Environmental
Science & Technology

The rush to shape
the cleaner car
512

Environmental
Science & Technology

contents

Feature

Interview

Outlook

Special Report

Departments

Solvent extraction of mercury from brine solutions with high-molecular-weight amines 525

F. L. Moore

Amines can be used to remove mercury from industrial waste solutions such as brine solutions from chlor-alkali plants, one of the major man-made sources of the metal. The commercially available amines—Aliquat 336 and Adogen 464—are especially useful since these quaternary amines extract mercury from either acidic or basic solutions. Either mixer-settler or countercurrent solvent extraction techniques can be employed.

Kinetics of oxidation of aqueous sulfide by O_2 529

K. Y. Chen and J. C. Morris

In some cases disagreeable odors and tastes in drinking water are caused by the presence of hydrogen sulfide or mercaptans at low concentrations. The conversion of these disagreeable constituents to innocuous materials is not a simple reaction; some of the aspects of the kinetic behavior are discussed. A chain mechanism is proposed.

Adsorption of lindane and dieldrin pesticides on unconsolidated aquifer sand 538

F. R. Boucher and G. F. Lee

Many chlorinated hydrocarbon pesticides can survive in both soil and water environments for years because of their relative stability. Naturally occurring dissolved organics which were present in two Wisconsin lakes reduced the adsorption of dieldrin on natural aquifer sand (Portage County, Wisc.) but had no effect on the adsorption of lindane.

Chemistry of catalytic nitrogen oxide reduction in automotive exhaust gas 543

R. L. Klimisch and G. J. Barnes

An exhaust emissions control catalyst—an alumina-supported mixture of copper and chromium oxides—first equilibrates the water-gas equilibrium; the reducing species are hydrogen and carbon monoxide. At low temperatures (less than 375°C) NO is converted to ammonia, but at higher temperatures lesser amounts of ammonia are formed owing to its dissociation.

Analysis of aliphatic fraction of air particulate matter 549

T. R. Hauser and J. N. Pattison

Aliphatic materials in the atmosphere are of interest because of their reported cocarcinogenicity, and a new, time-saving technique makes their determination possible. Direct determination of n-alkanes in air particulate matter is now possible by an improved technique which takes only 17 min, representing more than a fivefold saving in time over an earlier procedure.

Cadmium contamination of soil and its uptake by oats 555

M. K. John, H. H. Chuah, and C. J. VanLaerhoven

The extent of soil contamination by the heavy metal cadmium was evaluated for 33 agricultural samples taken from the Lower Fraser Valley (British Columbia, Canada). The cadmium content averaged 0.88 ppm, but a high Cd value of 95 ppm was found in a surface sample taken near a battery smelter. Oats grown on the contaminated soil contained very high amounts of cadmium in the roots, with smaller amounts in the aboveground portions.

Notes

Atmospheric lead and bromine concentration in Berkeley, Calif. (1963–70) 558

H. R. Bowman, J. G. Conway, and F. Asaro

Continuous monitoring of atmospheric lead is now practical using the technique of nondispersive X-ray fluorescence. The Berkeley data reveal that the ratio of bromine-to-lead appears to be higher in Berkeley than in six other cities previously studied.

Mercury and some other metals in urban soils 560

D. H. Klein

Eleven metals have been found in greater concentrations in industrial areas than in agricultural or residential areas. Data were taken from some 264 surface soil samples selected from a 300 sq mile region including metropolitan Grand Rapids, Mich. which earlier was ranked 50th in air pollution by the Public Health Service. The metals were cadmium, calcium, chromium, cobalt, copper, iron, lead, mercury, nickel, silver, and zinc.

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letters

Retraining aerospace engineers

DEAR SIR:

Your article, "New skills for out-of-work engineers," in the April 1972 issue was read with interest. However, I must vigorously disagree with your conclusion that "the Grumman program appears to represent just about the best sort of retraining an engineer could hope for, both in quality of instruction and length of program." The article goes on to state that if graduates of this program are unable to find employment, critics of all retraining programs will intensify their cries for alternative approaches to putting unemployed talent back to work.

The graduates of this program will be operating under many difficulties. First of all, because these trainees had been unemployed, they are not likely to have been among the best of those that had been employed in the aerospace industry. The environmental field does not op-

erate on "cost-plus," so quality is very important.

Secondly, these trainees would not have had the undergraduate background most appropriate to environmental studies. Most engineers drawn to the water programs in environmental engineering come from civil and chemical engineering. These trainees had come from mechanical and electrical engineering.
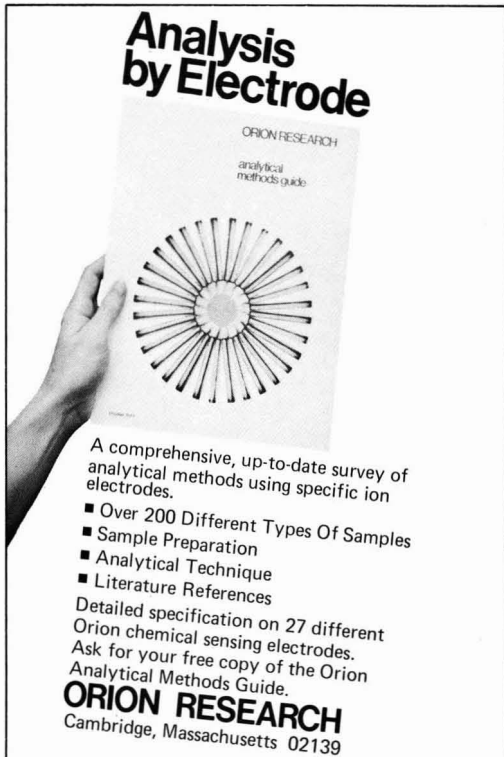
Thirdly, the program of study provides 620 hours of classroom instruction, which requires 5 hours a day five days a week over a period of six months. This type of approach is the antithesis of proper education. The typical master's degree program at an accredited university involves about the same number of classroom hours but extended over a 12-month period. This permits ample amount of time for work under faculty supervision in projects related to the program of study to provide a quality of instruction that cannot be met by being

lectured at in a continuous stream.

Graduates from the University of North Carolina with a Master of Science in Environmental Engineering are highly sought after every year, with each being offered a wide number of positions from which to choose. If it turns out that the Grumman graduates are not highly sought after, it is no condemnation of retraining. It may just possibly signify that retraining should be done in a university which is equipped for the purpose. After all, the University of North Carolina does not engage in manufacturing airplanes.

We do each year enroll a significant number of engineers making midcareer changes to the environmental field. These individuals have not had nor will they have in the future any difficulty in finding professional positions that are highly rewarding to themselves and to society. The 20 universities accredited by

How a Calgon bug count measures water quality in a mountain stream.

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the Engineers Council for Professional Development to provide graduate study in environmental engineering, plus many others besides, are involved in similar programs and can all testify to the high demand for their graduates. The most cursory survey of regulatory agencies, consulting engineering organizations, and other organizations that specialize in environmental engineering will testify to the shortage of highly qualified engineers in this field. A crash course for ill-prepared engineers will not satisfy this need.

Let me take this opportunity to comment on the posture of our national administration with regard to training in the environmental field. EPA is sharply curtailing its training grants because the administration claims that large numbers of unemployed and underemployed scientists and engineers are available. As any employer of environmental engineers can testify, the fact that an aeronautical engineer is available does not relieve the employer of the responsibility for obtaining qualified environmental engineers to meet his very special requirements. Curtailing resources for educating environmental engineers will have a very deleterious effect on the quality of work done, and the ultimate cost to society will be much higher than if a proper investment is made in qualified individuals.

Daniel A. Okun
Department of Environmental Sciences and Engineering
The University of North Carolina
Chapel Hill, NC 27514

Enforcement in Virginia

DEAR SIR:

We hate to quibble with your very helpful roundup, "Air pollution over the states" (ES&T, February 1972, p 111), but feel we must correct the statement that the Virginia State Air Pollution Control Board has taken "no enforcement actions" so far.

Enforcement has been a part of the Board's work since its beginning with a noticeable upsurge in early 1970. It has conducted enforcement proceedings that produced orders to some 10 industries and three localities to submit abatement plans with binding schedules, where they had failed to act. All complied. About half have already completed corrections or have installation of control equipment under way. Many other industries filed control programs earlier without the Board's having to go to this step. They are acting on those programs.

The Board has issued a half-dozen cease-and-desist orders to major and minor open burning violators. Our field staffers have taken many lesser enforcement actions without their having to reach the Board. The Board has taken two minor cases to court when its orders were ignored. It obtained a consent decree injunction in one and a conviction in the other. We are seeking a state law amendment sharply increasing court fines.

However, our purpose is to obtain results short of having to go to the last resort of court action.

William R. Meyer
Executive Secretary
Virginia State Air Pollution Control Board
Richmond, VA 23219

environmental currents

CEQ looks at need for deep water harbor facilities

Neither the East Coast nor the Gulf Coast has facilities for handling supertankers (more than 200,000 dwt) and although both Puget Sound and Los Angeles/Long Beach on the West Coast can presently handle some smaller intermediate tankers, it is becoming apparent that more deep water port facilities are needed for meeting U.S. energy needs. More than 300 supertankers are operating today and at least 200 such vessels are currently on order in the world's shipyards. CEQ's Gordon MacDonald told the Senate Interior and Insular Affairs Committee that their harbor facilities study began in January of this year and that it would concentrate on alternative superport location and terminal types and evaluate each by relative environmental effects, engineering feasibility, and costs.

EPA tries total approach to environmental problems

Jointly the Environmental Protection Agency and San Diego County (Calif.) have embarked on a project that could begin to solve the conflicting demands of environmental improvement. Under a $450,000 grant from EPA, the San Diego County Environmental Development Agency will establish a center for the analysis and management of all of their regional environmental problems. "Communities across the Nation are facing many difficult decisions in meeting the 1975 air quality standards as well as requirements for cleaning up waterways, disposing of growing amounts of solid waste, and controlling noise pollution," says EPA Administrator William Ruckelshaus. The project would pave the way for other communities.

OSHA calls for a year of the states

The Occupational Safety and Health Administration (OSHA) began its second year of operation on April 29. The agency sets and enforces job and health standards that cover 60 million employees in 5 million workplaces. George Guenther, Labor's assistant secretary for OSHA says, "This is a key year for the continued development and initial operation of state programs." He also pointed out that fiscal year 1973 will be the final year that states can receive 90% federal grants to plan their programs. In fiscal 1972, $6.8 million of the 90–10 grant money was already obligated, and an additional $1.69 million will be obligated to the 10 regional OSHA administrators before the end of this month. In the first nine months of the current fiscal year, OSHA conducted more than 20,000 inspections at work places and found 23% of them in compliance.

OSHA's Guenther

Water conferees meet; Supreme Court accepts pollution case

• At press time, both House and Senate conferees had been named to resolve the differences between the House and Senate versions of this year's clean water amendments. The conferees met for the first time the middle of last month. Earlier, it had been anticipated that the measure would have been on the President's desk for signature by this time.
• The U.S. Supreme Court has accepted original jurisdiction in a water pollution case that was brought by the state of Vermont against neighboring New York and the International Paper Co.; the case will be decided after its new term opens in October. At the same time, the Court refused two other original cases—those which have not been decided in the lower courts—Illinois against Milwaukee and other Wisconsin cities for alleged pollution of Lake Michigan, and 18 states against the big four automobile makers for alleged conspiracy to restrain development of air pollution control equipment.

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Problem:
Nitric oxide emissions from gas and oil fired utility boilers.

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Problem:
Lead particulates in the air.

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Problem:
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environmental currents

Smelter pollution controversy aired in Arizona

Proposed new air pollution controls for copper smelters in Arizona, which are supported by the copper industry, have produced a bitter internal dispute between health officials and the air pollution control officials. The revision would replace a mandatory 90% sulfur emission reduction with an industry-maintained monitoring system and voluntary operational cutbacks when sulfur levels are too high. The federal EPA questions the strength of the revised regulations; however, industry backers of the new controls say that more stringent rules would result in financial catastrophe for the copper industry.

Plea for high-lead gasoline denied in New York City

New York City's Environmental Protection Administrator Jerome Kretchmer has denied a plea by Mobil Oil, Sun Oil, and Getty Oil for permission to sell gasoline with a higher lead content and volatility than allowed by the city's air pollution control code. Since the beginning of this year, the lead content of gasoline sold in the city cannot be greater than 1.0 gram/gal., regardless of the octane rating. Also, gasoline sold in the city must not have a Reid vapor pressure (measure of volatility) greater than 12. Mobil, Sun, and Getty account for 33% of the gasoline sold in New York City.

Chicago bans phosphates; Feds act against Md. firms

How much phosphate?

Chicago's zero ban on phosphates in heavy-duty laundry detergents— accounting for about 90% of phosphates in all products on the market— becomes effective at the end of this month. Chicago's Department of Environmental Control will allow a six-month grace period for industrial and institutional cleaners to change over. The federal EPA initiated legal action against four industrial firms—American Sugar Refining Co., SCM Corp., American Smelting and Refining Co., and Allied Chemical Corp.—for water pollution violations in the Baltimore Harbor area. The four cases have been submitted to the U.S. attorney in Baltimore for action under the Refuse Act of 1899.

Particulate matter, wetlands under firm N.J. rule

The N.J. Air Pollution Code has been revised to include more stringent limitations on particulate emissions. The standards limit all particles emitted from the combustion of any fuel (earlier the standards applied only to combustion of solid fuel) and the new rules prescribe standards for all emitted particles from manufacturing processes instead of only solid particles. The N.J. Dept. of Environmental Protection adopted regulations which prohibit storage, disposal, or application of persistent pesticides and prohibit dumping solid waste or sewage or industrial wastes in certain sections of the state's wetlands. Two types of use permits will be issued—one for relatively small projects and another for full procedure projects requiring an environmental impact statement and public hearing.

New Jersey funds state recycling programs

Later this month, the N.J. Department of Environmental Protection will award six demonstration grants to selected community recycling programs. Involving $12,000 of state funds, three types of grants will become available: • grants to municipally supported programs that wish to regionalize • grants to municipally supported regional recycling programs already operating and • grants to municipalities for evaluating cost suitability of curbside pick-up of separated glass, newspaper, and metal.

environmental currents

Freezing removes dissolved solids from plating wastes

The best way to remove dissolved solids from metal finishing wastes may be to freeze them out, according to an engineer at Avco (Wilmington, Mass.). When water freezes, contaminants are excluded from the crystalline structure and concentrated in a brine which can be scraped from the ice. In Avco's process, cooled plating wastes are frozen by a fluorocarbon refrigerant. As the coolant evaporates, an ice–brine slurry is formed. Brine is separated from ice in a countercurrent washer, and ice is removed and melted. Process water purified in this way may then be reused. Avco has a 2500-gpd pilot plant in operation.

Listen! Humidity, not aromatics, is important for smog

Esso Research and Engineering finds that the formation of photochemical aerosols may depend more on humidity than on aromatic content of fuels. Working with a laboratory environmental chamber, Esso compared aerosol formation using two nonleaded fuels with 27% and 50% aromatic content, respectively (27% is approximately the aromatics concentration of regular grade commercial leaded gasoline). Esso found little difference in reduction of visibility due to photochemical aerosols, but in tests with relative humidities at 30% and 50%, aerosol formation was definitely increased.

Modular unit treats industrial waste waters

Marketed by Wastech, Inc. (Houston, Tex.), the Biota-Tron is a modular secondary treatment package that is capable of producing high-quality effluents. The prototype unit was designed to optimize oxygen transfer, mixing, and clarification and give positive control over as many parameters as possible. The modular concept gives the necessary reaction environment for treatment at the individual plant without prohibitive capital construction costs. Biota-Tron's cost of about $250/thousand gal. capacity compares favorably with the $1000/thousand gal. cost of conventional activated sludge plants.

Long-lived catalyst tackles auto NO_x . . .

Gulf Research and Development says it has a reduction catalyst for NO_x control on automobiles that lasts in excess of 50,000 miles. Gulf says in 1250 hr of engine dynamometer testing the catalyst still shows catalytic activity. Gulf won't give any details about the composition or physical form of the catalyst or support but says it is not poisoned by sulfur or lead and will probably be able to work with conventional, leaded fuels. Gulf also will not say how good the catalyst is at cleaning up emissions, but the company says that NO_x is reduced completely to N_2 and H_2O and that no NH_3 is emitted.

. . . while a catalytic process removes H_2S in water

A one-step catalytic process—called Cataban—for removal of H_2S from liquid streams has been developed by Rhodia, Inc., and is undergoing pilot tests by Rhodia at a Texas Gulf sulfur plant. The process uses a catalytic oxidation-reduction system in which a complex polyvalent metal ion—usually the ferric ion—oxidizes hydrogen sulfide to sulfur. Concurrently, the ferric ion is reduced to the ferrous state and simultaneously in the same vessel the ferrous complex is reoxidized to the ferric state. Sulfur produced may be recovered mechanically or simply left in the waste stream. Applications exist for hydrogen sulfide removal from effluent streams in pulp and paper mills, viscose rayon plants, and coal gas and coking operations, Rhodia says.
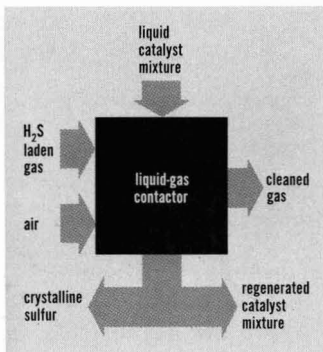
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A mercury analyzer accessory extends again the scope of AA spectroscopy in this field.
This non-flame technique provides a highly sensitive method for the determination of mercury in liquids.

Which all means that Varian Techtron has the expertise and the instrumentation to tell you what water is all about.

environmental currents
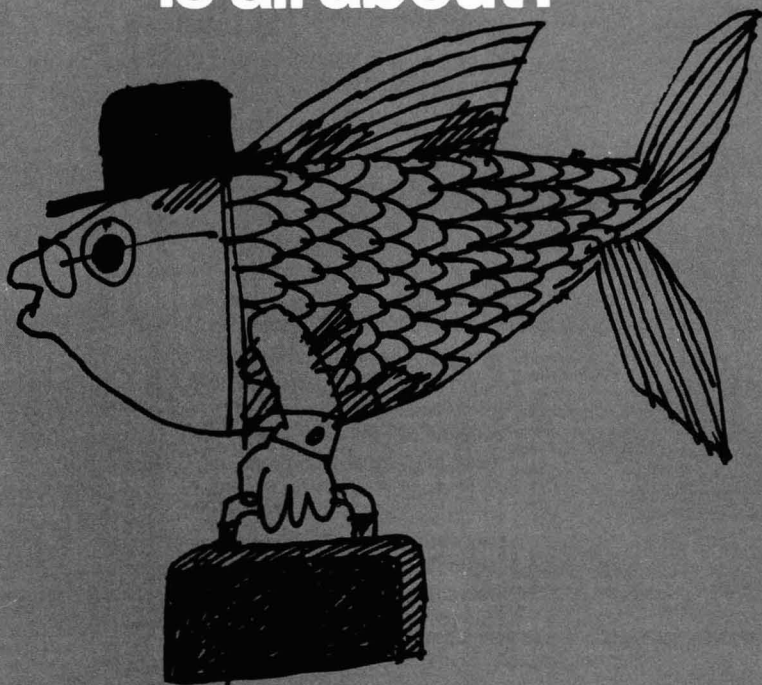
INDUSTRY

Getty Oil sues EPA over sulfur regulations

Getty Oil Co. has filed suit in federal court in Wilmington, Del., to halt enforcement of an EPA order requiring Delmarva Power and Light Co. to stop burning high-sulfur fuel at its Delaware City Power plant. (See ES&T, April 1972, p 305). A Getty subsidiary, Getty Oil Eastern, supplies Delmarva with fluid coke which, when mixed with other fuels, contains more than the 3.5% maximum sulfur content permitted by state regulations. Getty says EPA has not given sufficient consideration to the pollution control features of the refinery and that the EPA order wouldn't result in appreciable improvement of ambient air quality in the state. Getty Oil Eastern is seeking a variance from the regulations under state law.

TVA chief counts pollution control costs

Tennessee Valley Authority (TVA) Chairman A. J. Wagner notes that counting the cost of environmental cleanup is important in selecting priorities and determining the degree of cleanup needed. Wagner says, "Where health and safety are clearly endangered, there can be no compromise, but an environmental improvement which involves only aesthetics, particularly if it is extremely expensive, may have to accept a lower priority. Resources are too scarce to do everything." Cleaning up TVA's operations could cost as much as $800 million each year if regulations being actively proposed or considered take effect; TVA's revenues are only about $600 million per year. The cost of doing an adequate control job would be more like $75 million per year, according to the TVA chairman.

Cost impact on TVA for controls

Environmental problems	Annual costs (millions of dollars)	
	Maximum	Minimum
Strip mine regulation	$ 30–100	$10
Improved mine safety	30–45	15
Fly ash removal	35	15
SO$_2$ control	200–300	30
Sulfur tax	40–235	...
Waste heat control	50	5
Delays for environmental	55–65	...
Totals	**$440–830**	**$75**

Kodak offers industry rights on smoke suppression

Eastman Kodak Co. is offering rights to a new means for suppressing smoke from horizontal flares at no charge. Eastman says it is waiving all rights to an enforceable patent on the technique which was developed to prevent air pollution in the company's Texas petro-chemical complex so that other manufacturers with smoke emission problems will be encouraged to investigate the system's applicability to their particular problems. Eastman says the system uses water mist to hold the flame in check and to eliminate smoke. Operating costs are minimized because any water source, including industrial waste water, can be used. Installation costs are less than for other manually controlled smoke retardation systems.

Toxicology information service ready to go

Research scientists or health officials who need instant access to extensive and authoritative toxicology data will soon be able to hook into an on-line computerized data bank maintained by the National Library of Medicine through the Toxicology Information Program. The user—which may be any interested individual or organization—can utilize any one of a number of terminals such as phone or teletype lines to conduct a literature search. Called Toxicon, the program will be operated by Informatics, Inc.—a Rockville, Md.-based computer software and systems company. Users will be assessed a one-time subscription fee, plus a computer time charge and costs of additional special connections or terminal rentals.

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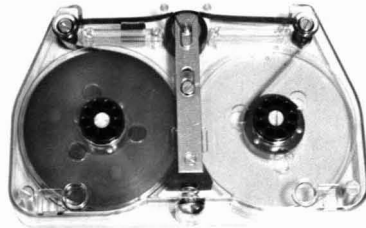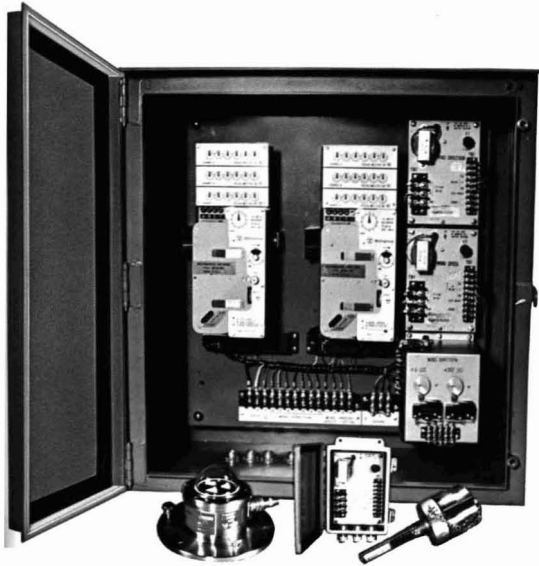
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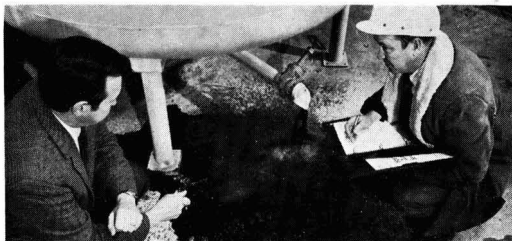
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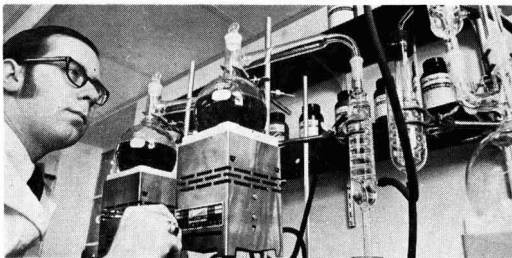
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Frank Zurn

An across-the-table discussion with a third-generation Zurn, a 45-year executive whose company is setting a fast business pace in the total environmental field

Frank W. Zurn is president of Zurn Industries, Inc., a company firmly dedicated to the concept of environmentalism. Sales totaled an estimated $185 million last year (year ending March 31, 1972). Frank Zurn tells ES&T's Stan Miller that the company was founded in 1900 by his grandfather, John A. Zurn, and grew into a multimillion dollar, family-owned corporation during the 30's-50's under the leadership of his father, Melvin A. Zurn, (who died in 1970) and his uncle, Everett F. Zurn, the present 64-year-old chairman of the board. The corporation went public in 1961, has acquired 18 companies during the past five years, and now has products and services in all four major environmental pollution control areas—air, land (solid waste), water, and noise.

Environmentalism

When did Zurn management direct itself to total environmental pollution control?

In the mid-sixties, we made a decision that if we were going to be in the business of pollution control, we were going to be involved on a total environmental control basis—air, land, water, and noise—because of the close interrelationships existing among these areas, both from a causative standpoint and the problem-solving mechanisms utilized. We set out to organize the growth program from within. We invested substantial monies in developing certain components in the air pollution control field, for example, but we concluded that the most efficient and economical method to growth within our time constraints was to initiate an acquisition program concentrated in the pollution control areas.

Our first major acquisition, in 1966, was a company known as Erie City Iron Works, one of the oldest corporations in Erie, Pa., and the third oldest corporation in Pennsylvania. The expertise that they brought into Zurn Industries was that of incineration, solid waste disposal, as well as a certain amount of air pollution control technology, primarily in the waste heat energy recovery field with emphasis on cooling and cleaning hot, noxious gases—all of which is tied in with generating steam from incinerated wastes.

What are some of the reasons for the changeover to a total environmental company?

Zurn customers were running into a problem with the disposal of solid waste which we entrapped in our water pollution control system. We had solved the water pollution control problem but ended up with a solid waste problem, and usually there were one of two answers—incineration or landfill. We
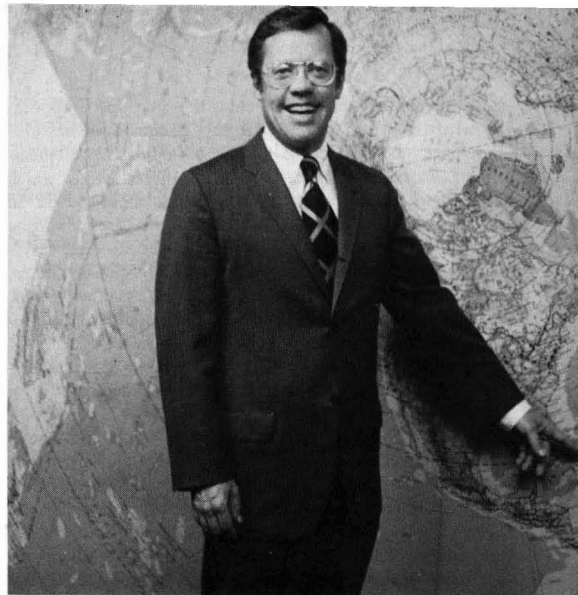
realized that if we were to incinerate, then we had to watch out for air pollution emissions.

All three control areas—air, land, and water—had to be done on a total basis or we were not doing the cleanup job thoroughly and properly. Before the move to environmentalism, Zurn was basically a hardware-oriented company; we dealt in water pollution control systems only.

After we had acquired various air, land, and water pollution control equipment companies, we recognized that we had the hardware, but we did not have the software which, in our parlance, consists of research, analysis, and design feasibility—the beginning of solving a pollution control problem; neither did we have the construction capabilities. We set about to find a company or companies that had both software and construction capabilities. After considerable searching, we came up with Ludwig Engineering and Science in late 1968. With that acquisition, Zurn then was ready to begin handling total turn-key projects because then we could start essentially at ground zero on a pollution control problem and take it to the ultimate solution, including training of operators, monitoring of plant effluents, and assuming total responsibility for round-the-clock performance of the plant.

What is the breakdown of industrial and municipal clients in the four categories of pollution control?

As a general statement, about 75% of the business is industrial, 25% municipal. However, this has been changing a percentage point or two each year in favor of the municipal. Starting this new year (April 1, 1972), we will probably be 70% industrial and 30% municipal. In water pollution control, municipalities are heavily involved with water and waste water treatment plants, but in air pollution controls the problems are with industries, power generation, and municipal incineration.

Noise pollution control is one of our newest directions; thermal pollution control is the other and is classified under the water pollution control activity of the company. Noise, our smallest business category, does about $3 million in volume—$2 million in hardware and $1 million in software. Zurn has been involved with the hardware side of the noise business primarily through the development of sound attenuation, mechanical, electrical, and hydraulic devices for nuclear submarines. Zurn's Mechanical Drive Division supplies

noise-attenuating drives for industrial machinery applications of the type developed for submarines. Zurn has also developed Accumultrol and Shoktrol products for attenuating or eliminating noise and shock from pipeline flow which are caused by quick-closing, actuating solenoid valves. In the absence of these shock arrestors, severe damage can be done to piping systems, not to mention shock noises reverberating through "quiet" buildings such as hospitals, schools, motels, and institutions. We don't see a huge market in noise pollution control in the immediate future, even in the equipment end of that business. Our work in the noise area, as far as the software is concerned is heavily oriented to municipalities—studies on airports, subways, and rapid transit.

On the other hand, thermal pollution control is our newest growth field. We regard this area as one of substantial growth with a very substantial market in dollar volume and potential profits. Balcke cooling towers, which Zurn can provide, are normal hyperbolics of the natural draft type as well as the induced draft type. The induced draft towers have a much lower silhouette than the natural draft. They are about one third the size of the natural draft towers in physical size. Of course, the advantage of the induced draft towers is that the flow rate across the water we are trying to cool can be varied regardless of the humidity of atmospheric conditions, and achieve extremely efficient cooling capability.

Products and services

Does Zurn have a complete line of products for air, water, solid waste, and noise?

We think we have a complete line capability in-house. However, we do specify and use other types of equipment that we do not manufacture. A good example is electrostatic precipitators. Zurn has investigated this market thoroughly, not only from design capability in this country but also from foreign licensing capabilities. We came to the conclusion that there is nothing really new and unique to offer in the electrostatic field. We are able to buy such equipment from a half dozen sources. The electrostatics market has peaked out; we feel that high-velocity wet-type scrubbers and bag-type filters are going to be taking over the market. Zurn has capabilities in both high-velocity wet scrubbers and bag filters; our bag filter work is coming on very strong.

Are the hardware items fabricated by Zurn?

We take responsibility for the equipment which we may specify and purchase which goes into the total pollution control system. It may be our design or it may be someone else's design and manufacture. Of all the products listed in various Zurn brochures, 99% of them are manufactured in-house and 95% of the 99% are proprietary. About 45% of the total Zurn manufacturing capacity is in the city of Erie, Pa., with more than a million square feet of manufacturing space. The other 55% of the capacity is spread all over the U.S. For example, scrubbers, mechanical dust collectors, and bag filters are manufactured in Birmingham, Ala.; metal bellows which go into our new instrumentation line of air-monitoring pumps are manufactured in Sharon, Mass., and Chatsworth, Calif.

Turn-key

Can Zurn perform turn-key operations in the four categories for both industrial and municipal clients?

We have been very successful in selling the turn-key concept to industries and are becoming successful in selling this concept to municipalities. With the economies, the quality of

"There is no reason why turn-key cannot be applied to the municipal market. We are 100% in the direction of turn-key."

installations, and performance and the efficiency of such installations that turn-key offers, there is no reason why turn-key cannot be applied to the municipal market.

Zurn Industries is 100% in the direction of turn-key. We think it's the most economical, efficient way to solve the massive pollution control problems. We think also in turn-key that there is plenty of business available for all available consulting engineering firms, for hardware equipment manufacturers, and for construction companies. We take total responsibility for the study analysis, for the design of the installations and the systems. We take responsibility for the equipment which we may specify or purchase. It may be our own design or it may be someone else's design and manufacture. It is true that Zurn does not produce every nut and bolt that goes into a pollution control plant. Take shredders as an example. We market a shredder under the Zurn name, but it's not produced by us. Electrostatic precipitators are another example; we do not produce these.

Are there examples of Zurn turn-key projects in the water category?

Although the project at the City of Cleveland (Ohio) which is being carried out by our affiliate—Zurn Environmental Engineers—is not specifically a turn-key contract, it contains the critical element of one. There, the Westerly plant project involves a departure in terms of liquid waste treatment; the untreated waste coming into the plant is a combined municipal and industrial waste that is quite complex and not suitable for treatment by conventional biological treatment means (activated sludge). Zurn submitted its proposal to the City of Cleveland three years ago in concert with Battelle-Northwest for conducting a feasibility study which included: • laboratory analysis of the incoming wastes and surrounding receiving waters • design, construction, and operation of a pilot plant facility at the plant site • analysis of pilot plant data • preparation of initial cost estimates for the full-scale facility. Now, Zurn Environmental Engineers is proceeding with preparation of final designs, plans, and specifications for the full-scale plant.

Initially, the plant will have a capacity of 50 million gal./day with provisions for handling storm water overflows up to a peak loading of 1600 ft/sec. Later, the plant can be expanded to 100 million gal./day. It will be located on approximately

8 acres of land adjacent to Edgewater Beach. When completed, the Westerly plant will be the world's largest municipal waste water reclamation facility utilizing physical-chemical treatment concepts. Construction cost alone approximates $35 million.

A good deal of the work that Zurn does in construction is more appropriately termed construction management. We do not necessarily use our own actual labor in all of these projects. We have made a point to use local available subcontracting construction companies in various locations. Of course, we would have the overall management responsibility for their proper performance, but we have made a point to use local available firms or the more talented construction engineering firms in joint ventures with Zurn where we are the lead responsible company. We use them on a subcontract basis and this has worked extremely well.

Technology markets

How many business agreements are being negotiated between foreign technology firms and Zurn for application of foreign technology to U.S. markets?

It's a two-way street. It's an international business challenge of tremendous magnitude. Our philosophy has been one of licensing our know-how and patents to overseas firms; Zurn has some 50–60 licensees to foreign companies. Then, through a cross-licensing arrangement Zurn brings their technology to U.S. markets. Balcke is a good example here. We brought over the thermal pollution control technology of Balcke (an engineering-manufacturing firm based in West Germany), and we have been negotiating with them to take on certain of Zurn's water pollution control technology. In the area of the Dusseldorf incinerator system, Zurn introduced this to the U.S. market. The patent for the system, as you know, is built around the cylindrical rotating inclined-plane grate for greater agitation of the solids and for cleaner and more efficient combustion of solid waste. In turn, we are negotiating with Deutsche B&W, the parent firm, to market our water pollution control products in the international market. In Japan, Mitsubishi has our water pollution control technology. Hawker Siddley, in England, also has this water technology. In South America, we have done feasibility studies

of watershed developments and waste treatment plants for Sao Paulo and Rio de Janeiro in Brazil as well as many comparable projects in other parts of the world.

Zurn also is doing construction work in many major free-world nations. Zurn developed certain techniques in slit forming concrete foundations that speed up the construction of waste treatment plants and similar waste control structures such as waterways, sluice ways, and the like.

Is there any reluctance by foreign countries to accept U.S. technology and vice-versa?

No, we have found that foreign countries eagerly look to the U.S. because they realize that the U.S. has the biggest industrial pollution problem. Japan, too, has a major pollution problem as well as certain European nations, but nothing of the magnitude that the U.S. has generated. Therefore, foreign countries eagerly look to us for the most economical solution to their problems. They eagerly await U.S. technological leadership in this area.

We know of some areas in the world where international state planners want nothing but U.S. technology in the particular area of pollution control. These are the new emerging nations such as Saudi Arabia. The whole group of Arab nations have discovered substantial oil reserves and are now building new communities literally from the 15th to the 20th century overnight. They want the latest, best, and most sophisticated approach to the problem, and they are coming to the U.S. for that pollution control technology.

Recent acquisitions

What can you tell ES&T about acquisitions?

Since 1966, Zurn has acquired 18 companies. We had a problem with three of the smaller acquisitions which resulted in a one-year moratorium on acquisitions (April 1, 1970–March 31, 1971) until we got our house in order. Zurn has an internal audit committee that travels to each of our operations on a regularly scheduled basis and makes a very thorough investigation of how things are coming along from a financial control standpoint. Because of the rapid rate that we were acquiring companies—one almost every two or three months—the audit committee did not get to a couple of the companies in sufficient time to initiate and implement the proper corporate controls. During the moratorium we continued to investigate potential acquisitions but we had a policy of no consummation. We felt that any company that wanted to come with us during the moratorium was worth waiting for.

Post moratorium, Zurn acquired the Robert Irsay Co. in June 1971. Their speciality is the design, engineering, and construction of air pollution control systems. Previous year sales were $13 million but sales for the current year will be close to $18 million. Robert Irsay does not produce any of the auxiliary equipment for these systems, such as induced draft fans, forced draft fans, and air pollution collecting equipment. These units are furnished through other Zurn subsidiaries and this again gives Zurn a total turn-key capability and responsibility in the design of air pollution control systems.

In the fall of 1971, we acquired Vulcan Manufacturing Co. (Cincinnati, Ohio). Their main expertise is in working with exotic metals, which is very important when air pollution controls are fabricated for highly corrosive liquids or gases such as in the continuous process industries—including petroleum refining and petrochemical manufacture. Vulcan will do about $8 million in volume this year.

Zurn profile at a glance
(estimated 1971 sales, millions of dollars)

Total sales: $185 million

Environmental management	Air and land pollution control	Water pollution control	Environmental safety and protection	Energy systems	Mechanical and leisure products
$50	$39	$30	$13	$29	$24

Note: Environmental management includes engineering, research, construction, and community development

. Wilkins Regulator Co. (suburban Los Angeles) was another
acquisition. Last year, sales were $1.5 million; this year they
will probably hit $2 million. Wilkins has developed and pat-
ented a pressure-regulating valve used in interior fire pro-
tection systems. In high-rise buildings, regulating the pressure
flow of a water supply system in a building of this type is very
difficult and costly, but the Wilkins pressure regulator does
this in a very economical way. For example, in a 40-story
high-rise building, these regulators might cut the cost of such
fire protection equipment by as much as 50 %, and it is all done
automatically.

In December 1971, Zurn acquired Crowell Designs, Inc.,
a company in the business of designing and producing bilge
pumps for all types of pleasure boats and recreational vehicles.
In the next several years, Zurn may broaden into two addi-
tional pollution control areas—instrumentation and chemi-
cals. We will probably get into the instrumentation field by
acquiring a company in the $10–20 million volume range.
With chemicals, Zurn will not manufacture the chemical itself.
We will buy these in bulk and do the mixing and compounding
and then merchandise them under the Zurn name. We see a
big market coming in this expendable products area as we as a
nation move more and more to the physical-chemical type
treatment of waste waters. A company in each of these two
areas will probably be acquired within the next six to 12
months.

Jack-of-all-trades

**By virtue of its activities in all areas, is Zurn the jack-of-all-
trades yet the master of none in the environmental area?**

I never thought that Zurn wanted to dispel the notion that it
did not have specialization in certain areas. Zurn is probably
the most renowned solids interception company in the world
with all types of interception devices and controls—screen-
ing, straining, and the like. The same holds true of our leader-
ship in various other speciality fields within the pollution
control market. I do not think any other company can touch
us in these areas of specialization. A company with a different
speciality might win out; they might manufacture a pump,
for example, or they might make valves or pipes. But Zurn as a
total environmental company already manufactures many of
these so-called specialties and could produce many others.

**Can you cite certain recent contracts in the total environmental
area?**

We, of course, have a large number of on-going and new
contracts too numerous to mention here. But of the more
interesting I would name the following: on the industrial
side, U.S. Steel (Gary, Ind.) has contracted Zurn for elimina-
tion of air pollution and recovery of waste heat, a project of
about $4 million. On the municipal side, I would mention
various feasibility and engineering studies, the most recent
being the James River study for the Commonwealth of Vir-
ginia. A main objective here will be the involvement of a
study leading to the preparation of a total water management
plan for the James River, which will not only consider ap-
propriate waste treatment criteria, but also recommend param-
eters for proper water utilization from the river.

In solid waste, Zurn constructed the new incinerator system
for Disney World in Florida for $1.1 million. In air pollution
control, we are about to "start-up" a breakthrough approach
for controlling sulfur dioxide gas at Key West, Fla., utilizing
a unique filtering medium for capturing the sulfur dioxide.
But municipalwise, the largest proposal outstanding to date is
for incinerators for New York City, totaling about $45 million.

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The problem: Taking the fish eyes out of polymer feeding

outlook

Building bricks from the waste pile

A new process offers an inexpensive way to turn inorganic solid wastes into quality building bricks, but acceptance by the construction industry may be slow in coming

The age of "gee whiz" technology is drawing to a close, but a process that takes almost any inorganic wastes and turns them into bricks that surpass American Society for Testing Materials (ASTM) building product standards is rousing some excitement nevertheless. Tekology Corp. (Palisades Park, N.J.), a majority-controlled subsidiary of Certain-teed Products Corp., and developer of the process, thinks it may contribute to a minor revolution in the low-cost, high-standard house-building industry. The patented technology is now available for license to firms interested in disposing of solid wastes and making money at it.

"Almost any inorganic material can be used," explains Jim Ryan, president of Tekology Corp. The company's method of brickmaking, called the Tek process, converts everything from gold mine tailings to oyster shells into high quality building blocks or bricks. The process does not involve heating in a kiln or autoclave which is essential for the familiar clay or sand lime bricks.

Process and products

Manufacturing bricks from inorganic solid wastes is simple and basic. Aggregate raw materials are dry mixed with Portland cement—usually the mixture is 90–96% raw material, depending on the nature or grain size of the raw aggregate. Next, water and a proprietary chemical admixture are added to the dry mixture. The now-moist mixture is loosely packed in a high-pressure mold and subjected to 3000–6000 psi pressure, which causes a binding chemical reaction between the cement, chemicals, and water.

The discharged "bricks" are stacked on pallets to "cure" (dry) for a minimum of 24 hr. A "green" or uncured brick taken directly from the press easily supports the weight of a grown man. Within 24 hours, some of these masonry units can withstand 3000 psi compression and have an eventual strength of over 5000 psi.

Except for the drying period, the entire operation is completed in 10 minutes in a plant that can be automated or semiautomated. A minimal manufacturing facility consists only of aggregate and cement hoppers, a chemical tank, a scale to weigh the mix, mixers, molds, a press, and stacking space.

The Tek process molds three basic bricks and blocks: Tekbrik (a regular sized brick), Tekblok (a brick in the shape and size of a concrete block), and Teklokblok (an interlocking block).

Advantages

The differences between the Tek process and conventional brick manufacturing account, in part, for the versatility of Tekology products. Clay brick factories require large kilns for heating and are usually located near clay deposits. Clay bricks cost less than a penny per pound at the factory, but transportation costs quickly raise prices. The Tek process, however, is relatively economical because heating is not required, manufacturing plants can be constructed near the market, and neither clays nor other special aggregates are necessary. Furthermore, brick factories have air pollution problems, while the Tek process emits no pollutants. Noise is integral in making concrete blocks with a vibrating press, but Tekology's hydraulic press is much quieter.

While bricks are in a kiln, heat distorts them and creates variations in the finished size. With the Tek molding process, says Ryan, all bricks and blocks are uniform in size. This uniformity, he explains, made possible the Teklokblok, which mechanically interlocks so closely with adjoining Teklokbloks that there is no need for mortar.

When completed, a Teklokblok wall is actually a double wall with the solid brick surface on both sides. The cavities or cores can be filled with sand or urethane or reinforced with metal rods. Teklokblok walls (without mortar) provide a breaking load that is about two and one-half times that of a conventional concrete block wall, Ryan claims. Housing components—doors, windows, electrical wiring—are easily integrated into Teklokblok walls.

Most conventional building units—brick, blocks, or stone—are held together with mortar. This mortar joint is the weak point in masonry construction—a brick wall is no better than its mortar joint. Epoxy plastics have been developed within the past few years that overcome joint weaknesses and reduce mortaring labor time. However, neither bricks nor concrete blocks have sufficiently regular surfaces

Potential bricks and blocks

Fly ash	Coral rock	Calcite
Frit	Asbestos	Iron ore
Ground glass	Laterite	Vermiculite
Foundry sand	Furnace slag	Granite
Aragonite	Volcanic ash	Lava
Mine tailings	Oyster shells	Mica
Cement dust	Ocean bottom sand	Limestone
Marble	Quarry tailings	Kaolin
Gypsum	Kyanite	Traprock
Sand	Dolomite	Glass fiber

Recycling. *The bricks in the house at the left were made out of ocean bottom and waste tailings. Tekology's Ryan (below) builds a model Teklokblok wall (the real thing is in the background)*

to enable them to be glued with thin, although extremely strong, epoxy plastic layers. The surfaces must be ground before an epoxy can be used since using large amounts of epoxy to fill in the irregularities is prohibitively expensive.

Epoxy can be used with the products of the Tek process, however, since their size is always uniform (eliminating the need for grinding), and the resulting wall is a much stronger entity. Using Tekbriks and epoxy, a good mason can lay at least 600 bricks per day, according to Ryan. This contrasts with an average 200 bricks per day for clay bricks and mortar.

Tekology bricks and blocks can be produced in a wide array of textures and colors. This is in part due to the varying colors and textures of the wastes used. Bricks made from fly ash are naturally smoother than those made from metallurgical slag. The natural textures of the bricks that ES&T examined were quite attractive, varying from semismooth to the normal coarseness associated with bricks. Tekology's Ryan explains that all Tek products can be rock-faced (chipped) to have a rough, stone-edged appearance, or glosses can be applied to give the walls a more finished look. Bricks made from lighter colored wastes can be tinted in a number of different shades for color variation.

Interlocking Teklokbloks eliminate the need for the high cost of masonry labor and materials, since the blocks can be set in place by unskilled labor. Wall building with Teklokbloks is simple because they go together only one way. Ryan terms them "idiot-proof."

Capital and manufacturing costs are lower than those for kiln operations. Equipment capable of producing 5000 bricks per hour (not including land or buildings) would cost about $450,000. Production cost of Tekbriks ranges from $17.50 to $20 per 1000 as contrasted with $35 to $40 per 1000 for conventional bricks.

Licensing and R&D

Tekology Corp. doesn't intend to go into the brick business itself, but licences its technology for a fee and royalty payments. The first licensee was New Providence Development Co., Ltd. (Nassau, Bahamas) which will make Tekbloks and Tekbriks out of ocean bottom and waste tailings.

Earlier this year, Ryan announced that Tekology has signed an agreement with Puerto Rican interests for exclusive licensing of the Tek process in Puerto Rico. Teklokbloks will be produced for low-cost buildings. The first Tek plant is expected to be in operation this year.

Certain-teed Products Corp., Tekology's parent company, has exclusive licensing rights in the U.S., with the exception of Hawaii and Alaska. At press time, Tunison Brick, Inc. (Lake Park, Ga.) has licensed the Tek process to produce bricks from phosphate mine tailings. The plant is expected to be in full production this summer.

Under contract with the Glass Container Manufacturers Institute, Tekology Corp. earlier this year successfully used ground-up, nonreturnable glass bottles to form building blocks which exceed ASTM specifications. "The glass wall, even the glass house, is now something that can be realistically achieved," Ryan points out.

Tekology researchers are also experimenting with using spent oil shale waste as a substitute for Portland cement in the Tek process. Tekology Corp. has applied for a patent on this newest development.

Firms the world over are sending samples of their various wastes to the Tek people to examine for the possibility of making bricks. The samples received are so numerous that Tekology now charges $150 for this service. After the first brick is made and tested, Tekology lists the characteristics, assets, and liabilities of the brick for the inquirer.

Problems

Although the Tek process for recycling waste materials is certainly potentially attractive, there are some potential problems. Despite the fact that Tek bricks and blocks pass ASTM tests with flying colors, local building codes are widely variable, and getting local approval for their use in buildings can be time-consuming and difficult.

Labor factors may rule out the use of the Tek process. For example, bricks from iron tailings weigh around eight pounds instead of the usual five pounds, an added burden that bricklayers probably would not accept. And, of course, there will inevitably be opposition and stiff competition from brick factories.

Many firms are hesitant about entering a field about which they know nothing, despite the opportunity to make money from wastes. Although Tekology Corp. is not at present prepared to make bricks from a customer's waste in any large quantity, the customer can license the Tek process and have Certain-teed Products Corp. handle the final building product, using its experienced sales and marketing forces. CKL

Reuse, recovery lower pollution from brewery

An environmental science writer's dream come true: the chance to do a story on pollution control in the brewing industry. Writers and Brew, after all, get on famously—the one extolling the virtues of the other; the second aiding and abetting the vice of the first.

Americans like beer. Last year, they drank more than 127 million barrels of it, according to U.S. Treasury Department statistics (one barrel contains 31.5 gal. of beer). And while Americans consume only about half as much beer per capita as northern Europeans—the world's most enthusiastic tipplers—the U.S. brews twice as much beer as the first runner up, West Germany.

The potential for pollution is high. Brewing consumes large amounts of water. Beer itself is about 93% water and the average brewery uses about 10 gallons of process water for each gallon of beer it makes. Effluent from even a small brewery—one which produces half a million barrels of beer annually—averages 700,000–800,000 gpd. BOD is in the neighborhood of 4000 mg/l. and total solids are in the 1000-ppm range. Solid wastes—spent grains, hops, and sludges of various composition—all add to pollution-abatement headaches for brewers.

Brewing process

The first step in the brewing process is malting. Whole barley is steeped in cool water and aerated for about 48 hr. The softened grain is then placed in germination bins at constant temperature and humidity for about a week. The germination process converts crude starch in the grain to soluble sugars and starches by enzymatic action. The barley is mechanically turned throughout the germination period to assure even sprouting.

With germination complete, the barley is transferred to drying kilns which gently toast the grain to caramelize it and stop further growth. The dry roasted grain is now called malt and needs only to be milled before it is used to give color and aroma to the finished beer.

Beer begins by mixing malt, brewer's rice, and water in large mash kettles and cooking through various temperature cycles to finish the conversion of starches into malt sugar. The cooked mash is filtered and the clear, amber malt extract is boiled with hops which add flavor and aroma. Spent hops are removed and the hot extract—called wort—is pumped to a coolship where undesirable proteins coagulate and settle out.

Cooled wort is mixed with brewer's yeast in primary fermentation tanks where malt sugars are converted to alcohol and CO_2. Secondary fermentation and aging complete the process and the clarified, finished beer is ready for bottling.

Waste treatment

Waste is generated at every step of the brewing process. Although virtually all the contaminants are biodegradable, the fact that they're present in such large quantities makes treatment essential. One brewer visited by ES&T—the Adolph Coors Co.—has been able to cut pollution considerably by reusing water and reclaiming brewing by-products, rather than discharging them directly to their treatment plant.

The Coors brewery—located near Denver in Golden, Colo.—is large by industry standards. It makes about nine million barrels of beer per year for distribution in 11 western states. Until 1953, according to Coors's general manager for environmental control, Howard V. Lewis, the brewery, industries associated with it, including a porcelain manufacturing plant, and the city of Golden all were discharging untreated wastes directly into Clear Creek, a tributary of the South Platte River. In 1953, Coors built a primary treatment plant to take care of the effluent from the brewery as well as the city's sewage.

The plant didn't work very well, according to Lewis, because of heavy initial loadings and fluctuating pH.

Coor's plant treats both industrial and municipal wastes
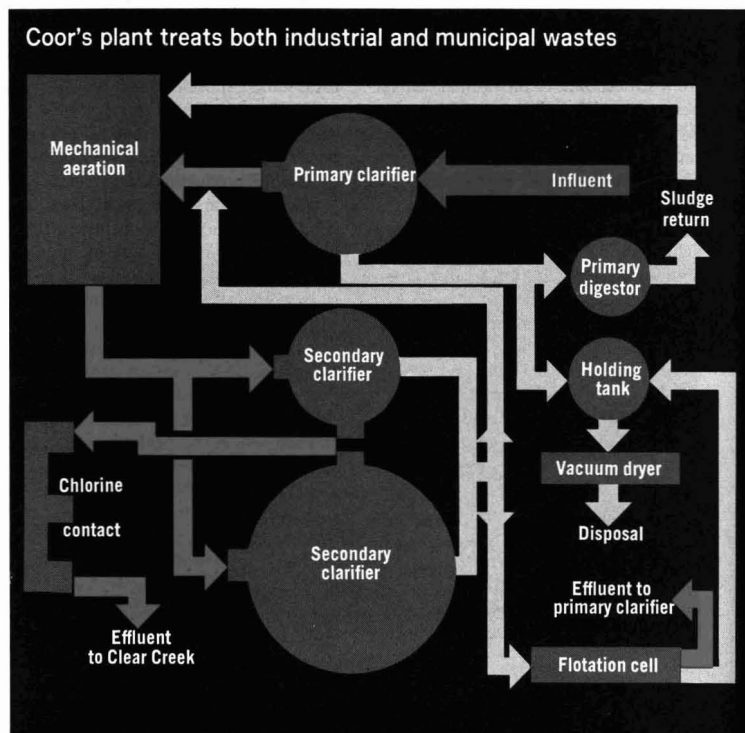
*By cutting initial loadings and
modifying sludge process, Adolph Coors
makes plant effluent sparkle*

Bits of solid waste—spent hops, grains, paper labels—choked the digesters. By adding screens and mechanical separators, Coors was able to upgrade the performance of the plant. Trapped solid wastes were pumped to anaerobic digesters modified with gas and steam recirculation systems to improve mixing.

Other problems remained, according to Lewis. Plant loadings were still extremely high, and the digesters had difficulty coping with shock loadings from batch brewing and malting operations.

Coors initiated a recovery program to cut loading and capture potentially valuable by-products. Recovering waste beer—overflow from the filling lines—rather than allowing it to flow into the treatment plant was particularly helpful, Lewis says.

Beer has a BOD of more than 125,000 mg/l., he notes, and by cooking waste beer in evaporative condensers, Coors not only reduced loading considerably,

but produced a syrup which could be used as a binder to form livestock pellets from spent grains and hops. Waste yeast was also dried, Lewis says, and made into a high-protein poultry feed supplement.

With such recovery procedures, Coors was able to reduce plant loadings from about 4000 mg/l. BOD to roughly 1600 mg/l. However, this was still not good enough since primary treatment continued to yield effluent with a BOD of about 1200 mg/l. and suspended solids content of about 125 mg/l. "Secondary treatment was clearly necessary," Lewis says.

Pilot studies indicated that activated sludge processes would need to be modified slightly because of the high carbohydrate content of the effluent. Carbohydrates promote rapid growth of *Spherotilus natans*—a filamentous plant which quickly clogs sedimentation basins. The solution to that problem, according to Lewis, was to inject small amounts of highly digested sludge di-

rectly into the activated sludge return.

Another problem was nutrient availability. The BOD:N:P ratio necessary for the secondary treatment unit to function properly, Lewis says, should be on the order of 100:5:1. But brewery effluent is both phosphate and nitrogen poor.

Wastes from the city of Golden currently supply ample phosphate, but Lewis says he must add anhydrous ammonia to make up for the nitrogen deficiency. Golden will soon join a metro municipal treatment plant, he adds, and Coors will have to supply phosphate as well.

Sludge handling

Waste activated sludge is thickened in a flotation cell with a cationic polyelectrolyte to an average solids concentration of about 4%. The activated sludge and primary settled sludge are pumped to a holding tank which is agitated to keep the solids evenly dispersed. Prior to 1963, Coors took this liquid sludge directly to landfill in tank trucks. But, says Lewis, that proved to be a costly, inefficient method of disposal which had to be operated around the clock. The sludge mixture is now fed to a vacuum filter. Dewatered sludge is trucked to company land, where it is mechanically turned with tracked machinery and farm equipment to minimize odors and work it into the soil. Experiments are under way to test the feasibility of drying sludge further. The sludge is 44% protein, Lewis points out, making it an ideal candidate for use in animal feeds.

Final clarified effluent from the secondary clarifiers is chlorinated in a contact cell before being discharged to Clear Creek. The final effluent shows a reduction of better than 95% in BOD and better than 97% reduction of suspended solids—well within the limits for discharge set by the State of Colorado.   HMM

Mash kettles. *Copper-capped vats,
lined with stainless steel, are the heart
of the brewery*
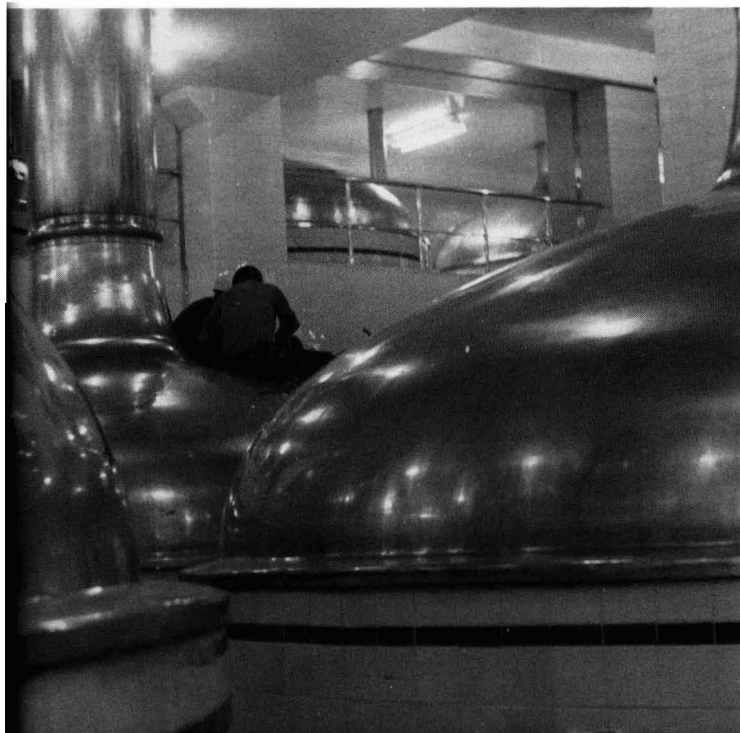
Reclaiming The Meadows

Trying to rationalize conflicting uses of New Jersey's last large space resource in a highly urbanized area is the Herculean task of the Meadowlands Commission
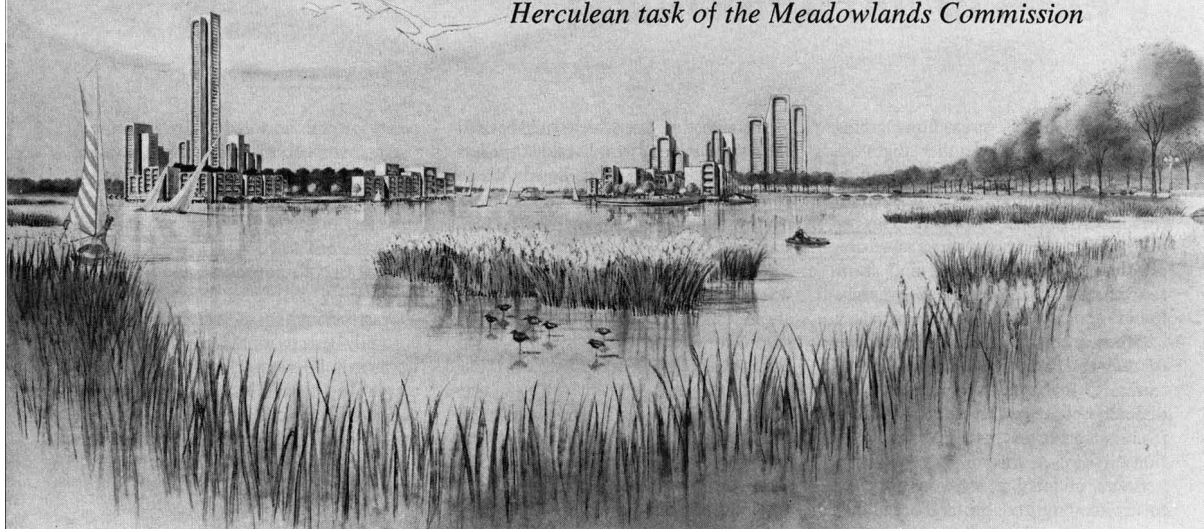
City in a swamp. *Master plan calls for self-contained residential clusters in harmony with the natural topography*

Less than five miles from the swarming press of Times Square there remains a sparsely populated salt marsh, larger than Manhattan Island and 20 times as large as Central Park. Ringed by people-packed municipalities, this 20,000 acre bog—The Meadows, as it is euphemistically called—has for centuries resisted man's efforts to subdue it.

The early settlers built wooden dams and dikes to wrest the land from the water, but their bulwarks were no match for the tides and burrowing muskrats. Later entrepreneurs substituted iron for wood and saw their investments swallowed whole as the drying land split open and engulfed the offending metal.

Not content with a swamp, man made a slough of The Meadows. Some 40,000 tons of garbage are dumped there each week. Many of the communities surrounding The Meadows are not even sewered. Through the heart of The Meadows runs the Hackensack River—one of the most seriously polluted streams in the nation.

What flows through The Meadowlands is not milk and honey, but to the New Jersey Hackensack Meadowlands Development Commission (HMDC), The Meadows is the Promised Land. If HMDC has its way, The Meadows will be transformed into a showcase for land use planning and reclamation. Under a master plan recently released by HMDC, the marsh would support various industrial, commercial, and residential uses coexisting in an "environmentally sound" fashion with natural scenic beauty and wildlife preserves. The plan provides for

• Self-contained island residential clusters on waterways, complete with shopping centers, churches, schools, and commercial and recreational facilities

• 1500 acres of public parks, commercial golf courses, marinas, and the like

• a water-oriented business, shopping, civic, entertainment, and cultural center

• water-based mass transit systems

• improved commuter transit facilities including transportation centers where commuters could transfer to rail or bus lines leading to major urban destinations

• transformation of used up landfill sites into parklands

• a large section of the southern end of the tract to be set aside as a wildlife preserve grown over with swamp grass, which would aid in combatting pollution.

The combined residential areas would make up a population center of about 400,000 people, making the Hackensack Meadows the third largest city in the state of New Jersey.

Orderly development

In 1968, the New Jersey legislature passed the Hackensack Meadowlands Reclamation and Redevelopment Act which established HMDC to oversee "orderly and environmentally sound" development of the vast marsh. The intent of the act was to avoid piecemeal development and erosion of virtually the last open space resource in the New York City metropolitan area.

The Commission held its first meeting in April 1969 and by late fall of the same year it had adopted Stage I of a master plan for land use. Stage I established interim zoning regulations to permit continuing development of about 2500 acres of The Meadowlands district where such development would not jeopardize future options for the master plan. At the same time, Stage I deferred development of about 10,000 acres for a period not to exceed two years. During those two years, HMDC would complete the master plan and hold public hearings to determine whether or not "useful modifications" of the plan might be in order before the final zoning ordinances were promulgated. At press time, that two-year moratorium was about to expire.

HMDC also prepared a number of technical support studies—dealing with the geological, ecological, and de-

velopmental history of the marsh—to support its proposed comprehensive land use plan. The complete master plan, released last December, has sparked considerable comment from both the public and private sectors. If adopted essentially "as is," implementation of the plan would take about 30 years—assuming, of course, that the money to make it a reality were available. As the situation now stands, legal challenges to the plan and the Commission's authority are likely to extend eventual completion well into the 21st century.

Legal tangle

From the outset, The Meadowlands development program has been plagued by legal questions. To begin with, the state laid claim to The Meadows under the doctrine of riparian rights. Loosely stated, riparian doctrine gives the state control of all lands presently

Meadowlands is hub of New York-New Jersey metro area

under water or touched by tidal waters at any time past or present.

Several local municipalities bordering The Meadows, as well as some individual property owners, have branded the state's move a "massive land grab" and are fighting the constitutionality of the enabling legislation in the state supreme court. Observers in the state capital say there are indications that the Court may find the act unconstitutional, but under a provision of the act that calls for revenue sharing with the communities. A bill recently introduced in the state's general assembly would amend the act to meet the court's objections.

But there are other problems as well. Environmentalists are nearly unanimous in their opinion that the master plan fails to provide adequate environmental safeguards. Charles Cooper, a biology major and chairman of Students for Environmental Action at Fairleigh Dickinson University, located on the fringes of The Meadows district, told the Commission at recent public hearings that the master plan was "economically opportunistic yet environmentally short-sighted."

Cooper, and various environmental groups as well, would like to see The Meadows restored for controlled recreational and educational purposes. The money spent building cities in the marsh might more profitably be spent in other ways, he suggests. "A state noted for an abundance of urban decay," Cooper says, "as evidenced by Paterson, Newark, and Jersey City, has chosen to divert the energies of repair and rehabilitation away from these recognized areas of crisis into the elimination of potential green space and the establishment of another metropolis."

Cooper isn't alone in his objections to building a city in The Meadows. Eugene P. Odum, Director of the Institute of Ecology at the University of Georgia, also doubts the wisdom of HMDC's plans. In a nine-page telegram to a hearing board, Odum said, "In concert with environmental utilization it appears to be ecologically unsound to structure a new city in an open space such as a salt marsh, especially since open space is already a limiting factor."

Facing reality

Restoration of The Meadows to its original state—or even keeping it open as a somewhat altered parkland—appears to be unlikely. Marsh conservation can only take place where there is marsh left to be conserved or at best

restored, and the Commission's findings indicate that relatively few acres with nearly intact ecosystems remain. HMDC's job, the plan says, was "to identify the limitations of the land, to determine the leeway for beneficial action, and to stretch the leeway and the benefits as much as possible."

At the ceremonies unveiling the master plan, then Commission Chairman Edmund T. Hume said, "the resulting pattern of land uses comes largely from the realities of the soils, existing uses, drainage requirements, and other incontrovertible facts, as well as from the desired future growth and other incontrovertible facts. No other method of planning would be practical or economically feasible."

Clearly, if any of the master plan is to be realized, economic feasibility will be a key consideration. HMDC declines to give figures for the cost of the total projects, but $10 billion is a figure frequently bandied about.

HMDC hopes that most of the money will come from private sources, but much state and federal money will be necessary as well. In April 1971, New Jersey Governor William T. Cahill announced a proposed massive sports and racing complex in The Meadows which the New York Giants will call home when they make their imminent move to New Jersey. Although HMDC is not saying it publicly, it's an open secret that the Commission hopes the complex will be a major catalyst in getting The Meadowlands redevelopment program under way.

Federal involvement

Much of the feasibility of building anything in The Meadows depends on adequate flood control measures. The U.S. Corps of Engineers reported, in a 1969 study, that without adequate flood control practices, damages to property in The Meadows would be around $5,868,000 annually. Most of the cost of adequate flood control would have to be met by the Corps.

But sources in Washington indicate that the Office of Management and Budget (OMB) early this spring advised the Corps to forget about building dams in The Meadows. Apparently, as part of a national policy, OMB wants to discourage the Corps from doing reclamation which would add population to already heavily populated areas. And if the Corps pulls out, it is highly unlikely that New Jersey's Department of Environmental Protection would see fit to foot the bill.   HMM
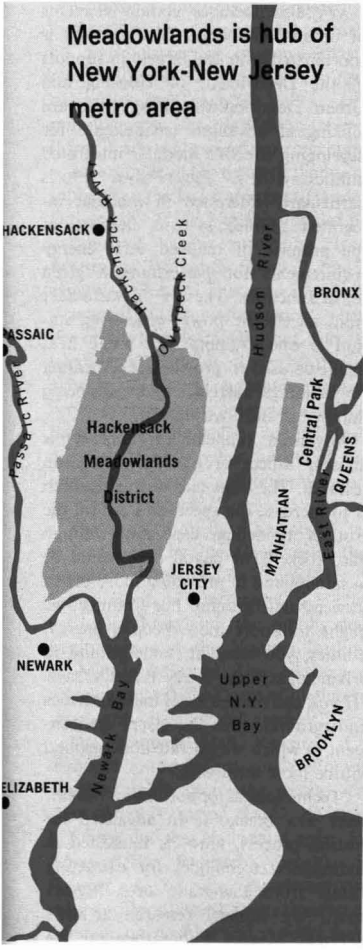
Federal research for long-term goals

The RANN program of the National Science Foundation is problem-oriented research at its best in search of knowledge for solutions to societal problems

RANN (Research Applied to National Needs) is housed in the newest directorate in the National Science Foundation (NSF), Research Applications. The RANN program is slightly more than one year old and supports problem-oriented research, applied or basic. The inclusion of applied research in the NSF charter was made possible by the NSF Amendments Act of 1968. Following the change in the charter, NSF created the IRRPOS (Interdisciplinary Research Relevant to Problems of Our Society) program in early 1970. This became a new program in the research directorate of NSF and brought together interdisciplinary teams—economists, social scientists, environmentalists, and the like—to work on societal problems. When RANN was created in March 1971, it was organized to include the IRRPOS projects and other established NSF programs as well as some entirely new programs.

"One of the first challenges that had to be met in developing the RANN program was to achieve effective coordination with the topical programs in other federal mission-oriented agencies to ensure that the RANN program complemented and supported these programs," says RANN's director Alfred J. Eggers, Jr. "The research we support in RANN strongly relates to the longer range and special requirements of other agencies. We support research on problems that overlap or fall between mission responsibilities of other agencies."

RANN involves about 65 people at NSF headquarters in Washington, D.C. "We do not do any in-house research," Eggers says. "All of the RANN research is carried out by universities, national laboratories, nonprofit institutions, and, to some extent, industry. The approximate splits are universities, up to 75%; nonprofit organizations, 10%; national laboratories, 12%; and industry, the remaining few percent."

Advanced technology applications

Eggers explains that there are four major divisions of RANN (see box) and offers some insights to RANN research. "Within the Advanced Technology Applications (ATA) program there are

four breakouts," Eggers says. "The first—the energy research and technology (ERT) element is, in fact, the single largest program in all of RANN. The funding level here is approximately $10 million." A first component of the ERT element is aimed at a study of energy systems which takes a total look at the problem, including everything from power plant choice and power plant siting to transmission systems and environmental impact of alternate energy sources.

Another component is devoted to energy resources and deals primarily with research on new technology to improve the utilization of existing energy resources. This program, too, has significant environmental concern. "In this area, for example, RANN supports a strong university research effort on the fly ash problem that is associated with the burning of low-sulfur fuels," Eggers explains. "The results from this research could be used to help design a better electrostatic precipitator, for example. What's involved is a deeper understanding of the physics of the problem of precipitating out fly ash."

In the third component—energy conversion research—the major effort is on solar power systems. Research is focused on both thermal collector and photosynthetic processes. RANN also has a strong research effort in advanced transmission technology. "We're particularly interested in super-conducting

RANN director Eggers. *"The name of the game is to support those new ideas that are ready to be applied in hard-hitting research efforts."*

technology for high-power transmission," the RANN director says.

The ATA program also includes elements of earthquake engineering, urban engineering, and technological opportunities. Earthquake engineering is particularly concerned with the issues of how to design structures of all kinds—for example, dams, buildings, and transmission lines—so that they will be more effectively resistant to earthquakes. The major research centers in this effort include Cal-Tech, University of California (Berkeley), University of Illinois, Purdue University, and MIT.

ATA also includes certain elements of urban technology. This research is coordinated with and largely in support of the Department of Housing and Urban Development (HUD). "We are looking at advanced technologies for developing effective modular integrated utilities systems," Eggers says. "HUD is particularly interested in modular integrated utilities systems because of the promise of reduced total energy requirements for performing a given set of functions. The use of waste heat from an electric power generating station is one example; the waste heat might be used to provide space heating for buildings, thereby avoiding its being dumped in the environment."

Advanced tunneling technology is another aspect of RANN's ATA urban research. The basic aim of this research is to increase the speed and reduce the cost of tunneling, especially through hard rock. "The payoff here would be in mining and in providing more urban services underground. For example, we might transport more people, energy, utilities, you name it, underground in urban areas," the RANN director says. "If you can move a lot of these activities underground, then the visual environment in which we operate aboveground will be more attractive."

"Technological opportunities" is another ATA breakout. In advanced industrial process, RANN is interested in finding new techniques for extracting metals from low-grade ores. Eggers says, "We support research at MIT's National Magnet Laboratory on the

use of high-intensity magnetic fields to remove 'nonmagnetic' metallic compounds from low-grade ores. Also in this area, we are interested in the development of new enzyme technology, particularly in relation to so-called immobilized enzymes—those that remain bound to the walls of enzyme reactors. Research is under way at the University of Pennsylvania, for example, on enzymes to eliminate phenols from industrial waste waters. Another effort in advanced industrial processes is taking a look at more mature industries with two aims in mind—increased productivity and reduced pollution."

Environmental systems and resources

The second major division within RANN (see box) is divided into research in the following areas:

• regional environmental systems
• weather modification
• trace contaminants

"In regional environmental systems," Eggers explains, "we support research on four classes of systems—coastal regions like the Chesapeake Bay, river basins like the Tennessee Valley, semi-primitive areas like the Galatin Canyon (Mont.), and urban-rural environments."

An example of the research that RANN supports in the latter area is at Harvard University. "It involves the study of the urban-rural region stretching from Boston to Plymouth, Mass.," Eggers explains. "We are interested in the environment under circumstances where the urban area is moving out into the rural area. This is a fairly rapidly urbanizing area and one that is imposing very important problems, including those of land use policy, zoning, waste disposal, water supplies, effects of new highways, airports, and other developments of rural areas."

The research on the Chesapeake Bay is performed by the Chesapeake Bay Research Consortium—comprised of Johns Hopkins University, the University of Maryland, the Smithsonian Institution, and the Virginia Institute of Marine Sciences. This research is coordinated with the Corps of Engineers, NOAA, and other federal agencies.

The National Hail Research Experiment is the biggest single effort in weather modification—the second segment of this major RANN division. Managed by the National Center for Atmospheric Research (NCAR) in Boulder, Colo., the experiment involves principal investigators from seven different universities and support from

five federal agencies; NSF/RANN has the lead federal responsibility.

"Of course, the reason we are interested in modifying hailstorms is to make them less destructive," Eggers explains. "In the agriculture area alone, hailstorms destroy as much as $300 million worth of crops each year. The basic objective of the experiment is to reduce the size of hailstones from a storm and thereby reduce their destructive effect."

The Hail Experiment is being funded at an annual level of $2–3 million. Field tests will start this summer and Eggers expects them to continue for several years. The main test area is a 600 sq mile area along the borders of Colorado, Nebraska, and Wyoming.

MetroMex is another weather modification research project in which RANN is involved. This project supports research in metropolitan St. Louis and vicinity on inadvertent weather modi-

RANN program at a glance

Major divisions

Advanced technology applications $19.5 million

Environmental systems and resources $19.5 million

Social systems and human resources $12 million

Exploratory research and problem assessment $5 million

Total $56 million (1972 fy)

Funding

million of dollars

request $80

estimate $56

$34

$12

1970   1971   1972   1973
Fiscal year

fication. "There is some evidence already that the amount of heat plus the pollution that goes into the atmosphere can modify the weather in and around St. Louis," says Eggers. "The weather in the area is monitored, and an attempt is being made to determine the correlation between the thermal and particulate loadings in the atmosphere and the effects on weather. A number of agencies are involved with Metro-Mex; EPA has the lead federal agency responsibility."

The trace contaminant work is concerned with the routes, targets, and rates of flow of trace contaminants in the environment. At present, special emphasis is on heavy metals with mercury and lead receiving major emphasis. Research in this area is closely coordinated with and primarily

in support of EPA, the Department of Agriculture, and the Food and Drug Administration, but Eggers says, "We support research by a team from the University of Missouri at Rolla on the cause and effects of effluents from the operation of lead mines (in the lead belt of Missouri) on hardwood forests and surrounding areas." This study offers another example of cooperation— the University of Missouri with the U.S. Forest Service and industry (the lead mine company)—to deal with a common problem. In the case of mercury, RANN supports studies on ion exchange resins for removing the metal from living organisms including man. This research is under way at the University of Rochester.

Social systems

Municipal systems and services and the upgrading of the cost-effectiveness of these services are the main concerns of RANN support in the social systems and human resources area. Examples here include studies by university teams who work in municipalities. A specific example is work with the New York EPA on problems of improving the productivity of the New York solid waste disposal service. A university team from the Stony Book campus of the State University of New York joined in this effort and contributed significantly to identifying operational means of improving productivity of the sanitation service.

Interim description and guidelines for proposal preparation for research under RANN are described in the publication, NSF 71-21, dated September 1971. Good new proposals are welcome, says NSF.

SSM

A monitor for 22 water pollutants

*The Enviro Monitor makes a continuous record of
pollutants and controls unattended operations at
remote locations under adverse weather conditions*

Industrial pollution control managers who are watching for monitors to record and control processing streams from their plants should sit back and take a look at what the new Enviro Monitor of Enviro Control (Washington, D.C.) is doing for some users in different locations in the U.S. Enviro Monitor is an all-weather monitor for as many as 22 parameters. It can be rigged to give a sound or light alarm when a particular parameter exceeds a preset value. It can also provide a permanent record of all parameters monitored.

Enviro Control, Inc., a subsidiary of Diversitron, Inc., was formed in September 1970 and although the first public announcement of its monitor came only at last year's meeting of the Water Pollution Control Federation (San Francisco, Calif.), a lot has happened since then. At press time, several users had told ES&T of their experiences with the Enviro Monitor and several others told of plans to get their hands on a monitor to check it out for their monitoring and control needs.

Who's using it?

Desert Research Institute (Las Vegas, Nev.) is using the monitor to record effluents from certain chemical and metal refining processing operations in the region. These industrial wastes are disposed of in a ditch, and the monitor has been placed at the end of the ditch to record several characteristics of the wastes. The continuous monitoring record is being established to see if there is any contamination of groundwaters which may eventually find their way to nearby Lake Meade. The monitoring program is part of a project supported by a four-year grant, totaling about $600,000, from the Environmental Protection Agency.

Alan Peckham, assistant director of the Center for Water Resources Research at the Institute, is also project director for the EPA grant. He tells ES&T that the grant has been in effect for two years and that, other than the Enviro Monitor, "we haven't found a monitor that we could operate under battery power in a remote location and leave out of doors under a wide range of climatic conditions." The parameters that are being checked in this desert application are conductivity, pH, temperature, and chloride.

Engelhard Industries (Newark, N.J.) uses the monitor to record effluents from its metallurgical separation operations. The parameters that are being continuously monitored are conductivity, copper, pH, and turbidity. Walter Drobot, engineering consultant, says Engelhard is using the monitor today for exploratory work but plans to monitor treatment processes and resultant effluent streams.

Municipal waste treatment operations are also finding the monitor useful. Levitt & Sons, one of the nation's largest home builders, uses the monitor at

Winslow township (N.J.). In this application, three parameters—dissolved oxygen (DO), pH, and temperature—are checked. The DO content of the aeration basin wastes must be carefully controlled before tertiary treatment of the wastes can proceed. Stanley Dea of the Levitt office at Lake Success, N.Y. says the unit works well on a daily basis to control and monitor the extended aeration of the process. The monitor is used to control the rate of oxygen introduction into the effluent in an aeration basin. Further details of this operation were reported at last month's meeting of the Instrument Society of America in San Francisco.

Another user is Mannington Mills (Salem, N.J.), a manufacturer of floor covering using latex. This company uses the monitor to record pH and to control addition of alum to its process waste waters. At a certain pH, the latex is flocculated by the addition of alum.

The pulp and paper industry is another potential user of the monitor. Its National Council for Atmospheric and Stream Improvement Council is checking the application of the monitor to this industry. Initially, the Council is interested in total oxygen demand (TOD), pH, sodium, chloride, and temperature.

What's ahead?

At press time, some active negotiations were under way with other users, including a food processing firm in Oregon, a leather tanner in Maryland, a canner in Delaware (interested in DO, temperature, pH, and turbidity), a refinery in Chicago (for DO, pH, conductivity, and chloride), and a plating plant in Oklahoma (for copper, cyanide, cadmium, chromium, and pH).

Roy Ricci, marketing manager for Enviro Control, says that the 22 parameters cover many of those included in the permit applications required by the Corps of Engineers. SSM

Advantages cited for monitor

Some of the advantages Ricci cites for the monitor are:

- range of operating temperature (−20° to 130°F)

- unattended operation

- battery-powered options

- operation in a submersible mode or a flow-through assembly

- sensor location independent of the monitor

- modular design for matching any industrial application.

Pollution-free power for the automobile

ES&T editorial staffers Marty Malin and Carol Lewicke
look at the progress made in controlling auto emissions
and the prospects for improvement in the future

They say the neon lights are bright on Broadway but sometimes it's pretty hard to tell because you can just barely make them out through the soupy air that chokes midtown Manhattan.

In Manhattan, as in major metropolitan areas across the nation, the automobile is without peer as a source of air pollutants. The experts don't always agree on precisely how much the automobile contaminates the air, but the estimates generally converge around 60 wt % of all air pollutants—including those from incinerators, space heaters, power plants and other industrial sources—released to the air each year. So the fastest way to cut air pollution is to eliminate automobiles.

And the fastest way to cut your income tax is to stop working.

As a symbol of the American Way, nothing—not even Motherhood—can match the allure of the private automobile. Nobody we know of has any good statistics, but we have the distinctly uneasy feeling that there are more two-car families in America than there are two-child families. While the national birth rate would seem to be leveling off, the number of cars on the streets grows apace.

Those two observations have recently led someone more prescient than we to predict that by 1985, one out of every four cars on the New Jersey Turnpike will be driverless. Since, by most accounts at least, there won't be any fewer cars on the road in the years to come, the need to make cars that pollute less is all the more compelling.

The search for a more nearly pollution-free power plant for the automobile—spurred by emission limits prescribed by federal law for the 1975–76 model years—has picked up considerable momentum. If the activity at times seems to border on the frenetic, it's because Detroit is feeling the pressures of eroding lead time and feeling them intensely. Auto makers say the deadline for signing initial supply contracts and firming up production schedules for 1975 model year cars has already passed. And Detroit is both unanimous and vociferous in its opinion that the industry can't possibly meet the so-called "Muskie numbers" for emission levels derived by EPA from the Clean Air Act.

EPA talks tough

The Clean Air Act of 1970 as amended provides the basic legal incentive for cleaning up the internal combustion engine (ICE). The act calls for a 90% reduction of hydrocarbons and carbon monoxide levels—as measured on 1970 model year cars—for all 1975 model year cars. The same HC and CO standards apply to 1976 and later model year cars. The law also provides for a reduction of 90% in emissions of oxides of nitrogen (NO_x) as measured in 1971 model year cars. Translated into numbers published by EPA on the basis of emission measurements, the 1975 standards are 0.41 g/mile HC, 3.4 g/mile CO, and 3.0 g/mile NO_x. For 1976 model year cars, NO_x emissions must be reduced to the 90% figure of 0.4 g/mile.

(See "New blueprint emerges for air pollution control," ES&T, February 1971, p 106.)

The Clean Air Act allows manufacturers to apply for a one-year suspension of the standards and requires the EPA administrator to hold public hearings and issue a decision within 60 days from the date of request. The EPA administrator can grant a suspension if he determines that:

• the suspension is essential to the public interest or public health and welfare

• the company requesting the suspensions has made a "good faith effort" to meet the standards

• the company has established that emission controls are not available or have not been available long enough to allow compliance by the deadlines and

• a study by the National Academy of Sciences (NAS) and other information available have not indicated that technology, processes, or other alternatives are available to meet the standards.

The preconditions—all of which must be met—are undeniably tough, and EPA Administrator William D. Ruckelshaus has made it no secret that the agency intends to exact strict compliance.

Carrot and stick

While EPA is apparently bent on vigorous application of the stick provided by the Clean Air Act, the agency seems equally willing to ply the carrot. Through the Federal Clean Car Incentive Program (FCCIP) EPA is funding

incentive contracts and awards to encourage production of low-emissions vehicles.

FCCIP is a standard federal R&D contract program except for the fact that there's no front money involved. It's a three-phase, multivehicle testing and evaluation program for demonstrating vehicles designed to meet the 1976 emissions standards.

EPA evaluates vehicles in terms of emission characteristics, safety, performance, reliability, serviceability, fuel availability, noise levels, and maintenance costs.

In Phase I of the program, would-be contractors receive a one dollar token payment from EPA. The contractor then develops a vehicle at his own expense and submits certified, independent laboratory tests covering several operating parameters. If the vehicle meets established specifications—which are considerably looser than the 1975–76 standards—EPA leases the vehicle for a three-month period and the agency runs its own tests.

If EPA likes the prototype, the agency negotiates a contract for production and delivery of 10 additional vehicles. In the process, specifications are tightened considerably so that by the end of this second phase, the vehicle must meet the 1975–76 emission numbers. Phase III allows the government to purchase 100–500 vehicles for fleet demonstration programs.

The incentive part of the program is this. Following the completion of Phase I, if EPA accepts the vehicle for Phase II testing, the agency will reimburse the manufacturer for his R&D costs. Moreover, the manufacturer retains patent rights (one of the strings usually attached to federal money is the stipulation that patent rights be assigned to the government). Thus, if the development proves to be successful, royalties from licensing agreements could sweeten the pot considerably. In addition, the government will buy production vehicles at premium prices—up to twice the statutory price limit set by GSA on vehicles—after FCCIP is wound up.

By edict of the EPA administrator, FCCIP is restricted to three general types of power sources—gas turbines, steam engines, and stratified charge engines. The idea is not to duplicate research—such as that on catalysts—which is being done by the auto industry. Current participants in FCCIP are Austin Tool Co., Chemico, International Materials, Petro Electric, Paxve, Schwitzer, and Stone Industrial.

Cleaning up the ICE

The auto industry, of course, has been doing a lot of research itself, most of it aimed at patching up the ICE. By some standards, they've been remarkably successful—the ICE isn't nearly as dirty as it once was. Emissions from autos are decreasing at an increasing rate, according to S. L. Terry, vice-president for safety and environmental relations at Chrysler Corp. Carbon monoxide emissions from today's cars are about $1/3$ of those from cars made in the 1930's, according to Terry. "If the industry stopped doing anything," Terry maintains, "emissions would continue to decrease" as new cars replace old ones.

To a large extent, just tinkering with the plumbing and wiring of the conventional ICE has aided in cutting emissions significantly. In addition, adapting engines for use with alternative fuels—propane, methane, liquefied natural gas (LNG) and even liquid hydrogen—has received considerable attention. Using alternative fuel systems, either separately or in tandem with conventional gasoline burning engines, does not appear to be feasible at this time.

Most of the proposed alternative fuels are already in short supply and it is doubtful whether any fuel other than gasoline could be made available in sufficient quantities by 1975. The petroleum industry has already reallocated significant portions of its refining capacity at not insignificant cost to meet the anticipated need for lead-free fuels.

Recirculating exhaust

One method that shows promise for reducing NO_x is exhaust gas recirculation (EGR). Returning 10–20% of the exhaust to the intake manifold cuts thermal formation of NO_x by reducing cylinder temperatures. But there is a penalty for cleaner operation. Precise control of the amount of gas recirculated is critical, and only small errors can lead to stalls and poor engine performance. Usually, carburetion ratios have to be enriched with fuel to assure smoother performance. That results in a fuel penalty ranging anywhere from 5–20%

While Detroit is saying that the 1975–76 emission numbers are too tough for present technology, two environmental groups, the Natural Resources Defense Council (NRDC) and Center for Scientists in the Public Interest (CSPI) are sueing EPA Administrator William D. Ruckelshaus for not being tough enough.

NRDC and CSPI charge that Ruckelshaus "acted in excess of his authority" by promulgating standards that are less stringent than those mandated by the Clean Air Act. The groups say the standards for hydrocarbons are about four times as high as originally intended by Congress. The discrepancy comes about over the use of correlation factors to equate results of the 1970, 1972, and 1975 Federal Test Procedures (FTP).

Citing the legislative history of the act, the plaintiffs say original air quality goals proposed by NAPCA were designed to cut pollutants to levels compatible with the public health. The 1980 goal for hydrocarbons was about 0.25 g/mile, the level determined by NAPCA to be necessary for achieving satisfactory air quality. Plaintiffs allege, and defendant Ruckelshaus agrees, that the intent of the Clean Air Act was to move the 1980 goals up by five years to 1975. But there is wide disparity over whose conversion factors should be used. EPA says that in terms of the currently used 1975 FTP, the 0.25 g/mile standard is equivalent to 0.41 g/mile. The plaintiffs do the arithmetic differently and come up with a standard of 0.11 g/mile.

In the first place, plaintiffs say, NAPCA itself rejected correlation factors as illogical, because 1975 vehicles would have completely different emission control systems than 1970 vehicles, and the relationship between the 1970 FTP and the 1972 FTP established by 1970 vehicles would have no application to 1975 vehicles. Furthermore, even if correlation factors were admissible, EPA's use of 1970 vehicles rather than precontrolled 1968 vehicles to set standards is erroneous, plaintiffs contend, because 1970 vehicles had been gimmicked to beat the 1970 tests—a practice referred to in the industry as cycle beating. Good results on 1970 tests did not necessarily mean better emission control since diluting pollutants by increasing exhaust volume fooled the machines. The effect was to incorporate a degree of successful cheating into the 1975 standards. Such policies, charges Louis V. Lombardo, an ex-EPA employee who served as a consultant to CSPI, "is analogous to a judge first finding a tax evader guilty of taking an illegal tax exemption in 1970 and then declaring that the evader could take the same illegal tax exemption every year thereafter."

Ruckelshaus denies suspension requests

EPA's tough stance may not be as tough as it appears to be
since the decision leaves Detroit plenty of room to maneuver

EPA Administrator William D. Ruckelshaus made what he called "the most important decision EPA has faced to date" last month when he denied requests of five automobile manufacturers—Volvo, International Harvester, Ford, General Motors, and Chrysler—for a one-year suspension of the 1975 emission standards for hydrocarbons and carbon monoxide. And his decision surprised practically everyone.

At a press conference May 12, Ruckelshaus told reporters that he had reached his decision—and informed the White House of it—10 days earlier, but had refrained from announcing it until a formal, written opinion could be prepared. Furthermore, EPA's General Counsel John R. Quarles said the only advance warning the auto industry got was a phone call he made to each of the applicants 1 hour prior to the public announcement of the decision, which was delayed until late afternoon to avoid possible repercussions on the stock exchanges.

All of that seemed to signal an end to the recently well-publicized industry–Executive bedfellowship. Detroit issued tight-lipped "no comments" and auto manufacturers said only that they would "carefully study" the 40-page opinion handed down by the EPA administrator. The Natural Resources Defense Council (NRDC), one of several environmental groups which participated in the hearings, crowed that the decision served "notice on Detroit that its days of obstruction are over." (Attorney David G. Hawkins, Counsel for NRDC—whose suit against Ruckelshaus for allegedly failing to set sufficiently strict emission standards was dismissed May 5 by Federal Judge Gerhard Gesell—says that, in light of the adminstrator's decision, NRDC has not yet decided whether to appeal the ruling.)

EPA's toughness with Detroit may be more apparent than real. Those who read into the administration's decision a promise that 1975 model year cars will meet the emission numbers for hydrocarbons and carbon monoxide may well be disappointed.

With his decision to deny suspension, Ruckelshaus placed himself squarely in the "strict constructionist" column—much to the chagrin of company counsels, environmental lobbies, and some newsmen who had openly bet on a suspension with simultaneous promulgation of more relaxed interim standards. The EPA administrator has said repeatedly that his decision would be based on the fact that the auto makers had not clearly demonstrated that presently available technology is inadequate to meet the standards.

Ruckelshaus does not say that technology is available. He says only that it "probably" is. And since auto makers couldn't prove that it isn't, he was legally constrained to rule against their request. The second part of the four part test (see p 512)—the good faith issue—didn't even enter into the decision, since the question of technical feasibility was unfavorably resolved.

EPA's decision left Detroit plenty of room for maneuvering. "I want to stress that the [technical feasibility] issue is a close one," Ruckelshaus said, leaving the door wide open for reapplication for a waiver when the auto makers feel they can marshal additional facts to support their contention. And at least one of the five applicants—Chrysler Corp.—is rumored to be considering trying to overturn the ruling in the courts.

Some hint of things to come may be gleaned from the opinion itself. The language is not unnecessarily rough nor does one detect a punitive tone. There are few admonitions, and any questioning of industry practices is done without being abrasive. The document also spells out what the agency will be looking for in case the auto makers can persuade EPA that technology is not available and the question of good faith has to be probed. EPA itself clearly expects to reconsider its findings at a later date.

Of course, purely political considerations appear to weigh heavily in whether or not Detroit will ever meet the Muskie numbers. National elections are only six months away. The present administration can ill afford to appear to be "soft on pollution" now. The fact that the White House has not commented on the hearings or EPA's decision lends credence to the conjecture that the Nixon administration does not wish to make an issue of the environment in the 1972 campaign. By avoiding comment on the issue now, the administration may be freer to press for relaxed standards should it wish to do so later. It's also no secret that Detroit will lobby hard—both on Capitol Hill and within the Executive—for changes in the law.

EPA's Ruckelshaus
The issue is close

and generally increases emissions of hydrocarbons and carbon monoxide.

Thermal reactors offer yet another partial solution for cleaning up exhaust. Such reactors usually take the form of greatly enlarged exhaust manifolds which provide a longer detention period for gases at elevated temperatures. The greater detention time allows more complete oxidation of carbon monoxide and unburned hydrocarbons to carbon dioxide and water. Thermal reactors have been designed which operate either on lean or rich fuel-air mixtures. But the high temperatures beneficial to CO and HC destruction only aggravate the problem of thermal NO_x formation.

Other engine modifications under intensive study by Detroit and some foreign auto makers are designed to offer more positive control over the combustion cycle. They include electronic fuel injection, quick heating intake manifolds, spark retard systems, new ignition systems which don't depend on spark plugs, and cylinder head modifications.

Catalysts

Despite encouraging results obtained by internal modifications of the gasoline engine, auto makers agree that their only hope of meeting the stringent 1975-76 standards rests with catalytic control devices.

Catalyst makers group catalytic units by physical types (monolithic or pellet), chemical types (oxidation or reduction), and composition (base or noble metals). A catalytic device generally consists of an active ingredient—a catalyst—deposited on some sort of support matrix and sealed in a "can." The catalytic device may then be positioned in the exhaust stream at the tailpipe (retrofitted) or incorporated into the exhaust manifold near the engine.

Much of the knowledge about catalysts remains heavily shrouded in secrecy, unknown even to the auto manufacturers who routinely sign agreements with catalyst makers promising not to analyze catalysts even in the event that they fail. Catalyst support materials are usually proprietary ceramics or alumina formulations. The physical configuration of the support may be pellets or beads, honeycombs, rolled or stacked plates. The idea is to achieve a support which will not degrade, break down, or shrink appreciably with high exhaust temperatures or vibration, but which will provide maximum area for catalytic activity and resist sloughing of the catalytic formulation.

During catalytic reactor manufacture, the support—or carrier—is charged with catalytic formulations. Industry spokesmen are tight-lipped, but it is generally thought that liquid formulations are preferred to solids because of superior adhesion characteristics. The catalyst itself may be either a noble metal such as platinum or palladium, or an exotic combination of base metals such as cobalt, copper, molybdenum, and certain rare earths.

Oxidation catalysts, used to convert hydrocarbons and carbon monoxide to carbon dioxide and water must generally be supplied with auxiliary air to do their job well. It is this type of catalyst which shows most promise. Reduction catalysts which convert NO_x into nitrogen gas or ammonia, depending on the technology, must operate in oxygen-poor environments. Reduction catalysts are not nearly as well developed as oxidation catalysts.

Catalysts available to date have shown rather poor durability, although some manufacturers claim to have catalysts which will last up to 25,000 miles. As a rule of thumb, however, catalysts with good durability have shown relatively poor activity. The converse holds true as well. Catalysts which show the most promise for meeting the 1975-76 standards are usually seriously impaired after 5000 miles of driving. Lead, sulfur, and phosphorus seriously interfere with catalytic performance and to date no catalytic device available has been able to stand up to the 50,000 mile maintenance free conditions required by EPA, no matter what the level of catalytic activity. Auto industry spokesmen also point out that tests on many of the longer lived catalysts have been carried out with essentially "sterile" fuel—fuel which contains about 100 times less lead than EPA will allow to be present in so-called lead-free fuel.

Despite all those problems, however, Detroit still has high hopes for catalysts. Ford recently signed a contract with Engelhard Industries to provide catalysts for half of its 1975 model year cars and is angling for suppliers for the remaining half.

Even with the catalysts—which Ford, like most other car manufacturers, will use in a highly integrated system with reactors, EGR, improved choke, throttle and ignition systems—the best Ford can do for 1975 is 1.6 g/mile HC, 19 g/mile CO, and 2.0 g/mile NO_x for 50,000 miles. GM says its integrated system could potentially achieve 0.3 g/mile HC, 2.5 g/mile CO, and 2.0 g/mile NO_x at

very low mileage, but that after 5000 miles the numbers will be above the standards.

Stratified charge

One modification of the ICE which may hold promise for the far term, if not by 1975, is the stratified charge engine—so termed because of the stratified air-fuel charge to the cylinder. Fuel is injected with only part of the intake air at the spark plug, the remainder of the intake air serving to reduce pollutant formation. Two major variations of the stratified charge engine are currently under development. One version, developed by Ford for the U.S. Army Tank–Automotive Command has given emission levels below the 1975 standards for low mileage. Called the PROCO (Programed Combustion) engine, it has recently been installed in test vehicles together with catalytic devices and EGR systems, Ford says, but the engine is prone to misfires, and durability of system components is low.

A second variant on the stratified charge engine uses a divided cylinder. The initial air-fuel mixture is ignited in a precombustion chamber and the exploding gases are mixed with intake air in the second chamber.

While the stratified charge engine is promising, it still appears to be a long way from the assembly line. Ford estimates that if development work on the engine could be completed by the end of December, 1974, the company could make "limited use" of the PROCO in 1979 model cars.

Wankel

The ICE that has received the lion's share of interest and publicity from the automobile industry is the Wankel. Among its major advantages are fewer parts, more power per chamber, and a smaller size. It should be cheaper to make than the conventional reciprocating piston ICE. But it has a serious flaw— it's dirty. It emits more pollutants than reciprocating ICE's but that may not be as bad as it sounds. Hydrocarbon emissions are as much as twice those from uncontrolled piston engines, but carbon monoxide emissions are not much worse. Furthermore, NO_x emissions are 20-60% lower than for piston engines, depending on various design parameters, and cleaning up NO_x is generally acknowledged to be a tougher job than controlling HC and CO. Since the Wankel need be only about $1/3$ the size of a piston engine to yield comparable horsepower, there is more room

under the hood for pollution control equipment.

The fundamental unit of the Wankel is a chamber shaped like an overweight figure eight. In the chamber is a rotor—roughly triangular in shape—with seals on each of the three apexes. Power to the wheels is provided by a gear arrangement in the center of the rotor which turns a shaft.

The rotor divides the chamber into intake, combustion, and exhaust zones. The air–fuel mixture entering from the intake port is compressed in the combustion zone where it is ignited by a single spark plug. The explosion forces the rotor to spin, ejecting combustion products from the exhaust port, and the process is repeated.

Unlike most of the other power plants of novel design, you can buy the Wankel today. Japan's Toyo Kogyo Co., Ltd., ships some 2000 Wankel-powered Mazdas to the U.S. each month, mostly for sale in California.

The major technical problem with the Wankel to date—apart from its heavy emissions—has been failure of the apex seals. That problem seems to have been solved, however. Laboratory prototypes have reportedly been made with seals that last more than 100,000 miles, and Mazda seals are guaranteed for 30,000 miles although Toyo Kogyo says they will last much longer.

Among American manufacturers, GM is in the best position to exploit the Wankel should it ever decide to do so. But periodic rumors from Detroit that

GM will put Wankels into production in the near future are quickly scotched.

Late last year, GM signed a non-exclusive licensing agreement with Audi-NSU; Wankel, GmbH; and Curtiss-Wright. The contract called for an initial payment of $5 million at the end of 1971 and $10 million payments at the end of each year for the next four years with a final $5 million payment at the end of the fifth year. For this outlay, GM has the right to make and sell the Wankel worldwide. GM can end its obligation at the end of any year.

Shortly after GM's decision to test drive the Wankel, Ford acquired the right to make the engine in West Germany through its subsidiary Ford-Werke, A.G. Both Chrysler and American Motors are quietly evaluating the Wankel although neither has a license to manufacture or sell the rotary power plant.

Alternatives to the ICE

As the lead times for the 1975–76 model years steadily diminish, it looks like the cleaned up ICE will be the only power plant on Detroit's assembly line for the near term. But there are several other less developed power plants which could find a place in the transportation market within the next two decades.

One of the more frequently mentioned is the electric car. Although the electric-powered vehicle promises zero pollution from the tailpipe, critics point out that generating stations do pollute and that the power needed to recharge storage

batteries will not be easy to obtain. The problem with electric passenger vehicles to date has been largely one of finding battery systems with sufficient storage capacity per unit weight to allow reasonable ranges between recharge and still provide the roominess of today's vehicles. Switching equipment and controls remain expensive, but it is reasonable to expect that mass production techniques and advances in technology could make the electric power plant competitive with the ICE, at least for some uses. Electric automobiles might be particularly useful under the "two-car strategy," frequently mentioned by EPA, where they could be used for short-distance commuting and driving around town.

Diesels have also been frequently mentioned as alternative power sources, since they emit practically no carbon monoxide. Theoretically HC and NO_x standards for 1975 could be met—but only theoretically, because to date there are no acceptable federal test procedures for reliably measuring pollutants applicable to the diesel. And meeting the 1976 NO_x standards borders on the impossible. Using EGR and modified engine designs it might be possible to attain NO_x levels of about 1.1 g/mile, says Rudolph Uhlenhaut, director, passenger car development, Daimler-Benz A.G. But since CO is not present in diesel exhaust, using a catalyst to reduce NO_x further is not possible. Furthermore, the diesel emits far more particulate matter than the ICE. "The diesel is not a simple magic bullet solution to the emission control system," Uhlenhaut says, adding bluntly, "It is not an alternative to the gasoline-powered engine."

Various other alternatives, including Sterling cycle engines—based on the alternate heating and cooling of an entrapped gas (typically hydrogen) which powers pistons—appear to be much further down the road. Among those frequently discussed but still in early development stages are cars powered by fuel cells or ammonia-burning engines, and hybrid vehicles, which use conventional power sources coupled with more experimental ones such as electric motors, flywheels, or cleaner fuels.

Gas turbine

Recent advances in engineering, however, have put two strong contenders into serious competition with the ICE—gas turbines and steam engines. The gas turbine has many inherent ad-

Williams Research gas turbine conserves waste heat to boost efficiency

air intake
compressor
rotating fuel inlet
combustion chamber
1700°F
igniter
370°F
1150°F
compressor turbine
power turbine
500°F
1280°F
heat exchanger
exhaust
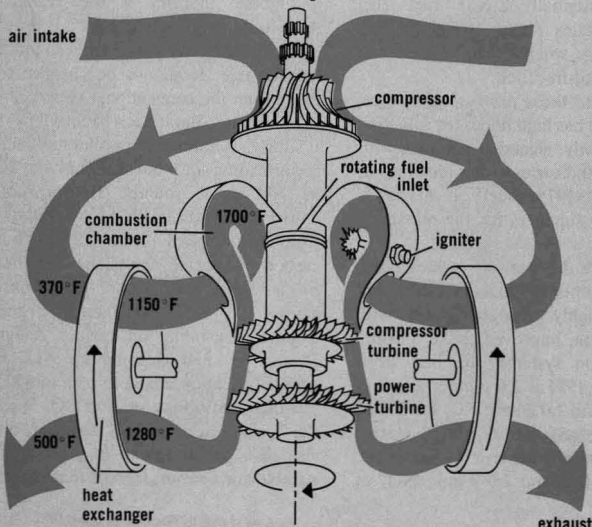
Peppy Wankel pollutes more than conventional ICE, but may be easier to clean up

exhaust port

rotor

intake port

shaft

spark plug
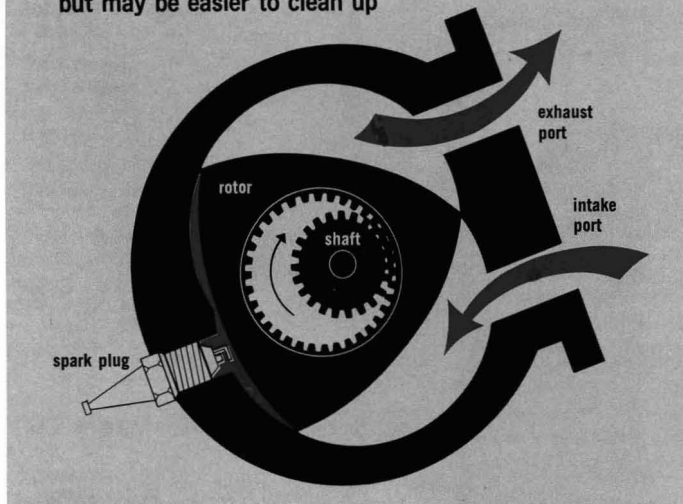
vantages over the ICE. It has less than half as many parts and needs no cooling system. It needs no warmup and boasts vibrationless operation. It can burn a variety of fuels—kerosene, gasoline, or diesel fuel, to name a few.

Emissions measured on an 80 hp gas turbine developed by Williams Research Corp., Walled Lake, Mich., are within the 1975 standards. Emissions measured under the unrevised federal test procedure are 0.34 g/mile HC, 4.5 g/mile CO, and 2.15 g/mile NO_x (unrevised federal standards were 0.46 g/mile HC, 4.5 g/mile CO, and 3.0 g/mile NO_x). Williams Research President Sam Williams expects to meet the more stringent 1976 NO_x numbers as well.

In the Williams turbine, intake air is drawn into a compressor, squeezed to four times atmospheric pressure, and preheated as it passes through the front half of rotating heat exchangers. From the heat exchangers, the heated air travels to the combustion chamber into which fuel is sprayed and burned, raising the temperature to 1700°F. Hot gases spin the compressor turbine and then the power turbine which provides power to the rear wheels. Exhaust passes through the heat exchangers where it is cooled, and heat is conserved to preheat intake air.

Williams says his gas turbine could be ready for initial mass production as early as 1978. If auto companies decided by 1975 to go with the gas turbine, three years lead time would be available—sufficient to train personnel, retool, and realign supplies, Williams says. The major auto makers, while not as optimistic as Williams, are, nevertheless, interested in turbines. GM, Ford, and

Chrysler have ongoing turbine programs. If indeed there is to be an alternative power source for the auto in the next decade, it would seem that the turbine is a definite front-runner.

Steam power

Right behind the turbine, however, is the steam engine. The reason it's behind doesn't seem to be as much a matter of technical feasibility as the fact that Detroit has more solid in-house grounding in gas turbines. And the auto makers are extremely reluctant to take a private inventor's claims on faith and limited testing.

In principle, the steam car uses vapor from water or some other working fluid—typically fluorocarbons—to drive pistons or spin turbines. Several inventors have developed proprietary steam designs including William P.

Lear's vapor turbine which uses water—Learium III—as a working fluid (Lear Motors Corp., Reno, Nev.), Edward Pritchard's reciprocating piston steam engine using water as a working fluid (Pritchard Steam Power Pty., Ltd., Melbourne, Australia) and Wallace L. Minto's hybrid piston–turbine engine which uses freon as a working fluid (Kinetics Corp., Sarasota, Fla.)

Virtually all the faults of earlier steam cars such as the Doble, White, and Stanley, have been corrected. Because of monotube boiler designs which contain only small volumes of working fluids at a time, explosion hazards have been eliminated. Engineering has improved heat transfer surfaces, and conservation of fluid is no longer a problem.

One advantage the steam engine has over the turbine is that it is inherently quieter. Like the turbine, it runs on cheap, readily available fuels. Emission characteristics also look good. Tests on Pritchard's car, for example, showed no measurable HC, 0.47 g/mile CO, and about 0.6 g/mile NO_x. With further efforts at controlling NO_x, Pritchard's engine should meet or better the 1976 NO_x standards. Lear's steam turbine —a 220 hp diesel bus engine—emits 2.0 g/mile CO, 0.1 g/mile HC, and 0.35 g/mile NO_x—well within the 1975–76 limits. Minto says his engine emits less than "$1/200$th" the pollutants allowed by law.

Clearly the ICE faces some tough competition from the newcomers. Meeting the 1976 NO_x standards—unless those standards are seriously eroded in the interim—will require some major breakthroughs in technology and that could cause Detroit to reconsider its commitment to the ICE.

Steam bus. *Newsmen in Reno, Nev., queue up for ride in prototype*

Hg Cr
Fe Cd
Zn Ni
Cu
Al
Sb Pb
As

Detection of mercury in water courses and in fish life above the standards established by the U.S. Public Health Service and growing concern with lead as an environmental contaminant stemming from its wide usage as a gasoline additive have sparked general interest in heavy metals as potential hazards in environmental control. The metals of most immediate concern are: chromium, manganese, iron, cobalt, nickel, copper, zinc, cadmium, mercury, and lead.

These metals are widely distributed in materials which make up the earth's surface. Igneous rocks, for example, typically average about 5% iron and contain other heavy metals at various levels ranging down to about 20 ppm lead, which is a relatively scarce element. These rocks are constantly weathered and leached by rainwater, and yet the natural runoff in rivers, even in extreme cases such as the Colorado River, is remarkably free of dissolved heavy metals.

Several of the so-called trace metals fill essential roles in life processes— e.g., manganese, iron, cobalt, copper, zinc, and molybdenum, while others such as mercury and lead are regarded with more suspicion as potential cumulative poisons. A remarkable compatibility exists, however, between the chemistry of heavy metals as encountered in nature and living organisms.

Heavy metals occur largely in natural mineral form as sulfides, oxides, carbonates, and silicates. These natural compounds are usually insoluble in water and only very slowly broken down by weathering and exposure to rainfall and groundwaters. For example, rainwater containing dissolved carbon dioxide attacks basic rocks such as peridotite which may contain 50% magnesium oxide and selectively dissolves magnesium in association with the bicarbonate ion, while iron, which may be similarly dissolved, oxidizes to the ferric form and precipitates as highly insoluble ferric hydrate even

Removing
heavy metals
from waste water

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feature

*Pending water pollution legislation requires heavy metal
removal not only before industrial wastes are discharged into
navigable waters, but also prior to ocean or land disposal*

when pH is as low as 2. Other heavy metals tend similarly to follow the behavior of iron and precipitate in the oxide residue while magnesia is carried off in groundwater as bicarbonate hardness. The order of precipitation from dilute solutions as the pH is raised is as follows:

Ion	pH	Ion	pH
Fe^{3+}	2.0	Na^{2+}	6.7
Al^{3+}	4.1	Cd^{2+}	6.7
Cr^{3+}	5.3	Zn^{2+}	7.0
Cu^{2+}	5.3	Hg^{2+}	7.3
Fe^{2+}	5.5	Mn^{2+}	8.5
Pb^{2+}	6.0	Co^{2+}	6.9

Very small heavy metal ion concentrations can be expected in neutral solutions. Ferric ion concentration in neutral water solution may even be far below the parts per billion (ppb) range subject to practical measurement. Iron is an extreme case but even lead shows extreme insolubility; for example, lead ion concentration at equilibrium with water containing 5 ppm or more of carbonate ion is less than 1 μg/l. or 1 ppb.

The heavy metals are, for the most part, responsive to practical treatment methods which have already been developed and utilized for water purification and metal recovery operations. Treatment methods which should be considered include chemical precipitation, cementation, electrodeposition, solvent extraction, reverse osmosis, and ion exchange.

Chemical precipitation

The most generally applied treatment method, particularly where complex chemical compounds are not involved and economic recovery is not a consideration, is the typical lime treatment plant (Figure 1), because of its relative simplicity and low cost of precipitant. Removing such metals as copper, zinc, iron, manganese, nickel, and cobalt requires almost complete precipitation as the hydroxide with no special modifications.

For cadmium, lead, and mercury, precipitation may be incomplete, however, and a modified flowsheet employing soda ash (for lead) or sodium sulfide (for cadmium and mercury) may be required. Where chromium is present, reducing the solution with sulfur dioxide, ferrous sulfate, or metallic iron before lime treatment is necessary. Chlorination may be needed to break down complex organic metallic compounds before chemical precipitation.

Where strong acidic wastes exist, part of the neutralization with limestone may be somewhat less expensive than lime. However, limestone must be evaluated carefully for each acid waste since it may not be effective as theoretically indicated owing to particle coating, need for fine grinding, and pH limitation of calcium carbonate. For example, nickel sulfate–sulfuric acid solutions treated first with crushed limestone, then with hydrated lime, show:

	Soln A	Soln B
$NiSO_4$, meq/l.	4	100
H_2SO_4, meq/l.	4	100
Nickel, ppm	117	2,935
pH	1.8	0.8

Agitation in a rotating reactor for 30 min with $-10 +40$-mesh crushed limestone at a rate of 100 g/l., filtered:

pH	4.9	4.9
Nickel	unchanged	unchanged

Agitation of filtrate with two times equivalent of the nickel with calcium hydroxide for 30 min, filtered:

pH	10.0	11.1
Ni, ppm	<1	<1

In the first step, coarsely crushed limestone readily reacts with the free acid but does not precipitate nickel. In the second step, hydrated lime precipitates the nickel below the detection point with sulfide ions. The nickel hydroxide precipitate settles quite readily and filters without difficulty.

The economic attraction of limestone is readily apparent when cost comparisons are made on an equivalent basis of contained calcium oxide (CaO). However, it is rarely possible to utilize the cheapest material—lump limestone—to anything approaching 100% effectiveness of its contained CaO. This is not true for pulverized limestone where neutralizing some mineral acids can be accomplished with high efficiency and pH below 5. To produce a neutralized effluent with a pH of 7 or above, either hydrated lime or quicklime (pebble lime) must be used.

Electrodeposition

Some metals found in waste solutions can be recovered by electrodeposition techniques, using insoluble anodes (Figure 2). Acid pickling of copper as done in wire drawing provides an opportunity for applying this method. Typical practice involves dipping the wire coils at intermediate stages of drawing in hot solutions of acid (10% H_2SO_4, for simple cleaning or 10% H_2SO_4–5% HNO_3, $Na_2Cr_2O_7$ for other oxidant for pickling). In cleaning, oxides are removed from the surface,

but when oxidants are used, the metal is etched. From 0.5 to 3% of the total copper fed to such operations may be dissolved. The copper content of solutions increases as the acid is consumed, and the dissolution rate declines. Finally, solutions must either be processed or replaced.

Spent solutions resulting from sulfuric acid cleaning of copper may be saturated with copper sulfate in the presence of residual acid. These are ideal for electrowinning where high-quality cathode copper can be electrolytically deposited while free sulfuric acid is regenerated. Anolyte from electrodeposition cells, after minor adjustments, can be recycled to the cleaning operation while cathode copper can be exchanged for credit to the basic supplier of copper bars. This type of recovery operation can be profitable while at the same time solving the bulk of the effluent disposal problem.

After the acid dip, copper coils must be thoroughly washed. Dragout (or carry forward) of acid copper sulfate solution can be minimized by use of a countercurrent system of first dipping in make-up water, but the final washing,

to be effective, inevitably produces a large volume of dilute acid–copper sulfate solution. This same solution may also carry finely divided cuprous oxide which is not readily soluble in dilute sulfuric acid solutions. Typical composition of the wash effluent may average 0.5 milliequivalents (meq) of copper per liter (0.5 meq Cu/l. = 15 ppm Cu) and 0.5 meq/l. H_2SO_4, along with other elements present in plant water supply.

Ion exchange is a possibility for recovering copper from weak solutions as a copper sulfate solution of sufficient concentration to warrant charging to the electrolytic recovery system. The presence of free acid as well as other metallic ions can reduce the efficiency of this operation and also not recover cuprous oxide which may approach colloidal dimensions. Thus far, straightforward lime or lime-soda precipitation seems to provide the greatest practical promise. The general procedure is to dose the water effluent continuously with hydrated lime which may be supplemented with calcium carbonate or soda ash (much as employed in hot lime-soda treatment of bicarbonate hard water).

Liquid-solids separation may be ac-

complished after appropriate reaction time by thickening and filtration or centrifuging. Solids are mainly a mixture of copper hydroxide and basic carbonate plus calcium sulfate and carbonate. In some instances, these solids have been sold for the copper content, but more frequently must be disposed of as landfill. The filtrate carries some sodium sulfate but is suited for repetitive reuse in many plant operations or direct discharge to a diluting stream or sanitary sewer.

Cementation

Another method to remove metals from waste streams, particularly where metal recovery is desirable, is cementation. Contracting a metal-bearing solution with the correct metal powder or scrap will precipitate certain selected metals as metallic "sponge" (Figure 3). In practice a considerable spread in the electromotive force between metals is necessary to ensure adequate cementation capability.

The most commonly used cementation metal is iron—often in the form of shredded detinned cans—and in the case of copper-bearing waste streams,

Figure 1

Typical lime treatment process

Figure 2

Typical electrolytic recovery plant

Figure 3
Copper cementation plant

Copper bearing solution — Iron scrap

Cone precipitators

Clear filtrate

Sponge copper

Lime treatment (Figure 1)

settlers" are used, and countercurrent flow, where feed and solvent enter at opposite ends of the system, is preferred.

Ultrafiltration

Reverse osmosis or ultrafiltration consists of semipermeable membranes which act basically as "molecular sieves" permitting soluble compounds having various molecular size ranges to pass through their pores. The membranes are synthetic organic materials and are frequently laminated. When set into pressurized ducts, these elements permit continuous flow, with the filtrate passing into parallel chambers. Pressures range from 50 to 600 psi, and 50 gal./ft^2/day, is the capacity. Power required for pumping amounts to about $^1/_4$ to $^1/_2$ hp/1000 gal. treated.

This technique has promise for removing and recovering metal ions from waste solutions, for, on a test scale, it successfully treated tertiary stage biological sewage and produced high-purity effluents.

Ion exchange

Developed to a high degree of efficiency for the recovery of uranium from its ores, ion exchange resins are well-known. In addition to systems that handled clarified solution, the so-called "resin-in-pulp" method, in which the resin is introduced directly into the ore pulp, works successfully. After separating the loaded resin, the metal is recovered in a more concentrated form by elution with suitable reagents.

Previously, industrial waste treatment has not responded well to this form of processing. This has been attributed to destructive effects of certain impurities on the resins, interfering ions, limited

offers the possibility of recovering most of the copper as a salable by-product called cement copper. The operation is carried out in an acid solution and results in dissolution of iron which is later removed by lime precipitation along with any residual copper.

A process employing cementation has been developed by the Connecticut Research Council and is installed in at least one brass mill for recovering copper from waste pickling liquor. Using zinc dust as a precipitant for gold and silver from cyanide solutions is a widely used cementation process that has interesting potential for recovering certain small amounts of metals, such as cadmium, mercury, and lead from industrial wastes.

Solvent extraction

One treatment scheme, liquid ion exchange, used in chemical and metallurgical industries involves extracting a particular metal from solution by contacting the solution with an organic reagent. This reagent reacts preferentially with the heavy metal ion of interest and converts it to a form soluble in appropriate organic solvents. A water-immiscible solvent for the organic reagent, such as kerosene, is intimately mixed with water, and then the two phases are separated. Acid-treating the organic fraction then releases the metal in a concentrated, water-soluble form which can be handled by conventional recovery methods.

This process, which has been adopted successfully by the uranium and copper industries, has possibilities for recovering metals from industrial wastes. A number of different types of "mixer-

Heavy metals found in major industries

	Al	Ag	As	Cd	Cr	Cu	F	Fe	Hg	Mn	Pb	Ni	Sb	Sn	Zn
Pulp, paper mills, paperboard, building paper, board mills					●	●			●		●	●			●
Organic chemicals, petrochemicals	●		●	●	●		●	●	●		●			●	●
Alkalis, chlorine, inorganic chemicals	●		●	●		●	●	●			●			●	●
Fertilizers	●		●	●	●	●	●	●	●	●	●	●			●
Petroleum refining	●		●	●		●	●	●			●	●			●
Basic steel works, foundries			●	●		●	●	●	●		●	●	●	●	●
Basic non-ferrous metals–works, foundries	●	●	●	●	●	●	●	●		●		●		●	●
Motor vehicles, aircraft – plating, finishing	●	●		●	●	●			●			●			
Flat glass, cement, asbestos products, etc.					●										
Textile mill products					●										
Leather tanning, finishing					●										
Steam generation power plants					●										●

Note: plastic materials, synthetics; meat products; dairy products; fruits and vegetables; grain milling; beet sugar; beverages; and livestock feedlot industries have no heavy metal discharges.

loading capacity, high cost of operation, etc. If a selected purified dilute stream from pretreated waste were contacted with a suitable resin, however, a successful recovery step might result.

Activated carbon adsorption

Similar to the resin-in-pulp technique, activated carbon adsorption, however, employs activated carbon instead of synthetic resins. Used successfully in commercial operation for extracting gold from cyanide solution, activated carbon adsorption has a number of advantages over ion exchange.

Relatively coarse (10 mesh) activated carbon is contained in stainless steel cylindrical screens which are submerged in the pulp, and the flow of suspended carbon from one screen to the next is countercurrent to pulp flow. The loaded carbon is then eluted with hot cyanide solution or sodium sulfide which dissolves the gold for later precipitation with zinc dust, and the carbon is recycled. The carbon is periodically reactivated by heating it in a small rotary kiln. Using activated carbon for metal removal has considerable promise in industrial waste treatment for removing the last trace of metal (in the range perhaps of 1 to 2 ppm) following electrodeposition or cementation, such as in the processing of electroplating wastes.

Each waste treatment problem must be regarded as a special case demanding a thorough study of the chemistry and economics involved. One of the critical factors, for instance, is the metal concentration in the solution to be treated. The various treatment schemes discussed are practical only within certain ranges of metal concentration in the feed solution. For example, processes that might be employed for various feed concentrations of copper are:

Feed soln, g/l. Cu	Treatment scheme
100 to 10	electrowinning
20 to 1±	cementation or electrostripping
1 to 0.01	lime precipitation, solvent extraction
0.2 to 0	ion exchange, activated carbon

As discussed earlier, copper can be concentrated in very weak solutions by ion exchange or solvent extraction to a level where electrowinning or electrostripping might be applied. In the case of "stripping cells," copper is recovered as a fine "sponge" which falls off the cathodes and can be collected as a commercial product by vacuum filtration.

Additional reading

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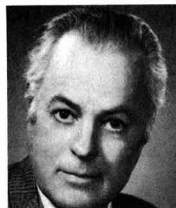
John G. Dean *is manager and general technical director of Dean Associates. Dr. Dean has specialized in the chemistry of metals, including their extractive chemical metallurgy, refining, electrochemistry, and conversion to derivatives for applications in many fields.*
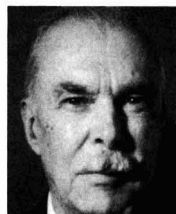
Frank L. Bosqui, *senior associate and project supervisor, has experience in South African gold and copper fields. His specialties include ore preparation, beneficiation, solids-liquid separation, furnacing, leaching, metal refining, precious metal recovery, and extractive metallurgy.*

Kenneth H. Lanouette *is vice-president of Industrial Pollution Control, Inc. He has extensive experience in water and waste water treatment plant engineering and sales and has presented papers on waste treatment and biofiltration. Address inquiries to Mr. Lanouette.*

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Solvent Extraction of Mercury from Brine Solutions with High-Molecular-Weight Amines

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■ High-molecular-weight amines are highly efficient solvents for the removal of mercury from brine solutions and other chloride systems. Mercury extracts essentially quantitatively at both the subnanogram and macro levels. The quaternary amines are especially attractive because of their ability to extract mercury from alkaline as well as acidic brine solutions. Regeneration of the amine solvent is readily achieved by stripping the mercury with aqueous solutions of nitric acid, ethylenediamine, or propylenediamine. Alternatively, the mercury can be stripped directly from the solvent by aluminum reduction-precipitation. A simple process is described for the abatement of mercury pollution in industrial brines and hydrochloric acid solutions.

Considerable interest has developed recently in discovering better methods for the removal of mercury from industrial waste solutions. The high toxicity of mercury and its presence in many hitherto unsuspected sources have prompted government studies to recommend that all controllable sources of mercury contamination be eliminated or maximally reduced. A recent review (Wallace et al., 1971) definitively describes the role of mercury in the environment.

It is highly desirable to eliminate mercury pollution at its source. A major man-made source of environmental mercury is the brine effluents from chlor-alkali plants. Our recent studies on the removal of mercury from brine solutions are described here.

Several methods are available for removing mercury from aqueous solutions (Roesmer and Kruger, 1970). The precipitation of mercury by a more active metal—e.g., aluminum, copper, iron, zinc—is effective, but it substitutes another metal in solution usually in considerably more than an equivalent amount. Methods based on the precipitation of mercuric sulfide suffer from the high toxicity and offensive odor of sulfide reagents. Sorption of mercury on preformed metal sulfides—e.g., iron sulfide, cadmium sulfide, zinc sulfide—is an effective removal method. However, the mercury in solution is replaced by another ion.

Ion exchange methods in use are expensive and suffer from problems arising from resin attrition and fouling due to the sensitivity to suspended solids (graphite, carbon, dirt) present in industrial solutions.

Solvent extraction techniques for the industrial removal of mercury from brine solutions have not been advocated previously. Popular cationic extractants used in analytical chemistry—e.g., dithizone—are too expensive and generally are unstable due to sensitivity to hydrolysis, oxidation, light, or heat. One class of solvents that does show considerable potential for the industrial extraction of mercury is the high-molecular-weight amines. Recently we have found that several of these amines possess the required properties for the extraction of mercury from brine solutions. In such solutions the mercury is already present as the $HgCl_4^{2-}$ complex—the species highly extractable by amines. No addition of other chemicals is necessary. Moreover, the amines are relatively inexpensive, readily available in large quantities, and amenable to processing by either mixer-settler or countercurrent techniques. The successful practical applications of the high-molecular-weight amines (Moore, 1960) in nuclear technology attest to their industrial potential for removing mercury from aqueous solutions.

Experimental

Apparatus. A NaI(T1) well-type scintillation counter, 1.75 × 2 in., was used for gamma counting.

Reagents. Primene JM-T is a mixture of primary amines, principally in the C_{18-22} range.

Primene 81-R is a mixture of primary amines, principally in the C_{12-14} range.

Amberlite LA-1 (N-dodecenyltrialkylmethylamine) and Amberlite LA-2 (N-lauryltrialkylmethylamine) are secondary amines. These secondary amines and the primary amines listed above are readily available from Rohm and Haas Co., Philadelphia, Pa.

Alamine 336-S (tricaprylamine) is a tertiary amine available from General Mills, Inc., Kankakee, Ill.

Aliquat 336-S (tricaprylmethylammonium chloride) is a quaternary amine chloride available from General Mills.

Adogen 464, methyltri(C_8–C_{10})ammonium chloride is a quaternary amine chloride available from Archer Daniels Midland Co., Minneapolis, Minn.

The amines were dissolved in reagent grade xylene or diethylbenzene.

Mercury-203 tracer is available from New England Nuclear Co., Boston, Mass.

Procedure. Five milliliters of the indicated aqueous phase containing 5 × 10⁵ gamma counts/min/ml of ²⁰³Hg tracer and <1 μgm/ml mercury was extracted at room temperature with an equal volume portion of the various solvents in 50-ml

Table I. Extraction of ^{203}Hg Tracer with 30% Aliquat 336-S-Cl-Xylene as a Function of HCl Concentration

HCl, M	^{203}Hg tracer extracted, %
0.003	85.1
0.015	86.6
0.03	93.0
0.2	99.8
0.4	99.8
0.8	>99.5
1.6	>99.5
3.2	>99.5
4.8	>99.5
6.0	99.0
8.0	99.0
9.6	98.4

Table II. Extraction of Macro Concentrations of Hg from Chloride Solutions with 30% Aliquat 336-S-Cl-Xylene

Initial aqueous phase			
NaCl, M	HCl, M	Hg, mg/ml	Hg extracted, %
...	0.1	8	99.8
...	0.3	6	99.8
...	0.3	2	99.8
...	1.7	2	99.9
...	6.1	2	>99.9
...	7.3	2	99.3
0.5	0.95	2	99.7
1.0	0.05	2	99.7
3.0	0.05	2	99.9
3.9	0.02	2	>99.9
1.0	0.10	6	99.7
3.0	0.04	15.2	>99.9

heavy-duty glass centrifuge tubes. Three-minute mixing periods were selected arbitrarily. High-speed motor stirrers equipped with glass paddles were used for the extractions. After extraction, the tubes were centrifuged in a clinical centrifuge for 2 min. Each phase was then analyzed for ^{203}Hg by counting 1-ml aliquots in a well-type gamma scintillation counter.

Results and Discussion

The mechanism of extraction of mercury from aqueous chloride solutions with a quaternary amine is of this type:

$$Hg^{2+} + 4Cl^- \rightleftharpoons (HgCl_4)^{2-}$$

$$2(R_4NCl)_o + (HgCl_4)_a{}^{2-} \rightleftharpoons [(R_4N)_2HgCl_4]_o + 2Cl_a{}^-$$

where R_4NCl = Aliquat 336-S-Cl or Adogen 464-Cl, o = organic phase, and a = aqueous phase.

The quaternary amine and its salt with the anionic chloro complex of mercury are essentially insoluble in aqueous solutions but possess high solubility in most organic solvents.

The quaternary amines are available as the chloride salts. Stock solutions—30% (w/v), 0.68M—were prepared in xylene and diethylbenzene (DEB). For the practical separations described in this paper, the solvents were scrubbed once by mixing with equal volume portions of 1M HCl for 5 min. After centrifugation, the pretreated solvents were used for the various studies. Appropriate dilutions were made from these solvents as required.

Extensive scrubbing of the solvent with aqueous reagents such as sodium carbonate, water, and various acids is sometimes used prior to the application of these reagents. However, we did not find such treatments necessary for our purpose. The 1M HCl pretreatment was quite adequate.

By use of the standard procedure described above, the pertinent variables were studied. The extraction of ^{203}Hg tracer with 30% Aliquat 336-S-Cl-xylene as a function of hydrochloric acid concentration is shown in Table I. Mercury-203 tracer extracts efficiently over a wide range of HCl concentrations. The slight decrease in the extraction of mercury at very dilute hydrochloric acid concentrations may be a reflection of increasing tendency to form hydroxy species of mercury. The addition of NaCl to the aqueous solution and pretreatment of the extractant with 1M HCl renders the ^{203}Hg tracer quantitatively extractable at the low acidities.

Excellent recovery of ^{203}Hg tracer is achieved from dilute to concentrated solutions of sodium chloride. Although most extractions in this study were performed for 3 min, mixing periods as short as $^{1}/_{2}$ min were adequate for essentially quantitative extractions of mercury. Rapid equilibrium is typical of such ion association–type extractions.

Macro concentrations of mercury also extract quantitatively from aqueous solutions of HCl and NaCl with 30% Aliquat 336-S-Cl-xylene (Table II). Further tests indicated that about 75 mg of mercury/ml of extractant could be loaded into the solvent. The amine:mercury mol ratio was about 2:1. The ability to extract large amounts of mercury is an important advantage of the amine because regeneration cycles can be minimized in large-scale work.

The organic:aqueous vol ratio in the extraction can be quite low, provided the amine:mercury molar ratio is $\gtrsim 2$. In a typical experiment, an organic:aqueous vol ratio of 0.06 afforded quantitative recovery of mercury in the system, 30% Aliquat 336-S-Cl-xylene—3M NaCl, 2 mg/ml Hg.

Table III. Extraction of Hg with 30% Aliquat 336-S-Xylene as a Function of HNO$_3$ Concentration

	Hg extracted, %	
HNO$_3$, M^a	R$_4$NNO$_3$	R$_4$NCl
1.8	94.8	99.7
3.2	82.9	99.6
4.2	65.0	96.0
5.0	47.2	90.7
6.2	28.9	75.7

^{a} Initial aqueous solutions contained 2 mg/ml Hg.

Table IV. Extraction of Hg from Brine Solutions with 30% Aliquat 336-S-Cl-Xylene as a Function of pH

Aqueous phase, pH		
Initial^a	Final	Hg extracted, %
1.0	1.1	99.9
3.2	5.4	99.7
5.1	5.6	99.9
7.2	6.2	99.6
9.2	6.5	99.6
10.0	7.1	99.8
10.9	10.9	99.2
11.5	11.5	71.4

^{a} Initial aqueous solutions contained 3M NaCl and 2 mg/ml Hg.

The extraction of mercury with 30% Aliquat 336-S-xylene as a function of nitric acid concentration is shown in Table III. Mercury extracts well from dilute nitric acid solutions with the nitrate salt of the amine. However, at a given nitric acid concentration, its extractability is greatly improved by use of the chloride salt of the amine—a fact which clearly demonstrates the greater extractability of the chloro complex of mercury over its nitrate complex.

To be a practical industrial extractant the solvent must function efficiently from alkaline brines as well as acidic brines. An important advantage of the quaternary amines is their ability to extract mercury from aqueous brine solutions of relatively high pH. Table IV shows results for the extraction of mercury with 30% Aliquat 336-S-Cl-xylene as a function of pH of the brine solution. The initial aqueous brine solutions contained $3M$ NaCl, 2 mg/ml Hg labelled with ^{203}Hg and varying pH. After 3-min extractions using 5-ml portions of each phase and centrifugation, the phases were analyzed for mercury.

The extraction of mercury from alkaline brine solutions as a function of amine class is shown in Table V. Pretreated solvents [indicated by (T) in the table] were prepared by mixing equal volume portions of the solvents for 3 min with $1M$ HCl followed by centrifugation. Although pretreatment is not required in some cases, the free HCl contained in the pretreated solvents serves to maintain the final aqueous pH at a lower level. This fact is particularly useful in aqueous systems containing no NaCl or free hydrochloric acid—cases in which the mercuric ion tends to precipitate. For all subsequent work, the pretreatment of solvents with $1M$ HCl was used.

The extraction of mercury from acidic brine solutions as a function of amine class gave results very similar to those obtained for alkaline brine solutions.

The extraction of mercury from alkaline or acidic aqueous solutions of potassium chloride were essentially identical to that obtained in the sodium chloride system. Excellent recovery of mercury was also achieved from aqueous solutions containing 0.1–1.0% sodium hypochlorite.

In all cases the quaternary ammonium chloride, Adogen 464, was as efficient as Aliquat 336-S-Cl for the extraction. Diethylbenzene was as satisfactory as xylene as a diluent for the amines.

Regeneration of the Quaternary Amine Solvent

Aqueous Strippants. For process applications, a satisfactory extractant must be regenerated for recycling operations. A number of reagents (Table VI) were evaluated for their ability to strip mercury from Aliquat 336-S-Cl-xylene solutions. The organic solvents initially containing 2 mg/ml Hg were stripped by extracting for 3 min with equal volume portions of the various aqueous strippants.

Nitric acid solutions of intermediate concentrations stripped the mercury from the solvents better than any other acidic reagent. Mercury stripped with nitric acid at both the tracer and macro level.

Ammonium hydroxide stripped the mercury effectively but some precipitate formed except at very high concentrations of ammonium hydroxide.

Among the numerous reagents tested, ethylenediamine and propylenediamine were superior as strippants for mercury. Aqueous solutions of these reagents as dilute as 1% stripped the mercury quantitatively from the solvent. Excellent mechanical behavior and material balances were observed with the

Table V. Extraction of Hg from Alkaline Brine Solutions as a Function of Amine Class[a]

Amine extractant in xylene	Class	Aqueous pH Initial	Aqueous pH Final	Hg extracted, %
30% Primene 81-R	Primary	10.6	9.6	>99.9
30% Primene JMT	Primary	10.5	9.5	>99.9
30% Amberlite LA-1	Secondary	10.5	7.4	70.0
30% Amberlite LA-2	Secondary	10.5	9.4	15.0
30% Alamine 336-S	Tertiary	10.5	8.6	40.0
30% Aliquat 336-S-Cl	Quaternary	10.6	8.7	>99.9
30% Primene 81-R(T)	Primary	10.6	8.3	>99.9
30% Primene JMT(T)	Primary	10.5	6.1	54.8
30% Amberlite LA-1(T)	Secondary	10.6	2.2	>99.9
30% Amberlite LA-2(T)	Secondary	10.5	4.2	>99.9
30% Alamine 336-S(T)	Tertiary	10.5	4.2	>99.9
30% Aliquat 336-S-Cl(T)	Quaternary	10.6	1.2	>99.9

[a] Initial aqueous solutions contained $3M$ NaCl and 2 mg/ml Hg.

Table VI. Stripping of Hg from Aliquat 336-S-Cl-Xylene Solutions

	Hg stripped, %	
	Concn of Aliquat 336-S-Cl in xylene	
Strippant	5%	30%
HNO₃, M		
1	<1.0	<1.0
3	12.0	0.4
5	52.6	8.0
6	71.6	17.0
8	85.9	48.0
10	88.8	76.0
12	83.9	87.4
Na₂SO₃, $1M$	55.0	41.1
Na₂S, $1M$	98.1	90.6
NaOH, $1M$	58.9	36.4
NH₄OH, M		
0.1	89.5	5.9
1	95.7	89.6
5	96.3	96.7
10	>99.0	98.6
15	>99.0	>99.0
Ethylenediamine, 2.5%	>99.0	>99.0
Propylenediamine, 2.5%	>99.0	>99.0

ethylenediamine or propylenediamine strippants. No precipitation of mercury occurred.

During the stripping studies an interesting tracer effect was observed. Surprisingly, the alkaline strippants—ammonium hydroxide, ethylenediamine, and propylenediamine—were discovered not to strip ^{203}Hg tracer containing <1 μgm/ml Hg carrier. Thus, each of these reagents easily stripped >99% of the mercury from the solvent containing 2 mg/ml Hg carrier but <2% from the solvent containing <1 μgm/ml Hg. Typically, the solvent initially containing <1, 5, 10, 25, and 250 μgm/ml of mercury showed strippabilities of <2%, 77%, 90%, 96%, and >99%, respectively. For practical applications in which macro concentrations of mercury are loaded into the solvent before regeneration, the tracer effect is inconsequential.

Reduction-Precipitation of Mercury with Aluminum. An alternative method for regenerating the solvent is to precipitate

Table VII. Reduction-Precipitation of Hg from 5% Aliquat 336-S-Cl-DEB by Aluminum

Reduction time, min	Hg reduced, %
3	2.0
10	8.1
25	22.5
40	35.9
60	46.9
75	65.0
90	77.0
105	83.4
135	90.3
Overnight (18.5 hr)	>98.0

the mercury directly from the organic solvent by reduction with a more active metal. Studies revealed that, indeed, mercury could be precipitated directly from the quaternary amine chloride solvent with aluminum, iron, copper, or zinc.

In a typical experiment, 8 ml of 5% Aliquat 336-S-Cl-DEB containing 2 mg/ml Hg was mixed for 3 min with 2.3 grams of aluminum turnings. After centrifugation, aliquots of the solvent were analyzed for mercury. The solvent was then allowed to sit in contact with the aluminum turnings. During each reduction period the solvent was shaken manually for 1 min to expose fresh aluminum surface. The results (Table VII) show that most of the mercury was removed from the solvent in about 2 hr; essentially quantitative removal was obtained when the solvent–aluminum mixture sat overnight, even in the absence of agitation. For faster reduction of the mercury, continuous mixing with aluminum shot or powder could be used.

As expected, reduction of mercury from the organic solvent was slower than from an aqueous brine solution. Thus, in an analogous experiment to that described above, the same quantity of aluminum turnings reduced 95% of the mercury from an aqueous 5M NaCl solution in the initial 3-min mixing period.

The behavior of tracer mercury (<1 μg/ml) in the aluminum reduction experiments was similar to that described previously for the alkaline strippants. Thus, <1% ^{203}Hg tracer stripped from the solvent after sitting in contact with aluminum for 65 hr.

In certain situations, regeneration of the solvent by aluminum reduction may be practical because it eliminates an aqueous stripping step. This demonstrates an important advantage of solvent extraction over ion exchange with solid resins. In the latter case direct reduction is not feasible.

Demonstration Tests. Yields of mercury were determined in numerous demonstration tests involving a two-cycle laboratory scale process. The feed solution contained 3M NaCl, 2 mg/ml Hg, ^{203}Hg tracer, 5 × 10^5 gamma counts/min/ml, pH 10.6. Twenty ml of the alkaline brine feed solution was extracted for 3 min with 20 ml of 5% Aliquat 336-S-Cl-DEB. The mercury was then stripped from the solvent by extracting for 3 min with 20 ml of the appropriate strippant. The strippants evaluated were 15M ammonium hydroxide, 2.5% ethylenediamine, and 2.5% propylenediamine.

The regenerated solvents were then used in a second cycle to extract fresh portions of the alkaline brine solution. Mercury was then stripped in a manner identical to that used for the first cycle.

Concentrated ammonium hydroxide (15M) stripped the mercury essentially quantitatively, but often a slight amount

of the mercury precipitated and material balances were poor. This fact along with the inconvenience of working with concentrated ammonium hydroxide probably eliminates it as a practical strippant for large-scale operation.

Dilute aqueous solutions of ethylenediamine and propylenediamine were excellent mercury strippants. The soluble "en" complexes with the mercuric ion prevent precipitation problems which arise with other alkaline strippants.

Some typical results shown in Table VIII indicate that mercury may be extracted from alkaline brine solutions essentially quantitatively with the quaternary amine. Stripping solutions of either 2.5% ethylenediamine or 2.5% propylenediamine readily strip the mercury from the solvent. The regenerated solvent is equally effective for a second-cycle extraction, if desired. Because of the high extraction coefficient for mercury in a single stage, multiple extractions will usually not be necessary.

Essentially identical results to those described above were obtained in tests of the recovery of mercury from acidic brine solutions with 5% Aliquat 336-S-Cl-DEB.

In further experiments we demonstrated that the primary, secondary, and tertiary amines listed in Table V could also be used for essentially quantitative recovery of mercury through the extraction and stripping steps, provided the brine feed solution was acidic.
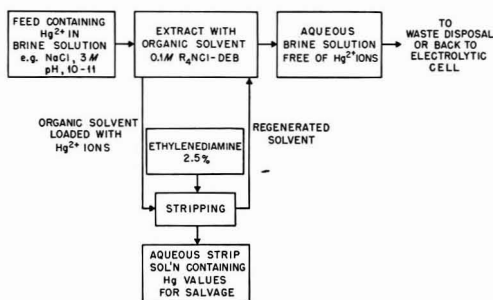
Figure 1. Solvent extraction system for removal of Hg from brine solutions

Table VIII. Recovery of Hg from Alkaline Brine Solutions with 5% Aliquat 336-S-Cl-DEB Via Two-Cycle Process

Process step	Hg recovered, %	Aqueous pH	
		Initial	Final
	(Run 1)		
Initial extraction	>99.9	10.6	1.9
2.5% Ethylenediamine strippant	99.6		
Second-cycle extraction	>99.9	10.6	10.7
Second-cycle strippant	99.6		
	(Run 2)		
Initial extraction	>99.9	10.6	1.9
2.5% Propylenediamine strippant	99.8		
Second-cycle extraction	99.9	10.6	10.8
Second-cycle strippant	99.7		

A schematic flow sheet of a typical solvent extraction system for the removal of mercury from brine solutions is shown in Figure 1. The process operates as effectively on saturated brine feed solutions as on dilute brine solutions. Satisfactory alternative strippants are 2.5% propylenediamine, $10M$ nitric acid or aluminum metal.

General Applications

The high-molecular-weight amines are promising solvents for the removal of mercury from industrial brine solutions. Especially attractive are the commercially available quaternary amines, Aliquat 336 and Adogen 464, because of their ability to extract mercury from alkaline as well as acidic brine solutions. These two amines show a solubility of <5 ppm in water. At such levels they do not present a toxicity hazard (Weeks et al., 1970).

The capacity of these reagents to extract mercury at both subnanogram and macro levels serves the dual purpose: (1) abatement of mercury pollution, the major objective of this work; and (2) the industrial recovery of large amounts of mercury from brine and other aqueous chloride solutions.

In addition to the extraction of mercury, the process described was also found to extract a number of other toxic metal ions—e.g., cadmium, zinc, lead, arsenic, and copper.

It is noteworthy that the method is not limited to the extraction of mercury from brine solution and other chloride systems. The mercuric ion forms amine-extractable anionic species in numerous other media—e.g., nitrate, sulfate, phosphate, organic. The described solvent extraction technique can be used to remove mercury from a wide variety of these aqueous solutions.

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Kinetics of Oxidation of Aqueous Sulfide by O₂

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■ Oxygenation of sulfide is characterized by an induction period at all pH values. It is concluded from the universal existence of this induction period and from the kinetic equation that the oxidation of sulfide by O_2 proceeds through a chain mechanism. Van't Hoff's method has been used for estimation of the initial order of reaction. For initial oxygen concentrations of 1.6 to $8.0 \times 10^{-4}M$ and initial sulfide concentrations of 0.5 to $2.0 \times 10^{-4}M$, reaction orders of sulfide and oxygen are 1.34 and 0.56, respectively. Variations of rate parameter k with pH shows a very complex pattern. In acid solutions, pH < 6, where H_2S is the predominating sulfide species, the rate is very slow. The specific rate increases greatly as pH increases through 7 to a maximum of pH 8.0 or so, then decreases to a minimum near pH 9, increases again to a second maximum about equal to the first near pH 11 and finally decreases again in more alkaline solutions. This unusual pH dependence of reaction rate was confirmed by the manometric measurement of oxygen uptake. However, with increasing initial sulfide concentrations, the first peak shifts from pH 8 to 7. This has been found to be connected with the presence of polysulfides as intermediates.

H ydrogen sulfide, its salts and closely related organic sulfides are significant environmental pollutants. Hydrogen sulfide and the mercaptans, CH_3SH and CH_3-CH_2SH, have unpleasant odors and very low odor threshold concentrations. Even in low concentration, they discolor many types of paint. Concentrations of a few tenths of a milligram per liter in drinking water cause noticeably disagreeable odors and tastes (Pomeroy and Cruse, 1969).

Sulfide occurs often in well water, lakes, and other surface waters as well as in anaerobic sewage and industrial waste waters. It is produced mainly by anaerobic microbial processes associated with the decomposition of organic matter. In polluted estuaries and lakes, the intrusion of seawater leads to the production of significant amounts of sulfide from the biological reduction of sulfate. Waste liquids discharged from industrial plants such as tanneries, paper and pulp mills, oil refineries, gas manufacturing works, and textile mills may also add important concentrations of sulfide.

For proper control and minimizing of the obnoxious tastes and odors associated with H_2S and the mercaptans, a thorough understanding of the chemistry of the reactions between aqueous sulfide and oxygen is urgently needed, for this is the

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Table I. Buffer Solutions For Different pH and Initial Total Sulfide

pH	Initial sulfide concn, mol/l.		
	$5 \times 10^{-5} - 2 \times 10^{-4}$	$1.0 - 3.0 \times 10^{-3}$	1.0×10^{-2}
4.5–6.0	0.04M $CH_3COOH + CH_3COONa$	0.08M $CH_3COOH + CH_3COONa$	0.2M $CH_3COOH + CH_3COONa$
6.0–7.0	0.04M $H_2CO_3 + NaHCO_3$	0.08M $Na_2HPO_4 + NaH_2PO_4$	0.2M $Na_2HPO_4 + NaH_2PO_4$
7.0–8.2	0.04M $(HOCH_2)_3CNH_2{}^a + NaOH$ or $H_3BO_3 + NaOH$	0.08M $Na_2HPO_4 + NaH_2PO_4$	0.2M $Na_2HPO_4 + NaH_2PO_4$
8.0–10.3	0.04M $H_3BO_3 + NaOH$	0.08M $H_3BO_3 + NaOH$	0.2M $H_3BO_3 + NaOH$
10.0–11.3	0.04M $NaHCO_3 + Na_2CO_3$	0.08M $Na_2HPO_4 + Na_3PO_4$	0.2M $Na_2HPO_4 + Na_3PO_4$
11.0–12.5	NaOH	0.08M $Na_2HPO_4 + Na_3PO_4$	0.2M $Na_2HPO_4 + Na_3PO_4$
12.0 up	NaOH	NaOH	NaOH

^{a} 2-Amino-2-(hydroxymethyl)-1,3-propanediol or tris buffer.

mechanism by which most sulfide is removed naturally from water.

In a previous paper (Chen and Morris, 1970), general characteristics of sulfide-oxygen reaction were described. It was found that oxygenation of sulfide is not a simple reaction. The induction periods, the complex dependence of reaction rates with regard to oxygen and sulfide, the sensitivity of the reaction to impurities, the number of intermediates and their products, and the dependence of the initial specific rate on pH all testify to a lack of simplicity. Indeed, the complications are so great that virtually no portion of kinetics or mechanism has been firmly established over the past half century of experimentation. It is the intention of this paper to present some aspects of the kinetic behavior and their interpretation.
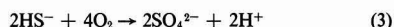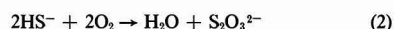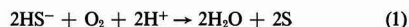
Experimental

Treatment of Glassware. All glassware for the preparation or storage of reagent solutions and all reaction vessels for spectrophotometric studies were soaked first in aqua regia and then in concentrated HCl for 4-hr periods. Then they were rinsed with 0.1M NaOH and finally several times with doubly distilled water. Reaction flasks for the manometric studies were first soaked overnight in toluene to remove grease and were subsequently boiled in distilled water and in a mixture of concentrated nitric and sulfuric acids before being rinsed like the other glassware.

Reagents. Stock sulfide solution, 10^{-1} to $10^{-2}M$, were prepared by dissolving appropriate amounts of ACS reagent grade $Na_2S \cdot 9H_2O$ (Mallinckrodt) in doubly distilled, deaerated water. The oxidized surface layers of sulfide crystals were carefully scraped off before dissolution. The stock solutions were standardized iodometrically and stored in stoppered volumetric flasks kept in a plastic glove box through which nitrogen was passed to maintain anoxic conditions. Fresh stock solutions were prepared daily.

Stock oxygen solutions were made up by bubbling artificial mixtures of O_2 and N_2 enriched in O_2 through suitable volumes of appropriate buffer solutions until saturation was reached. These solutions were maintained in dispenser bottles with the gas bubbling through slowly, and portions were added directly to the reaction vessels through the bottom tap. Oxygen concentrations in the stock solution were determined by the Winkler method.

Buffer Solutions. Oxidation of sulfide may either produce or consume hydrogen ions, depending on the products and other conditions. Thus

$$2HS^- + O_2 + 2H^+ \rightarrow 2H_2O + 2S \qquad (1)$$

$$2HS^- + 2O_2 \rightarrow H_2O + S_2O_3{}^{2-} \qquad (2)$$

$$2HS^- + 4O_2 \rightarrow 2SO_4{}^{2-} + 2H^+ \qquad (3)$$

So, buffering is necessary if constant pH is to be maintained during the course of the oxidation reaction. Buffer solutions used for pH control under the diverse conditions of experimentation are shown in Table I.

Sodium chloride was added to some solutions so that ionic strengths were approximately the same in each concentration range, but no effects attributable to ionic strength were noted. Phosphate buffers were found to catalyze the oxidation of sulfide to some extent in the low concentration range and so they were replaced by other buffers.

All chemicals used in this study were ACS reagent grade. Acetic acid and tris buffer were obtained from Fisher Scientific Co. Boric acid, sodium phosphates, and carbonates were obtained from Mallinckrodt Chemical Works and sodium hydroxide was from Merck & Co. All chemicals were used without further purification. They were dissolved in doubly distilled water.

Analytical Procedures. Two major methods were used in following the course of the oxidation of sulfide by O_2— manometric measurements of the uptake of oxygen as a function of time and spectrophotometric measurements of remaining sulfide. These were supplemented by occasional individual determinations of various oxyanions of sulfur and polysulfides.

The ion, HS^-, exhibits strong absorption in the uv from 260 to 190 mμ with a maximum at 230 mμ having a molar absorptivity of 7800 l. mol^{-1}cm^{-1}. Unfortunately, possible products of oxidation, such as $S_2O_3{}^{2-}$, $S_4O_6{}^{2-}$, and $SO_3{}^{2-}$, also absorb strongly in this region, the absorptivities at 230 mμ being 2250, 4300, and 500 l. cm^{-1}mol^{-1}, respectively. Ac-

cordingly, uv measurement was used only to obtain an approximate value for HS^- at each sampling time, and then accurate determination of total sulfide was carried out colorimetrically.

The colorimetric method used was the well-known formation of methylene blue by the mixing of ferric ions, N,N-dimethyl-p-phenylenediamine, and sulfide in HCl solution (Amer. Public Health Ass., 1965). The precision of this method was improved from the customarily accepted 10% to 1% on the basis of a foreknowledge of the approximate sulfide concentration obtained from uv absorption that permitted adjustment of the concentrations of the other reagents to the most appropriate values. Preliminary experiments had shown that the extent of color development is sensitive to the excess of reagents. With optimum excess of reagents the absorptivity per mole of sulfide for the formed methylene blue at 670 mμ, the wavelength of eventual measurement, was $3.25 \pm 0.02 \times 10^4$ l. mol^{-1}cm^{-1}.

Oxygen in stock solutions was determined by the Winkler method (Amer. Public Health Ass., 1965). The reduction of oxygen during the manometric experiments was followed by measurement of the change in gas-phase pressure at constant volume. No attempt was made to follow changes in oxygen concentration during the spectrophotometric studies when change in sulfide was being determined.

Precipitated product sulfur was determined by filtering samples through 100 mμ membrane filters, dissolving collected sulfur in acetone, adding cyanide and ferric chloride in acetone, and measuring the resulting ferric thiocyanate color (Bartlett and Skoog, 1954). Sulfur in acetone reacts rapidly and quantitatively with cyanide to give SCN^-.

Thiosulfate was determined by the procedure of Urban (1961) whereby thiocyanate is formed from cyanide in the presence of $CuCl_2$. Determination was preceded by deoxygenation with N_2, addition of $ZnCl_2$ to precipitate sulfide and filtration through a 220 mμ membrane filter. Thiosulfate alone was determined by treatment with cyanide in acidic solution, thiosulfate plus other polythionates except trithionate by treatment in alkaline solution.

The technique of West and Gaeke (1956) involving addition of tetrachloromercurate, p-rosaniline, formaldehyde, and HCl to form an intensely colored, red-violet material, was followed for determination of sulfite. Preliminary addition of zinc chloride and filtration through a 220 mμ membrane filter eliminated interference from sulfide and thiosulfate.

Polysulfides, mainly S_4^{2-} and S_5^{2-}, were measured from absorbance at wavelength 290 mμ where the absorbance of other sulfur oxyanions is at the minimum. The molar absorptivities at 290 mμ for S_4^{2-} and S_5^{2-} are 3900 and 5300 l. cm^{-1}mol^{-1}, respectively (Schwarzenbach and Fisher, 1960).

Measurements of pH value were made before and after each experiment with a precision of 0.02 pH unit with a Beckman Model 76 pH meter standardized at pH 4.01, 7.00, or 10.00 depending on the working range. All measurements were made at 25°C. Shift in pH was less than 0.05 unit for almost all runs.

Procedures. Two major types of experiments were used in obtaining the kinetic data. Runs in which the disappearance of sulfide as a function of time was measured spectrophotometrically and colorimetrically were used for formulation of a rate law for the reaction. In these experiments the initial sulfide concentrations ranged from 5×10^{-5} to 2×10^{-4} m (1.6 to 6.4 mg/l.) and the oxygen concentration from 1.6×10^{-4} to $8.0 \times 10^{-4}M$ (5.1 to 25.6 mg/l.). Manometric War-

burg-type experiments, in which the reduction of oxygen as a function of time was measured, were used to evaluate the rate of oxygen uptake. In these experiments the oxygen concentration was essentially the equilibrium value for atmospheric oxygen and the sulfide concentration ranged from 1×10^{-3} to $2 \times 10^{-2}M$ (32 to 640 mg/l.).

Standard kinetic studies were conducted in 250-ml volumetric flasks of borosilicate glass, a separate flask being used for each experimental point during the course of a run. Into each flask—usually 16 were used for a run—was dispensed first a suitable identical quantity of buffer solution and of O_2-free doubly distilled water, both of which had been deoxygenated by passing N_2 through them for at least 12 hr. The flasks were then purged of O_2 with gaseous N_2 for an hour or more. An equal, desired quantity of stock sulfide solution was next pipetted into each flask. Finally each flask was filled with oxygen-containing buffer solution, prepared as described previously, by feeding it through the bottom outlet of the dispensing bottle directly beneath the surface of the solution already in the flask until the vessel was completely filled. It was then stoppered, the contents were thoroughly mixed by inversion, the starting time was recorded, and the stoppered flask placed in the constant-temperature bath at 25°C. After the appropriate reaction interval, necessary samples were removed from the vessel for analysis and the remainder set aside.

Two additional flasks were prepared at the same time as the series of reaction vessels. In the first of these all the additions were the same except that an equal volume of oxygen-free water was substituted for the stock sulfide solution; this flask was used to obtain the initial oxygen concentration. The other flask also received the same additions except that it was filled with oxygen-free rather than oxygen-containing water; initial sulfide was determined iodometrically with this solution.

Manometric studies were conducted in Warburg equipment, using 20-ml, side-arm vessels. The volume of each vessel and its manometer were checked by the ferricyanide-hydrazine method (Umbreit et al., 1964). The volumes of sulfide solution used were fixed so that not more than 10% of the oxygen available in the gas space would be consumed in any run. Thus, these experiments were performed at essentially constant concentration of O_2.

For these studies the required quantities of sodium sulfide to give desired concentrations were dissolved directly in appropriate deaerated buffer solutions. Then 1–2-ml portions were pipetted into the Warburg flasks and, after they had been sealed, they were allowed 15 min to reach thermal equilibrium before readings were started.

Approach and Results. Evaluation of the specific rate parameters was done by the Van't Hoff (differential) method where the observed initial rates were measured after the induction period. The initial rates were determined graphically from (ΣS^{2-}) vs. time plot for various initial concentrations.

This method is based on the assumption that the expression for the initial rate has the form:

$$-\left[\frac{d(\Sigma S^{2-})}{dt}\right]_{t=0} = R_i = k(\Sigma S^{2-})_o^m(O_2)_o^n \quad (4)$$

Where R_i is initial rate and the parentheses represent molar concentrations.

The value of m can be obtained from the initial rates of experiments in which the concentration of O_2 is maintained constant and different initial concentrations of sulfide are employed. When initial concentration of oxygen is kept at the
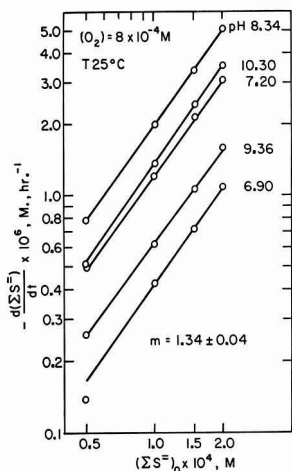
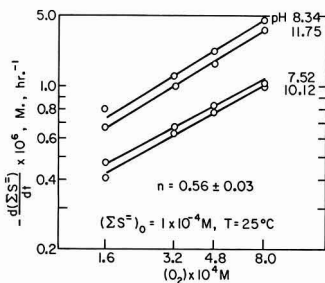Figure 1. Effect of sulfide concentration on initial rate of reaction

Figure 2. Effect of oxygen concentration on initial rate of reaction

Figure 3. pH dependence of observed specific rate of sulfide oxidation (see Table II for details)

same level with great excess in comparison with different initial sulfide concentrations, Equation 1 can be written

$$R_i = k_s(\Sigma S^{2-})_o^m \qquad (5)$$

Similarly, if $(\Sigma S^{2-})_o$ is kept at the same level while different initial concentrations of oxygen are employed, the overall equation can be reduced to

$$R_i = k_o(O_2)_o^n \qquad (6)$$

The true order obtained by the differential method deals with initial slopes, and the change in concentrations of reactants is small in the initial stage of reaction; therefore the validity of Equation 6 will not change materially even if sulfide concentration is not in excess.

These equations can then be used for evaluating the individual reaction orders.

Variation of Initial Rate with Sulfide Concentration. Experiments for estimation of the initial order of the reaction with respect to sulfide were conducted with an excess of O_2, $8 \times 10^{-4}M$ (25.6 mg/l.). Initial concentrations of sulfide ranged from 0.5 to $2 \times 10^{-4}M$.

In logarithmic form, Equation 5 becomes

$$\log R_i = \log k_s + m \log (\Sigma S^{2-})_o \qquad (7)$$

a linear equation. So, if R_i is plotted logarithmically against $(\Sigma S^{2-})_o$, linear traces should be obtained with slope equal to m. This is shown for sulfide dependence in Figure 1. These data do conform to straight lines of uniform slope giving a value of $m = 1.34 \pm 0.04$.

Variation of Initial Rate with O_2 Concentration. Studies for determination of order with regard to O_2 were conducted with sulfide concentration of $10^{-4}M$ in all experiments. The initial oxygen concentrations ranged from 1.6 to $8 \times 10^{-4}M$.

Similarly, these initial-rate data can also be treated by the Van't Hoff method. The logarithmic form of Equation 6 is

$$\log R_i = \log k_o + n \log (O_2)_o \qquad (8)$$

and so a logarithmic plot of values of R_i against $(O_2)_o$ should yield n as the slope. These plots are shown in Figure 2 and give from the slopes a fractional order of $n = 0.56 \pm 0.03$.
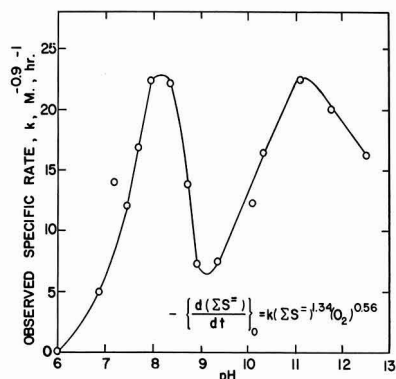
Combination of these results leads to an overall empirical equation:

$$-\left[\frac{d(\Sigma S^{2-})}{dt}\right]_{t=0} = k(\Sigma S^{2-})_o^{1.34}(O_2)^{1.56} \qquad (9)$$

A summary of k values, evaluated from kinetic experiments at varied total sulfide, O_2, and pH, is presented in Table II, which also lists observed induction or lag periods.

Good reproducibility of k values and good constancy over the range of sulfide concentrations studied are shown, both within $\pm 5\%$. A few of the k values for different O_2 concentrations show a greater scatter, up to $\pm 10\%$, but the majority are still within the 5% range. Consistency in the induction period at a given pH for different sulfide and O_2 concentrations is also shown.

Since the initial rate is the measurement of the slope after the induction period, possible complications owing to interference by products as well as change in the concentration of species during the course of experiments were avoided.

It is not essential, however, that a kinetic equation have the power series form assumed in application of the Van't Hoff method. Even when very good empirical agreement with experimental data is found for an equation of this form, theoretical or mechanistic reasoning often demands other forms particularly when fractional powers of the reactants appear to be involved. Often the more acceptable theoretical forms involve sums of terms that approximate to the fractional power.

An alternate expression that proved to fit all of the kinetic data for the varied total sulfide and O_2 concentrations except for those experiments in which visible precipitation of sulfur occurred is

$$-\left[\frac{d(\Sigma S^{2-})}{dt}\right]_{t=0} = k_A(\Sigma S^{2-})(O_2)\left\{1 + k_B\left[\frac{(\Sigma S^{2-})}{(O_2)}\right]^{1/2}\right\} \qquad (10)$$

When the second part of the last term is much greater than unity these equations reduce almost to the same form as the previous one.

pH Effect. In Figure 3, average values of the specific rates of sulfide disappearance, taken from Table II, are shown plotted as a function of pH. A very complex pattern is exhibited. In acid solutions, pH < 6, where H_2S is the predominating sulfide species, the rate is very slow. The specific rate increases greatly as pH increases through 7 to a maximum of pH 8.0 or

Table II. Specific Initial Rates, k, for Oxygenation of Sulfide at 25°C, k in $M^{-0.9}$ Hr^{-1}

pH	Initial total sulfide, M, $\times 10^4$				Induction period, hr
	0.5	1.0	1.5	2.0	
Initial O₂, M, $\times 10^4$ = 8.0					
6.00	<0.01	<0.01	<0.01	<0.01	
6.90	4.07	5.00	4.91	4.99	6.0
7.20	14.35	14.00	14.03	13.88	1.5
7.52	11.97[a]	11.63[a]	...	12.85[a]	0.75
7.72	17.14	16.82	...	16.53	0.5
7.94	22.12[a]	22.21	...	22.47[a]	0.75
8.34	22.19[a]	23.26[a]	22.92	23.60	0.2
8.75	...	15.53	...	12.30	0.75
8.95	7.16	6.98	...	7.40	0.80
9.36	7.47	7.83	7.12	7.40	2.0
10.12	12.45	12.21	...	12.29	1.50
10.30	16.35	16.28	16.57	16.64	1.0
11.10	22.24	22.91	...	22.20	0.50
11.75	20.65	20.11	...	19.42	1.05
12.50	17.05	16.28	...	15.45	1.0
Initial O₂, M, $\times 10^4$ = 4.8					
7.52	...	12.94	...	...	1.0
8.34	21.07	21.28	...	21.67	0.25
10.12	12.30	12.70	...	13.18	1.5
11.75	18.09	19.06	...	17.93	1.25
Initial O₂, M, $\times 10^4$ = 3.2					
7.52	...	12.83	...	...	1.0
8.34	20.21	21.48	...	22.28	0.25
10.12	11.99	12.36	...	12.67	1.50
10.30	14.44	14.68	...	14.99	1.20
11.75	18.48	18.91	...	19.62	1.25
Initial O₂, M, $\times 10^4$ = 1.6					
7.52	11.80	13.54	14.79	16.38	1.0
8.34	20.89	21.40	...	22.79	0.25
10.12	16.60	19.63	...	11.39	1.50
11.75	16.60	19.63	...	22.79	1.25

[a] Average values of three independent experiments, with ±5% deviation.

Figure 4. pH dependence of initial oxygen uptake by sulfide
$O_2 = 0.21$ atm, $T = 25$ °C
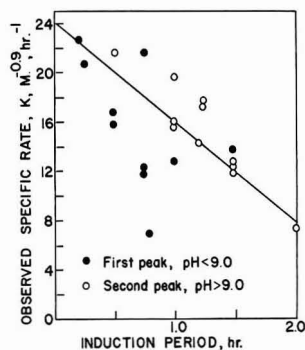
Figure 5. Inverse relationship of specific rate and induction period

so, then decreases threefold to a minimum near pH 9, increases again to second maximum about equal to the first near pH 11 and finally decreases again in more alkaline solutions.

The reality of this unusual effect of pH was confirmed by experimental studies on the rate of oxygen uptake. The initial rate of oxygen uptake was evaluated for the period just after the end of lag periods, as in the case of sulfide disappearance. Plots of the initial rate of oxygen uptake as a function of pH for sulfide concentrations from 10^{-3} to $1 \times 10^{-2} M$ are shown in Figure 4.

Induction Period. Figure 5 shows the correlation between the induction period and the specific reaction rate. Generally, the length of the induction period was constant for a pH over the range of experimental concentrations of reactants. Qualitatively, the induction period varied with pH in inverse fashion to the initial specific rate.

It is worthwhile to point out that the concentration of reactants remains unchanged during the induction period.

Intermediates and Products. Stoichiometry of sulfide-oxygen reaction depends on pH, concentration of reactants, and the
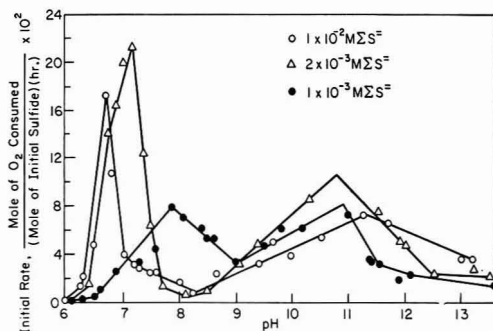
existence of extraneous substances or impurities (Chen and Morris, 1972). In a clean solution, polysulfides appear in the neighborhood of neutral pH region. It was found that the rate maximum coincided with the appearance of uv absorption at 285–290 mμ, observable at high sulfide concentrations. This is a region of wavelengths in which polysulfides, but no other sulfur species, exhibit absorption. Thus the first maximum in rate coincides with maximum polysulfide formation. Experimental results on the pH and time dependences of the polysulfide formation are shown in Figure 6. The maximum conversion of sulfide to polysulfides as intermediates is about 10% in a 3-hr period. For a solution saturated with pure oxygen and initially $1 \times 10^{-3} M$ in sulfide, the maximum percentage of conversion at the peak is about 15%. As the ratio of initial sulfide to oxygen increases, the percentage of conversion decreases steadily. A high sulfide-to-oxygen ratio results in the precipitation of sulfur while a low ratio results in direct oxidation to thiosulfate and other oxyanions at neutral pH regions. Depending on the pH values, the peak of polysulfides concentration is found to follow 1–4 hr of reaction.

It has been found that the concentration of formed polysulfides as well as the reaction rate generally follow the same pattern with respect to the change in pH values (Chen and Gupta, 1971).

It was demonstrated by the net stoichiometry of the reaction and analysis of products that thiosulfate is the principal product in pure laboratory solution at pH > 8.5 regardless of sulfide-to-oxygen ratio. Some sulfite is formed and is slowly

$\Sigma S^= = 3 \times 10^{-3} M$
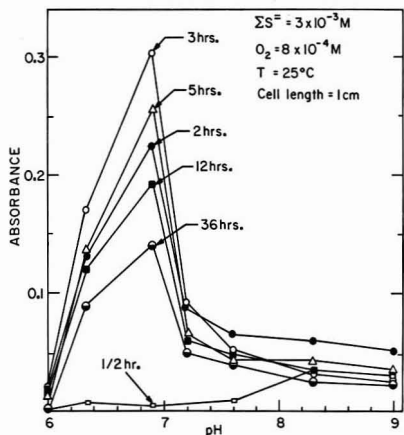$O_2 = 8 \times 10^{-4} M$
$T = 25°C$
Cell length = 1 cm

**Figure 6. Dependence of polysulfide formation at different time intervals**

Measurements at 285 mµ

oxidized to sulfate, the portion of sulfite becomes smaller with increasing pH. The formed sulfite may be eventually further oxidized to sulfate or may react with sulfur of polysulfides to form thiosulfate and is absent in the final solution. It is noteworthy that the rate of oxidation of sulfite is inhibited in a sulfide solution and its oxygenation proceeds much more slowly than that in the absence of sulfide. Theoretically, all sulfur and its oxyanions will be oxidized to sulfate in the presence of oxygen; however, this is not so within the period of observation, several weeks at most.

Discussion

A knowledge of species of reacting substances present in the reaction system is fundamental to the interpretation of kinetic behavior. In particular, pH effects on specific reaction rates are often a reflection of positions of acid-base equilibria for reactants. Such equilibria are insufficient to account fully for the unusually complex relationship between pH and oxygenation rates for sulfide solutions. Nonetheless, they comprise essential background data on which any eventual explanation must rely and may be the basis for trends in specific rate at pH less than 7 or greater than 12.

Equilibrium of Aqueous Sulfides. The concentrations of sulfide species in water are determined by two equilibria. When the weak dibasic acid H_2S or any of its salts is added to water, the equilibria

$$H_2S = H^+ + HS^-; \quad K_1 = \frac{(H^+)(HS^-)}{(H_2S)} \quad (11)$$

$$HS^- = H^+ + S^{2-}; \quad K_2 = \frac{(H^+)(S^{2-})}{(HS^-)} \quad (12)$$
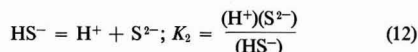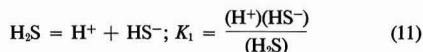
become established almost instantaneously. Here parentheses represent activities of the enclosed species and the K's are thermodynamic dissociation constants.

Then, when (H^+), K_1, K_2, and ΣS^{2-} are known, it is possible to compute the individual concentrations of H_2S, HS^-, and S^{2-}. The accuracy with which such computations of the relative concentrations can be made is determined to a great extent by the reliability of the equilibrium constants.

During the last 70 years, many investigators employing various techniques have measured and reported different

values for the first and second ionization constants of hydrogen sulfide. An extensive literature survey (Chen, 1970) shows that reported pK_1 values at 25°C vary from 6.97 to 7.06, and pK_2 values from 12.35 to 15. A reasonable mean value for pK_1 at 25°C is 7.02; on the other hand, no precision can be attached to any calculations involving K_2.

Simple computation from the values of K_1 and K_2 show that HS^- is the dominant species in sulfide solutions everywhere from pH 7 to pH 12.5 and that it comprises better than 90% of the sulfide species in aqueous solution from pH 8 to 11.5. It is natural therefore to attach the general oxygenation of sulfide in this mildly alkaline and acid pH range to the HS^- species as Abel (1956) has done. Moreover, the rapid decrease in rate of oxygenation as the pH decreases from 7 to 6 can be associated with the protonation of HS^- to give predominantly H_2S, which presumably is not readily oxidizable.
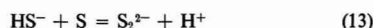
Equilibrium of Polysulfide Species. When crystalline sodium sulfide is added to oxygen-free water at room temperature, a clear solution is formed at any pH value. If, however, the water contains dissolved oxygen and has a pH between 6 and 9, a straw to greenish color soon develops, the intensity of which depends on the initial concentration of sulfide. Upon acidification, a whitish colloidal sulfur suspension forms and shows a Tyndall beam effect. The colored solution exhibits an absorption band in the uv region at 285–290 mµ wavelengths. When the colored solution is diluted to an initial sulfide concentration of $2 \times 10^{-4}M$, the color disappears completely; the uv absorption is still observable, however. It seems clear that some polysulfides have been formed in this partial oxidation and that the properties of the polysulfides need to be included in the interpretation of sulfide oxygenation.

Polysulfide ions, S_x^{2-}, may be formed through the interaction of sulfur and an aqueous solution of sulfide. Many investigators (Peschanski and Valensi, 1949; Maronny and Valensi, 1954–57; Schwarzenbach and Fisher, 1960) have confirmed that the polysulfuration index, x, is between 2 and 5 in aqueous solution. Schwarzenbach and Fisher (1960) also have shown that only S_4^{2-} and S_5^{2-} can be measured in aqueous polysulfide solution; S_2^{2-} and S_3^{2-} are either unstable or at such low concentrations that they cannot be detected.

It is noted that K_2 values of the acid dissociations of H_2S_4 and H_2S_5 are $10^{-6.3}$ and $10^{-5.7}$, respectively (Schwarzenbach and Fisher, 1960). So over the whole pH range from 6 up, S_4^{2-} and S_5^{2-} are the dominant polysulfide species present and comprise more than 90% of the polysulfide species at pH > 7.3.

Hartler et al. (1967), studying the rate of sulfur dissolution in aqueous sodium sulfide found that the rate of sulfur dissolution is influenced by factors related to each of these steps: the rate of mass transfer of reactant and also that of product, the specific active surface of the sulfur, and the rate of the chemical reaction. Moreover, it was found that the formation of polysulfide ions has an autocatalytic effect on the rate of sulfur dissolution.

Since in the reaction sequence

$$HS^- + S = S_2^{2-} + H^+ \quad (13)$$

$$S_2^{2-} + S = S_3^{2-} \quad (14)$$

$$S_3^{2-} + S = S_4^{2-} \quad (15)$$

$$S_4^{2-} + S = S_5^{2-} \quad (16)$$

each product is also a reactant for the next step, autocatalysis is to be expected if reactions after the first one are rapid. So,

it has been suggested that the mass transfer steps may become rate-determining in the presence of polysulfide.

In the oxidation of sulfide by dissolved oxygen the initial yield of sulfur is critical to the subsequent formation of polysulfide. When the concentration of sulfur in solution is less than its saturation value—i.e., $5 \times 10^{-6}M$ (LaMer and Kenyon, 1947), sulfur is present in homogenous solution and its reaction with sulfide should be much faster than that for the colloidal or solid state. So, whenever sulfur precipitation occurs, the concentration of total S^0 in solutions would be great enough to give equilibrium concentrations of all polysulfides as well as a saturation concentration of sulfur itself.

Saturation Concentration of Total S^0. It is now well-established that an x value greater than 5 is not likely in $S_x{}^{2-}$. The total S^0 concentration in solution may then be defined as the sum of the concentration of the sulfur itself plus that of the zero oxidation state sulfur combined with sulfide in each of the possible species of polysulfide up to $S_5{}^{2-}$, thus

$$\Sigma S^0 = S_{sol}{}^0 + S_2{}^{2-} + 2S_3{}^{2-} + 3S_4{}^{2-} + 4S_5{}^{2-} \quad (17)$$

For each of the polysulfide species an equilibrium may be written in the form

$$HS^- + (x-1)S = S_x{}^{2-} + H^+; \quad K_x = \frac{(H^+)(S_x{}^{2-})}{(HS^-)(S)^{x-1}} \quad (18)$$

The exact form of the dependence on sulfur activity is not known, for the formula of dissolved elemental sulfur is uncertain. If, however, the equilibrium is measured and used only under saturation conditions, the sulfur activity may be taken as unity, so that one may write, regardless of the sulfur formation,

$$K_x = \frac{(H^+)(S_x{}^{2-})}{(HS^-)} \quad (19)$$

Values of pK_x for the following equilibria have been reported by Maronny (1959):

$$HS^- + S = S_2{}^{2-} + H^+; \quad pK_2 = 12.16 \quad (20)$$

$$HS^- + 2S = S_3{}^{2-} + H^+; \quad pK_3 = 10.85 \quad (21)$$

$$HS^- + 3S = S_4{}^{2-} + H^+; \quad pK_4 = 9.86 \quad (22)$$

$$HS^- + 4S = S_5{}^{2-} + H^+; \quad pK_5 = 9.18 \quad (23)$$

Combination of expressions for each of these equilibria with that for the first acid dissociation of H_2S with neglect of the second ionization of H_2S yields equations for the variation in the position of equilibrium with pH, valid for pH < 11:

$$\log (S_2{}^{2-}) =$$
$$-12.16 + \log (\Sigma S^{2-}) + pH - \log\left[1 + \frac{(H^+)}{K_1}\right] \quad (24)$$

$$\log (S_3{}^{2-}) =$$
$$-10.85 + \log (\Sigma S^{2-}) + pH - \log\left[1 + \frac{(H^+)}{K_1}\right] \quad (25)$$

$$\log (S_4{}^{2-}) =$$
$$-9.86 + \log (\Sigma S^{2-}) + pH - \log\left[1 + \frac{(H^+)}{K_1}\right] \quad (26)$$

$$\log (S_5{}^{2-}) =$$
$$-9.18 + \log (\Sigma S^{2-}) + pH - \log\left[1 + \frac{(H^+)}{K_1}\right] \quad (27)$$

It is clear from these equations that concentrations of poly-

Table III. Concentrations of Polysulfide Species in Equilibrium with Sulfur at $(\Sigma S^{2-}) = 1 \times 10^{-4}M$

Species	pH				
	6	7	8	9	10
$pS^0{}_{sol}$	5.30	5.30	5.30	5.30	5.30
$p(S_2{}^{2-})$	11.20	9.46	8.20	7.16	6.16
$p(S_3{}^{2-})$	9.89	8.15	6.89	5.85	4.85
$p(S_4{}^{2-})$	8.90	7.16	5.90	4.86	3.86
$p(S_5{}^{2-})$	8.22	6.48	5.22	4.18	3.18
$p(\Sigma S^0)$	5.30	5.19	4.48	3.50	2.52

sulfides corresponding to sulfur saturation are functions of pH and sulfide concentration.

Computations of the concentrations of each of the $S_x{}^{2-}$ in equilibrium with a saturated solution of sulfur can be made for specific pH and ΣS^{2-} from the following relationships:

$$\text{Total sulfide} = H_2S + HS^- +$$
$$S_2{}^{2-} + S_3{}^{2-} + S_4{}^{2-} + S_5{}^{2-} \quad (28)$$

$$(HS^-)(H^+) = K_1(H_2S) \quad (29)$$

$$(S_x{}^{2-})(H^+) = K_x(HS^-) \quad (30)$$

Results of such computations for 10^{-4} molar total sulfide and pH values from 6 to 10 are shown in Table III. It is noted that the concentrations of $S_2{}^{2-}$ and $S_3{}^{2-}$ are small compared to $S_4{}^{2-}$ and $S_5{}^{2-}$ which is in agreement with the general finding that in polysulfide solution only $S_4{}^{2-}$ and $S_5{}^{2-}$ are present in sizable quantity (Schwarzenbach and Fisher, 1960).

Table III includes also computed data for ΣS^0 in a solution with saturated sulfur at pH values from 6 to 10.

$$\Sigma S^0 = S^0{}_{sol} + S_2{}^{2-} + 2S_3{}^{2-} + 3S_4{}^{2-} + 4S_5{}^{2-} \quad (31)$$

where $S^0{}_{sol}$ was estimated to be about $5 \times 10^{-6}M$ (LaMer and Kenyon, 1947). It may also be noted from these relationships that whenever the sulfide concentration is increased tenfold, the concentration of each polysulfide species in a saturated sulfur solution is increased correspondingly.

In a reaction solution, sulfur has to be formed from oxygenation of sulfide. Therefore, the actual upper limit of polysulfide concentration for pH 6 and 7 will be slightly less than the figures presented in Table III. For higher pH values it will be much less because of the limitation on the amount of sulfur formed.

Another model, which is closer to the actual solution condition in this study, is based on the assumption that sulfur is the only reaction product and the fact that no sulfur is initially added. The computations are based on the following equations:

$$\text{Total sulfide} = H_2S + HS^- + 2S_2{}^{2-} +$$
$$3S_3{}^{2-} + 4S_4{}^{2-} + 5S_5{}^{2-} + 5 \times 10^{-6} \quad (32)$$

$$(HS^-)(H^+) = K_1(H_2S) \quad (33)$$

$$(S_x{}^{2-})(H^+) = K_x(HS^-) \quad (34)$$

$$\Sigma S^0 = 5 \times 10^{-6} + S_2{}^{2-} + 2S_3{}^{2-} + 3S_4{}^{2-} + 4S_5{}^{2-} \quad (35)$$

The concentration of each polysulfide species and the saturated concentration of sulfur for specific pH and $(\Sigma S^{2-})_o$, based on these equations, are shown in Table IV. Although the assumption that sulfur is the only product from oxygenation is not in accord with the general pattern of experimental results, never-

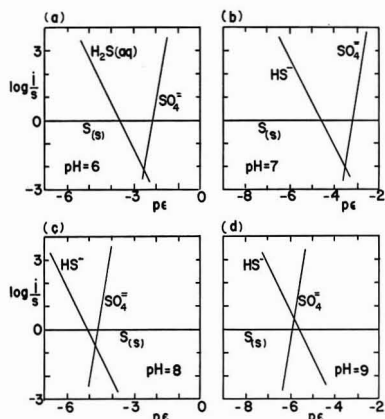| Species	pH				
	6	7	8	9	10
pS^0_{sol}	5.30	5.30	5.30	5.30	5.30
$p(S_2^{2-})$	11.22	9.49	8.35	7.87	7.78
$p(S_3^{2-})$	9.92	8.18	7.04	6.56	6.47
$p(S_4^{2-})$	8.92	7.19	6.05	5.57	5.48
$p(S_5^{2-})$	8.24	6.51	5.37	4.89	4.80
$p(\Sigma S^0)$	5.30	5.19	4.60	4.19	4.10

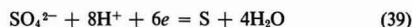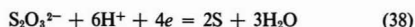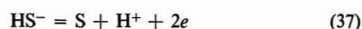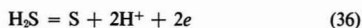Figure 7. Relative activity of sulfur species at different redox potentials

theless, this simplification provides a basis to compute the upper limit of concentration of each polysulfide species and the saturated sulfur concentration. It also partially explains the pH dependence of sulfur precipitation in the absence of catalyst.

Again, it is demonstrated that sulfide has a higher holding capacity for sulfur at higher pH; thus with the increase of pH beyond 7.5, precipitation of sulfur becomes more and more difficult.

It may also be noted that, at pH 6, polysulfide concentrations are negligible compared with that of dissolved elemental sulfur, whereas at pH 7 the equilibrium concentration of sulfur in polysulfides is a significant fraction of the total dissolved S^0 and at pH 8 the sulfur in polysulfide is dominant.

These remarks are pertinent, of course, only when there is enough sulfur to saturate the solution. Because the major polysulfides are S_4^{2-} and S_5^{2-}, their relative concentrations may be expected to drop off greatly as the sulfur activity decreases.

Figure 7 shows the relative activity of sulfide, sulfur, and sulfate using the activity of sulfur as unity. The dependence of log (SO_4^{2-}/S), and log (HS^-/S) or log (H_2S/S) are expressed as a function of $p\epsilon$ at different pH values by using Equations 36–39. The methodology for the construction of such diagrams is detailed elsewhere (Stumm and Morgan, 1971).

$$H_2S = S + 2H^+ + 2e \qquad (36)$$

$$HS^- = S + H^+ + 2e \qquad (37)$$

$$S_2O_3^{2-} + 6H^+ + 4e = 2S + 3H_2O \qquad (38)$$

$$SO_4^{2-} + 8H^+ + 6e = S + 4H_2O \qquad (39)$$

Free energy data are obtained from oxidation potentials (Latimer, 1952).

It is clear from these calculations that activity of sulfur drops drastically with increasing pH value at any $p\epsilon$ state. It is for this reason that computations on the distribution of polysulfides break down at pH values greater than 10 when, according to the calculation, the concentrations of S_4^{2-} and S_5^{2-} species should dominate the mass balance relationship.

Interpretation of Kinetic Behavior. A primary problem in the interpretation of the kinetics of oxygenation of sulfide is the explanation of the unique and complex dependence of the reaction rate on pH. There are two maxima to be accounted for plus changes in stoichiometry and induction periods. Also the maximum in the lower pH range shifts its location from pH 8.0 to pH 6.7 and becomes relatively much greater as compared with the second maximum as the initial total sulfide concentration is increased from 10^{-4} to $10^{-2}M$.

Abel, in 1956, hypothesized that the drastic increase in the rate of oxygenation from pH 6 to 8 represented increasing dissociation of H_2S to HS^- with HS^- as the specific active reactant with oxygen. Such a hypothesis does seem to explain the kinetic results at pH 6 to 8 when the total sulfide is only $10^{-4}M$, and a molar excess of oxygen is present. At pH 6, HS^- constitutes less than 10% of the total sulfide while at pH 7 it is about 50% and pH 8 more than 90% of the total sulfide. The data in Table II for k values in the $10^{-4}M$ concentration range vary quantitatively as well as qualitatively directly with the percentage of HS^- in solution.

On the other hand, Abel's explanation is inadequate to account for the decrease in the rate at pH > 8.3 nor for the occurrence of the second maximum near pH 11. For, HS^- remains predominant as more than 90% of the total sulfide over the whole pH range from 8 to about 12. Abel was, of course, unaware of the detailed complexities of the pH dependence. Also, the shift in the first maximum to lower pH values with increase in sulfide concentration is inexplicable with Abel's hypothesis.

It is clear that other factors showing a pronounced change near pH 7 must be adduced to account for all the observed rate phenomena in this pH region. One such change is the stability of the polysulfides, which are insignificant at pH 6 but predominate at pH 8 in solutions saturated with sulfur. Yet, when sodium sulfide is dissolved in various oxygen-containing buffers between pH 6 and 9, as previously described, the resulting uv absorption at 285–290 μ due to polysulfide is strongest near pH 7 and very little appears at either pH 6 or 9 as shown in Figure 6. The observation is expected for pH 6 where polysulfide is unstable; at pH values greater than 9 the polysulfide must fail to appear because sulfur is not being produced by the oxygenation of sulfide in this range. This assumption seems reasonable judging from the computation on the activity of sulfur with reference to its oxyanions and hydrogen sulfide as shown in Figure 7.

Since the maximum observed formation of polysulfide near pH 7 coincides with the pH of maximum oxygenation rate for relatively concentrated sulfide solutions, $10^{-2}M$, it is suggested that this accentuated maximum results from a more rapid reaction of polysulfide with O_2 than that of HS^- with O_2. Polysulfide thus acts as a catalyst for oxygenation of sulfide, as proposed by Bowers et al. (1966), and leads to the accentuated maximum at pH 7. Consistent with this hypothesis is the observation that sulfur is precipitated on the acid side of the maximum during the oxygenation of $10^{-2}M$ sulfide.
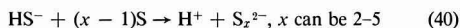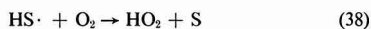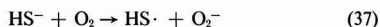
It is implicit in this hypothesis that little polysulfide is formed at pH 8 and greater because of a lack of available sulfur and thus the autocatalytic action of polysulfide is not observed in these alkaline solutions. There are a number of other phenomena related to the sulfide–oxygen system that exhibit change in mildly alkaline solutions and so might be associated with the decline in rate in this region. Because the second dissociation of $HSO_3^- = H^+ + SO_3^{2-}$, has $pK_2 = 7.2$ this is a pH region in which predominant HSO_3^- becomes predominant SO_3^{2-} as pH increases. Moreover, the position of equilibrium for the reaction

$$HSO_3^- + S \rightleftarrows S_2O_3^{2-} + H^+ \qquad (36)$$
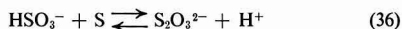
shifts to favor thiosulfate rather than sulfite plus sulfur just in this region. It may be that the lack of available S for poly-sulfide formation is in part the result of its consumption to form thiosulfate. A third noteworthy fact is that the inter-mediate products of the oxygenation at low sulfide concen-trations shift from a mixture of sulfite and thiosulfate to almost pure thiosulfate as the pH increases beyond 8.5 (Chen and Morris, 1970). It seems likely that these phenomena are interrelated and that some aspects of them are responsible for the decline in oxygenation rate in mildly alkaline solutions.

Conclusion

Based on the observations of reaction intermediates and products, the change in reaction rate and stoichiometry with reagent proportions, and on the study of catalysis and in-hibition (Chen and Morris, 1972), a reaction pathway is pro-posed for the neutral and slightly acid or alkaline solutions.

$$HS^- + O_2 \rightarrow HS\cdot + O_2^- \qquad (37)$$

$$HS\cdot + O_2 \rightarrow HO_2 + S \qquad (38)$$

$$HS\cdot + O_2^- \rightarrow S + HO_2^- \qquad (39)$$

$$HS^- + (x-1)S \rightarrow H^+ + S_x^{2-}, \; x \text{ can be 2–5} \qquad (40)$$

The reaction scheme following the polysulfide formation is presented in Figure 8.

In natural waters, in the absence of biological activity, sul-fide can be slowly oxidized to sulfur which then combines with the remaining sulfide to form polysulfides. It is possible that oxygenation of sulfide in the interface of oxygen and sulfide layers undergoes a sulfide–sulfur–polysulfide cycle, with the initial oxidation of sulfide to sulfur as a rate-determining step.

Since sulfide oxidation in nature is largely biologically mediated, the reaction scheme present in this paper is ap-plicable only to chemical oxidation. However, oxidation of sulfide to sulfur by sulfur bacteria can eliminate the rate-determining step on the initial sulfur formation; subsequently, chemical and biological factors may each play a significant role in the further oxidation.

Nomenclature

k = specific rate constant
k_A = rate constant
k_B = rate constant
k_o = rate constant with same initial sulfide concentra-tion and different initial oxygen concentration
k_s = rate constant with same initial oxygen concentra-tion and different initial sulfide concentration
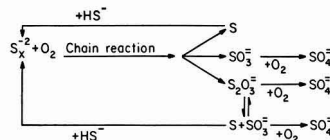
Figure 8. Reaction pathway of oxygenation of sulfide

M = molar or mol/l.
m = reaction order with respect to sulfide concentration
n = reaction order with respect to oxygen concentration
$p\epsilon$ = $-\log(e)$, relative electron activity, equivalent to $(nF/2.3RT)\cdot E$
R_i = initial rate, slope taking after induction period
(ΣS^0) = total sulfur in zero oxidation state, including por-tion bound in polysulfides
(ΣS^{2-}) = concentration of total sulfide at any time, including H_2S, HS^-, and S^{2-}
$(\Sigma S^{2-})_0$ = concentration of total sulfide at $t = 0$
S^0_{sol} = free soluble sulfur, not chemically bound
X = polysulfuration index

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Adsorption of Lindane and Dieldrin Pesticides on Unconsolidated Aquifer Sands

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■ The adsorption of lindane and dieldrin on natural aquifer sand from Portage County, Wis., was investigated in laboratory batch tests. From aqueous solutions whose concentrations were in the range of 5 to 500 μg of pesticide/l., the corresponding adsorption capacity of the sand was in the ng/g range. The range of temperature and pH likely to occur in an aquifer would have no significant effect on the uptake of dieldrin and lindane. The naturally occurring dissolved organics present in two Wisconsin lake waters were found to reduce the adsorption of dieldrin. However, lindane adsorption was unaffected by the same organics. Nearly 70% of the adsorbed lindane was leached in three successive washes of distilled water. In contrast, less than 20% of the dieldrin adsorbed by the aquifer sand was removed after three washes.

The intelligent use of pesticides requires an understanding of the many ecological interrelations of a pesticide following its application to soil or water. Because of their relative chemical stability, most of the chlorinated hydrocarbon pesticides may survive in soils and water for years (Lichtenstein et al., 1960; Rudd, 1963). A number of cases involving the contamination of groundwater by pesticides has been reported (Nicholson, 1965; Public Health Service, 1964, 1965). This paper reports the findings of an investigation of the uptake of two chlorinated hydrocarbon pesticides on a natural aquifer sand (Boucher, 1967). The objectives of the study were: (1) to determine the sorption capacity of the sand, (2) to determine the effects of temperature, particle size, pH, and dissolved organics on the uptake of the pesticides, and (3) to consider the influence of the chemical structure of the adsorbate pesticides on their uptake.

Experimental Materials and Procedures

Adsorbents. The adsorbent substrates used in this study included: natural aquifer sand taken from the Little Plover River basin; Ottawa sand standard, 20–30 mesh (Fisher Scientific Co., Cat. No. S-23); and silica sand, 80–120 mesh (Fisher Scientific Co., Cat. No. S-151). The latter two sands were selected for use as a standard substrate against which the results gained from the aquifer sand could be compared. Aquifer sand samples were collected from the Little Plover River basin, Portage County, Wis. Samples were taken from four test holes 15 ft apart at 5-ft intervals from the surface to bedrock, approximately 90 ft below surface. The sand was air-dried at 22° to 25°C and stored in the dark in cloth bags for later use. Particle size analysis showed that the sand was well sorted with an effective size and uniformity coefficient of 0.18 mm and 2.0 mm, respectively.

The cation-exchange capacities of the natural aquifer sand, 80–120 mesh silica sand, and 20–30 mesh Ottawa sand, determined according to Jackson's procedure (Jackson, 1958), were 0.8, 0.2, and 0.04 meq/100 grams, respectively.

Adsorbates. The pesticides used in this study were γ-1,2,3,4,5,6-hexachlorocyclohexane, the active principle of BHC (100% purity City Chemical Corp., New York, N.Y.), and 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo-exo-5,8-dimethanonaphthalene, the active component of dieldrin (anal ref grade Shell Chemical No., New York, N.Y.), referred to as lindane and dieldrin. These compounds were chosen as representative of the chlorinated hydrocarbon class of organic pesticides and are commonly used.

Pesticide standard stock solutions were prepared in Nanograde benzene (Mallinckrodt) and stored at 4° or 5°C. Benzene was used because it freezes at these temperatures, eliminating concentration due to evaporation. Working standards for injection into the gas chromatograph were prepared by appropriate dilution of the stock solutions with Nanograde N hexane (Mallinckrodt).

The aqueous pesticide solutions used in the sorption experiments were prepared by evaporating to dryness an appropriate volume of an acetone pesticide solution in a 9- or 18-l. carboy. The particular water was then added and a minimum of five days was allowed for the pesticide to dissolve. The mass of pesticide added to the carboy was kept below the solubility limit of the total solution being prepared. These solutions were diluted as necessary to provide the desired range of concentrations. The concentration of the pesticide water was determined at the time of each sorption experiment. When solutions of water from Lake Mendota, Dane County, Wis., and Lake Mary, Vilas County, Wis., were prepared, the water was passed through a 0.45-μ pore size Millipore filter prior to adding it to the carboy. The carboys were covered with aluminum foil and stored in the dark.

The two lake waters were used in experiments designed to evaluate the influence of dissolved organic carbon on adsorption capacity. Assuming that relative dissolved organic carbon can be estimated from COD data, Lake Mary water (COD = 25 mg/l.) has a concentration of dissolved organic carbon approximately three times that of Lake Mendota water (COD = 9 mg/l.).

Batch Experiments. The adsorption batch tests were designed to permit the development of an isothermal relationship to describe the adsorption data. All experiments were made under controlled temperature conditions. The temperature range under investigation was 5° to 40°C. Periodic ob-

servation of the water bath temperatures indicated variations less than ±0.2°C.

For the adsorption tests, 100 grams of sand and 55 cc of pesticide water were added to a 125-cc ground glass–stoppered Erlenmeyer flask. The flasks were shaken in the controlled temperature baths for 24 hr when equilibrium conditions were desired. For rate experiments, the time of shaking was varied accordingly. After shaking, the supernatant was centrifuged for 15 min at approximately 12,000 g. A 5- to 25-cc aliquot of the centrifuged solution was extracted three times with 10, 5, and 5 cc of Nanograde hexane which was then brought to 25 cc in a volumetric flask. Prior to extraction, sodium sulfate was added to the water to minimize potential emulsion formation.

Gas chromatographic analysis for the pesticide was made directly on the hexane extract or dilution thereof.

To estimate the total amount of lindane desorbed, the following procedure was used. To a 250-cc ground glass–stoppered Erlenmeyer flask were added 100 grams of sand and 50 cc of pesticide water. The flasks were shaken for 24 hr, after which time 20 cc of supernatant were pipetted off and centrifuged. A 5-cc sample of the centrifuged water was extracted and analyzed for lindane. The adsorption test mixture was washed three times in the constant temperature bath with 150 cc of distilled water for 24 hr. At the end of each wash period, 140 cc were pipetted from the supernatant and analyzed for lindane.

Because smaller volumes were used for the dieldrin desorption tests, the procedure was modified by the use of a 125 cc Erlenmeyer flask and by using 60-cc wash volumes.

Analytical Procedures. The hexane extracts of the aqueous pesticide solutions used in the study were analyzed for their pesticide content by injecting a 1-μl sample of the extract or appropriate dilution thereof into a Model 1520 Wilkins Aerograph gas chromatograph equipped with an electron capture detector. The mass of pesticide in the test solution injected was determined by comparing its peak height response occurring at the appropriate retention time to a standard curve prepared from standard solutions of the pesticide. A new standard curve was prepared at the time of each analytical run. For lindane, the concentration range of the standard solutions was 1 to 16 pg/μl. In the case of dieldrin, a range of 4–24 pg/μl was used. The gas chromatographic column consisted of a single borosilicate tube, $1/8$ in. by 6 ft, extending from the injection port into the electron capture detector. The column was packed with 2.5% DC-200 coated on 80–100 mesh Chromosorb-W, HMDS. Carrier gas flow was 30 cc/min of high-purity nitrogen. For lindane, operating temperatures for injection port, column oven, and detector oven were 230°, 188°, and 220°C, respectively. The column oven temperature was increased to 206°C for dieldrin. Electrometer attenuations of 4× or 8× were used for all analyses. The electrometer output was recorded on a 1-mV Brown Electronik recorder.

Percent Recovery. In the recovery studies, the pesticides were introduced into triplicate water samples by adding 1 cc of an acetone solution to 50 cc of water. The concentration in the water was determined using the extraction and gas chromatographic procedures described previously. The data indicate that recovery is essentially complete (91–102%) with no meaningful loss of pesticide during the analytical procedure. Water from Lake Mary and Lake Mendota did not affect the recoveries.

Reproducibility of Data. To estimate the precision of the experimental data, a simple statistical analysis was made on results of replicate sorption tests of lindane on aquifer sand
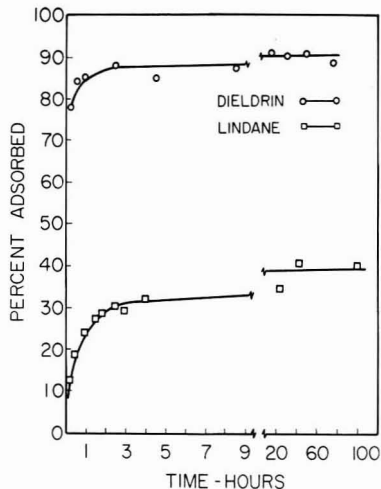
Figure 1. Adsorption of lindane and dieldrin

50 cc of lindane water (47.8 μg/l.), 50 cc of dieldrin water (63.0 μg/l.), 100 grams of aquifer sand, temperature = 5°C

and of replicate analyses of pesticide water standards. Standard procedures previously described were used for the adsorption tests, extractions and analytical determinations. The variability of the data from the adsorption tests is slightly greater than that from the analyses of water standards. The mean and standard deviation of 20 determinations of the lindane concentration of the supernatant from adsorption tests were 34.9 ± 1.6 μg/l. Six replicate determinations of the lindane concentration of a water standard yielded a mean and standard deviation of 51.6 ± 0.9 μg/l.

Results

Adsorption Rates. The rate of lindane and dieldrin adsorption on aquifer sands was determined at initial concentrations of 47.8 and 63.0 μg/l., respectively. Pesticide solutions were equilibrated with the sands for periods ranging from 15 min to more than 100 hr. Duplicate tests were made. A comparison of the percent of lindane and dieldrin adsorbed from solution by the sand is shown in Figure 1. The data show that initial uptake is rapid during the first 4 to 5 hr. However, slight additional adsorption may continue after 100 hr.

Isotherms for Lindane and Dieldrin. The adsorption of lindane and dieldrin on aquifer sand as a function of concentration is illustrated by the isotherms shown in Figure 2. The plotted data were derived from four replicate adsorption tests at 5°C shaken for 24 hr. For the concentration range tested, the adsorption of both pesticides fits the Freundlich isotherm. Dieldrin uptake on aquifer sand is approximately 20 times greater than the uptake of lindane on the same substrate.

A comparison of lindane adsorption on aquifer sand and the two silica standard sands was made to evaluate the influence of particle size and cation-exchange capacity of the adsorbent substrate. Figure 3 shows the results derived by averaging the data from the four replicate tests using aquifer sands and duplicate tests with 80–120 mesh standard silica. The results plotted for 20–30 mesh Ottawa sand are from a single test. The isotherm plot shows a general trend of increasing adsorption capacity for lindane from Ottawa sand to 80–120 mesh
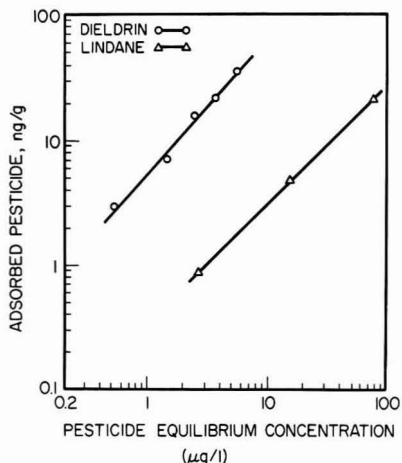
Figure 2. Lindane and dieldrin uptake on aquifer sands

Equilibration time = 24 hr, 50 cc of pesticide water, 100 grams of aquifer sand, temperature = 5°C
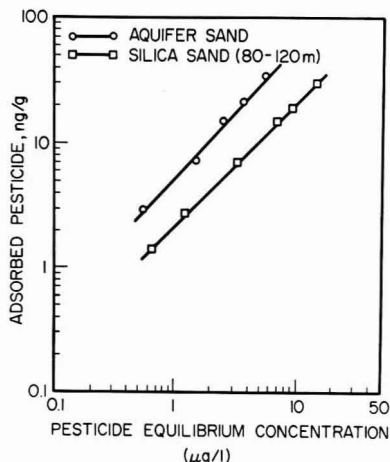

Figure 4. Dieldrin uptake on aquifer and silica sand

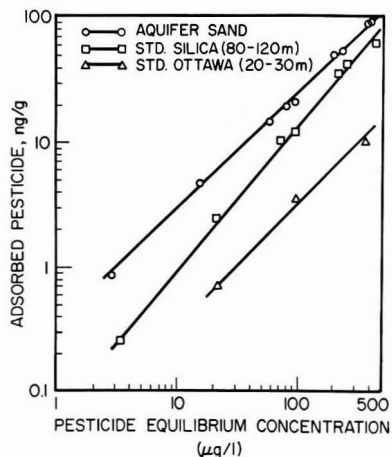50 cc dieldrin water, 100 grams of sand, equilibration time = 24 hr, temperature = 5°C

Figure 3. Lindane uptake on aquifer and standard sands

50 cc of lindane water, 100 grams of sand, temperature = 5°C, equilibration time = 24 hr

standard silica to aquifer sand. The increased capacity of 80–120 mesh sand over the 20–30 mesh substrate indicates that the increased surface available on the smaller sized sand results in greater adsorption capacity. Because of the wide range of particle size for the aquifer sand, it is difficult to attribute its increased capacity to surface area considerations alone. Correlation of adsorption capacity with cation-exchange capacity appears significant from the data in Figure 3. The adsorption capacity of aquifer sand is approximately 2.5 times greater than that of 80–120 mesh silica sand, while their cation-exchange capacities differ by a corresponding factor of 4.4. Similarly, the adsorption capacity of 80–120 mesh silica is about three times that of 20–30 mesh silica, while their cation-exchange capacities vary by a factor of 4.

Isotherms for the adsorption of dieldrin on aquifer and

standard silica sands are shown in Figure 4. The datum points are mean values of three replicate tests of each substrate. The resultant log-log plots fit the Freundlich equation. Similar to the case of lindane uptake, the adsorption of dieldrin on aquifer sand is approximately two times greater than that on 80–120 mesh silica.

Effect of Temperatures. Although the range of temperature variations generally found in a groundwater aquifer would not be expected to significantly affect the adsorption equilibria, the effect of temperature was considered in the hope that it might further the understanding of the sorption process. Both lindane and dieldrin show significantly reduced adsorption on aquifer sand at 40°C as is illustrated in Figures 5 and 6. The plotted values are means of triplicate adsorption runs at 5° and 40°C.

By analogy to the Clausius-Clapeyron equation (Daniels and Alberty, 1955), the apparent heat of adsorption of lindane and dieldrin on aquifer sand was found to be about 5 and 3 kcal/mol, respectively. The magnitude of the apparent heats of adsorption falls within the range usually expected for physical adsorption.

Effect of pH. To estimate the influence of pH on the uptake of lindane on aquifer sands, standard adsorption tests were run in which the pH of the test solutions was varied from pH 4.3 to 8.9. Solutions of HCl and KOH were used to maintain a constant pH. The results of triplicate tests made at each pH indicate no significant difference in the adsorption of lindane as a function of pH within the range tested.

Effect of Dissolved Organic Carbon. The effect of dissolved organic carbon on the adsorption of lindane by aquifer sands was investigated by running standard adsorption tests with pesticide waters prepared with Lake Mendota water which had been passed through a 0.45-μ pore size Millipore filter to exclude particulate matter. The results of triplicate tests of both distilled and Lake Mendota waters indicate no significant difference in uptake due to Lake Mendota water.

To determine the influence of dissolved organic material on the adsorption of dieldrin on aquifer sands, an analogous experiment was run using distilled Lake Mendota and Lake Mary waters. The mean values of duplicate tests are shown in
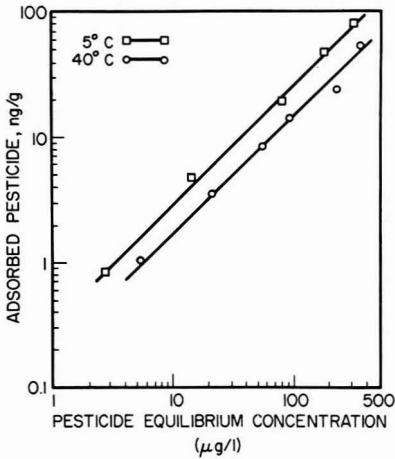
Figure 5. Effect of temperature on lindane adsorption on aquifer sand

Equilibration time = 24 hr, 50 cc of lindane water, 100 grams of aquifer sand
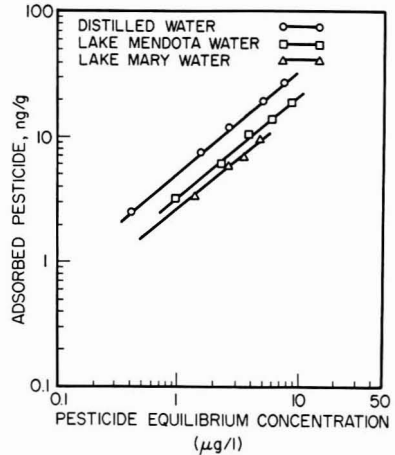
Figure 7. Effect of Lake Mendota and Lake Mary water on dieldrin uptake on aquifer sand

50 cc of pesticide water, 100 grams of aquifer sand, equilibration time = 24 hr, temperature = 5°C
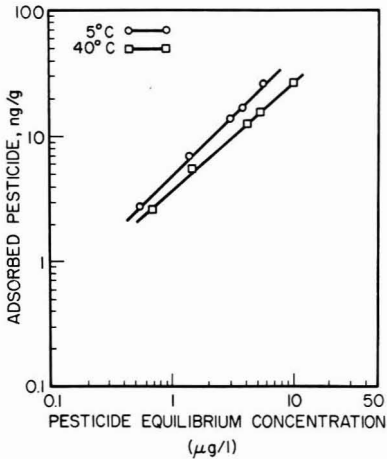
Figure 6. Effect of temperature on dieldrin adsorption on aquifer sand

Equilibration time = 24 hr, 50 cc of dieldrin water, 100 grams of aquifer sand
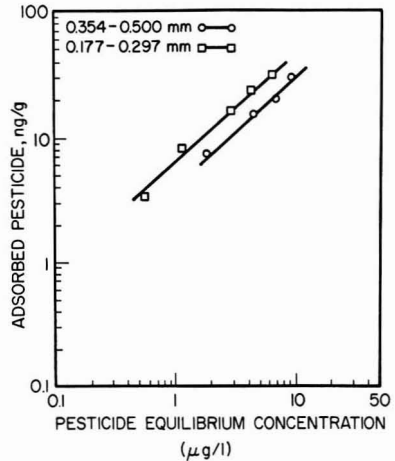
Figure 8. Effect of particle size on uptake of dieldrin on aquifer sand

50 cc of dieldrin water, 100 grams of aquifer sand, equilibration time = 24 hr, temperature = 5°C

Figure 7. The isotherms indicate a distinct reduction in the uptake of dieldrin as the dissolved organic concentration of the adsorbate solution is increased. The greatest reduction occurs between the Lake Mendota and distilled water isotherms. Using the distilled water results as a basis, the reduction in the adsorption capacity of the sand in the cases of Lake Mendota and Lake Mary water is approximately 40 and 47%, respectively.

Effect of Particle Size. To estimate the effect of particle size on the uptake of dieldrin on aquifer sands, two size fractions, 0.35 to 0.50 mm and 0.8 to 0.3 mm, were obtained by sieving. The standard adsorption tests were run using each fraction. Figure 8 presents the results obtained. The plotted data are means of duplicate tests of each size fraction. The results indicate an increased adsorption capacity for the smaller size

fraction as would be expected. However, the increased uptake does not appear to be related to adsorbent surface area alone. Although the capacity of the smaller fraction is approximately 40% greater than that of the larger fraction, the total surface area of the former is estimated to be about eight times that of the latter.

Desorption Characteristics. Experiments were run to evaluate the differences in dieldrin desorption at equilibrium conditions as a function of: dissolved organic carbon content of the adsorbate solution, and aquifer vs. silica sand. Standard desorption tests were made under equilibrium conditions. A single wash was used to obtain the data shown in Figure 9. Each bar value represents the mean of four replicate tests. The results indicate greater desorption from the standard silica sand than from aquifer sand. Similarly, increased
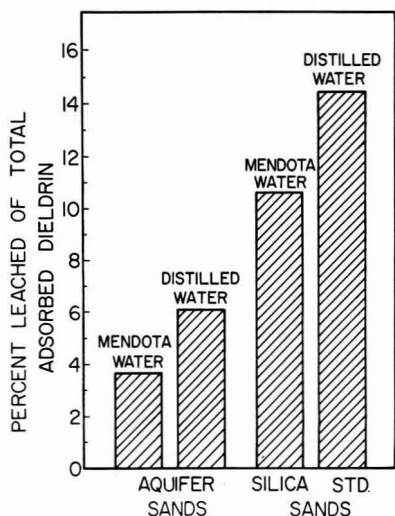
Figure 9. Effect of Lake Mendota water on the desorption of dieldrin from aquifer and standard silica sands, adsorbed dieldrin (4 replicates)

Aquifer sand–Mendota water = 24.0 ± 0.2 ng/g, aquifer sand–distilled water = 22.9 ± 0.2 ng/g, silica sand–Mendota water = 20.9 ± 0.3 ng/g, silica sand–distilled water = 20.5 ± 0.2 ng/g, single wash = 50 cc of distilled water, 100 grams of sand, wash time = 24 hr, temperature = 5°C

desorption occurred from adsorbate solutions of distilled water than from Lake Mendota water solutions. The pesticide–sand association is strongest for the Mendota water–aquifer sand system and weakest for the distilled water–silica sand system.

The total amount of dieldrin desorbed from aquifer sand in successive washes was also estimated. The results of triplicate tests are shown in Table I. Approximately 17% of the dieldrin initially adsorbed on the aquifer sand is leached by three successive washes with distilled water.

Similar tests were made to determine the total lindane leached from aquifer sand in consecutive washes. Table II presents the results of four replicate tests. The data indicate that approximately 70% of the lindane initially adsorbed on the aquifer sand is leached in three washes. The greatest percentage is removed by the first wash followed by successive decreases.

Discussion

For both lindane and dieldrin, adsorption increases with increasing concentration of pesticide. The resulting isotherms can be described by the Freundlich equation; however, the constants for each isotherm were not evaluated, since they have no particular meaning relative to the sorbent properties, nor can they be related from one system to another. Because of the low concentrations required by solubility limitations, multilayering apparently did not occur in either case.

The increased uptake of dieldrin over lindane may be due to solubility differences as well as the asymmetry of the dieldrin molecule which may influence its electron density causing increased polarization compared to lindane. The increased polarity may result in stronger binding forces between dildrin and the sand particles.

The rate data suggest that an equilibrium interfacial concentration is reached rapidly and may be followed by a much slower penetration or diffusion of the pesticide molecules into the amorphous silica structure of the surface of the sand particles.

The decrease in the adsorption of dieldrin due to the presence of natural dissolved organics present in the adsorbate solution may be due to an insulating function of the organic fraction. That is, the dissolved organics, whose concentration is approximately 100 to 1000 times greater than that of the pesticide, can be expected to associate with the sand surface and effectively insulate the negatively charged surface of the sand. For lindane, this insulation may have negligible effect because of the more neutral character of the molecule. In the case of dieldrin, assuming a more polar nature than that of lindane, the possibly less polar surface presented by the organic coated sand would be expected to reduce the association between adsorbate and adsorbent. The observed effect of dissolved organic compounds in the adsorbate solution may also be due to a preferential association of dieldrin and the dissolved organic species remaining in solution resulting in less dieldrin being taken up by the sand.

It appears that the observed adsorption of lindane and dieldrin is the result of more than a single mechanism. Physical adsorption and hydrogen bonding may contribute to the total uptake. The dominant effect may be determined by the nature of the adsorbate and is influenced by competitive effects of the dissolved species. Impressed on these functions may be a rate-controlling penetration reaction brought about as a result of the amorphous nature of the sand surface.

Environmental Conditions. The results of this investigation on the sorption of lindane and dieldrin on Little Plover River basin aquifer sand in batch tests coupled with limited column tests, reported by Boucher (1967), can be used to characterize the general aspects of pesticide transport in the aquifer. Based on studies on the sorption of pesticides by soils in areas of high rates of precipitation, combined with low-permeability soils, little movement of surface contaminants to the groundwater would be expected because of the high sorption capacity shown by most soils for pesticides (Bailey and White, 1964). However, in areas of high-permeability soils and low precipitation rates, the conditions are ripe for groundwater contamination. Once the pesticide enters the aquifer it may be attenuated by dilution and sorption. Dilution

Table I. Desorption of Dieldrin from Aquifer Sand

ng Dieldrin adsorbed/g of aquifer sand	% Leached of total adsorbed dieldrin			
	Wash 1	Wash 2	Wash 3	Total
29.6	4.36	6.95	6.12	17.4
30.0	6.13	5.30	4.90	16.3
29.7	6.74	7.78	4.15	18.8

Table II. Desorption of Lindane from Aquifer Sand

ng Lindane adsorbed/g of aquifer sand	% Leached of total adsorbed lindane			
	Wash 1	Wash 2	Wash 3	Total
22.8	52.0	12.2	3.6	67.8
25.3	29.5	6.7	2.4	38.6
20.9	31.0	29.4	11.9	72.3
26.5	47.3	16.9	9.0	73.2

may or may not adequately attenuate the pesticide to an acceptable level.

In the case of lindane, little effective attenuation through adsorption to the sand substrate would be expected from a continuous source. If the pesticide entered the aquifer in a slug, it might be adsorbed immediately and effectively removed from causing potential harm to the water interests. The leaching by uncontaminated waters may cause sufficient dilution to negate potential problems. However, the initially adsorbed lindane would be expected to be readily removed and transported, which could possibly cause harmful results to interests susceptible to chronic low-level exposure.

An aquifer contaminated by dieldrin might be expected to react somewhat differently. The considerably increased capacity of the sand for dieldrin would result in an attenuation over a short distance. Once attenuated, the dieldrin might be expected to travel at a much slower rate and in lower concentrations than lindane. This difference would be expected to be magnified in areas where the groundwater contained appreciable amounts of dissolved organics.

Variations of pH, particle size, and temperature likely to be found in most subsurface environments would have little effect on the disposition of either pesticide in the aquifer. Simple batch-type tests on the other chlorinated pesticides for comparison of uptake capacity can be expected to yield insight to permit an estimation of their relative disposition in a given aquifer.

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Chemistry of Catalytic Nitrogen Oxide Reduction in Automotive Exhaust Gas

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■ The catalytic control of nitrogen oxide emissions in automobile exhaust was investigated in laboratory and engine dynamometer tests. A typical base-metal catalyst, an alumina-supported mixture of copper and chromium oxides, was used in all tests. The chemical reactions that control product formation during the reduction of nitrogen oxides over this catalyst were identified. It was shown that the catalyst first equilibrated the exhaust gases with respect to the water gas equilibrium:

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$
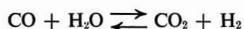
This changed the dominant reducing species in the exhaust gases from CO to H_2. The H_2 so formed was effective in promoting the conversion of NO to NH_3, especially at low temperatures ($<375°C$). At high temperatures ($>600°C$) the lesser amounts of NH_3 produced were shown to be due to the elemental decomposition of NH_3.

Catalytic systems are currently being investigated for the control of automotive nitrogen oxide emissions. Recently, the presence of ammonia has been detected in the exhaust of cars equipped with such catalytic emission

control systems (Bernstein et al., 1971; Meguerian and Lang, 1971; Hunter, 1971). Since the emission of ammonia is undesirable, it was of interest to try to determine the mechanisms by which ammonia is formed and those by which it is destroyed. The work was carried out using an alumina-supported mixture of copper and chromium oxides, a typical base-metal exhaust emission control catalyst. Initial work, which concentrated on the effect of various engine and exhaust parameters on catalyst performance, was followed by a series of laboratory studies to identify the nature of the reactions involved. All studies were carried out with small-scale catalytic reactors.

Experimental

Engine Studies. A 350 CJD production V-8 engine was operated at constant speed and load to produce exhaust gases of the desired composition. The engine was coupled to a dynamometer by which speed and load were controlled. The fuel used in this study was unleaded Amoco Premium gasoline. A portion of the exhaust gas stream was pulled from the main exhaust line through the small-scale catalytic reactors by a pump, as shown in Figure 1. The reactors were constructed from 1-in. o.d. thin-walled stainless steel tubing, mounted vertically in an electric furnace, which maintained the catalyst bed at the desired temperature. A shielded thermocouple, placed in the center of the bed, measured catalyst temperature. The catalyst ($1/8$-in. spheres, 36 cm^3 total volume,

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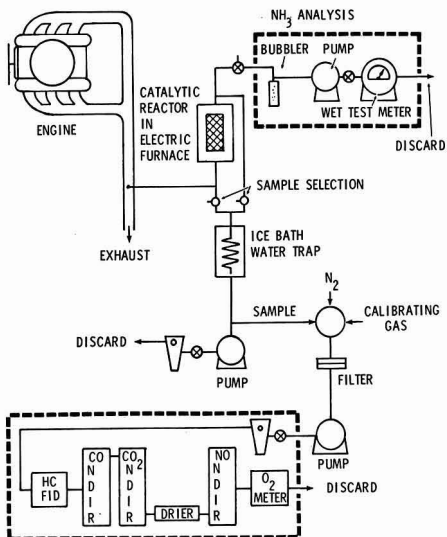
Figure 1. Experimental set-up for engine studies of catalysts

4-in. bed depth) was retained in the tube by stainless steel screens. Flow control over the catalyst bed was achieved by throttling a diaphragm pump placed downstream of an ice-bath water condenser.

Laboratory Studies. The laboratory studies were carried out with the continuous flow system shown in Figure 2. The reactor, which consisted of a $^3/_4$-in. stainless steel pipe, was situated in an electrically heated furnace. The furnace temperature was regulated by a proportional controller. The catalyst was supported by a piece of stainless steel screen. Thirty cm^3 of $^1/_8$-in. silicon carbide pellets were used on both sides of the catalyst bed to ensure complete reactant mixing. The catalyst charge, 15–30 cm^3, resulted in a bed depth of 2–4 in. Four thermocouples were spaced an inch apart along the vertical axis of the catalyst bed. The temperature at the middle of the bed was used as the catalyst bed temperature.

The desired inlet gas concentration was obtained by metering cylinder gases through calibrated rotameters. The cylinder gases used were: 2% CO in prepurified nitrogen, 40% H$_2$ in prepurified nitrogen, 0.40% NO in prepurified nitrogen, 100% nitrogen (prepurified), 100% air (dry), and 100% CO$_2$ (liquid).

Water was metered by a Milton-Roy minipump into a vaporizer which consisted of a 20-ft coil of $^1/_8$-in. stainless steel tubing in an electrical furnace at 300°C. The gases and the steam were brought together, preheated, and mixed in the 4-in. section of $^1/_8$-in. silicon carbide pellets, immediately upstream from the catalyst in the stainless steel pipe.

Sampling and Analyses. CONTINUOUS ANALYSES. A throttled diaphragm pump was used to pump a portion of the exit gas stream through the analysis train. Valving was arranged so that the converter inlet and exit gases could be compared with calibration gases of accurately known composition. CO, CO$_2$, NO, and N$_2$O were measured by nondispersive ir analyzers. NO$_2$ was measured with a nondispersive uv analyzer. O$_2$ and H$_2$ were analyzed for with a paramagnetic and a thermal conductivity instrument, respectively. Significant corrections for CO and CO$_2$, about half the total instrument response, had to be made for the nitrous oxide analyzer and for the hydro-

gen analyzer. This instrumentation allowed continuous analysis of either the inlet or exit gases, as desired.

AMMONIA ANALYSIS. Two methods were used for the ammonia measurements. The first, a wet absorptiometric method, based on a procedure described by Tetlow and Wilson (1964), was used in the engine experiments. The samples were collected by bubbling raw exhaust gas through a dilute sulfuric acid solution. The sample lines were kept as short as possible and were heated to avoid water condensation and subsequent loss of ammonia in the lines.

The method is based on the measurement of the optical density of the indophenol blue solution, produced when ammonia reacts with sodium phenate and sodium hypochlorite in the presence of acetone.

The second method, based on the catalytic oxidation of ammonia to nitric oxide, was used in the laboratory experiments. Several platinum catalysts, which quantitatively oxidized ammonia to nitric oxide, were effective in this application. Total nitric oxide concentration was measured by the continuous NDIR instrument, and the ammonia concentration was obtained by difference. Simultaneous measurements showed that the two methods agreed quite well, but the latter method, continuous oxidation and analysis, was faster and more reliable. Nitrous oxide formation was avoided by use of a rather heavily loaded platinum catalyst (0.5–2.0% Pt), and excess oxygen in the analysis stream. It was necessary to maintain the catalyst temperature at 650°C. Below this temperature, extensive formation of nitrous oxide, N$_2$O, occurred.

Catalyst Preparation. The catalyst was prepared in a two-step procedure. First, alumina in the form of $^1/_8$-in. spheres (Kaiser KA201, surface area = 260 m^2/g) was impregnated by soaking in a concentrated aqueous solution of cupric nitrate [3.75 moles Cu(NO$_3$)$_2$/l.]. The resulting material was air-dried overnight and calcined for 5 hr at 620°C in an airstream at a gas hourly space velocity (ghsv) of 500. A second impregnation was carried out on the resulting material in a concentrated aqueous solution of chromium nitrate [3.13 moles Cr(NO$_3$)$_3$/l.] followed by the same drying and calcination
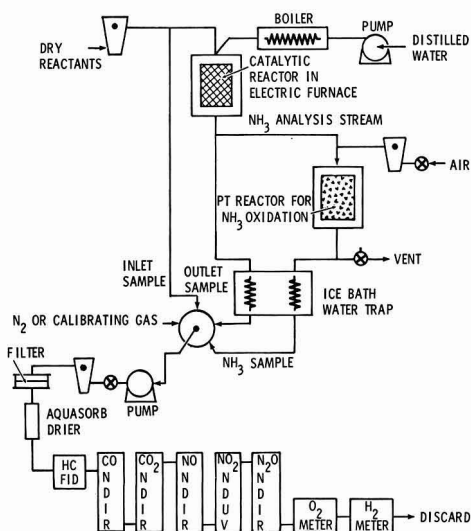
Figure 2. Experimental set-up for laboratory studies of catalysts

FEEDSTREAM: EXHAUST FROM A 350 C.I.D. CHEVROLET ENGINE

G.H.S.V. = 15000

CATALYST TEMPERATURE = 320°C
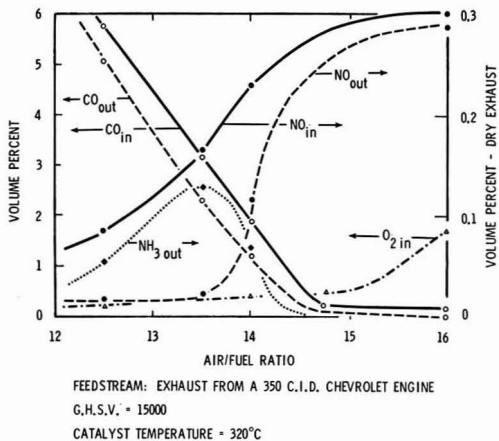
Figure 3. Air-fuel ratio effect on catalytic converter inlet and outlet compositions

FEEDSTREAM: EXHAUST FROM A 350 C.I.D. CHEVROLET ENGINE

G.H.S.V. = 15000

CATALYST TEMPERATURE = 320°C
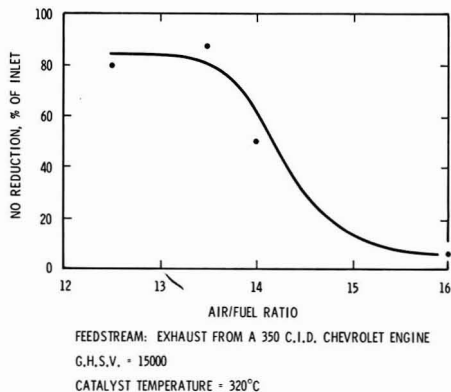
Figure 4. Air-fuel ratio effect on catalytic NO reduction

FEEDSTREAM: EXHAUST FROM A 350 C.I.D. CHEVROLET ENGINE.

G.H.S.V. = 15000

CATALYST TEMPERATURE = 320°C

Figure 5. Relationship between NO removal and NH_3 formation

FEEDSTREAM: EXHAUST FROM A 350 C.I.D. CHEVROLET ENGINE

A/F = 14.0

G.H.S.V. = 15000
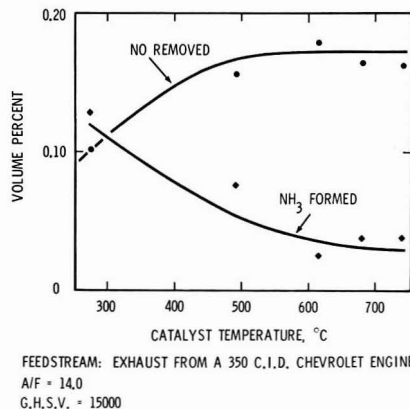
Figure 6. Effect of catalyst temperature on NO reduction and NH_3 formation over an alumina-supported copper and chromium oxide catalyst

sequence. The chemical analysis of the finished catalyst showed 6.3% copper and 4.4% chromium. Before the NO activity measurements were made, the catalyst was reduced by passing a stream of gas containing 1% CO in nitrogen over the catalyst at 650°C for 1 hr (ghsv = 15,000). All the tests described here were carried out with the catalyst in the reduced condition. Typically, after several hours of testing in either the laboratory or the engine installation, the surface area of the catalyst was 140 m^2/g, as measured by the standard BET method (Brunauer et al., 1938).

Results and Discussion

Engine Studies. STOICHIOMETRY EFFECTS. The effect of the air-fuel ratio on NO concentrations at the inlet and outlet of the catalytic reactor is shown in Figure 3. The ghsv was 15,000 and the catalyst bed temperature was 320°C.

The NO inlet concentrations decreased as the air-fuel ratio was decreased from 16:1. A slight variation in the engine power output was unavoidable so that the engine could be made to operate over the desired air-fuel ratio range.

Ammonia concentrations at the reactor outlet are also shown in Figure 3. Ammonia concentrations into the converter were not significant (<10 ppm). Apparently, little am-

monia was formed during either the combustion process or by post-combustion reactions in the exhaust system.

At low air-fuel ratios (<13.5), absolute reduction of NO was low since NO emissions from the engine were low. However, a relatively large percentage reduction in NO was achieved at air-fuel ratios less than 14 as shown in Figure 4.

The relationship between ammonia formation and nitrogen oxide removal is shown in Figure 5. Peaks in both ammonia formation and NO reduction occur at the same air-fuel ratio (~13.5). At high air-fuel ratios, NO reduction was poor because of the lack of reducing agents in the exhaust gases.

TEMPERATURE EFFECTS. Effect of catalyst temperature on ammonia formation was studied in a series of experiments carried out at an air-fuel ratio of 14.0. The influence of temperature on nitric oxide and ammonia concentrations is shown in Figure 6. The alumina-supported copper chromia catalyst in the reduced condition removed NO at quite low temperatures (<375°C). Ammonia formation decreased as the temperature increased. It was assumed that the other product formed in the NO removal process was elemental nitrogen, since significant concentrations of nitrous oxide (N_2O) were not detected in these experiments.

Table I. Copper Oxide–Chromia Catalysis of the Hydrogen–Nitric Oxide Reaction

Feedstream: 0.3% H_2, and 0.10% NO in a nitrogen atmosphere at a ghsv of 38,000

Temp, °C	NO reduction/% of inlet NO concn	NH_3 formation/% of inlet NO concn
370	78	13
455	94	36
540	98	44
650	98	23
735	99	9

Table II. Equilibrium Concentrations (Vol %) of CO and H_2 According to Water–Gas Equilibrium at Air-Fuel Ratios of 13.6 and 14.1

Temp, °C	Equilibrium constant	A/F = 14.1		A/F = 13.6	
		CO	H_2	CO	H_2
1,930	5.2	1.55	0.33	2.76	0.58
1,480	3.6	1.45	0.43	2.58	0.76
1,040	1.79	1.19	0.69	2.17	1.17
815	0.97	0.93	0.95	1.76	1.58
480	0.17	0.30	1.58	0.77	2.57
260	0.013	0.03	1.85	0.33	3.01

Laboratory Studies. REDOX MODEL AND AMMONIA FORMATION. Effect of air-fuel ratio on the catalytic reduction of NO was shown in Figure 4. At rich ratios (<13), there was very little NO present, while at high (lean) air-fuel ratios, the NO was not reduced because there were no reducing agents available. Previously, these air-fuel ratio effects have been rationalized by a simple stepwise oxidation-reduction scheme involving Reactions 1–4 (Bernstein et al., 1971)

$$CO + MO \longrightarrow CO_2 + M \qquad (1)$$

$$H_2 + MO \longrightarrow H_2O + M \qquad (2)$$

$$\tfrac{1}{2}O_2 + M \longrightarrow MO \qquad (3)$$

$$NO + M \longrightarrow MO + \tfrac{1}{2}N_2 \qquad (4)$$
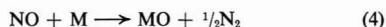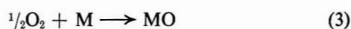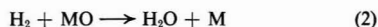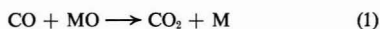
where MO and M are, respectively, the oxidized and the reduced forms of the catalyst.

It is presumed that the reoxidation occurs via Reaction 3 at lean air-fuel ratios and via Reaction 4 at rich air-fuel ratios. This mechanistic interpretation is deficient in one important aspect since it does not account for one of the major products, ammonia. Obviously, the chemistry of the system is more complex than this simple scheme indicates. Accordingly, a series of laboratory studies was carried out to explain the formation of ammonia as a major product.

Two possible routes were considered for ammonia formation. The first was the production of ammonia from elemental nitrogen and hydrogen (Reaction 5).

$$N_2 + 3H_2 \longrightarrow 2NH_3 \qquad (5)$$
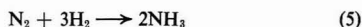
This reaction was thought to be unlikely, and indeed, ammonia could not be detected when N_2 and H_2 were passed over the catalyst at higher-than-exhaust concentrations. Thus, the second possibility, the reaction between hydrogen and nitric oxide (Reaction 6) seemed to be the more likely source of ammonia.

$$2NO + 5H_2 \longrightarrow 2NH_3 + 2H_2O \qquad (6)$$
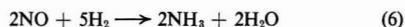
Table I shows that these two components, at typical exhaust concentrations, readily form ammonia with the catalyst used in these studies. Reaction 6 has been studied by others with related catalysts (Ayen and Peters, 1962; Sourirajan and Blumenthal, 1961).

COMPETITION BETWEEN REDUCING AGENTS. Much of the work on catalytic control of automotive NO_x has concentrated on CO as the dominant reducing agent in exhaust gas (Roth and Doerr, 1961; Shelef, 1968). This is due to the fact that CO is a powerful reducing agent for NO in the presence of redox catalysts and also because the concentration of CO is about three times that of hydrogen in exhaust (D'Alleva and Lovell, 1936). Therefore, it was somewhat surprising that hydrogen competed so effectively with CO, as indicated by the ammonia yields, particularly at low temperature. In contrast, it can also be seen that CO (Figure 3) was converted to CO_2 concomitant with NO reduction. As a matter of fact, the laboratory studies consistently showed a greater CO removal than could be accounted for by the oxygen in the nitrogen oxides. Engine studies also showed this seemingly unaccountable decrease in CO concentrations, particularly at very rich conditions. It was more difficult to do an oxygen balance in the engine studies, since even at rich A/F ratios, there was always a sizable oxygen concentration (0.3–0.5%) in exhaust gas, apparently due to flame quench phenomena (Daniel, 1970).

The Water–Gas Equilibrium. These considerations led to an examination of the water–gas equilibrium (Reaction 7),

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad (7)$$
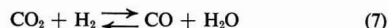
which is an important factor in determining the composition of exhaust gas at fuel-rich stoichiometries. It has been known for some time that this equilibrium is frozen in the combustion and expansion processes and that the concentrations of the four species involved correspond to an equilibrium constant of approximately 3.6, which in turn corresponds to a temperature of 1480°C. Thus, equilibrium is not maintained as the combustion gases are cooled by expansion during the power stroke. Table II shows the concentrations predicted, however, if Reaction 7 had been equilibrated in the exhaust at the lower temperatures. It can be seen that the equilibrium ratio of H_2 to CO increases dramatically at lower temperature. Thus, if exhaust catalysts are able to re-establish this equilibrium at the catalyst operating temperature, the domi-

Table III. Effect of CO and Hydrogen on Ammonia Formation from Nitric Oxide Over a Cu–Cr–Al_2O_3 Catalyst[a]

Constant feed components: 10% H_2O, 10% CO_2, 0.10% NO, balance nitrogen with ghsv = 38,000
Temperature: 650°C

Variable inlet concn		Conversions, %[b]		
CO, vol %	H_2, vol %	NO → NH_3	$CO → CO_2$ Obsd	$CO → CO_2$ Predicted[c]
1	0	61	57	65
1	0.3	52	35	57
1	1	50	7	35
0	0.3	46	−9	−10
0	1	50	−29	−30

[a] NO conversion for all these experiments was constant at 98 ± 2%.
[b] Numbers refer to conversions of the component specified. Positive conversion values indicate a decrease in concentration of a particular component over the catalyst and a negative conversion indicates an increase in concentration caused by the catalyst.
[c] CO conversions predicted are based on the water–gas equilibrium.
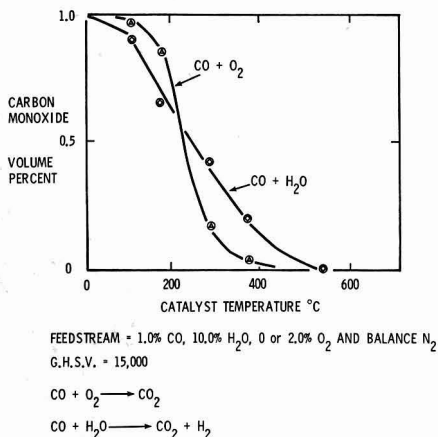
Figure 7. Comparison of the water–gas shift reaction and the catalytic oxidation of CO over a Cu–Cr–Al$_2$O$_3$ catalyst

FEEDSTREAM = 1.0% CO, 10.0% H$_2$O, 0 or 2.0% O$_2$ AND BALANCE N$_2$
G.H.S.V. = 15,000

$$CO + O_2 \longrightarrow CO_2$$
$$CO + H_2O \longrightarrow CO_2 + H_2$$
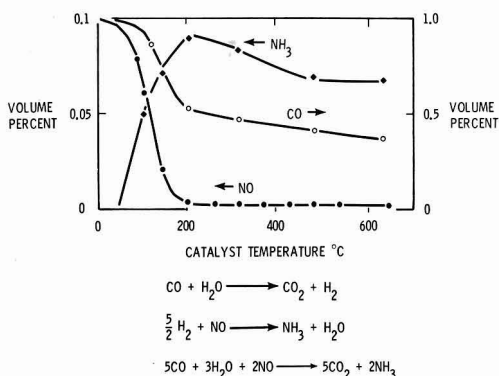
Figure 8. Water–gas shift reaction and NO reduction over a Cu–Cr–Al$_3$O$_8$ catalyst

$$CO + H_2O \longrightarrow CO_2 + H_2$$
$$\tfrac{5}{2} H_2 + NO \longrightarrow NH_3 + H_2O$$
$$5CO + 3H_2O + 2NO \longrightarrow 5CO_2 + 2NH_3$$

nant reducing species in exhaust will be hydrogen rather than CO. It has already been shown that hydrogen competes with CO quite well in NO reduction over a similar catalyst (Sourirajan and Blumenthal, 1961).

WATER–GAS CATALYSIS. A laboratory experiment was carried out to determine the activity of the catalyst with respect to the water–gas equilibrium. Figure 7 shows that the catalyst was quite active for this conversion in the appropriate temperature and space velocity range. It is interesting to compare the efficiency of this process (Reaction 7) with the normal oxidation of CO over the same catalyst in the presence of water (Reaction 8). Data for this reaction are also shown in Figure 7.

$$CO + \tfrac{1}{2}O_2 \xrightarrow{\;H_2O\;} CO_2 \qquad (8)$$

It can be seen that the two rates are quite comparable—i.e., that water converts CO to CO$_2$ about as efficiently as O$_2$ does over this catalyst. It should be noted that the state of oxidation of the catalyst was different in the two cases. The comparison of these two processes will be discussed later. Precious metal catalysts have also been shown to promote this equilibrium in exhaust gas (Jones et al., 1971).

EFFECT ON AMMONIA FORMATION. To determine how the water–gas process effects ammonia formation, a similar experiment was carried out, but this time 1000 ppm of nitric oxide was added to the feedstream. From these results (Figure 8), it can be seen that water and CO react and that there is a concomitant removal of NO which results primarily in the formation of ammonia. Since no hydrogen was present in the original feedstream, the reaction is forced to proceed through Reaction 7 to form hydrogen which reacts with NO via Reaction 6 to form ammonia. The overall process can be represented by:

$$5CO + 3H_2O + 2NO \longrightarrow 5CO_2 + 2NH_3 \qquad (9)$$
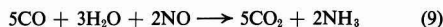
Table III summarizes additional data which illustrate the process in more detail. In these experiments, the inlet CO and H$_2$ concentrations were varied, and the concentrations of CO$_2$, H$_2$O, and NO were held constant. Nitric oxide was apparently reduced to NH$_3$ and N$_2$, since no N$_2$O was formed. The system is complex and does not lend itself to simple explanation; however, the importance of the water–gas shift reaction for ammonia formation is quite apparent. For example, it can be seen that the largest amount of ammonia was formed when hydrogen was not present in the feedstream.

The last two columns in Table III show the CO conversions observed and those predicted from the water–gas equilibrium (Reaction 7). It can be seen that the catalyst promoted the equilibrium in both directions as required by the basic principles of catalysis (Bond, 1962).

Ammonia Removal Processes. Figure 7 showed that ammonia formation tends to decrease at higher catalyst temperatures. The other product is presumed to be elemental nitrogen since significant concentrations of nitrous oxide or nitrogen dioxide could not be detected. Two processes were considered for the removal of ammonia. These were the decomposition of ammonia (Reaction 10) and the reaction between ammonia and nitric oxide (Reaction 11), (Otto et al., 1970).

$$2NH_3 \longrightarrow N_2 + 3H_2 \qquad (10)$$
$$2NH_3 + 3NO \longrightarrow \tfrac{5}{2}N_2 + 3H_2O \qquad (11)$$
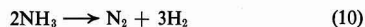
A series of experiments was carried out with feedstreams containing ammonia. These results are shown in Figure 9. It can be seen that the ammonia decomposition proceeded at about the same rate whether or not nitric oxide was present
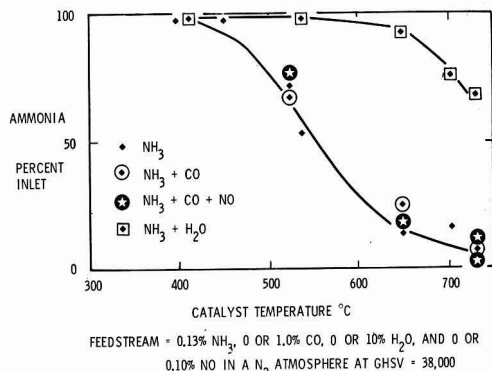
Figure 9. Effect of various exhaust constituents on ammonia decomposition over a Cu–Cr–Al$_3$O$_8$ catalyst

FEEDSTREAM = 0.13% NH$_3$, 0 OR 1.0% CO, 0 OR 10% H$_2$O, AND 0 OR 0.10% NO IN A N$_2$ ATMOSPHERE AT GHSV = 30,000

Table IV. Effect of O_2 on Ammonia Formation from Nitric Oxide Over a Cu–Cr–Al$_2$O$_3$ Catalyst

Constant feed components: 1% CO, 0.1% NO, 0.3% H$_2$, 10% CO$_2$, 10% H$_2$O, balance N$_2$ with ghsv = 38,000
Temperature: 650°C

Inlet O_2 concn, vol %	Total NO conversion, %	NO → NH$_3$ conversion, %
0	98	65
0.2	98	62
0.4	94	32
0.5	87	9

in the gas stream. It was necessary to include CO in the NO experiments in order to maintain the reduced state of the catalyst. In this connection, data in Figure 9 also show that CO by itself did not affect the ammonia decomposition significantly. Thus, it seems fairly clear that the instability of ammonia at high temperatures was accounted for by the elemental decomposition process (Reaction 11), and that the reaction between NH$_3$ and NO (Reaction 12) is not of major importance. It can also be seen in Figure 9 that water had a large retarding effect on the ammonia decomposition and displaced the reaction to higher temperature. This retarding effect of water is not surprising in view of the similarity in chemisorption behavior of ammonia and water (Peri, 1965). It would thus be expected that the high exhaust concentrations of water would severely inhibit the absorption of ammonia on the catalyst surface and subsequent ammonia decomposition.

Effect of Oxygen on Ammonia Formation. Figures 6 and 8 indicate that ammonia formation in the engine experiments was lower than in the laboratory experiments. This difference can be explained by the effect of oxygen on ammonia formation. As previously noted, engine exhaust contains 0.3–0.5% oxygen even at rich air-fuel ratios.

Table IV shows data from laboratory experiments in which inlet oxygen concentration was varied. It can be seen that oxygen causes substantial reduction in ammonia formation with little effect on total NO conversion. This oxygen effect would seem to account for the differences in ammonia formation between the laboratory and the engine studies. Work is currently in progress to explain this effect and utilize it in the control of NO emissions in automotive exhaust gases.

Summary

Reduction of NO in exhaust gases over a copper-oxide chromia catalyst was observed to be influenced by engine A/F ratio, and to result in the production of NH$_3$. These observations have been explained by a series of laboratory experi-
ments. From these experiments, the following conclusions were drawn:

A simple oxidation-reduction mechanism can satisfactorily explain the low reduction of NO and the effective oxidation of CO at lean air-fuel ratios. However, at rich air-fuel ratios, the catalyst tended to equilibrate the exhaust with respect to the water–gas reaction and this equilibration changed the dominant reduction species from CO to H$_2$.

A substantial amount of the NO reduction which occurred at rich air-fuel ratios was accomplished by reaction with H$_2$ to form ammonia. At low temperatures (<375°C), most of the NO reduced is converted to NH$_3$ and as the temperature increases (>600°C), less ammonia is produced, primarily due to its decomposition to nitrogen and hydrogen. Finally, the residual oxygen present at rich air-fuel ratios appears to mitigate ammonia formation.

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Analysis of Aliphatic Fraction of Air Particulate Matter

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■ A new method applicable to the analysis of the aliphatic fraction of air particulate matter is presented. The method, coupled with aerometric data, enables the first direct determination of n-alkanes in air particulate matter and extends analytical capability to the C_{15}–C_{36} range. The method was applied to ambient air samples (both urban and nonurban); to particulate matter emanating from the burning of coal, gasoline (both raw and irradiated exhaust), and diesel fuel; and to source samples such as gasoline, diesel fuel, motor oil, and coal. Results indicate that most of the aliphatic fractions analyzed contained measurable amounts of both normal and isomeric alkanes. Additionally, the method can be used to estimate the contribution of cigarette smoke to indoor pollution and also the contribution of the internal combustion engine to ambient air pollution.

The aliphatic fraction of air particulate matter as defined by Tabor et al. (1957) has been shown to constitute between 20 and 65% of the benzene-soluble portion (organic fraction) of air particulate matter as collected on a glass fiber filter using a high-volume air sampler (Tabor et al., 1957, 1958).

The interest in the aliphatic material in air arises from their reported cocarcinogenicity. Horton et al. (1957) has shown that the induction and incidence of tumors on the skin of mice by benzo(a)pyrene and 3-methylcholanthrene was increased and accelerated when the carcinogens were applied in conjunction with certain high-molecular-weight hydrocarbons, including n-alkanes. Additionally, the cocarcinogenic activity of some long-chain aliphatic hydrocarbons has also been demonstrated by Shubik et al. (1956).

Since the aliphatics constitute between 20 and 65% of the organic particulate matter found in the atmosphere, they may contribute greatly to the carcinogenic activity of the polynuclear aromatic hydrocarbons also present in air particulate matter. Wynder and Wright (1957) and Van Duuren (1958) have also speculated that the presence of n-alkanes in the atmosphere may enhance the carcinogenicity of these type compounds.

Prior to this study the aliphatic fraction was analyzed by gas chromatographic procedures (Sawicki et al., 1965; McPherson et al., 1966) that measured only the n-alkane range from C_{17} to C_{26-28}, and to obtain this area of the chromatogram required 60 min. To obtain the gas chromatogram of the entire aliphatic fraction required over 96 min and the n-alkanes in the sample above C_{28} were lost. To actually measure the n-alkanes, a subtractive technique was used and at no time was the actual

gas chromatogram of an n-alkane subfraction obtained. The new analytical procedure presented requires less than 17 min to obtain the gas chromatogram of an aliphatic fraction and the chromatogram contains much more detail than any previous procedure. This represents better than a fivefold savings in time required to obtain the chromatogram. Additionally, chromatograms were obtained for both the n-alkane and isoalkane subfractions. The ability to analyze n-alkanes is now increased from C_{26-28} to C_{36}. Hence, the new method gives better chromatograms than ever previously available in much less analytical time.

Experimental

Apparatus. A Beckman Model GC-4 gas chromatograph equipped with a dual hydrogen flame ionization analyzer was used for all gas chromatographic analyses. A matched pair of 20 ft $\times$ $^1/_8$ in. diam stainless steel chromatographic columns packed with 3% SE-30 on 100–120-mesh Chromosorb W were employed. The flash vaporization inlet and inlet line of the GC-4 were maintained at 350°C while the differential hydrogen flame detector and detector line were kept at 360°C. Column temperature was programmed so that the initial temperature of 150°C was maintained for 3 min; temperature was then raised to 315°C in 6 min (temperature rise is 27.5°C/min), and the temperature was held at 315°C until the end of the chromatogram.

The carrier gas, helium, was passed through the columns at a rate of 40 ml/min while the air and hydrogen rates to the detector were 250 ml and 55 ml, respectively. The columns were conditioned by heating them at 325°C while purging with helium (40 ml/min) until a stable base line was established. Samples were placed on the column using a Hamilton 1.0 μl syringe graduated in 0.1 μl.

Reagents. All organic solvents used were reagent grade (distilled in glass) quality supplied by Burdick and Jackson Laboratories of Muskegon, Mich. The n-alkane standards were purchased from Polyscience Corp., Evanston, Ill.

Pellet from Linde Type 5A Molecular Sieve was treated and activated in the following manner: The sieve was pulverized in a mortar, passed through a 40-mesh screen, and activated by heating in a muffle furnace at 450°C for 24 hr. The Molecular Sieve was transferred to a bottle and cooled to room temperature over silica gel in a desiccator. The bottle was then capped and stored in the desiccator as a precautionary measure.

Procedure

The air sampling and analytical methodology involved in the collection of atmospheric particulate matter, the Soxhlet extraction procedure to obtain the benzene-soluble organics, and the separation and isolation of the aliphatic fraction have been adequately described (Tabor et al., 1957; "Tentative Procedure for Determination of Suspended Particulates in the Atmosphere," 1969). Once the aliphatic fraction is obtained,

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EXAMPLE OF SEPARATION OF STANDARD n-ALKANE MIXTURE.
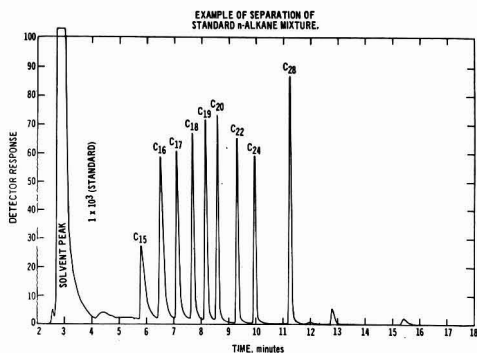
Figure 1. Chromatogram of a standard *n*-alkane mixture

it is immediately subjected to gas chromatographic analysis using the chromatographic parameters described earlier in this paper. One tenth microliter (0.1 μl) of the aliphatic fraction is injected into the column, and the overall gas chromatogram is obtained. The sample may have to be gently warmed under a hot water tap for complete liquification depending on the nature and source of the sample. This chromatogram is used to determine differences in aliphatic fractions from various sources.

The remaining portion of aliphatic fraction (up to 100 mg where possible) is weighed, dissolved in reagent grade isooctane (100 ml), and placed in a separatory funnel equipped with a ball and socket joint on the bottom so that it can be used as a reservoir for wet column chromatography later in the analysis. Ten grams of the activated powdered 5A Molecular Sieve is then added to the reservoir and the mixture is allowed to stand, with intermittent shaking, for 3 hr. The mixture is then transferred to an already packed chromatographic column by simply attaching the bottom of the reservoir to the top of the column and opening the stopcock. The column (~35 cm in length × 1.5-cm i.d.) is already packed to a height of 12 cm with additional activated powdered 5A Molecular Sieve. After all the mixture is transferred to the top of the column (isooctane was used as a wash), the isooctane is allowed to run into the column—i.e., the column is allowed to run dry to ensure that any portion of the aliphatic fraction that is dissolved in the isooctane and not absorbed on the Molecular Sieve is now travelling down the column. Three portions (5 ml each) of isooctane are added to the column and each portion is allowed to run into the column before the next is added. Finally, 100 ml of isooctane is added to the reservoir and allowed to elute through the column. Elution during the entire operation was aided by the use of vacuum, and the eluent was collected in a 500-ml vacuum flask attached to the bottom of the column by a rubber stopper. This portion contains everything in the aliphatic fraction except *n*-alkanes.

After all the isooctane is removed from the column, a second 500-ml vacuum flask is attached to the bottom of the column, and the column is eluted with 250 ml of reagent grade *n*-pentane. This portion contains the *n*-alkanes in the aliphatic fraction.

Both eluents, isooctane and pentane, are then concentrated by evaporation transferred to a tared centrifuge tube, and evaporated to dryness in a vacuum oven—the isooctane at 60°C and the pentane at room temperature. The residue in the tube is weighed and percent recoveries determined.

One tenth microliter (0.1 μl) of each residue is then subjected

to gas chromatographic analysis using the previously described chromatographic parameters. These gas chromatograms are then compared with the chromatograms obtained for the original aliphatic fraction and *n*-alkane standards.

Standardization. Standardization was achieved by subjecting synthetic mixtures of known concentrations of *n*-alkanes in the C_{15}–C_{36} range to gas chromatographic analysis to establish retention data, reproducibility, and linearity of detector response. Figure 1 represents a chromatogram of a synthetic mixture, and Table I lists the response (in cm^2/Nmol) and retention time (in min) data. Both actual data and data relative to C_{24} are given in Table I. Tetracosane (C_{24}) is the hydrocarbon found in the middle (based on carbon number) of the aliphatics present in atmospheric particulate matter.

Discussion of Procedure. Numerous variables involved in the gas chromatographic procedure were investigated. These included flow rates of the carrier gas, column length, and temperature programming. The flow rate of hydrogen and purified air to the flame ionization detector were optimized in accordance with directions supplied by the Beckman Instrument Co. and were set at 55 and 250 ml/min, respectively.

Silicone gum (SE-30) columns were used because numerous studies have shown them to be effective in separating hydrocarbons, and they are relatively stable up to 320°C. At first, a matched pair of columns 6 ft long were used in attempts to achieve the desired separation. These were replaced with 20-ft columns, and even 40-ft columns were employed in attempts to separate the huge mixture of isomers present in the aliphatic fractions.

In general, a 20-ft column gave a better separation than a 6-ft column; the 40-ft column did not significantly enhance the desired separation.

Numerous temperature-time programs were employed to determine the best possible method to separate the mixture of *n*-alkane standards in a reasonable length of time. The combination of a 20-ft column and the temperature program previously described were finally selected to give a decent separation in a reasonable length of time. The time required for gas chromatographic analysis was less than 20 min. This represents a fourfold savings in time over existing procedures.

The efficiency of Molecular Sieves for absorption of *n*-alkanes is a function of dryness and surface area of the Molecular Sieve, and the contact time between the *n*-alkane and the Molecular Sieve. Hence, care must be taken in keeping the Molecular Sieve dry after activation. Initial attempts in using the Molecular Sieve involved solution of the *n*-alkane in isooctane, addition of the powdered activated Molecular Sieve followed by shaking for a variable time period, centrifugation, and removal of the supernatant isooctane. The supernatant isooctane was then evaporated, and the residue was subjected to gas chromatographic analysis to determine if all the *n*-alkane was captured by the Molecular Sieve. The results indicated that in approximately a 2-hr agitation/standing time, about 90% of the *n*-alkane was absorbed by the Molecular Sieve. An increase in standing time gave very slightly increased absorption efficiencies, and an equilibrium seemed to be established between the amount of *n*-alkane in the Molecular Sieve and the amount remaining in the isooctane solution. Therefore, it seemed necessary to have two successive absorption steps in the procedure. This was accomplished by first bringing the isooctane solution of the *n*-alkane into contact with the Molecular Sieve (accompanied by periodic shaking) for a 3-hr period followed by passage through a second, fresh quantity of Molecular Sieve that had been placed in a chromatographic column. This procedure effectively removed 99+ %

of the *n*-alkanes from the isooctane solution when the amount of *n*-alkanes added was 100 mg or less. This amount is enough to analyze the aliphatic fraction but represents two to five times the amount found in an average high-volume air sample. Hence, it may be necessary to pool aliphatic fractions for analysis.

The Molecular Sieve passing through a 40-mesh screen was used for analysis. Although larger mesh size (smaller particles) may give better absorption efficiency for the *n*-alkanes because of increased surface area, it is not advised for this procedure because of the difficulty of getting isooctane to flow through a chromatographic column packed with Molecular Sieve. Even using a 40-mesh Molecular Sieve, a vacuum was applied to the column to assist in column flow, and it took approximately 3 hr for the 250 ml of isooctane to pass through the column.

Sawicki et al. (1965) employed a bromination–wet column chromatography procedure to remove any unsaturated aliphatics that may be contained in the overall aliphatic fraction. His procedure was applied to a large aliphatic fraction, and the gas chromatograms and ir spectra of the sample both before and after the bromination procedure indicated that the aliphatic particulate matter did not contain much, if any, unsaturated material that could be removed by bromination. Additional attempts to remove any olefinic material (reaction with mercuric perchlorate or acid hydrolysis with concentrated sulfuric acid) again indicated that the fraction was free from unsaturated material.

Recovery Studies. Recovery studies were performed to determine the amount of the aliphatic fraction recovered from the various steps in the overall analytical procedure. A quantity of the *n*-alkane mixture was placed on each of two glass fiber filters, dried, and extracted (Soxhlet) with benzene.
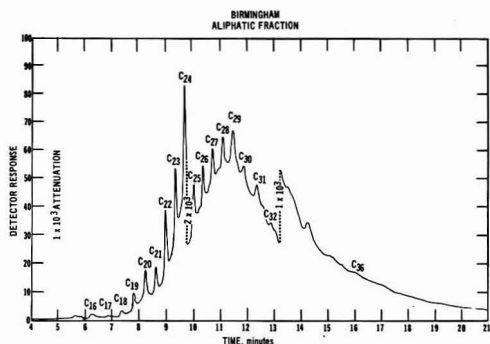
Figure 2. Chromatogram of Birmingham aliphatic fraction

It was found that 99.5% of the mixture was recovered from the paper by this technique. This aliphatic fraction was then isolated and 87.6% of the *n*-alkane mixture was recovered.

The mixture was then dissolved in isooctane, carried through the Molecular Sieve separation and the two subfractions were obtained. The isomeric alkane fraction isooctane eluent contained 3.8% of the *n*-alkane mixture; the *n*-alkane (*n*-pentane eluent) contained 44.2% of the mixture.

Combining all the recovery percentages, it was found that none of the aliphatic fraction was lost during benzene extraction, and the isolation of the aliphatic fraction and Molecular Sieve recoveries combine to give a net recovery of 42.1%. Therefore, of the *n*-alkanes present in the original benzene extract, 38.7% is recovered in the pentane fraction, and 3.3% is recovered in the isooctane fraction.

Application. The analytical procedure was applied to air particulate matter (urban, nonurban, and indoor), to suspected air pollution sources of aliphatics (particulate matter from raw and irradiated auto exhaust, diesel exhaust, and coal soot), and to other possible sources (raw gasoline, diesel fuel, automobile oil, and coal). Thirty-eight gas chromatograms representing the individual aliphatic, *n*-alkane, and isomeric alkane fractions of each of these samples are available (Hauser, 1971).

Analysis of an organic fraction representing the air over Birmingham, Ala., gives rise to three chromatograms. Figure 2 is the gas chromatogram obtained for the aliphatic fraction, Figure 3 represents the *n*-alkane subfraction, and Figure 4 depicts the isomeric alkane fraction left after *n*-alkane removal. These three chromatograms are typical of chromatograms observed for most samples analyzed. Figure 2 illustrates the ascending and descending base line observed for all aliphatic samples regardless of source and demonstrates that direct gas chromatographic determination of individual compounds in the aliphatic mixture is very difficult if not impossible to obtain. The percent of the various *n*-alkanes in all aliphatic fractions analyzed is given in Table II. The data in Table II have been corrected for both detector response for the individual hydrocarbons relative to C_{24} and the 44.2% recovery of the *n*-alkanes reported earlier in the paper. Table III lists the percentage of total alkane portions in the entire aliphatic fractions for all samples analyzed. These data were calculated by determining the total area under the curve using a planimeter and dividing this area into the area under the corresponding peaks based on a standard *n*-alkane mixture. Neither the response correction nor recovery factors were applied to the data in Table III because a range of alkanes was

Table I. Gc Calibration Data for Standards

	Response, cm²/nm		Retention time, min	
n-Alkane	Obsd	Rel. to C_{24}	Obsd	Rel. to C_{24}
C_{15}	1.86	1.62	5.82	0.58
C_{16}	1.80	1.58	6.50	0.65
C_{17}	1.48	1.30	7.10	0.71
C_{18}	1.40	1.23	7.68	0.77
C_{19}	1.31	1.15	8.16	0.82
C_{20}	1.28	1.13	8.59	0.86
$C_{21}{}^a$		1.09		0.90
C_{22}	1.19	1.04	9.31	0.93
$C_{23}{}^a$		1.02		0.97
C_{24}	1.14	1.00	9.96	1.00
$C_{25}{}^a$		0.97		1.03
$C_{26}{}^a$		0.94		1.07
$C_{27}{}^a$		0.91		1.10
C_{28}	1.05	0.88	11.24	1.13
$C_{29}{}^a$		0.87		1.17
$C_{30}{}^a$		0.85		1.21
$C_{31}{}^a$		0.84		1.25
C_{32}	0.94	0.82	12.80	1.29
$C_{33}{}^a$		0.80		1.36
$C_{34}{}^a$		0.79		1.42
$C_{35}{}^a$		0.77		1.49
C_{36}	0.86	0.75	15.41	1.55

a Extrapolated data due to unavailable standards.
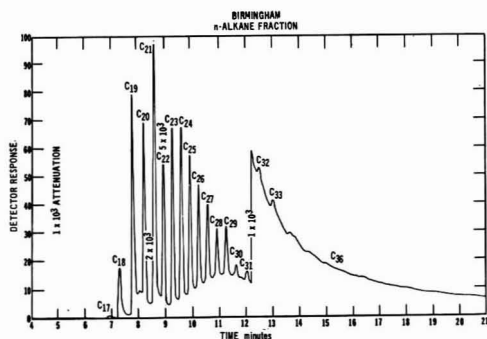
Figure 3. Chromatogram of Birmingham n-alkane fraction
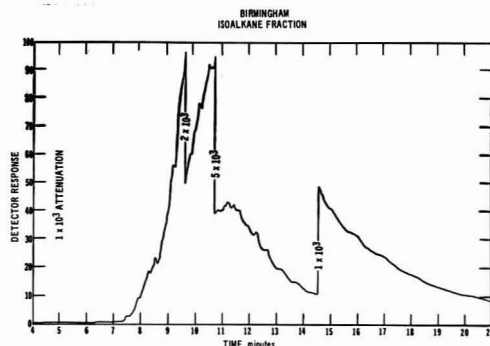
Figure 4. Chromatogram of Birmingham isomeric alkane fraction

Table II. Percent n-Alkanes in Aliphatic Fraction

n-Alkane	Bir-mingham	Los Angeles Sept.	Los Angeles Jan.	Amboy	Indoor	Auto exhaust Raw	Auto exhaust Irrad.	Diesel soot
C_{14}				0.24				
C_{15}				1.29				
C_{16}				1.29			0.02	
C_{17}	0.003		0.004	1.13	0.02	0.02	0.02	
C_{18}	0.02		0.03	1.13	0.05	0.03	0.09	
C_{19}	0.09		0.12	1.08	0.09	0.90	0.29	1.0
C_{20}	0.15		0.25	1.08	0.17	1.34	0.61	3.4
C_{21}	0.20		0.38	1.13	0.30	1.37	0.99	4.4
C_{22}	0.24	0.11	0.59	1.46	0.39	0.97	1.88	6.9
C_{23}	0.32	0.23	0.94	2.16	0.44	0.70	3.32	5.9
C_{24}	0.35	0.43	1.13	2.59	0.80	0.57	3.00	5.5
C_{25}	0.30	0.48	1.42	2.88	0.64	0.40	2.71	5.1
C_{26}	0.26	0.70	1.30	3.63	0.53	0.35	2.33	3.8
C_{27}	0.25	1.02	1.38	3.80	1.21	0.40	2.13	3.6
C_{28}	0.23	1.05	1.27	3.80	0.42	0.27	1.70	3.4
C_{29}	0.26	0.97	1.15	3.38	0.89	1.56^a	1.26	2.8
C_{30}	0.12	0.50	1.12	2.25	0.33		0.65	2.3
C_{31}	0.13	0.37	0.85	1.96	1.29		0.45	1.7
C_{32}	0.75^b	0.35	0.63	1.50	0.28		0.38	1.5
C_{33}		0.17	0.33	1.13	0.39		0.27	3.1^a
C_{34}		0.06^a	0.28^a	0.67	0.15^a		0.16	
C_{35}				0.58			0.07	
C_{36}	0.32^a			0.33			0.07^a	
C_{37}				0.70^a				
Total	3.99	6.44	13.17	41.66	8.39	8.88	22.4	54.4
C peak	24	28	25	27	27	21	23	22

^{a} In excess of indicated carbon number.
^{b} C_{32}–C_{36}.

being considered and neither the number of isomers in the range nor the detector response was known.

Two ambient air samples from Los Angeles were analyzed. These samples were collected in September 1969 and January 1970 less than one mile from the San Bernardino Freeway near Alhambra, Calif. The analytical results for both samples are recorded in Tables II and III. For the September sample, 1.9% (2.3 $\mu g/m^3$) of the particulate matter was found to be aliphatic while for the January sample, 3.6% (3.0 $\mu g/m^3$) was aliphatic. The concentration of the various n-alkanes in the Los Angeles samples are recorded in Table IV.

Two nonurban ambient air samples were analyzed. One was composite background sample supplied by the National Air Surveillance Network and the other a sample taken in Amboy, Calif. by the San Bernardino Air Pollution Control Office. The n-alkane data for the Amboy sample are reported in Table II while the data for specific carbon atom portions in the aliphatics of both samples are given in Table III.

An aliphatic fraction was obtained from particulate matter collected on a filter used in an air-conditioning system of a large office building. The air inside the building plus any needed make-up air was conditioned as necessary, passed through a Cambridge filter capable of retaining particle matter of 1 μ with 85% retention, and piped to the rest of the building. The dirty filters were treated as a large air sample and the aliphatic fraction was obtained in the usual manner. The

Table III. Carbon Atom Range (%) of Aliphatic Fraction

Carbon no. range	Bir-mingham	Los Angeles		Background			Auto exhaust		Auto oil	Diesel		Coal	
		Sept.	Jan.	NASN	Amboy	Indoor	Raw	Irrad.		Soot	Fuel	Ext.	Soot
<19	1.1	0.06	0.2	1.7	25.3	0.3	1.2	1.4	0.5	4.0	85.7	11.6	2.3
19–22	3.4	1.6	2.1	16.7	9.4	4.5	22.0	13.3	5.3	20.0	11.4	11.0	15.2
22–24	5.1	4.6	5.5	21.7	7.3	9.5	16.7	11.7	12.5	19.1	2.0	8.7	13.5
24–26	10.9	12.0	11.5	19.3	7.8	15.4	20.2	14.4	22.3	12.4	0.3	12.5	17.0
26–28	16.8	19.7	17.2	14.1	11.3	14.2	16.8	20.4	22.5	13.2	0.1	12.8	15.8
28–30	18.4	19.5	19.5	11.3	11.4	14.6	10.7	13.9	15.3	11.6	0.2	13.4	16.4
30–32	17.1	18.2	18.0	7.4	10.1	20.5	6.6	9.4	11.1	8.3	0.1	10.2	8.3
32–36	17.4	19.4	19.8	6.7	12.9	16.8	4.4	14.1	8.3	9.3	0.2	13.4	9.1
>36	9.7	5.0	6.3	1.1	4.5	4.2	1.3	1.5	1.8	2.1	...	6.4	2.4

results obtained from the gas chromatograms of the aliphatic, n-alkane, and isomeric alkane fractions are tabulated in Tables II and III.

Two auto exhaust particulate samples were obtained. One represented particulate matter from raw, nonirradiated exhaust; the other was a gum deposited in the throat of a Venturi tube used to meter the quantity and flow rate of irradiated exhaust being transported to exposure chambers. The raw exhaust particulate matter was collected on a high-volume glass fiber filter while the gum deposited in the Venturi was simply washed out with chloroform. Aliphatic fractions of both samples were obtained, fractionated, and analyzed in the usual manner. The gas chromatograms were very similar to Figures 2–4 and the data obtained are given in Tables II and III.

The analytical procedure was also directly applied to four automobile oil samples. The gas chromatograms approximated each other to a great degree and closely resembled the chromatograms given in Figure 4. The data given in Table III represent an average of all four oil samples analyzed.

The gasoline used in the auto exhaust study was analyzed via the gas chromatographic procedure. It was found that 99+ % of the gasoline had less than 19 carbon atoms. One liter of the gasoline was cautiously evaporated to a volume of 10 ml by heating on a hot plate and quickly removing the vapors. During this operation, the temperature of the gasoline rose to 250°C. Gas chromatographic analysis of this concentrated sample still indicated that 93+ % of the sample had less than 19 carbon atoms. Hence, gasoline itself should not be considered as a major source of aliphatic particulate matter in air.

Also analyzed were diesel fuel, diesel soot, coal, and coal soot. The data derived from these samples are also given in Tables II and III as indicated.

Discussion of Results

In general, the characteristics of the gas chromatograms obtained for the various ambient air aliphatic fractions (both urban and nonurban) were quite similar. All the chromatograms of the aliphatic fraction (Los Angeles, Birmingham, Indoor, Amboy, and NASN Background) exhibited well-defined peaks corresponding in retention time to n-alkanes in the approximate range of C_{17} to C_{34}. With the exception of the two background samples (Amboy and NASN), the rest of the ambient air samples peaked in the $C_{27}-C_{28}$ range. This range was also the midpoint of the sample on a weight basis—i.e., 50% of the aliphatic fraction was composed of alkanes of 28 carbon atoms or less and 50% was greater than 28 carbon atoms (See Table V). This is to be compared with raw gasoline and diesel fuel in which greater than 95% is less than 19 carbon

atoms. The particulate matter formed by the combustion of gasoline and diesel fuel in internal combustion engines gives rise to aliphatic fractions in which this 50% midpoint is about C_{24+}. The midpoint for the coal sample was C_{25+} and for the coal soot sample, C_{24+}. The composite NASN and the Amboy, Calif., ambient air background samples had a 50% midpoint of C_{24} and C_{25}, respectively. Therefore, the following observations can be made. The combustion of gasoline and diesel fuel gives rise to the formations of aliphatic material of higher molecular weight than the fuel itself but somewhat lower than is found in ambient air particulate matter. The 50% midpoint by molecular weight of this particulate matter formed by various combustion processes does not exactly correspond with the molecular weight of particulate matter observed in the ambient atmosphere of Birmingham and Los Angeles. The 50% midpoint for combustion particulate matter is $\sim C_{24}$ while that observed for the two cities is $\sim C_{23}$. It is interesting to note that Sawicki (1965) has determined an average molecular weight of ($C_{24}H_{43}$) for a combined aliphatic fraction accumulated from 100 communities all over the U.S. This number agrees with the particulate matter obtained from the various combustion processes and the two background samples but does not agree

Table IV. Concentration of n-Alkanes in Los Angeles Air[a]

n-Alkane	Sept. 1969	Jan. 1970
C_{17}		0.1
C_{18}		0.8
C_{19}		4
C_{20}		8
C_{21}		11
C_{22}	3	18
C_{23}	5	28
C_{24}	10	34
C_{25}	11	43
C_{26}	16	39
C_{27}	23	41
C_{28}	24	38
C_{29}	22	35
C_{30}	12	34
C_{31}	9	26
C_{32}	8	19
C_{33}	4	10
C_{34}	1[b]	8[b]
Total	148	396.9

[a] All values in ng/m³.
[b] In excess of indicated carbon number.

Table V. Summary Data for Aliphatic Fraction

Sample	50% Breakpoint[a]	% n-Alkane[b]	Ratio[c]
Diesel fuel	$<C_{19}$		
Concd gasoline	$<C_{19}$		
Raw auto exhaust	C_{24}	8.9	0.10
Diesel soot	C_{24}	54.4	1.19
NASN background	C_{24}		
Irrad. auto exhaust	C_{25+}	22.4	0.29
Amboy	C_{25+}	41.7	0.72
Coal soot	C_{25+}		
Coal extract	C_{26}		
Motor oil	C_{26+}		
Birmingham	C_{28+}	4.0	0.04
Indoor	C_{28+}	8.4	0.09
Los Angeles, Sept.	C_{28+}	6.4	0.07
Los Angeles, Jan.	C_{28+}	13.2	0.15

[a] Carbon number at which 50% of sample is greater or less by weight.
[b] n-Alkanes in aliphatic fraction.
[c] Ratio of n-alkanes to isomeric alkanes in fraction.

with what was found in air samples of Los Angeles, Birmingham, or the indoor sample. If some of the lower molecular weight (C_{10}–C_{19}) were lost from the urban ambient air samples through vaporization under the conditions of sampling, this would explain the shift to the higher 50% midpoint range of C_{28+}. It is quite possible that a portion of these low-molecular-weight alkanes are removed from the high-volume filter by a mechanical phenomenon based on air-sampling rate, particle size, and filter-retention characteristics.

Inspection of the gas chromatograms obtained from the various air and source samples gives rise to the following observation: The Birmingham and indoor samples gave gas chromatograms that had better detail for normal alkanes than did either of the Los Angeles samples. This indicates that there was probably a more even distribution of isomers in the Los Angeles samples. The NASN background sample has some well-defined peaks after C_{24}, and the Amboy background sample exhibited numerous well-defined peaks from C_{13} to C_{36} (Figure 5). The raw auto exhaust sample showed distinct peaks in the low-molecular-weight range of C_{17}–C_{21} while the auto exhaust gum illustrated distinct peaks from C_{19} to C_{34}. All of the raw oil samples somewhat resemble the Los Angeles samples in that the gas chromatograms are somewhat ill-defined and nonspecific.

The indoor sample gives rise to an interesting phenomenon. The gas chromatographic peaks observed in the C_{29} to C_{34} range of the indoor sample are higher (relative to the unresolvable background) than the same peaks observed in ambient air samples; additionally, the concentrations of the odd-numbered n-alkanes in this same range are greater than the even-numbered n-alkanes (Figure 6). This phenomenon may be due to the presence of cigarette smoke particulate matter being trapped on the filter and hence present in the sample. Carugno (1962) analyzed some of the paraffin waxes in tobacco and tobacco smoke by gas-liquid chromatography. His data demonstrate that this same phenomenon exists for both tobacco and tobacco smoke extracts. The isomeric alkane fraction of the indoor sample also differs from ambient air samples in that some very well-defined peaks are present in the carbon range in question. From this data it seems reasonable to postulate that the contribution of cigarette smoke to an indoor air pollution problem can be ascertained by the degree to which these deviations from ambient air samples occur.

The two background samples present some interesting possibilities. The NASN background sample which is composed of samples taken in various rural nonpolluted areas of the U.S. The particulate loading on these samples have a geometric mean of 32 $\mu g/m^3$. Amboy, Calif., is in a relatively noninhabited nonpolluted rural area that mainly serves as a gasoline and refreshment stop for tourists and truckers. The sampler was located 300 yd north of Highway 66 and the particulate loadings were low, having an annual geometric mean of 30.5 $\mu g/m^3$. Even though the particulate loading was low enough to be considered a background ambient air sample, the sampler was located relatively close to a major highway, and it is probably safe to assume that the great majority of the organic particulate matter came from auto and diesel exhaust. The 50% midpoint for raw auto exhaust, diesel particulate matter, irradiated auto exhaust gum, the NASN background, and the Amboy exhaust sample was between C_{24} and C_{25}. Forty-two percent of the Amboy sample was found to be n-alkanes. The corresponding data for the NASN sample were not obtainable because of small sample size. Approximately 9% of the raw auto exhaust particulate matter, 22% of irradiated auto exhaust gum, and 54.4% of diesel particulate matter were found to be normal alkanes and are highly suspected of producing the large amounts of n-alkane in the Amboy sample. Further extrapolation of this data can lead to the observation that areas having a relatively high n-alkane content in its aliphatic fraction are the areas that have a high auto and diesel exhaust problem. For example, the January Los Angeles
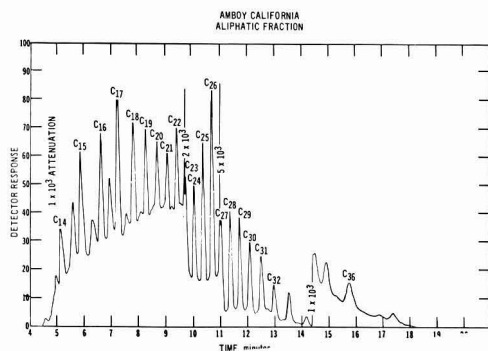
Figure 5. Chromatogram of Amboy background aliphatic fraction
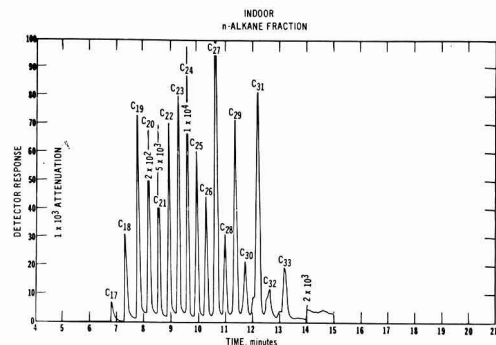
Figure 6. Chromatogram of indoor n-alkane fraction

sample was 13.2% *n*-alkane as compared to Birmingham at 4.0% *n*-alkane.

The ratios of normal alkane to isoalkane for the various substances analyzed are given in Table V. From this data it is shown that the highest ratios are exhibited by the diesel soot and Amboy samples. The Amboy samples had a higher ratio than irradiated auto exhaust gum indicating that the Amboy sample was primarily polluted with diesel soot.

The NASN sample does not necessarily represent any specific type of pollution. In fact, APCO went to great efforts to locate the samplers in areas where pollution in general was absent. Since the air samples taken in these areas did exhibit an aliphatic fraction, however small, it must be assumed that either there is a small background source of *n*-alkanes or that pollution from the various mobile and stationary combustion sources has now dispersed over the entire country.

Conclusion

All ambient air samples, both urban and nonurban, contain an aliphatic fraction that includes measurable amounts of normal alkanes in the C_{16} to C_{36} range. The burning of gasoline and diesel fuel, neither of which contain substantial amounts of alkanes in excess of 16 or 20 carbon atoms respectively, in internal combustion engines gives rise to aliphatic particulate matter containing both normal and isomeric alkanes in the C_{16} to C_{36} range. Of the samples analyzed, diesel particulate matter and irradiated auto exhaust gum appear to be major contributors to the low-molecular-weight normal alkanes in ambient air particulate matter. Hence, this ratio may serve as an indicator of the total pollution in an area caused by the internal combustion engine.

The phenomenon observed for the indoor sample indicates

the method may serve to determine the tobacco smoke contribution to indoor air pollution. Conversely, the method could be used to determine the effectiveness of filters (or other devices) in removing tobacco smoke from air.

Finally, the aliphatic fraction of air particulate matter is void of unsaturated material as determined by bromination, oxidation, and gas chromatographic analysis.

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Cadmium Contamination of Soil and Its Uptake by Oats

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■ The extent of cadmium contamination of soils in the Lower Fraser Valley (S.W. BC, Canada) was evaluated. Nitric acid-soluble cadmium in the surface samples among 33 agricultural soils averaged 0.88 ppm. However, nitric acid-soluble cadmium reached as high as 95 ppm in a surface sample taken near a battery smelter, but this level decreased considerably with distance and depth. The effect of soil application of carbonate, nitrate, chloride, sulfate, and phosphate salts of calcium on cadmium uptake by oats was determined in a growth chamber study involving soils taken near a battery smelter and from farmland. Oats grown on the contaminated soils contained very high amounts of cadmium in the roots, with smaller amounts in the aboveground portions. Soil treatments affected the cadmium content of roots significantly but did not affect the cadmium content of tops.

C admium accumulation in man has been related to emphysema and chronic bronchitis (Lewis et al., 1969; Nandi et al., 1969). It has also been shown that the level of cadmium in humans who die from hypertensive diseases is higher than that in humans whose deaths are due to other causes (Schroeder, 1965). The association of cadmium with these health problems has lead to studies of cadmium levels in the human body, animals, plants, and foodstuffs (Kropf and Geldmacher-v. Mallinckrodt, 1968; Kubota et al., 1968; Schroeder et al., 1961; Schroeder et al., 1967).

Cadmium is found in the earth's crust in association with zinc (Vinogradov, 1959). The presence of cadmium in the atmosphere is predominately due to the smelting, roasting, and electroplating of metals. The joint presence of zinc and cadmium in oils and motor vehicle tires was established and implicated as a source of cadmium contamination of roadside plants and soil (Lagerwerff and Specht, 1970). Use of cadmium

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Table I. Vertical Distribution of Nitric Acid–Soluble Cadmium in Soil Profiles Near a Battery Smelter

Profile 1 at 15 meters[a]		Profile 2 at 30 meters[a]		Profile 3 at 90 meters[a]	
Depth, cm	Cd, ppm	Depth, cm	Cd, ppm	Depth, cm	Cd, ppm
0–5	44.25	0–5	0.87	0–8	0.45
5–10	2.45	5–10	0.67	8–15	0.32
10–15	0.67	10–15	0.64		
15–20	0.62				
20–25	0.39				
25–30	0.32				

[a] Distance from the smelter.

Table II. Nitric Acid–Soluble Cadmium Content (Ppm) of Surface Samples in Vicinity of a Battery Smelter

Distance from battery smelter flume, meters	Obsd	Mean	Std dev	Range
15	4	48.96	31.07	7.92–95.40
30	3	1.59	0.68	0.87–2.50
90	3	0.56	0.09	0.45–0.68
125	1	0.73		
200	1	0.91		
300	1	1.65		
Overall	13	15.81	28.03	0.45–95.40

compounds as fungicide sprays on broad beans, tomatoes, wheat, and turf grasses was mentioned by Ross and Stewart (1969).

The present study was conducted to add more information about cadmium in man's environment and to provide a clearer picture of factors affecting the entry of cadmium into the food cycle.

Materials and Methods

Soil samples for a growth chamber experiment were sampled from 0–16 cm at two locations near Vancouver, BC, Canada. Delta silty clay loam was taken from farmland away from any industrial activity, and Richmond sandy loam was obtained at a site near a battery smelter. For both soils, a pH of 6.4 was measured for a 1:1 soil–water suspension. The percent organic matter determined by wet oxidation with chromic acid was 5.3% for Delta soil and 7.4% for Richmond soil. The soil samples were placed in 8-oz styrene cups and treatments of C, Cl, S, P, or N at two rates (100 and 1000 ppm for C, Cl, S, and P; and 25 and 250 ppm for N) were applied by mixing appropriate amounts of $CaCO_3$, $CaHPO_4$, $CaCl_2 \cdot 2H_2O$, $CaSO_4 \cdot 2H_2O$, and $Ca(NO_3)_2 \cdot 4H_2O$ throughout the soil. A check pot was also included and three replications of the soil pots were incubated at field capacity for a 30-day period in a darkened growth chamber at 25° ± 3°C. Oat seeds (*Avena sativa L.*, cv. Fraser) were germinated, using a modified Stanford-DeMent bioassay (Stanford and De-Ment, 1957), in 400 grams of quartz sand and thinned to seven plants per pot. After 14 days, the bottom portion of cups containing seedlings was removed, and seedlings were nested on top of soil cups. The three replicates of the two soils with the various treatments were arranged in a completely randomized block design in a growth chamber. Oat tops were harvested after 21 days of growth in a controlled environment consisting of a 16-hr light (provided by cool fluorescent lamps) and 8-hr darkness cycle. To maintain vigorous growth of oats, deionized distilled water and a nutrient solution were

used throughout the experiment. The nutrient solution added 50 mg N, 8 mg P, 60 mg K, 15 mg S, 50 mg Ca, 10 mg Mg, 125 µg B, 125 µg Mn, 12.5 µg Zn, 5 µg Cu, and 2.5 µg Mo per pot. The roots in the quartz portion were harvested for both soils, whereas roots from the soil were harvested for the Richmond soil only. The dry weight yields of shoots and roots from the quartz zone were recorded. Plant samples were digested with nitric–perchloric acid mixture and levels of cadmium were determined by atomic adsorption.

To study the extent of cadmium contamination in agricultural soils, 33 surface samples at depths of 0–16 cm were collected from various sites in the Lower Fraser Valley (S.W. BC). Near the battery smelter, samples were collected at various depths and distances from the flume as described previously (John, 1971). Samples were air-dried and ground to pass a 20-mesh screen. One gram of soil was shaken with 5 ml of N HNO_3 for 30 min and cadmium was determined with atomic absorption.

The computer methods for acquisition, reduction, and statistical analysis of the data were employed as described previously (John, 1970; John et al., 1969).

Results and Discussion

Cadmium Contamination of Soils. The nitric acid–soluble cadmium levels of the two surface samples used in the growth chamber study were found to be 46.4 ppm for the Richmond soil (near the battery smelter) and 1.3 ppm for the Delta soil. Analysis of the profile samples taken near the smelter indicated that accumulation of cadmium occurred in the surface layer. The cadmium level decreased progressively with depth (Table I). These results indicated that downward movement of cadmium in the soil profile may occur at a limited rate. The rapid decrease of cadmium level in surface samples with increased distance from the smelter flume (Table II), suggested that cadmium contamination was localized. Although soil was sampled in various random directions from the flume, no relationship to prevailing wind direction nor other causation was found to explain the large range (7.92–95.40 ppm) in the cadmium content of surface samples at 15 meters. Since cadmium is jointly present with zinc (Vinogradov, 1959) and the smelting of batteries containing these metals results in volatilization of cadmium, its escape

Table III. Effect of Various Soil Treatments on Cadmium Content (Ppm) of Oat Plant Parts Grown on Two Soils

Treatment	Rate, ppm in soil	Richmond soil			Delta soil	
		Oat shoots	Oat roots in quartz	Oat roots in soil[a]	Oat shoots	Oat roots in quartz
Control		16.1[a][b]	36.3[a]	237[b]	0.51[a]	1.11[a]
C	100	17.4[a]	67.5[b]	174[c]	0.77[bcd]	2.22[a]
	1000	15.5[a]	23.5[a]	187[b]	0.66[abcd]	1.81[a]
Cl	100	17.8[a]	30.1[a]	206[bc]	0.83[cd]	1.39[a]
	1000	15.9[a]	34.1[a]	275[b]	0.51[a]	1.81[a]
S	100	15.5[a]	24.6[a]	187[c]	0.57[ab]	1.25[a]
	1000	17.2[a]	27.8[a]	210[bc]	0.54[ab]	1.88[a]
P	100	18.3[a]	26.4[a]	183[c]	0.83[cd]	1.46[a]
	1000	15.1[a]	22.6[a]	135[d]	0.54[ab]	1.74[a]
N	25	17.1[a]	20.0[a]	177[c]	0.86[d]	1.53[a]
	250	19.5[a]	29.6[a]	286[a]	0.60[abc]	1.74[a]

[a] Oat roots in soil were harvested for plants grown on Richmond soil only.
[b] Means of three replicates. Means in a column subscripted by the same letter do not differ significantly at the 5% level according to Duncan's Multiple Range Test (Duncan, 1955).

Table IV. Effect of Various Soil Treatments on Soil pH and Yield

Treatment	Rate, ppm in soil	Richmond soil			Delta soil		
		Soil pH	Dry wt of oat shoots, grams/pot	Dry wt of oat roots in quartz, grams/pot	Soil pH	Dry wt of oat shoots, grams/pot	Dry wt of oat roots in quartz, grams/pot
Control		$6.42_a{}^a$	5.64_a	0.93_a	6.45_a	5.89_a	0.79_a
C	100	6.51_{cd}	4.95_a	0.75_a	6.64_d	4.91_a	0.70_a
	1000	6.52_d	5.20_a	0.69_a	6.82_e	4.99_a	0.57_a
Cl	100	6.45_{ab}	5.24_a	0.77_a	6.48_a	5.55_a	0.90_a
	1000	6.44_{ab}	4.66_a	0.66_a	6.52_b	5.55_a	0.70_a
S	100	6.46_{ab}	5.84_a	0.68_a	6.53_{bc}	4.65_a	0.58_a
	1000	6.45_{ab}	5.42_a	0.78_a	6.44_a	5.30_a	0.74_a
P	100	6.45_{ab}	5.19_a	0.60_a	6.45_a	5.56_a	0.70_a
	1000	6.45_{ab}	5.73_a	0.69_a	6.47_a	5.27_a	0.70_a
N	25	6.48_{bc}	5.76_a	0.76_a	6.53_{bc}	4.92_a	0.64_a
	250	6.52_{cd}	5.41_a	0.77_a	6.56_c	5.36_a	0.68_a

[a] Means of three replicates. Means in a column subscripted by the same letter do not differ significantly at the 5% level according to Duncan's Multiple Range Test (Duncan, 1955).

into the atmosphere via the flume, and the subsequent deposition on the surface explain the presence of more extractable cadmium in surface than subsurface samples and the localized nature of soil contamination in the vicinity of the smelter.

Amounts of nitric acid–soluble cadmium present in agricultural soils were much lower than in the surface soils from the smelter site. The cadmium content of the 33 soils ranged from undetectable amounts to 4.67 ppm and averaged 0.88 ± 0.79 ppm. The five agricultural soils, collected from sites nearest Vancouver, contained substantially higher levels (1.92 ± 1.40 ppm). Increased contamination of those soils may be attributed to the greater proximity of the sites to the industrial port and metropolitan center. However, the higher amounts of extractable cadmium in these soils may also result from their common glacio-marine parent material. The present study did not attempt to conclude whether either or both of these factors were responsible for the higher levels of nitric acid–soluble cadmium in the five soils.

Cadmium in Oat Plants. Roots in contact with contaminated Richmond soil accumulated large amounts of cadmium (mean = 205.1 ppm for the 11 treatments replicated three times). Cadmium content of the roots from the quartz zone placed above the contaminated soil was relatively smaller (mean = 31.1 ppm), while the shoots contained still smaller amounts (mean = 16.8 ppm). These results suggest that although cadmium is translocated from root to top portions, accumulation takes place at root absorption sites. The oats grown on the farmland soil (Delta) contained relatively smaller amounts of cadmium, but the levels in roots were consistently greater than in aboveground portions.

Effects of various salt treatments applied to the soil on cadmium absorption and translocation by oat plants are shown by data in Table III. Cadmium content of oat shoots was not significantly affected by any of the high-rate treatments for either soil; however, Cd content was generally increased significantly by the low-rate treatments for Delta soil. Cadmium level in roots from quartz layer was increased when 100 ppm carbon was applied as $CaCO_3$ to Richmond soil but was otherwise unaffected by treatments applied to either soil. Roots in contact with contaminated Richmond soil contained significantly reduced cadmium levels when low rates of elements (except chloride) were applied. It is of par-

ticular interest to note that application of 1000 ppm phosphorus to Richmond soil reduced cadmium in roots by 43%; however, the same treatment failed to alter the cadmium content of oat shoots or roots in quartz.

Effects of these various treatments on the cadmium content of the plant portions are not easily explained by physiological considerations alone. Dry weight yields were not affected by the treatments (Table IV). (Yields of roots from Richmond soil were unavailable.) Therefore, the differing cadmium concentrations associated with various salt treatments could not be attributed to the accumulation of absorbed cadmium in a reduced volume of plant material. The application of the calcium salts altered the soil pH (Table IV), but differences in soil reaction were not large enough to explain variations in cadmium uptake. The results obtained indicate that further research with various rates of phosphate and lime application should be conducted to elucidate cadmium absorption and translocation phenomena.

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NOTES

Atmospheric Lead and Bromine Concentration in Berkeley, Calif. (1963–70)

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■ Lead and bromine aerosols collected in downtown Berkeley, Calif., for one-week periods over the past eight years, have been analyzed using nondispersive X-ray fluorescence analysis. Typical analyses times were 2 min. The results suggest that X-ray fluorescence is a practical technique for routine lead monitoring, and that continuous monitoring stations are feasible. Seasonal lead variations similar to those found in the San Diego area were observed and appear to be correlated to data for wind and wind direction. The ratio of bromine-to-lead collected on filters appears to be higher in Berkeley than in the six other U.S. cities previously reported.

This study was undertaken to determine if nondispersive X-ray fluorescence analyses (Bowman et al., 1966) for lead, bromine, and other elements can be made rapidly enough that continuous sampling by remote automated monitoring systems would be possible.

Earlier measurements on filter papers using X-ray fluorescence analysis with difference-filter techniques (Sciaraffa and Ziegler, 1970–71) as well as those using a mass spectrometer (Chow and Earl, 1970) usually concentrated on a single element in a single analysis, whereas this method is capable of a multielement analysis in a single run.

In this study, work has been limited to just lead and bromine aerosols because of the complications introduced by the relatively high concentrations of iron and zinc present in HV 70 filter paper fabric. The use of low-ash filter paper for collection purposes eliminates some of these problems.

Sample Collections

A series of filter papers was collected weekly over the past eight years in downtown Berkeley, Calif. by the safety-service department of the Lawrence Radiation Laboratory as part of an environmental survey system (Cantelow et al., 1962). The downtown sampling station is located on a busy street (Shattuck Avenue between Hearst and Berkeley Way), and the air intake to the system is located about 8 ft from the curb and about 7 ft above the street level facing the street. The air

was filtered through HV 70 filter paper at an average flow rate of 4 ± 0.5 cfm, and the aerosols were collected on an open area of ~196 cm².

Counting Assembly and Procedure

Each of the over 400 filter papers was analyzed for 2 min on the X-ray fluorescence spectrometer. The filter papers were folded twice (to increase by a factor of 4 the effective lead and bromine seen by the X-ray detector) and placed in a holder that compressed the papers and held them at a fixed geometry with respect to the X-ray fluorescence system.

A source-target-assembly similar to one described by Giauque (1968) was used. The main advantage of the source-target two-step excitation method is that it allows one to choose the X-ray energy which is used to excite the sample, and thereby optimize the measurement. The target material used here was zirconium metal. The primary radiation was a 100-mCi source of ^{125}I.

Eight hundred channels of pulse-height information were taken on each 2-min run and stored on magnetic tape in digital form at the end of each run. Figure 1 shows the lead-bromine region of the spectrum for a sample collected over a seven-day period in December of 1969 and counted for 2 min. The data could be processed by hand or, more quickly, by a computer or a pulse-height analyzer with summing capability. A blank piece of HV 70 filter paper showed negligible lead and bromine but significant amounts of iron and zinc.

Each filter paper was analyzed twice, once with a slow amplifying system for which count rate corrections were needed, and a second time with a high-rate pulsed optical feedback amplifying system (Goulding et al., 1970) for which
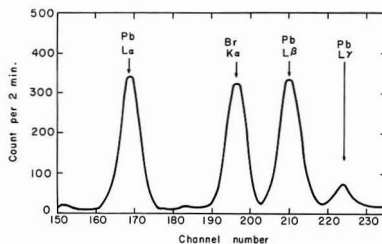
Figure 1. Lead and bromine intensity distribution measured in a filter paper using a multichannel pulse-height analyzer (background has not been subtracted)

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count-rate corrections were negligible. The results from both sets of runs agreed, with an average reproducibility of better than 5%.

Lead and bromine concentrations were obtained by summing a number of channels over the Pb Lα and Br Kα peaks, subtracting the nearly negligible background and comparing the results to standards treated in the same manner.

Calibration

A number of techniques was used to calibrate the filter papers for lead and bromine. These included: analyses of weighed amounts of lead metal and of KBr which had been vaporized onto Al foils; wet chemical analyses of foils and some filters; and independent X-ray fluorescence analyses of some of the filters by R. D. Giauque. The lead and bromine results agreed within standard deviations of 7 and 13%, respectively.

Results

The atmospheric lead and bromine concentrations for the years 1963–1970 are plotted in Figure 2. The seasonal variations are similar to those reported for San Diego by Chow and Earl for lead (Chow and Earl, 1970) and correlate very well with climatalogical data for wind direction and speed. In the summer, the San Francisco Bay area has winds averaging 9–10 mph and these winds are from the Pacific Ocean. The winter winds average 5–7 mph and have no predominant direction. The higher-speed winds from the cleaner areas of the ocean result in the cleansing of the Bay area, and as a result the lead and bromine concentrations are lower in the summer. There seems to be no correlation with rainfall.

Table I shows the average lead and bromine concentrations for each of the eight years. The averages are essentially constant over the eight years, within a standard deviation of 5% for lead and 7% for bromine.

An average bromine-to-lead wt ratio of 1:60 has been reported for six cities of the U.S. (Blossen and Thompson, 1971). Our study indicates a ratio of 1:3.2, which is closer to the ratio found for automobile exhaust gases. We have no explanation for this difference.

To determine which additional elements could be detected, a one-week collection (January 1971) was made on Whatman No. 40 paper. In addition to the lead and bromine, iron and zinc were detected in a 2-min X-ray fluorescence analysis. The spectrum is shown in Figure 3. The air volume was 11,884 ft^3.

Summary

Analysis of lead and bromine aerosols collected over 7-day periods on air-monitoring filter papers appears to be particularly suited to nondispersive X-ray fluorescence analysis. Lead and bromine concentrations can be determined in many cases in 2- or 3-min runs. The technique is nondestructive so that the papers can be reanalyzed if needed or saved for future reference.

With an increase of less than an order of magnitude in the airflow and the excitation source and no folding of the filter paper, results comparable to those reported here would be obtained with 2-hr collections and 2-hr counts. A system of continuous air-monitoring could be installed in which the data from many remote locations could be fed to a single central computer, which could give bihourly concentrations of lead, bromine, iron, and zinc at any of the remote locations. As the equipment is easily made portable (Frierman et al., 1969), temporary stations could also be established.
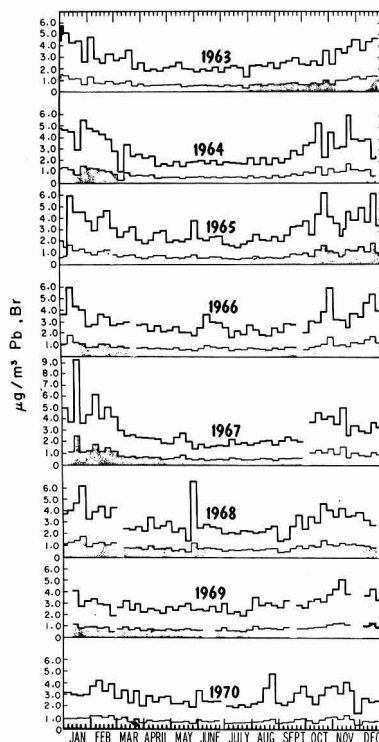
Figure 2. Atmospheric lead (upper solid line) and bromine (shaded area) concentrations in downtown Berkeley (1963–1970)

Table I. Daily Average of μg/m^3 for Bromine and Lead

Year	Bromine	Lead
1963	0.75	2.8
1964	0.75	2.8
1965	0.83	3.0
1966	0.85	3.0
1967	0.90	3.1
1968	0.90	3.2
1969	0.84	3.0
1970	0.82	2.9
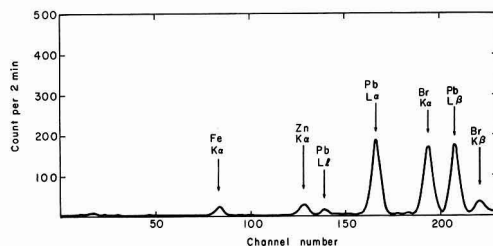
Figure 3. X-ray spectrum from aerosols collected on Whatman No. 40 filter paper

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Mercury and Other Metals in Urban Soils

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■ A suite of 264 surface soil samples, selected from a 300 sq mile region which includes industrial, agricultural, and residential areas, has been analyzed for mercury and Ag, Ca, Cd, Co, Cr, Cu, Fe, Ni, Pb, and Zn. All these metals are more concentrated in industrial areas than in residential and agricultural areas. All except lead are more concentrated around the airport. An asphalt plant appears to act as a point of mercury discharge.

T he flux of mercury from the continents to the atmosphere appears to be about 10^{11} grams/year (Weiss et al., 1971). The fraction of the total flux attributable to industrial activity may be small, but within a confined area, short-term fallout of Hg originally discharged as a result of industrial activity may be significant. This paper reports the results of a study of the concentration of Hg and 10 other metals in soil samples collected from regions of different land use.

Study Area

The area chosen for sampling was a rectangle, 19 miles (E-W) by 16 miles (N-S), enclosing the metropolitan area of Grand Rapids, Mich. The municipalities within the region have a combined population of about 300,000, and occupy 120 of the total 304 sq miles. The total area includes industrial, residential, and agricultural uses, and unimproved wooded land. Figure 1 shows the study area, subdivided according to land use. The area classified Industrial includes all land actually in industrial use, plus a zone extending one mile in all directions beyond the industrial land. Thus the Industrial classification includes industry, most commercial uses, and most of the high-density residential areas. The area classified

as Agricultural includes only land in agricultural use. The area classified Airport includes the airport plus a one-mile fallout zone which encroaches on the adjacent agricultural land. The Residential area includes everything else, primarily low-density residential areas and substantial amounts of unimproved woodlands.

Wind direction and velocity in the study area show very wide day-to-day variations, but the most common wind direction is from the west, and the next most common, the south. Wind velocities average about 10 knots. Temperature inversions are common at night, but they almost always break up during the day, so that prolonged inversions are quite rare. Annual total precipitation averages about 30 in.

According to a study by the Michigan Department of Public Health (1968), the Grand Rapids area ranks about 50th in air pollution in the U.S. Roughly 1000 tons of total pollutants are discharged to the atmosphere daily, 75% of which is from motor vehicles, and 14% from industry. About 100 tons of the daily total is particulate matter, 80% of which is from industry. Emissions of metal or metal oxide dusts total about 7 tons daily. Burning of refuse in the city dump was discontinued in 1963, and the burning of refuse by individuals was banned in 1970.

Sampling and Analysis

The sampling pattern followed the street layout, and was on a one-mile grid, except along the southern and eastern edges, where sampling was at two-mile intervals. A total of 264 samples were collected over a two-day period in early November, before the first snowfall. The samples were 2-in. cores of the surface soil, collected 30–50 ft from any road and usually from an established grassy area. Care was taken to avoid golf courses and institutional lawns, since some of these might have been treated with mercurials.

The samples were freeze-dried, homogenized, and screened

to remove small stones, roots, etc. Two-gram samples were oxidized at room temperature with nitric acid and potassium permanganate. Aliquots of the clear supernatant were analyzed for Hg by the method of Hatch and Ott (1968), with a Perkin-Elmer Model 303 atomic absorption spectrophotometer. After the Hg analyses were completed, the Ag, Ca, Cd, Co, Cr, Cu, Fe, Ni, Pb, and Zn were determined in the solution, by standard AA techniques.

Results and Discussion

The concentrations of the metals were initially plotted as contour maps. The distribution shown by zinc, Figure 2, is typical. Comparison of Figure 2 with the land use map (Figure 1) shows that the industrial and airport zones are clearly enriched in zinc compared to the agricultural and residential zones, and that the highest concentrations of zinc are found within the industrial zone. The results for all the metals are presented in Table I. The medians are usually smaller than the means, indicating that the distributions are not normal. The conventional standard deviations are included in Table I, to give some measure of the spread of the values. For every metal, the concentration in the industrial zone is greater than in the residential zone. For Ca, Cd, Co, Fe, Hg, and Ni, industrial soils show enrichment by about ×1.4. For Cu, the enrichment is ×2. For Ag, Cr, Pb, and Zn, the enrichment is about ×2.7. The reason, if any, for this grouping of the results is not clear.

For all the metals except Ca and Pb, agricultural soils are slightly richer than residential soils.

For every metal except Pb, the airport soils are significantly enriched; for seven of the metals, the highest mean values are for airport soils.

Because of the skewness of the data, they are best tested for significance by a nonparametric test, the Mann-Whitney U test. This test indicates, for example, that the concentration of Hg in agricultural soils (mean = 0.11) is not significantly different from that in residential soils (mean = 0.10), but that concentration in industrial soils (mean = 0.14 ppm) is higher, with greater than 99.5% probability. Figure 3 shows the frequency distribution of Hg for the various land use classifications. As the figure shows, the higher mean value in the industrial soils is not the result of a few very high values, but is
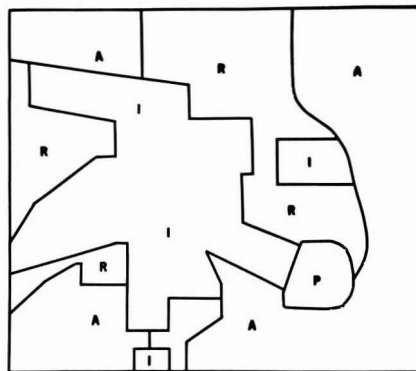
Figure 1. The study area, a 19 (E-W) × 13-mile (N-S) rectangle, with land use classified as residential (R), agricultural (A), industrial (I), airport (P)
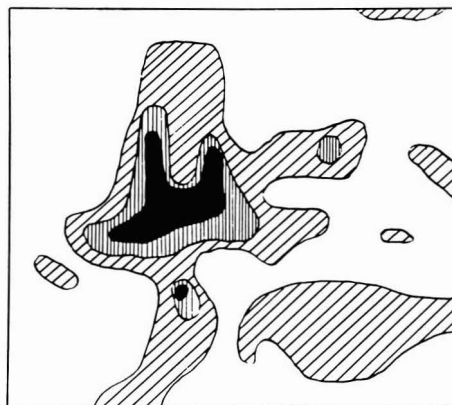
Figure 2. Zn in soils of the study area

Unshaded, 0–30 ppm; diagonal, 30–60 ppm; vertical, 60–120 ppm; black, above 120 ppm; highest obsd values, 314, 267, 254 ppm

Table I. Metal Concentration (ppm) Related to Land Use Patterns

		Ag	Ca	Cd	Co	Cr	Cu	Fe	Hg	Ni	Pb	Zn
Residential	median	0	1,000	0.4	2	1.6	7.5	2,000	0.07	4	15	17
N = 70	mean	0.13	2,300	0.41	2.3	3.2	8.0	2,200	0.10	5.4	17.9	21.1
	std dev	0.19	2,600	0.44	1.5	3.3	4.5	1,100	0.10	4.1	12.6	12.5
Agricultural	median	0	800	0.4	2.5	3.9	5.6	2,200	0.09	6	11	17
N = 91	mean	0.19	1,400	0.57	2.7	4.6	8.8	2,600	0.11	5.6	15.4	22.1
	std dev	0.25	1,900	0.52	1.5	3.6	6.0	1,600	0.09	4.4	14.9	12.9
Industrial	median	0.4	1,900	0.7	2	6.0	11.2	3,200	0.11	7	22	32
N = 86	mean	0.37	3,200	0.66	2.8	8.5	16.3	3,100	0.14	8.3	47.7	56.6
	std dev	0.33	3,000	0.54	1.8	9.0	14.3	1,400	0.10	5.2	59.6	63.1
Airport	median	0.4	3,700	0.7	8	22	9.4	7,000	0.17	11	14	36
N = 7	mean	0.29	4,100	0.77	7.9	17.6	10.4	6,200	0.33	12.3	17.9	36.6
	std dev	0.30	3,800	0.56	2.7	8.9	2.1	1,600	0.18	5.9	8.4	15.0
Industrial/residential		2.85	1.39	1.61	1.22	2.66	2.04	1.41	1.40	1.54	2.62	2.68
Airport/residential		2.24	1.78	1.88	3.43	5.50	1.30	2.82	3.30	2.28	1.00	1.74
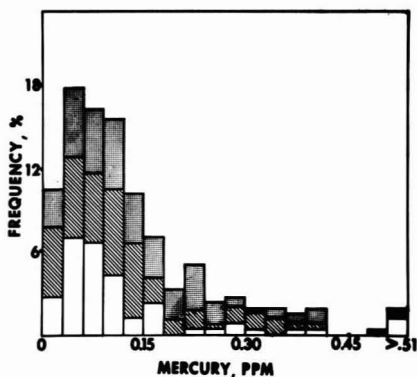
Figure 3. Frequency distribution diagram for Hg in soils of the study area

Unshaded, residential; diagonal, agricultural; shaded, industrial; airport values not included

Figure 4. Hg in soils of study area

Unshaded, 0.00–0.06 ppm; diagonal, 0.06–0.15 ppm; vertical, 0.15–0.30 ppm; black, above 0.30 ppm; highest obsd values 1.44, 1.27, 0.95 ppm

owing to a general shift of the frequency distribution to higher Hg concentrations.

Figure 4 is the concentration contour map for Hg, drawn to the same scale as Figures 1 and 2. Compared to the typical pattern shown by zinc, the mercury distribution is much more diffuse, with many small regions in which Hg is considerably enriched. Most of these regions are close to several potential Hg sources, so usually it has not been possible to define specific discharge sources. However, the far northeast corner of the study area shows a well-developed fallout pattern for Hg. This region is primarily undeveloped woodlands, with some fruit and dairy farming. The only potential discharge site is an asphalt plant, located within the fallout pattern. Other asphalt plants in the study area are in the general industrial zones, and any fallout they might produce cannot be distinguished from that produced by other nearby sources.

Literature Cited

Hatch, W. R., Ott, W. L., *Anal. Chem.*, **40,** 2085–7 (1968).
Michigan Department of Public Health, "Air Pollution Study of Kent County, 1966–1967" (1968).
Weiss, H. V., Koide, M., Goldberg, E. D., *Science,* **174,** 692–4 (1971).

industry trends

Chem-Trol Pollution Services, Inc. (Niagara County, N.Y.) has arranged $1.1 million worth of financing to be used for installing a new chemical reclamation and disposal operating facility at Model City, N.Y.

Battelle-Northwest (Richland, Wash.) has received a $300,000 contract for a two-year study to determine the environmental effects of Atlantic Richfield's Cherry Point Refinery near Bellingham, Wash.

Research-Cottrell will provide two hyperbolic natural draft cooling towers for the Tennessee Valley Authority's Watts Bar Nuclear Plant. Total value of the contract is about $11,400,000.

Culligan has received a $165,000 contract from the Office of Saline Water (OSW) to test an improved ion exchange method for desalting brackish water. Culligan will field-test equipment at Davis Dam, Ariz., Artesia, N.M., Gallup, N.M., and La Junta, Colo.

Krebs Engineers (Menlo Park, Calif.) will supply Minnesota Power and Light with the world's largest gas scrubber. The 1.4 million ACFM scrubber will be used to remove fly ash in stack gases from a 350-MW coal-fired steam generator at Cohasset, Minn.

American Petroleum Institute (API) has awarded a research contract to Av-Alarm Corp. (Mountain View, Calif.) to study a system of repelling migratory waterfowl and seabirds from areas where oil spills have occurred.

Cryogenic Technology, Inc. (Waltham, Mass.) is delivering cryogenic refrigerators for the first tonnage LNG plant to be installed in the U.S. using the Stirling refrigeration cycle. The machines are being installed at Yarbro, Ark., providing LNG to a 55,000-barrel cryogenic storage plant.

International Recycling Corp. (Sayerville, N.J.) is a new corporation formed to explore engineering and marketing techniques and approaches to pollution and refining problems which have been difficult to solve. The firm is now accepting precious metal–bearing salvage.

Hydronautics, Inc. (Laurel, Md.) will analyze data collected by Johns-Manville Corp. on performance of oil recovery booms in recent tests off the coast of Santa Barbara, Calif. Tests, conducted on slicks of soybean oil, were conducted for the Coast Guard.

Burns and Row Construction Corp. (Chula Vista, Calif.) has received a $1.6 million contract from the Office of Saline Water (OSW) for management, operation, maintenance, and systems development of the San Diego Desalination Test Facility. The facility consists of seven major experimental plants for seawater desalination.

S. W. Brown and Associates (New York, N.Y.) has received an award from the New York Association of Consulting Engineers for work in waste heat reclamation.

Dow Chemical Co. has received a contract from the Interior Department to project energy costs and their influence on the economics of desalting at various U.S. locations to the year 1990. Value of the contract is $22,110.

Academy Computing Co. (Oklahoma City, Okla.) has formed a new subsidiary—Separator Technology Corp.—to market oil–water separators.

Aqua-Chem, Inc. has received an order for an evaporator of its patented spray design for concentrating radioactive wastes at the Prairie Island nuclear generating station of Northern States Power Co., Red Wing, Minn.

SCA Services, Inc. (Boston, Mass.) has agreed to acquire Commercial Removal, Inc., a solid waste management and disposal company in Southfield, Mich.

new products

Atomizer

GLOMAX electrothermal analyzer produces strong reproducible signals from subnanogram samples of metal analyte. Chamber allows observation and easy accessibility to tantalum ribbon during the process. Barnes Engineering Co.
61

Salinity meter

New design instrument gives soil salinity readings in 3 min and water salinity readings in seconds. Calibration accuracy of portable unit is factory set and needs no adjustment. GLA, Inc.   **62**

NO$_x$ analyzer

New analyzer measures NO, NO$_2$, and NO$_x$ in separate modes. Instrument does not require a vacuum pump and features a built-in ozone generator and solid state electronics. Bendix Corp.
63

Scrubbers

New line of packed scrubbers have been computer-designed for high-efficiency control (99%+ removal) of hydrochloric, nitric, hydrofluoric, and similar mists or fumes from cleaning, pickling, and plating baths. Beetle Plastics, Inc.
64

Spectral source

High-intensity light source for use in atomic absorption spectrometers and fluorescence instruments boasts improved stability which boosts sensitivity by as much as 50 times. Helpful for trace metal pollution analysis. Scintillonics   **65**
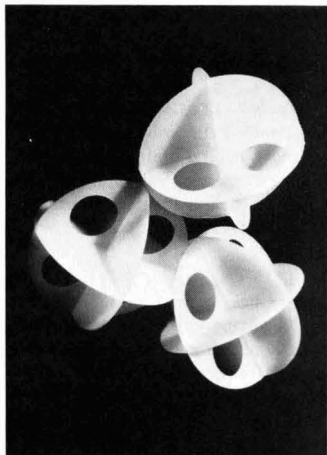
Packings

Protak plastic tower packings incorporate desirable features of liquid-gas contact media with added advantages of polypropylene and saran plastics. Plastics Industries Co.   **66**
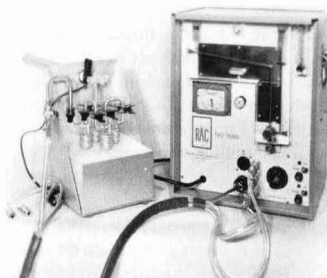
SO$_2$ sampler

Portable system takes accurate samples of gaseous pollutants or moisture in stacks or ducts. Control module has push to test flowmeter, controls for probe heater, vacuum pump, and totalizing dry gas meter. Research Appliance Co.   **67**

Water standard

Ecolo-Trol is ideal water standard for laboratories which test water quality. Standard provides known values for BOD, COD, SS, conductivity, total carbon, organic carbon, and pH. Based on APHA methods. Alpha Associates **68**

Bottle disposer

Bottle-Buster will crush containers quietly at minimum rate of 20–25 per min. Ertel Engineering Co. **69**

Ozone monitor

Self-contained industrial ozone monitor measures concentrations up to 10 wt %. Instrument measures ozone in real time by monitoring absorption at 2540Å. Dasibi Corp. **70**

Reverse osmosis

New bench ultrafiltration/reverse osmosis unit fills gap between strictly laboratory units and large-scale pilot plants. System uses replaceable externally wound, tubular membrane elements. Universal Water Corp. **71**

Chromatograph

Liquid chromatograph offers resolution, speed, and sensitivity of units costing many times more. Features high-pressure operation to 3000 psi. Chromatronix **72**

Boom

Boa-Boom is nylon reinforced polyvinyl chloride floating oil containment boom. Air-inflated collar supports reinforced weighted skirt and conforms to water surface to give maximum oil retention. Environetics, Inc. **73**

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new literature

Solid waste. Story of solid waste and what is being done to combat it is focus of booklet prepared by trade association. Glass Container Manufacturers Institute **91**

Catalog. Combined catalog 72 is two catalogs of available scientific equipment bound together for users convenience. Scientific Glass Apparatus Co., Inc. **92**

Tank liner. Brochure features cutaway illustration of installed, free-hanging, electronically welded bag-type flexible liner for oil field tanks. Unit Liner Co. **93**

Sewage Grinder. Bulletin describes and illustrates continuous operation grinder for efficient grinding of sewage. Engineered Products **94**

O_2 Removal. Information is available on Ridox reagent for high-efficiency removal of O_2 in calibration gases. Fisher Scientific Co. **95**

Pitot pumps. Ten-page brochure covers broad line of Roto-Jet pitot pumps and gives detailed specs on capacities and performance ratings. Kobe, Inc. **96**

Water services. Bulletin CS-1 describes company's five-step program for water treatment servicing and lists available test equipment. Gamlen Chemical Co. **97**

Conductivity meter. Bulletin describes features of conductivity and salinity meter. Gives complete specs, price, and ordering information. Yellow Springs Instrument Co. **98**

Conversion chart. High-purity materials company offers promotional summary chart listing frequently used scientific conversion factors. Aremco Products, Inc. **99**

Catalog. New 68-page catalog lists full line of analytical instruments for the chemical laboratory including GC's, osmometers, spectrometers, and the like. Hewlett-Packard **100**

Polystyrene. Answers to tough questions about effects of polystyrene foam are contained in ecologically oriented, illustrated booklet. Society of the Plastics Industry **101**

Air. Catalog lists specialty gases among which are two grades of research grade air for vehicle testing calibration. Matheson Gas Products, Inc. **102**

Liners. Bulletin details specs and technical information on applications of polyvinyl chloride pit and pond liners. Fabrico Mfg. Corp. **103**

Catalog. New 16-page catalog listing chemically inert polyethylene piping systems includes specs, physical properties, installation diagrams, and instructions on heat-fusing methods for plumbing. Nalgene Piping Systems Division **104**

Recycling. Pair of bulletins discusses agglomeration systems for pollution abatement, raw material by-product processing, and waste recycling. Ferro-Tech Industries, Inc. **105**

Catalog. New 1972 catalog lists available reagents and laboratory accessories. Apache Chemicals, Inc. **106**

Thermoplastic pipeline. Bulletin describes case history of world's largest thermoplastic pipeline for sewage treatment plant. M. L. Sheldon Plastics Corp. **107**

Reverse osmosis. Information on reverse osmosis, purification, waste water reclamation and recovery of valuable industrial materials is contained in a new leaflet describing company's reverse osmosis membrane. Eastman Kodak Co. **108**

Temperature control. Bulletin lists line of incinerator temperature-control devices to minimize pollution. Burline Instrument Co. **109**

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bookshelf

New Energy Technology: Some Facts and Assessments. H. C. Hottel, J. B. Howard, xi + 364 pages. M.I.T. Press, 50 Ames St., Cambridge, MA 02142. $2.95, paper.

A product of several teaching and research projects, the book reports the status of today's energy problems, assesses the technical and economic adequacy of existing or proposed processes and their consistency with developing standards of environmental quality, and suggests where additional effort—research, development, demonstration plant—is needed to accelerate change. ∎

Global Environmental Monitoring. 67 pages. Editorial Service, Swedish Natural Science Research Council, Box 23136, S-104 35 Stockholm 23, Sweden. 1971. $2.00, paper.

Report prepared by the Scientific Committee on Problems for the Environment for the UN Conference on the Human Environment (being held in Stockholm this month). Contains recommendations, environmental problems, monitoring, and operational and institutional arrangements. ∎

Your Environment: Air, Air Pollution and Weather. Collins M. Henson, 206 pages. The Interstate Printers & Publishers, Inc., 19–27 N. Jackson St., Danville, IL 61832. 1971. $4.95, hard cover.

Written specifically for students in grades six through nine. Designed to meet the needs of students by involving their young minds in scientific inquiry. Begins with basic facts and proceeds through complex processes, thus building a comprehensive scientific background in the area of air, weather, and man's use and misuse of his environment. ∎

Water Pollution Microbiology. Ralph Mitchell, Ed. x + 416 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, NY 10016. 1972. $19.50, hard cover.

Begins with a chapter on sources of water pollution. Following papers are grouped into six parts: microbial

changes induced by inorganic and organic pollutants, intestinal pathogens as pollutants, pollution and community ecology, microbial parameters of pollution, and microbiological approaches to pollution control. Compiled to promote understanding of the role of microorganisms in water pollution and water pollution control and to stimulate interest in microbial ecology of polluted waters among biologists and engineers. ∎

Hydrogen Sulfide Removal Processes. P. G. Stocher. vi + 288 pages. Noyes Data Corp., Park Ridge, NJ 07656. 1972. $36, paper.

Book is based on U.S. patents since 1960 relating to hydrogen sulfide removal from gases and liquids. Supplies detailed technical information and can be used as a guide to the U.S. patent literature in this field. ∎

Geothermal Overviews of the Western United States. approx. 192 pages. Geothermal Resources Council, P.O. Box 1033, Davis, CA 95616. 1972. $6.00, paper.

Contains papers from western states which include information on geology, geothermal potential, future power needs, regulation agencies, and references. Presents geothermal data from all those western states with geothermal potential. ∎

Environmental Chemistry: Air and Water Pollution. H. Stephen Stoker, Spencer L. Seager. iv + 186 pages. Scott, Foresman and Co., Glenview, IL 60025. 1972. $2.95, paper.

Book was written in hope that a more realistic picture of the pollution problem, its dangers and solutions, will emerge. Specifically, the book takes an objective look at the chemistry and chemical compounds of air and water pollution. ∎

A Nationwide Survey of Environmental Protection. Erdos & Morgan, Inc. 92 pages. The Wall Street Journal, 30 Broad St., New York, NY 10004. 1972. $3.00, paper.

Report on issues of environmental protection based on a survey among Wall Street Journal subscribers. Reveals what businessmen say their companies will be doing to solve the pollution problems of the 70's, a definitive report on what business is doing and thinking. ∎

meeting guide

June 19–22
Air Pollution Control Association
65th Annual Meeting and Exposition
Miami Beach, Fla.
Open to all individuals in industry, government, science, and education concerned with air pollution control. Includes equipment exhibition plus 150 technical papers. Write: Public Relations Dept., Air Pollution Control Association, 4400 Fifth Ave., Pittsburgh, PA 15213

June 21–24
National Solid Waste Management Association
8th Annual International Refuse Equipment Show & Congress
Denver, Colo.
Topics include land disposal, stationary compaction/container systems, management of collection operations, manpower development & incentives, new developments in resource recovery, and trends in the solid waste industry. Contact: NSWMA, #214, 1145 Nineteenth St., N.W., Washington, DC 20036

June 25–30
Engineering Foundation
Environmental Engineering in the Food Industry Conference
Henniker, N.H.
Purpose of the conference is to examine the latest technology for measuring, sampling, and analyzing all environmental wastes which originate during food processing. Fee: $160. Contact: Engineering Foundation, 345 E. 47th St., New York, NY 10017

June 26–28
American Society of Civil Engineers
Specialty Conference
Rochester, N.Y.
Titled "Nutrient Removal—How to Do It." Contact: ASCE, 345 E. 47th St., New York, NY 10017

June 26–28
Association of Professional Engineers of the Province of Ontario
International Conference on Automobile Pollution
Toronto, Ontario
Politicians, public health officials, city planners, engineers, scientists, and representatives of the major automobile industries will attend and contribute. Contact: Anthony E. O'Donohue, Conference President, P.O. Box 5653, Station A, Toronto, Canada

June 26–29
American Meteorological Society
Third National Conference on Weather Modification
Rapid City, S.D.
Over 60 papers on materials and delivery systems, mathematical models, field experiments, and ecological, sociological, and legal aspects of weather modification programs. Write: Richard A. Schleusener, Institute of Atmospheric Sciences, S.D. School of Mines and Technology, Rapid City, SD 57701

June 27–30
American Society of Agricultural Engineers
65th Annual Meeting
Hot Springs, Ark.
Includes sessions on treatment and management of animal and poultry wastes. Write: American Society of Agricultural Engineers, St. Joseph, Mich. 49085

July 2–7
National Environmental Health Assoc.
1972 Environmental Health Conference and Exposition
New York, N.Y.
Topics include air and water pollution, solid waste disposal, environmental chemicals, transportation, noise, and environmental education. Write: National Environmental Health Association, 1600 Pennsylvania, Denver, CO 80203

July 2–7
Engineering Foundation
Technological Futures for Offshore Oil Conference
South Berwick, Me.
Topics will include future technologies for developing offshore petroleum resources and their likely economic, environmental, legal/political, and other social impacts. Contact: Engineering Foundation, 345 E. 47th St., New York, NY 10017

July 9–14
Engineering Foundation and others
Public Transportation in Urban Areas Conference
Henniker, N.H.
Contact: Engineering Foundation, 345 E. 47th St., New York, NY 10017

July 10–14
American Society for Testing Materials
ASTM Third International Conference on Measurement of Air Quality
Johnson, Vt.
Subject will be sampling techniques and problems. Write: P. M. Giever, Rt. 8, Allison Park, PA 15101

July 10–14
International Atomic Energy Agency
Symposium on the Interaction of Radioactive Contaminants with the Constituents of the Marine Environment
Seattle, Wash.
Aimed at elucidating the influence of radioactivity on the marine ecosystem and providing some background material for estimating capacity of the sea for assimilating radioactive waste without harmful effects on man and the ecosystem. Contact: John H. Kane, Special Assistant for Conferences, Div. of Technical Information, Atomic Energy Commission, Washington, DC 20545

July 11–15
National Society of Professional Engineers
Annual Meeting
Denver, Colo.
For further information: Len Arzt, PR Director, NSPE, 2029 K St., N.W., Washington, DC 20006

July 18–20
University of Rhode Island
Annual North East Regional Antipollution Conference (ANERAC-72)
Kingston, R.I.
Theme will be economics of pollution. Write: Professor D. L. Sussman, Rm. 207, Bliss Hall, University of R.I., Kingston, RI 02881

July 24–26
Public Technology and the American Institute of Aeronautics and Astronautics
Second Annual Urban Technology Conference
San Francisco, Calif.
Will concentrate on transportation, environment, and technology transfer. Contact: Advance Registration, Second Annual Urban Technology Conf., American Institute of Aeronautics and Astronautics, 1290 Avenue of the Americas, New York, NY 10019

Courses

June 19–22 and 23–24
University of California
Airport Planning and Design Short Course and Airport Noise Developments in California Short Course
Berkeley, Calif.
Fee: $150 and $85, respectively. Write: Dept. B, University Extension, Univ. of Calif., 2223 Fulton St., Berkeley, CA 94720

June 19–30
University of Colo. and NOAA
Remote Sensing of the Troposphere Short Course

Boulder, Colo.

Introduction to basic scientific background for study of the environment—principally the atmosphere—by remote probing methods, specific systems for remote probing, and atmospheric physics. Fee: $325. Contact: S. W. Maley, Engineering Center, Univ. of Colo., Boulder, CO 80302

June 19–July 28
National Science Foundation and others
Advanced Institute on Statistical Ecology

University Park, Pa.

Covers topics in statistical ecology (modeling, sampling biological populations, etc.). Contact: G. P. Patil, Director, Advanced Institute on Statistical Ecology, 330 McAllister Bldg., University Park, PA 16802

June 25–30
Lehigh University
Kinetics, Catalysts, and Chemical Reactor Design Short Course

Bethlehem, Pa.

Emphasis on environmental and biochemical processes. Contact: Robert W. Coughlin, Dept. of Chemical Engineering, Lehigh Univ., Bethlehem, PA 18015

June 26–30
Union College
Third Annual Industrial and Product Noise Institute

Schenectady, N.Y.

Covers basic nature of sound and noise control, federal and state noise laws, and noise measurement equipment. Contact: Special Programs Office, Union College, Schenectady, NY 12308

June 26–30
Massachusetts Institute of Technology
Engineering Aspects of Heat Disposal from Power Generation

Cambridge, Mass.

Designed for engineers, ecologists, educators, members of the utility industry, and regulatory agencies concerned with the problem of heat disposal associated with fossil and nuclear power generation. Write: Director of Summer Session, Room E19-356, MIT, Cambridge, MA 02139

June 26–July 7
Southern Illinois University
Conservation Education Workshop

Carbondale, Ill.

Contact: Paul F. Nowak, Conservation and Outdoor Education, Southern Illinois University, Carbondale, IL 62901

June 26–July 21
Southern Illinois University
World Man/World Environment Workshop

Carbondale, Ill.

Total fee: $350. Write: Summer Workshop, Dept. of Design, Southern Illinois Univ., Carbondale, IL 62901

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JUNE 1972

VALID THROUGH
AUGUST 31, 1972

ADVERTISED PRODUCTS:

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
46	47	48	49	50	51	52	53	54	55	56	57	58	59	60

NEW PRODUCTS, NEW LITERATURE:

61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
76	77	78	79	80	81	82	83	84	85	86	87	88	89	90
91	92	93	94	95	96	97	98	99	100	101	102	103	104	105
106	107	108	109	110	111	112	113	114	115	116	117	118	119	120

Name _____

Position _____

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BUSINESS ☐ Other _____

WATER AND WASTE CONTROL NEWS

CHRYSLER WASTE CONTROL. Plant wastewater containing light machining oils and plating rinse solutions is treated in three tanks like that shown above at new Dayton (Ohio) waste treatment facility to destruct chromates and decant waste oil. Centralized graphic control panel shown below was furnished and installed by Honeywell; puts the operator in instant touch with all functions of the facility to help the automaker meet city standards on PH, phosphates, chromates, and suspended solids. Thomas Sturr, manager of plant utilities, points out the effluent flow recorder, a Servoline instrument adapted to receive the 4-20 ma signal from a 12-inch magnetic flow meter in the main effluent line from the facility to the Dayton municipal waste treatment plant.

Automate Your Water Cycle

Inefficient use of plant process water costs American industry millions of dollars yearly. How to automate plant water processes to save water costs is described in "Instrumentation For Industrial Water Processes", a descriptive paper by Honeywell water management marketers A. H. Keyser and C. P. Blakeley. Reprints are available.

AUTOMATION KEEPS IT COOLER. This induced draft, cross-flow cooling tower is typical of the majority of industrial plant cooling tower installations. Trouble areas in cooling efficiency can come from scale, corrosion, and microbiological growths in water. A well-designed control system automates the feeding of inhibitors to cut tower maintenance costs and increase cooling efficiency.

Aeration of Industrial Wastes

Measurement and control of dissolved oxygen as the key to successful aeration of sewage and industrial wastes is described in Honeywell Application Bulletin AB-16, "Dissolved Oxygen in Sewage and Industrial Wastes". The bulletin describes how Honeywell D. O. measuring systems are used in waste treatment processes with air diffusers or surface aerators. Write for free copy.
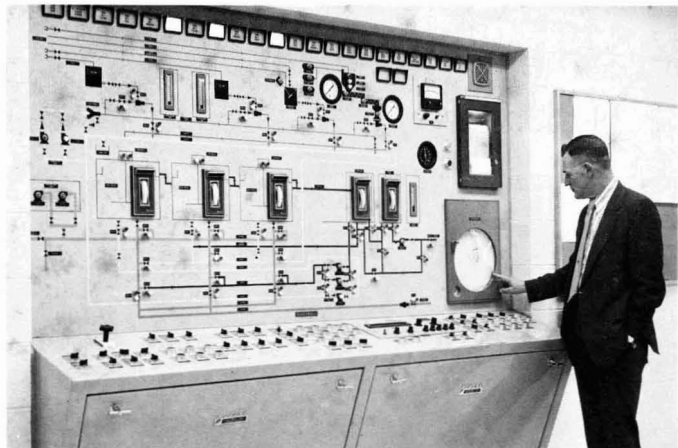
Cutting Cooling Tower Costs

Summer months mean heavy loads on plant process and environmental water cooling systems. Honeywell control systems can help cut costs of cooling tower operation where the water used requires chemical treatment. Majority of the problems of cooling tower water involve scale, corrosion, and fouling by microbiological growths. Growths are retarded by shot-feeding chlorine and other biocides. Scale and corrosion are minimized by adding inhibitors to both system and makeup water in proportion to flow. Honeywell's wide line of flow transmitters (both pneumatic and electric), recorders, controllers, and control valves apply here.

The treatment also demands accurate control over conductivity and pH. Honeywell supplies a complete line of sensors, sensorholders, transmitters, recorders, and control instruments for this application.

How sophisticated a cooling tower control system should be depends more on environmental factors and the quality of the raw water used than the physical size of the cooling tower itself.

Typical control systems for five different configurations of cooling towers are described in Honeywell Application Data Sheets AD 59-08-12 through -16. Write for a free set.
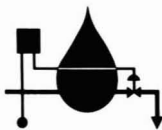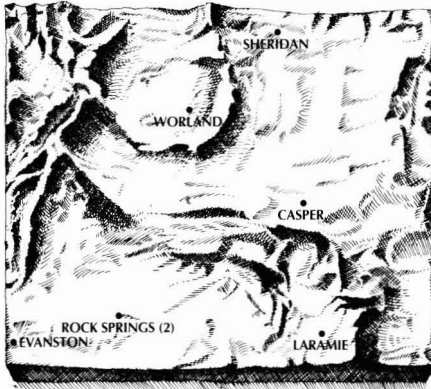
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