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LEAD
the specter of poisoning 30

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contents

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Features

Interview

Outlook

Departments

Current research

Measurement of suspended solids concentrations in sewage using a depolarization method 43

J. W. Liskowitz and G. J. Franey

The concentration of suspended solids in sewage in the range of a few parts to 5000 ppm can be measured by this method. The degree of depolarization is unaffected by other parameters such as size distribution of articles, density variations, source of samples (industrial or municipal), color variations, and other items in sludge samples. Perhaps, the degree of polarization is the result of averaging or cancellation of efforts.

Development and validation of a generalized mechanism for photochemical smog 47

T. A. Hecht and J. H. Seinfeld

A 15-step mechanism is proposed for the formation of photochemical smog, but it is by no means a unique model. The mechanism accurately simulates the effect of carbon monoxide on smog chamber photoxidation kinetics and the inhibitory effect of high initiation concentration of nitric oxide on the maximum concentration of ozone attained. The role of sulfur oxides and the generation of photochemical aerosols are not included.

A numerical method for computing equilibria in aqueous chemical systems 58

F. M. Morel and J. J. Morgan

A computer program has been developed which covers the chemical reactions in aqueous chemical systems. The program uses the stability constant approach and the Newton-Raphson method for digital computation of equilibria. An application of the program is presented for a system of 780 soluble species, 64 possible solids, and one gas-phase component.

Gaseous bromine and particulate lead, vanadium, and bromine in a polluted atmosphere 68

J. L. Moyers, W. H. Zoller, R. A. Duce, and G. L. Hoffman

Atmospheric concentrations of bromine are less than suspected from the amounts of bromine added to ethyl gasoline. A significant portion of the bromine produced by the combustion of leaded gasoline can be released to the gaseous phase. But gaseous and particulate species may have different atmospheric resident times or the collection procedure may discriminate against a particular form of atmospheric bromine.

Photooxidation of sulfur dioxide 72

H. W. Sidebottom, C. C. Badcock, G. E. Jackson, J. G. Calvert, G. W. Reinhardt, and E. K. Damon

The first stage of studies for removing SO_2 from the atmosphere via homogeneous paths is described. Theoretical maximum rates of photochemical oxidation of SO_2 are presented. These data should be useful in determining the importance of alternative homogeneous or heterogeneous removal mechanisms for specific atmospheric systems.

Correction

Effect of peroxyacetyl nitrate (PAN) in vivo on tobacco leaf polysaccharide synthetic pathway enzymes 71

L. Ordin, M. J. Garber, J. I. Kindinger, S. A. Whitmore, L. C. Greve, and O. C. Taylor

This article appeared originally in ES&T, July 1971, p 621

Communication

Proton activation analysis for trace elements 79

S. Fiarman and G. Schneier

Bombarding water samples with a proton beam from a Van der Graff accelerator can be used to determine trace elements in water samples at the ppb level. Typical measurements include phosphorus at the 28-ppb level, nitrogen at 190-ppb level, sulfur at 50-ppb level, and fluoride and sodium at the 0.1–1.0-ppb level.

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letters

Adsorption of solvent vapors

DEAR SIR:

After reading your article in the November 1971 issue of *Environmental Science & Technology* on "Solvent vapors under fire," (p 1086), we were quite disappointed that nothing was mentioned about carbon adsorption for controlling hydrocarbon emissions from industrial processes.

Our company has been manufacturing carbon adsorption equipment for recovery and reuse of solvents for over 20 years and has more than 10,000 units installed throughout the world. We are experienced with recovering chlorinated solvents and many others used in industrial finishing and processing. We have units installed in dry-cleaning plants, metal degreasing, all the way to printing operations. Most of these solvents can be recycled and reused as they come from our system.

The Environmental Protection Agency has made very clear that control of existing solvents is more desirable than substituting the "less reactive" or "nonreactive solvents" mentioned in your article, because there is evidence that no solvent is nonreactive. They have stated this in the Federal Register, Volume 36, No. 158, dated August 14, 1971, under Title 42, Chapter 4, Appendix B, Section 4.0, Control of Organic Compound Emissions. Under Section 4.6 they state that reduction of at least 85% can be accomplished by: (A) Incineration and (B) Carbon adsorption.

We believe your article could have had a more positive approach to the problem of solvent control if carbon adsorption had been mentioned.

Dennis M. Larson
Vic Manufacturing Co.
Minneapolis, Minn. 55413

• *Al Gaber of Calgon Corp. has also written us to make the same point—Ed.*

Haste and waste

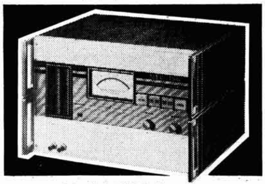
DEAR SIR:

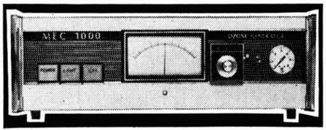
Dr. Abel Wolman (Viewpoint, October 1971, ES&T, p 981) quoted Publilius Syrus to the effect that haste (on the part of "vociferous groups") makes waste (in environmental improvement).

His quotation could not be more apropos to the sewage crisis in the Washington, D.C. metropolitan area. However, it should be clarified that not all the haste is attributable to vociferous groups. Much waste indeed has originated from such public agencies as the Washington Suburban Sanitary Commission (WSSC) of Maryland, which has until recently always hastened to approve sewer hookups regardless of the quality of treatment available. This policy has resulted in heavy overloading of all sewage treatment plants in the area and the well-known situation on the Potomac River.

The situation has become so bad that our citizen group recently took legal action against this agency. I think it is pertinent to mention that Dr. Wolman has been the chief consultant of WSSC and that he has consistently favored large-volume over high-quality treatment. Consequently, citizens have been forced to attribute a certain amount of haste to his own actions.

Robert F. Mueller
Prince George's (Maryland)
Environment Coalition
Lanham, Md. 20801





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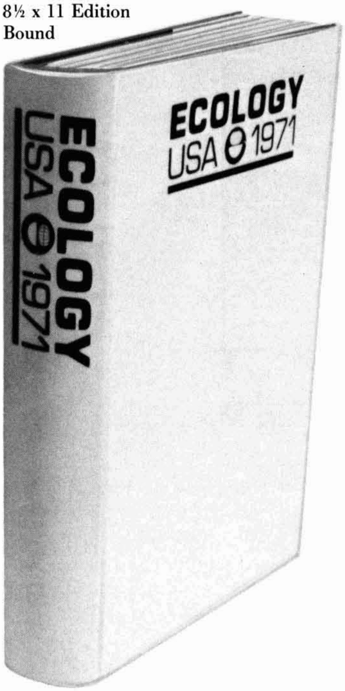

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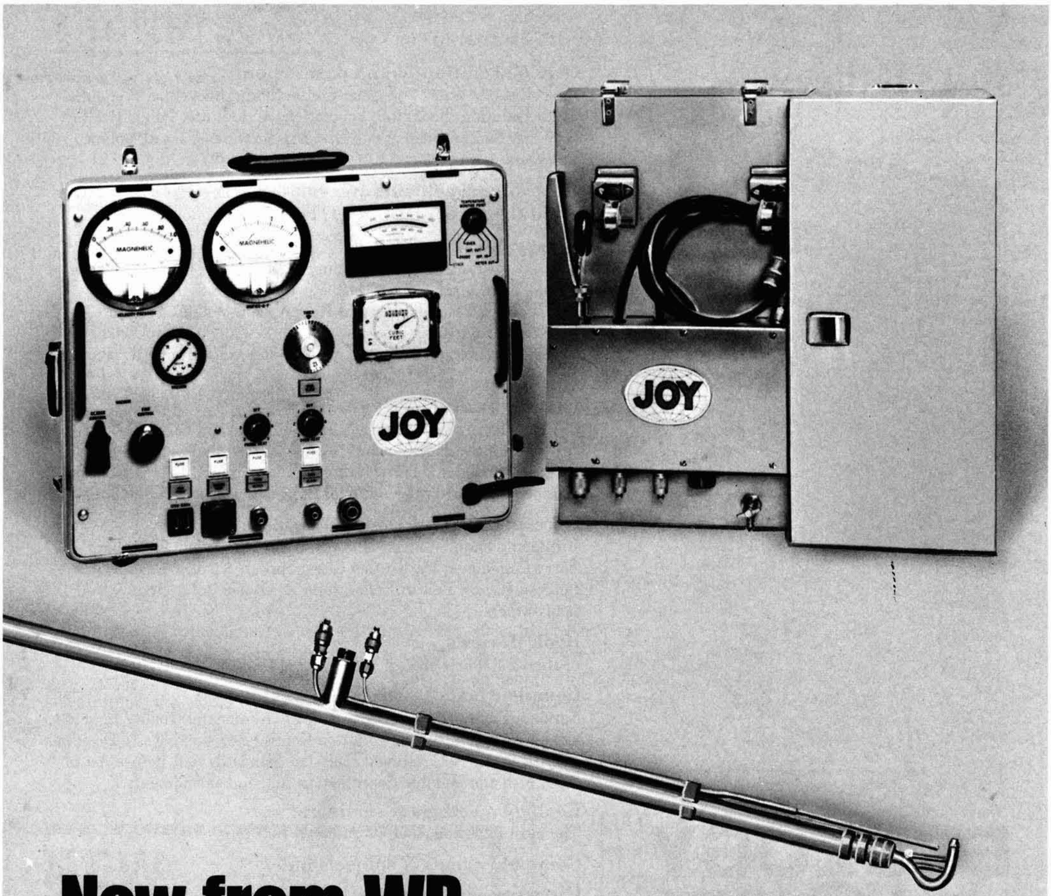

Playing the environmental numbers game

It's time for those who make measurements and those who use them to start communicating with one another

The average man-in-the-street, if there is such an animal, has a longstanding love affair with numbers. Percent completions, games behind, yards rushing, earned run averages, you name it, your average man will rattle it off. And now he has a new figure to relish—the pollution index. Locally, newspapers, radio, and TV publish an air pollution index—parts per million of oxidant (in the summer) or sulfur dioxide (in the winter) in the air for the previous day. We've often wondered what John Q. Public thinks—if he even notices—when the index makes its twice-yearly shift from one criterion of pollution to the other. If he doesn't notice the changing basis for the index, then he is really not being much less scientific about numbers than people who ought to know better.

For there is an awful lot of monkey business being played with numbers, especially now that a penchant for being at least superficially quantitative has arrived on the environmental scene. It used to be that terms like "zero tolerance," "zero residue," and the like really meant something useful. Now that the technology of measurement has become highly refined, "zero" is a number that can hardly be believed, let alone written into some sort of regulation.

Apart from the semantic mischief that can be wreaked on even accurate numbers—a half-empty bottle can be accurately described as half full, for instance—the most dangerous aspect of numbers appears to be that they are rarely quoted with an indication of how they were measured. While such qualifications are the stock-in-trade of technical papers such as those ES&T publishes each month, it is rarely that numbers are aired in public forums with even the slightest reference to their accuracy or applicability. Typically, one group might argue that lead in the air is on the increase while another maintains that it is declining. Both could be right, but we'll never know until we discover how each group made its measurements, where and when. Quite commonly we would find that neither group actually made any measurements but instead used someone else's numbers.

It is perhaps critically important that legislators and regulation setters recognize that there is more in a number than meets the eye. The history of regulations regarding the permissible emissions from auto exhausts is fraught with good examples of this point. Practically every time the U.S. government has recommended a new test method for a pollutant, the standard for that pollutant has had to change because every method seemed to give different results.

That sampling and measurement techniques have their drawbacks is widely recognized in the technical community, of course. (See the story on ASTM's Project Threshold on page 23 of this issue, for an example.) But it is by no means so clear that the lay public understands the situation. As an example, consider the case of carbon monoxide alerts in Los Angeles; the number of these alerts is up sharply in 1971. The simple explanation is that the concentration at which an alert is called has been reduced from 100 to 50 ppm. But an impression of rapidly rising atmospheric CO levels may remain nonetheless.

If numbers are going to be used as the goals of a clean environment—and promulgation of emission limits, performance standards, and all the rest of the paraphernalia of regulatory agencies indicates that they are—then the numbers game is too important to be left to those with no knowledge of analysis and measurement. Analysts and other number-getters will have to abandon their traditional independent stances and start mixing it with the number-users. The conflict may be a bruising one, but the cause is just.

D. H. Michael Bowen


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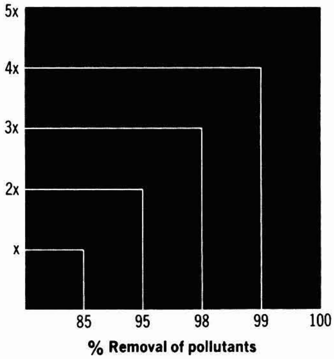
Costs of water treatment



CEQ's Train offers views on water pollution

At last month's reopening of hearings on proposed water pollution amendments by the House Public Works committee, Russell Train testified that the concept of water quality standards should not be abandoned. One of the fundamental questions is whether very high expenditures should be made in cases where such expenditures are not necessary in order to achieve water quality standards. Total recycle costs five times more than 85% removal (see diagram). Further, Train supported the objectives of • achieving water quality for swimming and other high quality use by 1981 • requiring precise effluent limitations for individual sources of discharge to achieve water quality objectives • requiring best practicable technology for industrial pollution control by 1976. But on this last point, he cautioned that some provision should be made available for an extension, not more than two years, for facilities under certain circumstances.

EPA: awards, hazardous pollutants, and warnings

At the celebration of its first anniversary on December 2, EPA presented awards to 29 employees for their individual contributions to the nation's environmental problems. One of the three gold medals for exceptional service went to Kenneth Biglane for his role in developing the national contingency plan for dealing with oil spills and hazardous materials in the U.S. waters. Three materials—asbestos, beryllium, and mercury—have been classified as hazardous air pollutants. Within 180 days, EPA will hold hearings and set emission regulations unless information presented at the hearings demonstrates that the pollutants clearly are not hazardous. EPA and the Department of Labor jointly established a dislocation warning system to avoid or minimize unemployment resulting from pollution control enforcement actions.

National Water Commission hits two-thirds mark

The National Water Commission, a temporary body established by Congress in 1968, was given five years in which to prepare a comprehensive and independent review of the nation's water problems (ES&T, March 1970, p 202). The scope of the NWC review includes everything from pollution to inland navigation, from irrigation to ecology, from institutions to aesthetics. A draft of the NWC final report will be completed by the fall of this year; the final report will be submitted next January. Meanwhile, a dozen reports have been released on specific problems including reports on groundwater management, interstate water compacts, and waste water reuse. These reports are available from NTIS, Springfield, Va. 22151.

Congress and the President receive noise findings

Authorized by the Clean Air Amendments of 1970 (P.L. 91-604), the noise report basically contains contractor findings and includes the following topics: • effects of noise on living things and property • sources of noise and their environmental impact • control technology and estimates for the future • laws and regulatory schemes for noise abatement • government, industry, professional, and voluntary programs • assessment of noise concern by others.

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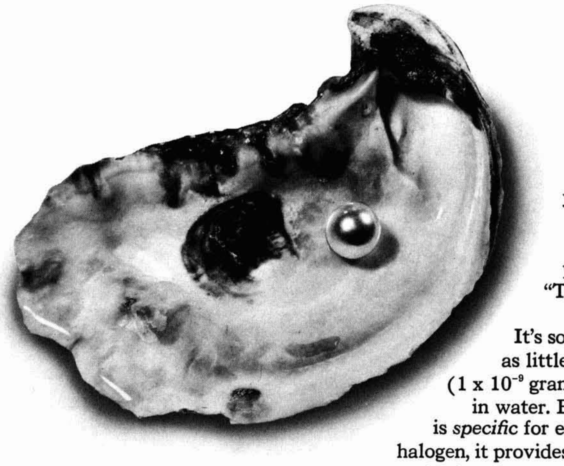

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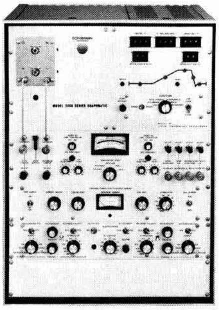

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STATES

N.J. pipes wastes to ocean, cites military polluters

The New Jersey Department of Environmental Protection has approved a $3,526,000 state grant for constructing an outfall pipe almost a mile into the Atlantic Ocean diverting effluent that would otherwise be discharged into Raritan and Sandy Hook Bays. The facility will ultimately handle the combined wastes from 12 municipalities. Nine federal military installations—Camp Charles Wood, Camp Evans, Fort Dix Military Reservation, Fort Hancock, Fort Monmouth, Lakehurst Naval Air Station, McGuire Air Force Base, Pedrickstown Military Reservation, and Picatinny Arsenal—received water pollution abatement orders with a compliance deadline by the end of next month (see ES&T, December 1971, p 1176).

Gov. Richard Ogilvie

P&G loses Fla. market; Ill. pays 25% sewage costs

Proctor & Gamble withdrew its laundry detergents last month from the market in Dade County, Fla. "until new product developments permit us to return." P&G's action is based on a law making it illegal to sell detergents containing phosphates in the Miami area after December 31. Last month, Illinois Governor Richard Ogilvie released over $900,000 for full or partial payment of the state's 25% share of eligible costs for municipal sewage improvements. Thus far, these proceeds authorized by the Anti-Pollution Act of 1970 brings the total amount paid by the state for projects already completed or currently under construction to $8,888,611. "Clean water is an attainable resource for all residents of Illinois," emphasizes Ogilvie.

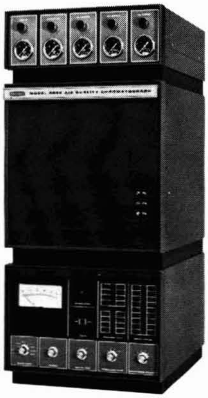
Ga. county cited; Philly fines auto owners

In a decision of state and possible national significance, a Georgia court ruled that a county is responsible, under Georgia constitution, for the health and well-being of the people within its jurisdictional borders. Walton County was made a codefendant in a civil action against a small municipality for operating an illegal garbage dump. The matter is being appealed to the State Supreme Court. The Philadelphia (Pa.) Municipal Court fined 22 vehicle owners for automotive air pollution. Most defendants were fined $25 plus court costs, but those who failed to appear were fined $100 plus court costs. A joint Police-Air Management Team patrols the streets for smoking auto exhausts.

Nuclear power plant under tight control in Illinois

The Illinois Pollution Control Board granted Commonwealth Edison and Iowa-Illinois Gas & Electric Co. a permit to operate a new nuclear generating station but under extremely strict conditions. Rejecting the argument that the federal government had preempted the field of radioactive emission control, the board ordered the companies to reduce, by December 1973, gaseous radioactive emissions by a factor of 30 times the amount the companies had requested to discharge. A maximum recycle system for liquid radioactive discharges is required; the board also ordered the companies to install a diffuser pipe to distribute more equally heated wastes in the river. The companies can only operate one of the two 809-MW boiling water reactors until adequate controls are installed.


Polluted air isn't new.



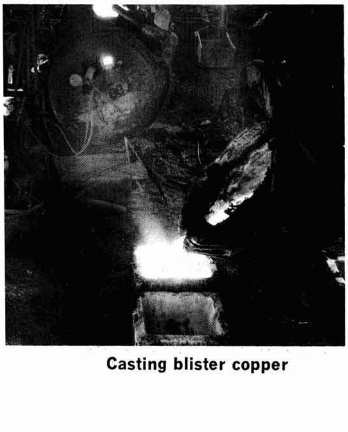
TECHNOLOGY

Chimneys could safely store nuclear wastes

Underground chimneys, created by detonation of small nuclear devices, could be used for permanent disposal of radioactive wastes, according to scientists at the Lawrence Livermore Laboratory (Livermore, Calif.). Such chimneys—actually cavities filled with broken rock—could be located under nuclear fuel reprocessing plants and eliminate hazardous shipping and storing of nuclear wastes aboveground. The Livermore team suggests that heat produced by the radioactive decay of high-level wastes would boil the solutions dry in the chimneys. Steam given off in the process could be recycled. When capacity of the chimney is reached—in about 20 years—heat would melt the rock. When radioactivity decreased sufficiently, the rock would cool and solidify, permanently trapping wastes underground.

Plastics make debut in concrete bridge

The first use of recycled plastics as a component of structural concrete will be in a bridge connecting Elgin, Ill.'s Civic center grounds with Walton Island in the nearby Fox River. Residents of Elgin will collect some 25,000 scrap plastic bottles which will be ground into chips and used to replace 30 vol % of the normal sand aggregate in the bridge's concrete footings and span. The 100 ft long, 7 ft wide arch will be about 9 % lighter in weight than it would have been with conventional concrete, with insignificant loss of strength. Tests have shown that the plastic-concrete mixture has "zero slump" when wet—a valuable property, suggesting that the mixture might be used in slanting architectural forms where bulging due to gravity flow induced by weight of conventional concrete must be overcome.



Casting blister copper

Copper smelting process developed by Japanese

Mitsubishi Metal Mining Co. Ltd. has developed a new copper smelting process which it says will be the industry standard in the near future. The process eliminates air pollution from refining operations, Mitsubishi says, because it allows complete recovery of sulfur dioxide generated during smelting. Conventional copper making consists of two separate processes—making of copper matte from concentrates in a reverberatory furnace and then batch production of blister copper from the matte in a converter. Mitsubishi's process strings the two steps together, improving efficiency and allowing better control over the process. Mitsubishi is building a 1500-tpm semicommercial unit in Onahama, Japan to test the process.

Model incinerator to be built and tested by MIT group

A research team at the Massachusetts Institute of Technology has built and tested a model incinerator that simulates combustion conditions in traveling-grate incinerators. Funded by the EPA's Bureau of Solid Waste Management, the project has two objectives: • to find an easily monitorable index of incinerator burnout that can be used in servomechanisms to control incineration • to obtain data from which to design better air distribution within and above the fuel bed. The device is a cylindrical chamber, separated into upper and lower sections. Twelve nozzle ports in the top supply overfire air to ignite the top of the fuel bed. The lower section houses analytical probes. One result to date—changes in CO_2 emissions may be a simple measure of burnout.

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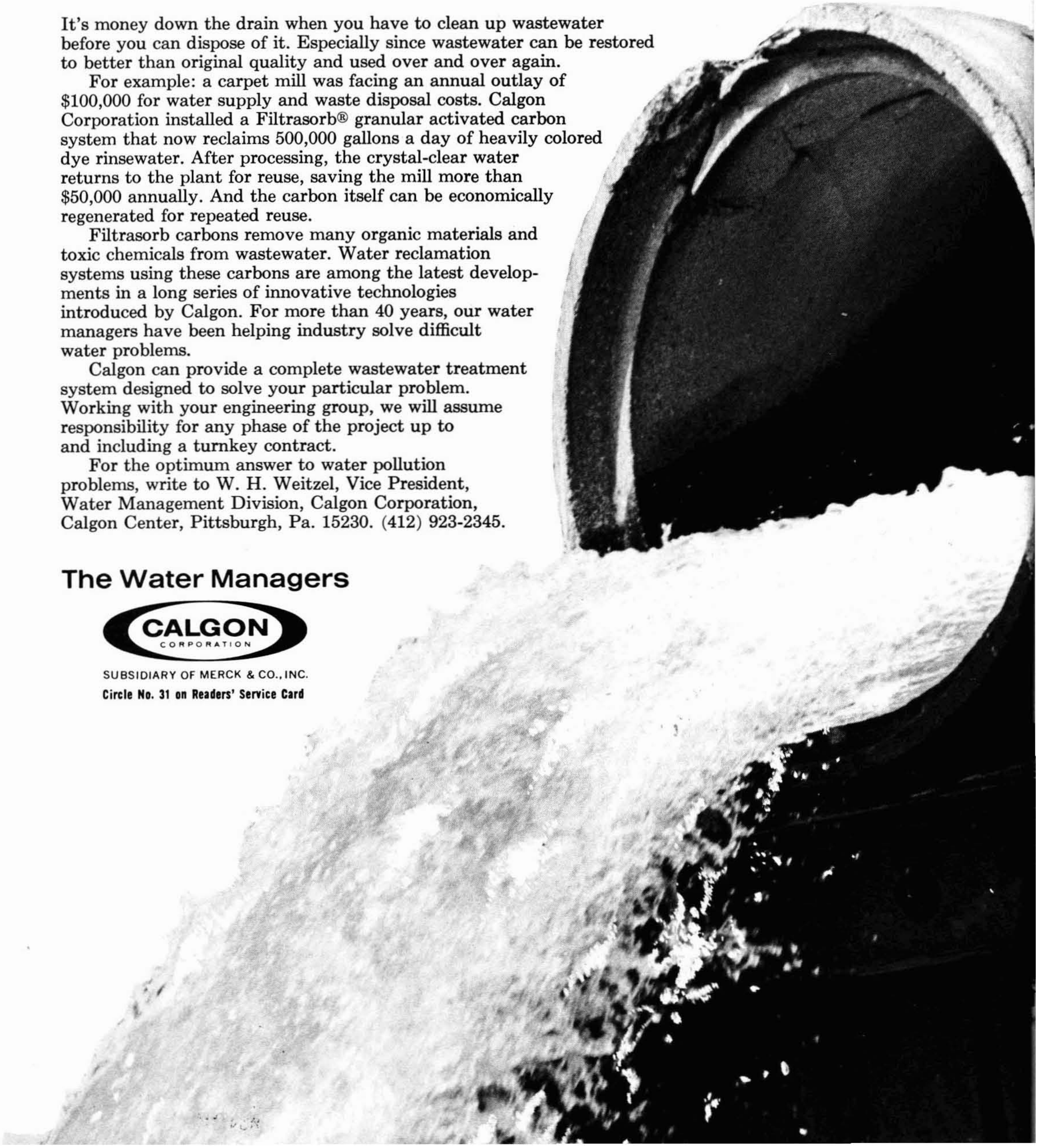


INDUSTRY

API earmarks $5 million for air, water pollution

The American Petroleum Institute will spend about $5 million in the institute's program to combat air and water pollution in 1972, according to API's President Frank Ikard. API has added about $2.6 million to the $2.5 million previously appropriated and already largely committed to projects which will be completed during 1972. Ikard says the bulk of the money will be spent for research on oil spills ($1.3 million) and automobile emission control ($2.8 million). A major part of the research on auto emissions has joint sponsorship of the Automobile Manufacturers Association, EPA, and API. The rest of the budget will be spent on other programs for improving the quality of the environment.

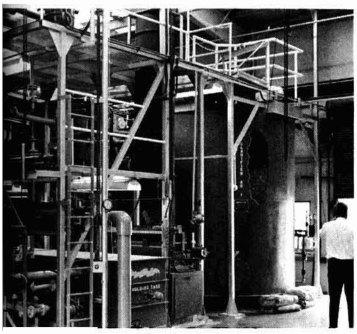
ICI claims catalyst for exhaust emissions reductions

Imperial Chemical Industries Ltd. says it has a catalytic muffler system that will cut levels of nitrogen oxides, carbon monoxide, and unburned hydrocarbons in automobile exhaust sufficiently to meet the 1976 EPA emission standards. ICI gives no details about the composition of the catalyst, but says the dual-catalyst muffler system has worked well in limited tests. Federal regulations require that catalytic devices be serviceable for up to 50,000 miles, and ICI will not speculate whether or not its system will hold up for that many miles, but the company is reportedly discussing its development with potential customers in the U.S. ICI assumes that lead-free gasoline will be widely available in this country by 1976.

TVA will implement stricter strip-mining controls

The Tennessee Valley Authority (TVA) will require tougher specifications for reclaiming strip-mined land from would-be suppliers of coal for the agency's electric generating stations. TVA is the largest domestic consumer of coal, using some 35 million tons annually to fuel steam-electric generating plants. Roughly half the coal comes from strip or auger mining while the remaining half comes from deep mines. Although TVA has routinely required some land reclamation in its contracts since 1965, future contracts will involve two-step bidding. Under the plan, the coal producer has to submit a detailed plan of operations and reclamation to be approved by mining and reclamation specialists before a company will be qualified to bid. Part of the awarded contract money will then be held in reserve and paid only when reclamation is completed.

Municipal treatment plant to test PhoStrip process



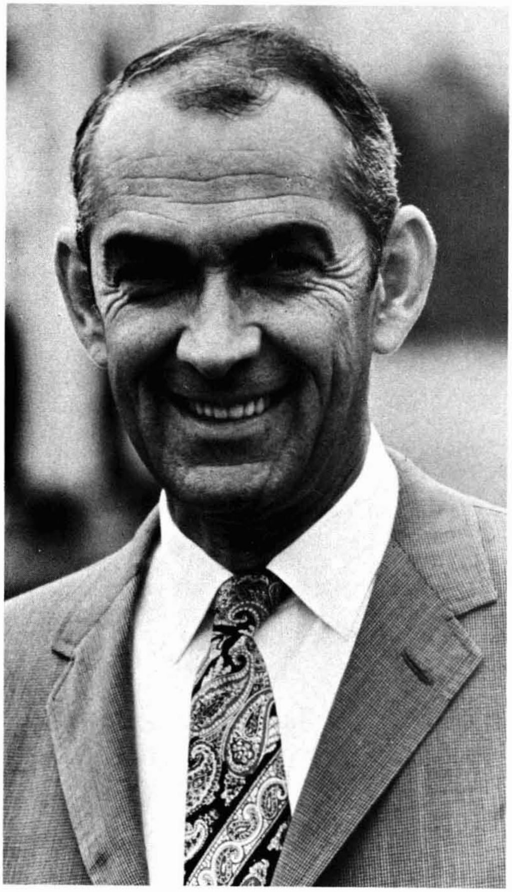
Municipal plant

Two Washington, D.C. area sewage treatment plants will serve as sites for Biospherics' PhoStrip phosphorus removal process. The process relies primarily on biological processes, rather than the addition of chemicals (see ES&T, January 1971, p 15). The District of Columbia Department of Environmental Services and the Washington Suburban Sanitary Commission have signed agreements with Biospherics to conduct 180-day tests of the process at the D.C. Blue Plains Water Pollution Control Plant on the Potomac River near the District's southern tip and the Piscataway Plant in Prince George's County, Md. Advantages of the PhoStrip process are said to include compatibility with existing activated sludge processes, low chemical dosages, and lower sludge volumes than with conventional processes. Costs of the tests will be borne by Biospherics.

ES&T Interview

JOHN SCHORK

A candid talk with Research-Cottrell's, mild-mannered executive who has some interesting things to say and whose company is unique in pollution controls



John Schork is chairman of the board and president of Research-Cottrell, one of the nation's leading environmental management companies. R-C went public in 1967 and hit $100 million in sales last year. Schork tells ES&T*'s Stan Miller how the company broadened its business scope and moved ahead in today's environmental management arena including recent acquisitions, internal concentration on profit centers, legislative pressures specifying cleanup deadlines, and its move to a total environmental management team.*

Opportunities

How is business? Was 1971 the seventh year of uninterrupted growth in sales, earnings, and new orders for R-C?

Yes, there is no question about it. Sales were up, backlog orders were up, and earnings were up. Although we are moving into pollution solving, products and systems are still by far the largest dollar volume part of our business. The engineering-consulting part is perhaps 20% of the total. The four major areas of business are the steel industry, power generating plants, pulp and paper industry, and the cement industry. The company has doubled in size since 1969. New orders for precipitators, for example, are more than double what they were last year. This is also about twice what we forecasted.

What effect has the recent round of environmental laws had on R-C business?

Almost all of the increase in precipitator orders for older plants is due to legislation and either enforcement actions or threatened enforcement actions. Newer plants have good pollution control equipment; they have been putting it in for years. Noticeably, legislation is effective in the back-fitting of existing installations. Here, the customer is putting in pollution control equipment and not getting any additional capacity out of his plant. Half of the new 1971 orders for precipitators went for such existing installations; some of them did not have anything much in the way of air pollution control equipment and others had obsolete controls installed years ago.

Restructured management

Beginning in 1970, R-C operated with a completely restructured management. How did this change come about and how successful has the changeover been?

The conceptual idea of becoming an environmental management company is something we worked out in-house. After that decision was made we then got some help from the management consultants, Lybrand Ross Bros., Montgomery. In 1965, R-C was a one-product company—precipitators—but it was then that we put together our so-called game plan. The plan called for expansion into the capital equipment business—fabric filters, scrubbers, mechanicals, cooling towers, and tall stacks. In 1969, R-C ended up with a complete line of products. Then, we had to see what else it could do. Obviously, selling hardware was going to be one aspect of this total environmental management picture. Everyone is going to have to buy hardware.

We had many people coming to us who didn't even know what their problems were. So, we decided to change our approach; the object was to sell the customers on our services. Understanding their problems is one of R-C's real strengths. We don't just sell out of a handbook. Our sales engineers and applications people know the customer's process. They talk to the steel mill superintendent and power plant superintendent not about R-C equipment but about their whole operation. All of this is an advantage when it comes to sizing and designing equipment.

The changeover has given R-C a lot of growth capability we didn't have before. Of course, nothing is perfect, but I think if R-C had stayed just with selling hardware, we could not hope to reach the position we expected to be in 1975 or 1980.

Profit centers

How many divisions are there within R-C and how profitable are they?

There are two groups—the Environmental Control Group with about 800 people and the Environmental Engineering Group with about 900. They are both profitable. The Control group is mainly concerned with air and thermal pollution controls. It is headed by William Jones and represented about 81% of last year's business. The engineering group is concerned with water pollution control, waste disposal, and land use planning. It is headed by Peter Gianacakes and represented 17% of the business. Oxy-Catalyst was the remaining 2%.

In the Engineering Group, Metcalf & Eddy is by far the largest of the three (see box). About 70% of their total business is in the municipal water and waste treatment field. They didn't grow as fast in 1971 as we had thought. But a lot of municipal projects were held up temporarily. We will probably see more activity now in 1972.

Can you elaborate on the business rationale for sale of Degremont-Cottrell and acquisition of Oxy-Catalyst?

R-C was in the water pollution control hardware business with the Degremont-Cottrell division; we lost money every year for four years. Whether it was our fault or the market's fault, we cannot say. We just couldn't produce a profit. Selling hardware to municipalities is a tough competitive business. Municipalities are almost forced to buy the equipment on the basis of low bid. So, R-C was in the field competing for large dollar volume and small profit. It just seemed that we could better apply our money, people, and talents elsewhere. So we sold the operation. No regrets. Had we not sold it in 1970, we would have had a problem with the consulting-engineering groups, because some municipalities are reluctant to have a consultant do the study if he is associated with a hardware supplier.

We acquired Oxy-Catalyst to complete our product line in air pollution control. Our line was complete for particulate collection; we also had developed one process for SO_2 removal and licensed another. But other gaseous pollutants were not covered. We knew that gaseous pollutants were going to be a growing business and that many of the problems with these pollutants are solved by catalytic oxidation. Oxy-Catalyst was a small company, but it had been in the air pollution control business since 1959 and was a leader in its field. Sales were about $2 million annually. They had been making catalytic mufflers to solve the hydrocarbon emissions problem for 15 years. Some of their expertise is applicable to the automotive emissions control problem.

Technology

Is the present technology that is available from R-C adequate to control emissions from every stationary source? What are the exceptions?

For control of particulate matter, there is a solution to every problem. There is no reason to see dust or dirt coming out of any chimney in the U.S. Certainly, this is a broad statement, and there may be a process somewhere that cannot be controlled, but, in general, the controls for particulate matter are well developed. For gaseous emissions, it is an entirely different story. You pretty much have to take them one at a time. SO_2 controls are only experimental today. When you put them into commercial operation on a day-to-day basis it may be a different story. Collectively, utilities have spent a total of $80 million on SO_2 removal systems over the past four years, but there is no company that can sell such a system with the same degree of confidence and guaranteed performance as with a particulate control system. After we all get a little commercial experience—I guess in another few years—we will then be able to have the same assurance for SO_2 systems we have for particulate collection, but we cannot do them today. We can put the system in today, and it works, but you get a variety of efficiencies. Everything has to be done quickly these days. We had 50 years to develop controls for particulate; we've had only four years for SO_2 controls!

How many SO_2-fly ash removal systems have been purchased?

Commercially, about a half dozen systems have been sold. Recently, we sold one system to a western utility—Arizona Public Service. When its 115-MW plant was built 10–12 years ago, the entire cost of electricity produced was about $65/kW. Now, we are going back and putting in our control system which will cost them $48 a kilowatt additionally. This is the extreme case, but in every case the controls are expensive.

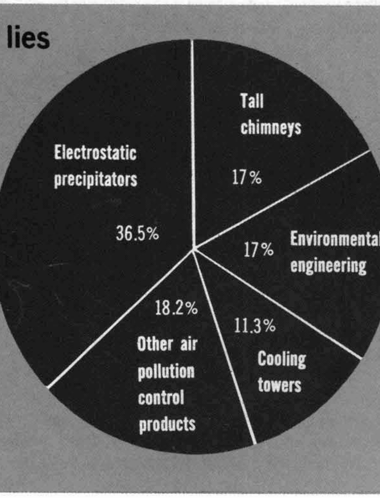
Where its strength lies

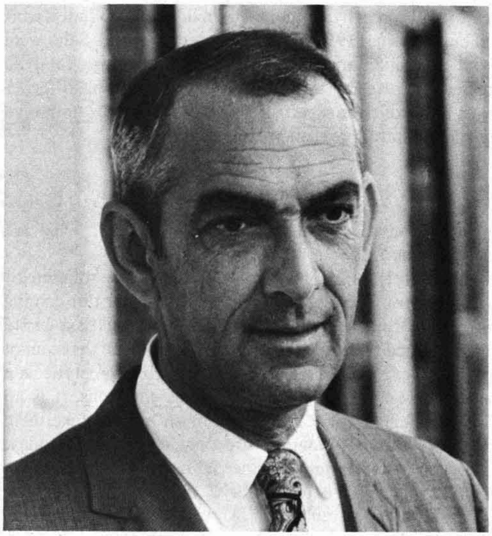
Environmental Control Group

Air Pollution Control
Hamon Cooling Towers
Custodis Chimneys
Flex-Kleen Corp.
Research-Cottrell (Canada) Ltd.
Custodis Canadian Chimney Co., Ltd.

Environmental Engineering Group

Metcalf & Eddy, Inc.
Connell Associates, Inc.
Sun, Low, Tom & Hara, Inc.
Cottrell Environmental Systems, Inc.





"We are the only company who is 95% or better in environmental control—products and services. . . . We have the broadest line because there is nobody else who competes with us in everything we do."

Research-Cottrell's Schork

Out unit will be in operation sometime toward the end of 1972 or early 1973.

What is the status of control technology for other pollutants?

Recently, R-C licensed the Swedish process of A. B. Bahco. This SO_2 control process is useful on smaller installations of the 100-MW size—smaller boilers, industrial boilers, and small power plant boilers. The Bahco process is a tried and true process. It has worked very effectively in Sweden and Japan. But it is important to note that the process would not be applicable to the large 800–1000 MW units that are being built today.

R-C is working on the oxides-of-nitrogen problem, but it is going to be a number of years before hard answers begin to come up.

Marketing

When did the R-C marketing function begin?

A formal program of customer-oriented marketing began only in 1970. But we have been trying to anticipate the customer's needs for several years. There is the old story, for example, that precipitators did not work with low-sulfur fuel. But R-C developed the hot precipitator in 1964 to solve that problem. At that time, we sold one to Con Ed, but no one else seemed to be interested. We developed one, and the world didn't care. Now, the story is different. A third of our 1971 precipitator orders were for hot ones.

R-C has a common marketing function for all products, but the three companies in the Environmental Engineering Group operate independently today. However, there is a blank spot on the organization chart for a marketing business development function for that group.

What is unique about R-C that distinguishes it from other environmental companies?

The unique thing about R-C is that we are the only company who is 95% or better in environmental control—products and services. In each one of our product lines we have good competitors, but no one company competes with us in all of our products. Nor is there any one company that competes with us in all our services. That is why I say we have the broadest line because there is nobody else who competes with us in everything we do. We are careful that we give our customers good products and services because this is all we have to sell.

Research

How much research does the company sponsor?

We have much to do in research. Many dollars will be spent on upgrading the SO_2 removal system capability so that it can move to mid or high ninety percent removal in delivered efficiencies. What we have to do is get the system down to the point where we can guarantee a specific performance for the unit. It is not going to be easy. In 1971, research expenditures were approximately $750,000. In 1972, we have budgeted $1.5 million for research, doubling last year's expenditure. Much of the money will be spent on the SO_2 control problem.

R-C profile at a glance

History in a nutshell

1912–1952 Sold electrostatic precipitators

1952–65 developed mechanical collectors and wet scrubbers

1965 acquired fabric filter product line

1966 entered capital equipment end of the water and waste treatment market by acquisition of an American subsidiary of a French company

1967 entered thermal pollution control market by acquiring a cooling tower company

acquired Custodis Construction Co. which builds tall chimneys for dispersion of gaseous pollutants

went public

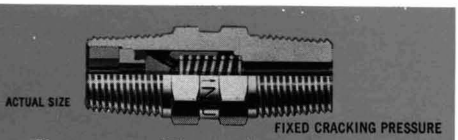
1970 sold the water and waste treatment company acquired in 1966

1971 redirected company to environmental management concept and broadened business base from equipment manufacturer and supplier

acquired three firms in environmental engineering

- Metcalf & Eddy (Boston, Mass.), a consulting firm with major strength in municipal water and sewage treatment, industrial waste water, and solid waste disposal
- Connell Associates (Miami) a consulting firm with major strength in land planning, development, and architecture
- Sunn, Low, Tom and Hara (Honolulu), a consulting firm with major strength in water and waste, coastal engineering, and land use and planning

acquired Oxy-Catalyst, a leading supplier ($2 million sales) of gaseous pollution abatement equipment for industry by thermal and catalytic processes and catalytic mufflers for use with internal combustion engines.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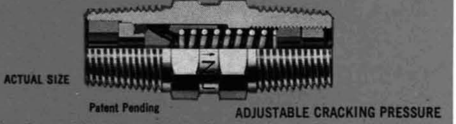
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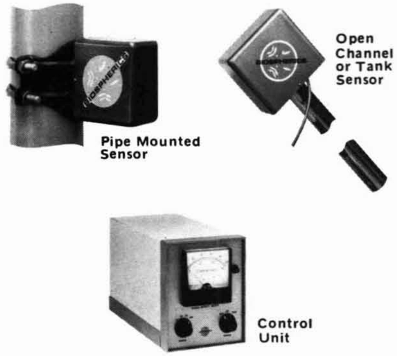
Patent Pending
ADJUSTABLE CRACKING PRESSURE


Open Channel or Tank Sensor
Pipe Mounted Sensor
Control Unit

outlook

Turn-key turns on construction firms

Construction of municipal waste treatment plants is a rapidly growing business; it merits a test of the turn-key option to get on with cleanup of the Nation's waters

Now that banks have changed their business operations, for the first time in 34 years, to a floating prime rate from the prime lending rate, how much longer can it be before the U.S. government allows turn-key construction of federally funded municipal waste treatment plants? Under the traditional method, consulting engineers prepare a plant design for a municipality. Then, contractors bid competitively for construction based on that design.

The furor touched off by the turn-key proposal that was announced by the EPA administrator last September 15 stirred the hottest environmental conflict in years. The issue, simply, is whether or not to permit turn-key operations as an alternative option that would be open to municipalities. The EPA proposal would open the option.

Whether turn-key operations are in the public interest only tests and time can tell. Judging from the sharp comments made on the EPA proposals, it may be months before the regulations are finalized, if indeed they are finalized at all. At press time, the deadline for comments (November 29) had passed, but it was too soon to know the fate of the proposal.

According to Webster's, a turn-key job is a job or contract in which the contractor agrees to complete the work of building and installation to the point of readiness or occupancy. (For a commonly accepted definition, see box.) In any event, turn-key involves three elements—engineering, procurement, and construction.

The turn-key approach has been around for years; it's been used in the industrial sector with much success. Although turn-key is a radical departure from the traditional way of performing municipal waste treatment plant construction in this country, it's common practice in foreign countries. It is used in just about every other country of the world except the U.S. on public works projects involving water and water treatment.

In the past, because of state regulatory bodies, there has been neither competition in municipal treatment construction nor advances in process design or technology. Nor has there been a single source of responsibility to ensure that a municipal plant employing traditional treatment methods will even operate as designed. This, at any rate, is what the turn-key proponents say.

The advantage most often cited as the prime consideration for turn-key is the fact that plants are built at a lower cost and in a shorter time. Savings accrue because one or more of the three elements of turn-key operations are provided concurrently. The turn-key contractor has complete control of the work because he normally employs mechanical and other workers directly, rather than through subcontractors. Other advantages, according to proponents, are that turn-key operations:

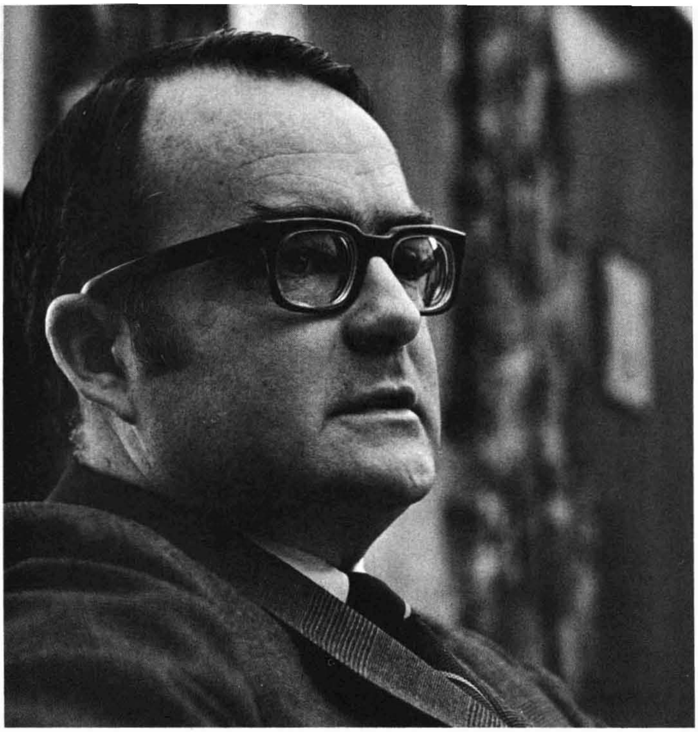
- are used in many foreign countries
- promote technological competition
- pinpoint one responsible management
- guarantee performance after construction.

Why EPA made the turn-key proposal in the first place is not certain. One school of thought maintains that pres-

Turn-key proponents

The 29 regular members of the National Constructors Association (NCA) have provided extensive turn-key operations in the industrial sector and two thirds of them have capabilities in all or some phases of waste water treatment, according to a 1971 NCA survey.

The Austin Co., Cleveland, Ohio
The Badger Co., Inc., Cambridge, Mass.
Bechtel Corp., San Francisco, Calif.
Blaw-Knox Chemical Plants, Inc., Pittsburgh, Pa.
C. F. Braun & Co., Alhambra, Calif.
Burns and Roe Construction Corp., Paramus, N.J.
Catalytic, Inc., Philadelphia, Pa.
Chemical Construction Corp., New York, N.Y.
Crawford & Russell Inc., Stamford, Conn.
Dravo Corp., Engineering Construction Div., Pittsburgh, Pa.
Ebasco Services, Inc., New York, N.Y.
The H. K. Ferguson Co., Cleveland, Ohio
Fluor Corp., Los Angeles, Calif.
Ford, Bacon & Davis Construction Corp., Monroe, La.
Foster Wheeler Corp., Livingston, N.J.
Kaiser Engineers, Oakland, Calif.
The M. W. Kellogg Co., Houston, Tex.
Koppers Co., Inc., Pittsburgh, Pa.
The Litwin Corp., Wichita, Kan.
The Lummus Co., Bloomfield, N.J.
Arthur G. McKee & Co., Independence, Ohio
The Ralph M. Parsons Co., Los Angeles, Calif.
J. F. Pritchard & Co., Kansas City, Mo.
Procon Inc., Des Plaines, Ill.
The Rust Engineering Co., Pittsburgh, Pa.
Sanderson & Porter, Inc., New York, N.Y.
Stearns-Roger Corp., Denver, Colo.
Stone & Webster Engineering Corp., Boston, Mass.
United Engineers & Constructor Inc., Philadelphia, Pa.



EPA Administrator Ruckelshaus

"What I am asking is not that you take a calculated risk on unproved methods, but that you take . . . advantage of systems that already have been shown to work."

sure for the EPA announcement came from the top—the administration. The story goes that construction firms, contributors to the coffers of political candidates, see business opportunities in construction of waste treatment facilities and want their share of the action. What truth, if any, there is in this line of reasoning is left to the environmental speculator.

More importantly, turn-key proponents say they want to be given the opportunity of having one, two, three, or dozens of tests cases—the exact number is unimportant—to prove that the alternative choice of construction method can work. Turn-key, then, is a basis issue.

Pro arguments

R. M. Santaniello, vice-president and general manager of Gulf Degremont, Inc., says, "The turn-key approach has been and is being used in just about every other country of the world, except the U.S., on public works projects involving water and waste treatment—with a high degree of success. A form of turn-key bidding is now being utilized on planned construction of a 30-million gpd waste water treatment facility for Garland, Tex. It is proving to be successful in reducing costs and developing new technology, all with true guaranteed performance of proposed facilities."

The pressure is on to make turn-key a test case for a construction grant from the federal government. Many municipal plants treat industrial wastes and need more technology than that offered by run-of-the-mill plants.

Harvey A. Stephenson, mayor of the city of Keokuk, Iowa (a city that plans to build a secondary sewage treatment plant), says, "Keokuk requires more than a conventional sewage plant design. Three manufacturers in this city of 14,500 people contribute waste components sufficient to produce a waste strength approximately 10 times that of a normal city of this size. In order to obtain the best design at the most satisfactory capital and operating costs, we wish to obtain the benefits of design competition. We could do this, as I see it, by inviting bids against performance specifications if we were certain that we would not sacrifice our eligibility for a federal construction grant."

Monsanto Enviro-Chem, the catalyst for the Keokuk case, started talking about 2–3 years ago with the responsible federal, state, and local officials on ways to introduce alternative business views in the waste facilities construction field.

C. C. Kemp of Monsanto Enviro-chem Systems, Inc. says, "We have long advocated use of the turn-key contraction method as a means of obtaining competition at the technical level in municipal treatment plant construction. We believe that the proposed change will be especially important in ensuring effective design for the increasing number of joint industrial and municipal treatment plants."

C. C. Pascal, president of Zurn Engineers (Upland, Calif.), notes that "the turn-key concept adds one of the more important functions of engineering design—economics. The incentive to design economically is practically nonexistent with the separation of builder and engineer. Indeed, the incentive is to design uneconomically—i.e., the greater the construction cost, the greater the engineering fee, generally."

R. E. Siegfried, president of The Badger Co., notes, "We strongly feel that the same progressive chemical engineering expertise which we have provided for years to the petroleum and chemical process industries can also be applied to the field of municipal waste treatment. . . .We expect to function in the waste treatment field in much the same way as we do in the process field, namely, to develop and offer a more economical competitive technology than our competition."

Another turn-key supporter is John B.

Dwyer, vice-president for research and engineering of The M. W. Kellogg Co. He notes that, "This (turn-key) undoubtedly reduces the burden of costs which will have to be borne by the public, by permitting utilization of best available technology. Furthermore, it will encourage private companies to invest in research and development of improved processes, since business will be available to them provided they guarantee performance. This move is certainly in the public interest."

John H. Robertson, manager of the environmental systems division of Catalytic, Inc., notes that "We (Catalytic) would strongly favor a proposal which permitted a design and construct approach to municipal projects." Robertson goes further and offers suggested language on turn-key: "It is recommended that a qualified environmental engineer certify, in such cases (turn-key), that alternatives have been considered, and the solution proposed is economically feasible as well as technically approved."

J. D. Spink of The Rust Engineering Co. notes that "The turn-key contracted method will be available to municipalities whose waste treatment facilities must not only treat the domestic waste in that municipality, but also, in many cases, various industrial wastes. This situation alone in the past has been detrimental to some form of traditional treatment processes which municipalities have had to use because of the state regulatory bodies."

Additional support for the turn-key proposal was received from Westinghouse Electric Corp. (Pittsburgh, Pa.); R. B. Humphreys Construction Co., Inc. (Indianapolis, Ind.); and Fluor Utah Engineers & Constructors, Inc. (Los Angeles, Calif.)

Organizations, too, are behind the turn-key proposal. The National Constructors Association (Washington, D.C.) is an association of engineering-construction firms (see box) that have provided turn-key operations in the industrial sector for years. The firms have regularly provided the engineering, procurement, and construction of plants to deliver performance in accordance with the design. Under the right set of circumstances, these firms do not see why they would not be interested in the construction of municipal waste treatment facilities.

Con arguments

On the other side of the proposal is the consulting engineering profession. So too are state water pollution control officials. From coast to coast and in every state, consulting engineers are not happy with the proposal, which is putting it quite mildly. In fact, Wesley Gilbertson, deputy secretary of the Pennsylvania Department of Environmental Resources, says, "We have talked with no one who has indicated they favor the proposal."

The fear of competition is never so evident than in considering their comments. "My experience in foreign turn-key projects indicates that we would be taking a step backward if such a proposal is adopted," says Philip Abrams of Consulting Engineers, Inc. (Palm Springs, Calif.). "Quality of construction and contract negotiations are subject to irregularities, which are difficult to resolve."

Turn-key: how it works

A contracting method under which all major activities—engineering-design, procurement of plant equipment, and construction—are included in a single contract, with the contractor having a professional relationship with the owner or client to produce optimum end results as to the quality of work, lowest possible cost, and earliest possible completion. Turn-key contract terms vary but may include performance guarantees and such price guarantees as lump sum or guaranteed maximums. For example, if a contract were negotiated for $10 million, and the actual cost exceeded that figure, then the contractor would absorb the overrun up to an agreed amount such as all or part of his fee.

R. H. Albanese, a consulting civil and sanitary engineer of Port Washington, N.Y., points out, "It is our opinion, as practicing professional sanitary engineers, that such approval would eventually lead to contractors dictating the designs of treatment works to professional engineers (retained by the contractor) and that the engineer would no longer be protecting the interests of the municipality, but instead his client, namely the contractor."

"Not only will the effectiveness of the projects suffer," he continues, "but also the well-established competitive bidding on a well-defined design will be lost. Such a loss will be detrimental to the sanitary engineering profession as it may lead to the substitution of substandard equipment once a contractor (not a design) is selected."

One consulting engineer points out a few examples of turn-key projects which are in operation today, and that they are in trouble. "City of Omaha is currently undergoing problems with two waste treatment and paunch manure plants that are of the turn-key variety," says Raymond G. Alvine of the Nebraska-based R. G. Alvine & Associates. He comments, "I know from personal observation and experience that turn-key contractors will cut every corner possible on a project to increase their profit."

But one real concern regarding turn-key that is not easily dismissed is that public bodies will be held accountable for their choices. "The tragedy of the turn-key proposal is that public bodies will necessarily be required to make decisions which they are not competent to make without experience, re: costs, the adequacy and fairness of which they are incompetent to judge, and under a plan where the acceptance of the finished work is by the same party that performs the work," says R. Howson of Alvord, Burdick & Howson Engineers (Chicago, Ill.).

A similar theme is found in the comments of Thomas McMahon, director of water pollution for the Commonwealth of Massachusetts, who objects to the EPA proposal, saying that the turn-key approach might result in "marginal" construction and greatly increase responsibility of state and federal agencies.

Looking ahead

Perhaps many of the apparently conflicting views on the merits of turn-key stem from the fact that the September 15 announcement was not specific enough. Presumably, the language will be more specific if and when it is finalized.

Given the opportunity of test cases in the waste water construction field, turn-key operations may pave the way for construction in the future. But it is important to note that instant answers are not possible. For example, even if a turn-key operation were approved for municipal construction tomorrow, only after several years—when the construction would be turned over—would the results be available for a final decision on the merits of the approach. But how much longer can we continue to try and solve pressing problems with yesterday's, if not yesteryear's, procedures? SSM

Philadelphia-based American Society for Testing and Materials has put together a three-year program to validate analytical methods for measuring selected atmospheric contaminants

Project Threshold: testing the tests

In the battle to clean up dirty air, regulatory officials operate on a basic assumption: that testing methods are accurate and precise. Examining that fundamental assumption is the purpose of Project Threshold—a venture of the American Society for Testing Materials (ASTM). The Philadelphia-based organization will look at some 35 different methods for measuring various atmospheric pollutants in a three-phase program spanning three years and costing about $2 million.

Project Threshold was launched early last year, and the results of the first phase should be available shortly. Phase I is designed to evaluate seven test methods (see table) for measuring sulfur dioxide, nitrogen dioxide, lead, sulfation rate, and dustfall. Phases II and III will focus on methods for some hydrocarbons, nitric oxide, hydrogen sulfide, mercaptans, and certain particulate matter.

The need for a project such as Threshold is obvious when one considers that few if any methods for detecting atmospheric contaminants have been subjected to rigorous accuracy and precision studies, according to Walter V. Cropper, ASTM's director of New Projects and manager of Project Threshold. "As of this time last year," Cropper says, "there was not even one good standard method which had been satisfactorily checked for accuracy and reproducibility." There were, according to Cropper, some good "single-operator results"—statistically valid precision experiments carried out by single investigators—but no experiments had been done to check variance between laboratories or operators and thereby to establish appropriate confidence limits.

Such testing, Cropper explains, is the bailiwick of ASTM which has some 75 years of experience in standardizing test methods by the so-called "consensus method." That method, ASTM's Managing Director William T. Cavanaugh explains, involves far more than a conclave of experts who simply agree on the best way to do things.

The consensus system relies on expertise, but firmly resists the notion that there is any such thing as unbiased expert opinion. Rather, ASTM assembles a panel of expert advocates, clearly labels their professional biases, and then referees the proceedings as the panel thrashes out solutions that are, on balance, beneficial to all. The result is a standard that is arrived at voluntarily and subscribed to voluntarily, but which carries enormous professional clout.

ASTM's system, Cavanaugh insists, is the best in the world for setting measurement standards. State and federal governments routinely accept ASTM standards for materials and methods as the basis for their regulatory activities, he points out. Hopefully, the methods used for arriving at consensus standards for concrete and other structural materials early in ASTM's history will serve pollution control efforts as well.

Round robin

To determine the accuracy and precision of its testing methods, ASTM has relied on "round robin testing." It works like this: After the committee has decided on the best procedure for a given test—say the determination of octane ratings for gasoline—several cooperating independent laboratories make separate analyses of a split sample, following the Committee's written procedure letter by letter.

By comparing results among laboratories, ASTM can determine statistically valid accuracy and precision parameters which give some frame of reference for subsequent test results. Laboratories usually sandwich the verification tests in between their normal duties, so that the testing costs ASTM nothing. While such an approach to the problems of Project Threshold might have been desirable, several problems unique to the

Project Threshold will validate methods for:

PHASE I

Nitrogen dioxide
(Griess-Saltzman reaction)

Sulfation rate
(Lead peroxide candle)

Sulfur dioxide
(West-Gaeke method)

Particulate matter
(Optical density of filtered deposit)

Lead in atmosphere

Collection and analysis of dustfall

PHASES II and III

Nitric oxide

Nitrogen oxides

C_1-C_5 hydrocarbons

Formaldehyde

Inorganic fluoride

Polynuclear hydrocarbons in particulate matter

Oxidants

Sulfur dioxide

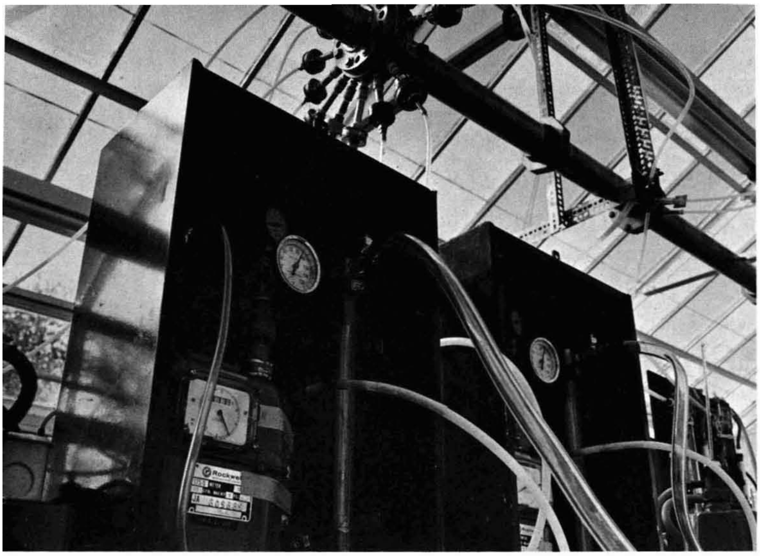
Sulfur oxides in stacks

Hydrogen sulfide

Mercaptans

Beryllium

Others as appropriate



Spider. *Sixteen-armed wheel splits air intake to assure sample uniformity*

analysis of the atmosphere made ASTM modify its traditional approach.

First of all, the sheer amount of work to be done and the need to complete it as soon as possible make voluntary efforts unsatisfactory, Cropper explains. "Furthermore," he says, "you can't just bottle up a big chunk of air and divide it into identical parts" and ship it to participating laboratories. Some components would react with others on standing, dust would settle out, and the sample would degrade with time, he adds.

To overcome these problems, ASTM decided that independent testers would have to be transported to the sampling sites to make simultaneous determinations under identical conditions. Obviously, Cropper notes, independent laboratories were reluctant to give up personnel and large blocks of time necessary to make the tests on site.

ASTM decided on a contract approach which would pay some independent laboratories for their work while encouraging others to donate their efforts if they so chose.

ASTM Committee D-22 on Methods of Atmospheric Sampling and Analysis settled on six laboratories to do the bulk of the work. Battelle Memorial Institute was named contract coordinator, with responsibility for planning and supervision. George D. Clayton and Associates, Arthur D. Little, Inc., Midwest Research Institute, Research Triangle Institute, and Walden Research Corp. were named contract cooperators.

Sampling sites

Three sampling sites—chosen to represent a variety of atmospheric conditions—were selected for Phase I of the project. The first series of tests was conducted during the week of August 15, 1971 at the University of Southern California at Los Angeles. The Los Angeles site was selected because of relatively high concentrations of oxidants, NO_2, and lead in the air during the summer months. The second site, Bloomington, Ind., was selected because of a nearly flat pollution profile. "The methods we are testing aren't any good if they work only at the high pollution concentration," Cropper points out. "We need methods that work at lower concentrations as well." Testing at the Bloomington site was finished late last October.

The third site is to be in the metropolitan New York area, chosen because it represents the opposite end of the pollution spectrum from Los Angeles—low levels of photochemical smog, but higher concentrations of certain pollutants from fuel oil burning and automobile emissions such as SO_2 and NO_2. Preparations for the New York test were under way at press time.

Funding for the program comes entirely from interested private sources. At present, some 50 corporations have chipped in $420,000, all of which is budgeted for Phase I of the program. Government participation in the funding is not being actively solicited, Cropper says, because "If the study is going to mean anything, it's got to have the involvement of the private sector." Federal money would not be refused, however, should some government agency wish to sponsor part of the work.

In order to keep the work as objective as possible and to avoid charges of conflict of interest, no industry will be allowed to contribute more than a quarter of a million dollars. "That way nobody can have more than $^1/_8$ of the action," Cropper says.

Procedures

The experimental procedures for validating the methods have been carefully worked out and details have been painstakingly specified. It is especially important that the tests be statistically valid, according to Cropper, and ASTM's committee E-11 on Statistical Methods has been actively involved in the experimental design. Committee E-11 decided, for example, that a minimum of five analysis teams would be necessary for statistically meaningful results—hence the five contract cooperators. The on-site sampling laboratories, on the other hand, can accommodate up to eight teams, allowing laboratories who wish to donate manpower to work side by side with the contract labs.

The experimental sampling setup allows simultaneous but independent sampling and analysis during a test run. Air is drawn into the laboratory through two stacks—high enough to minimize effects of local point sources of pollution such as nearby exhaust systems, but not high enough to reflect local conditions accurately. "After all," says Cropper, "we're testing the tests, not testing the air." The air samples are split by an eight-legged "spider" valve system, allowing simultaneous tapping of the airstream by the independent teams. Provision is made to inject "spiked" samples of standards prepared for Project Threshold at the National Bureau of Standards. Operators report their results only to the test manager. Sampling ports are rotated to minimize equipment variables. Teams begin monitoring and stop sampling on a countdown command to ensure that they are sampling the same air supply. Other variables, such as pressure, flow rate, and temperature are continuously monitored during the testing.

Each test site generates about 1000 bits of data which must be integrated and statistically manipulated to produce accuracy and precision information and to establish permissible margins of error. ASTM hopes to have preliminary results of its tests available by March of this year. Plans for Phases II and III are somewhat less certain (the two phases may even run concurrently), but all of the tests should be completed by the end of 1973 with final reports due by mid 1974. HMM

Waste lube oils pose disposal dilemma

Reprocessing seems the answer, but new technology would add to costs in an industry already under severe pressure

Ever wonder what happens to the oil drained out of the crankcase of your car at the local service station? If you do, you're in good company; others, including the U.S. Environmental Protection Agency (EPA) and the American Petroleum Institute (API) are wondering too. Just how large amounts of used lubricating oils in this country apparently disappear is something of a mystery, although there is a strong suspicion that much of it ends up in the environment, usually in an unacceptable fashion.

Consider some facts:

- About 1.1 billion gal of automobile lubricants and 1.5 billion gal of industrial lube oils are bought each year in the U.S. EPA estimates that 50% of the auto oils and 30% of the industrial oils are not consumed and are disposed of in some way
- A study performed by A. D. Little, Inc. for the state of Massachusetts in 1969 estimated that the ultimate fate of 18% of all automotive used oils in the state was "unknown," that another 23% was dumped on the ground at the source (presumably at or near a service station), and that a further 11% was used as road oil
- The API determined in 1966–67 that 43% of a sample of service stations did not know the ultimate fate of the oil removed from their premises, although less than 2% admitted to dumping it on the ground or into a sewer

In view of the fact that these figures lead to an estimate of at least 500 million gal/year of used auto oils in need of disposal, it is particularly striking to note that the annual capacity of the U.S. oil re-refining industry is pegged at only 100–150 million gal and that, in fact, it has declined from about 300 million gal in 1960.

Traditionally, service stations have stored their waste oils in underground tanks of several hundred gallons capacity and periodically have them taken away by small trucking operations—"scavengers" to the trade. Only 5% of the 1966 API sample of service stations did not have any such arrangement. Whereas many stations used to be paid by scavengers for the oil, it is now more common for the station to have to pay a small fee—perhaps 5 cents a gallon—for the service.

Precisely what some of the scavengers have been doing with the oil after collecting it from service stations is a subject of speculation rather than hard fact. EPA suspects that many small operators routinely dump oil from their trucks into sewers, onto vacant ground, or into the nearest convenient waterway. Since a scavenger generally requires no permit for plying his trade beyond obtaining road licenses for

Waste oil burning yields metals in combustion products

(lbs of products as oxides/10,000 gal waste crankcase oil)

	Jackson Miss.	Okla. City Okla.	Washington D.C.	Doraville Ga.	San Carlos Calif.	Dearborn Mich.	St. Louis Mo.	Houston Tex.	Lyons Ill.
Zinc	36	46	58	33	54	45	32	32	44
Copper	1.1	0.9	1.4	1.2	1.6	1.4	1.2	1.3	1.5
Aluminum	4.6	5.1	2.6	5.1	4.4	4.8	4.5	4.4	6.3
Barium	43	25	57	20	31	9.3	33	45	38
Calcium	136	220	162	131	220	147	120	162	168
Nickel	0.2	0.3	0.3	2.4	0.5	0.6	0.3	0.9	0.7
Chromium	2.6	2.9	4.8	1.5	3.8	2.6	2.2	2.9	1.2
Iron	34	32	17	30	28	36	32	30	42
Silicon	29	22	13	24	24	27	64	19	24
Lead	650	650	400	570	480	720	650	570	650
Tin	0.6	0.6	0.6	1.0	0.9	1.0	0.9	1.3	0.9
Phosphorus	225	225	255	211	173	264	189	189	173
Boron	3.6	3.6	2.8	4.3	3.6	5.9	3.6	3.8	5.9
Magnesium	23	10	23	36	19	31	25	61	25
Total	1188.7	1243.4	997.5	1070.5	1043.8	1295.6	1157.7	1122.6	1180.5

Source: EPA, based on tests conducted at various U.S. sites by members of APR his vehicles, there really is no good way to keep a check on his activities. EPA's Hal Bernard, chief of the Water Quality Office's Agricultural and Marine Pollution branch, believes that many scavengers sell their oil to fuel oil distributors who blend it in with regular heating oils and sell it to unsuspecting customers.

The recognized outlet for the waste oil from scavengers is a re-refining plant which treats the oil so as to remove impurities and resells it to blenders who add virgin lube oil and sell the resulting product as "reclaimed oil" through regular wholesale and retail channels. The re-refining industry is sufficiently well organized to have a trade association—the American Association of Petroleum Re-refiners—but the industry is going through bad times for several reasons. Probably the main one is the increasing number of additives in oils and in gasolines (degraded gasoline additives reach the crankcase by bypassing the pistons). The additives have been a boon to motorists by extending the mileage that can be driven between oil changes, but they have increased the difficulty of treatment at the re-refinery. The second reason for the decline of re-refining is that the industry has lost a tax advantage that its product once had over virgin lube oils; both products now bear the same excise tax.

The last straw for re-refiners, ironically enough, has been the pollution potential of their operations. The almost universal method of waste oil treatment is contact with sulfuric acid to extract most of the impurities, followed by clay treatment to remove color. These operations yield, as well as the re-refined oil, mountains of acid sludge and contaminated clay: 20–40% of the waste oil ends up either as acid sludge or spent clay. Disposal of these semisolid by-products poses real problems for the industry which is increasingly being prevented from landfilling leachable materials. In addition, spills such as occurred on the Schuylkill River above Philadelphia in November 1970, in which 3 million gal of oily waste escaped through a broken dike after a heavy rain, have done much to sour the reputation of the re-refiners.

Better treatment

Upgrading the technology used in waste oil treatment is being explored. The Institut Francais du Petrole, a French group in the business of developing and licensing technology for the petroleum industry, has come up with what it claims is a big improvement over conventional acid and clay treatment. In essence, the IFP process involves a technique similar to that used in a propane deasphalting process in the petroleum industry, although the process conditions are completely different. Liquid propane is used to extract most of the impurities, and this step is followed by acid and clay treating. However, claims IFP's Robert Dutriau, the amounts of acid and clay needed are reduced by 80–90%, with a corresponding decrease in the amounts of acid and clay sludges needing disposal.

The IFP process has been licensed to an Italian company which has successfully operated it for three years at a plant in Milan. Dutriau explains that the Italian government pays re-refiners a bounty for each gallon of waste oil reprocessed; so in fact does the government of West Germany. Significantly, perhaps, Dutriau is not particularly optimistic about chances of licensing the process in the U.S., where there is no such government bounty. However, some scavenger operations are subsidized by cities like Baltimore on the basis that waste oils constitute a fire hazard.

EPA, too, is interested in having the re-refiners upgrade their technology. But, says EPA's Bernard, the agency has stressed conversion of waste crankcase oils to products other than lubricating oil. Bernard believes that production of diesel oils or fuel oils from the wastes would be preferable because the amounts produced in a year would be very small fractions of the total sales of virgin products, and so would be less disruptive in the marketplace. (In contrast, the 1960 capacity of the re-refining industry—300 million gal—probably provided at least 25% of the total market for automotive lube oil.)

The National Oil Recovery Corp. (Bayonne, N.J.), with financial support from EPA, has demonstrated that zero-sulfur heating oil and diesel oil can indeed be produced from waste lube oils through vacuum distillation.

However, burning tests using waste oil alone indicated that the metals in the waste oil which remained in the fuel oil product contributed to scale buildup on heat transfer surfaces that would be entirely unacceptable in commercial, and certainly in residential, heating installations. In addition, EPA is understandably concerned about the composition of the combustion gases resulting from burning such a fuel, which contains in addition to lead—the subject of most traditional concern—iron, phosphorus, zinc, and barium.

API, for its part, believes that the best solution probably is to blend waste lube oils directly with virgin fuel oil and to burn them together. Burner tests conducted by API member companies in 1968–69 reportedly showed no ill effects when the fuel contained 25% waste oils, but the lead content of the gases produced during soot blowing was almost 1 $\mu g/m^3$, albeit not enough to affect overall air quality adversely. EPA's concern about the blend-and-burn approach centers around the difficulty of providing adequate assurance that the oil users will be properly supervised.

According to Ray Wright, director of marketing for API, the institute is working on criteria that would permit waste oils to be reprocessed by the primary refiners (API member companies) and used as refinery feedstock.

Potential problems, however, might be posed by physical and chemical properties of waste oils that could adversely affect refinery processes. The overall problem with this approach, and indeed with any approach that converts waste oil to a product less valuable in the marketplace than lube oil, seems to be that there is little if any room for a profit. Re-refiners presently make a bare few cents per gallon on their reprocessing operations, and any investment required to upgrade their technology would appear to require either a more valuable product or an outright subsidy to make it worthwhile.

The story of waste crankcase oils is yet another case, with which the environmental field is replete, in which better technology is only a part answer to a problem. Without control of scavenger collecting procedures and a profit incentive for reprocessors, it is difficult to see progress being made.

In the meantime, things may be getting worse. API's Wright says that 35–45% of all auto oils are now bought at retail outlets other than service stations. It is intriguing to wonder what people who buy oil at the drug store do with the waste they drain from the crankcase at home.

Furthermore, points out Bernard, automotive oils represent only part of the waste oil problem. EPA is increasingly concerned about the proper disposal of industrial cutting oils, tank bottom sludges, and oily ballast waters from ocean-going tankers. DHMB

Environmental lobbies want Congress to outlaw surface mining, but coal companies argue that stripping is far too important to the nation even to be phased out gradually

Feds eye regulations for strippers

Big Muskie is not a senator from Maine. It's the granddaddy of all the earthmovers—a $25 million behemoth of a power shovel with a boom as long as a football field and a maw that strips away some 200 cubic yards of dirt with every mouthful. Big Muskie, and its somewhat smaller cousins, the Silver Spade and the Gem of Egypt, ply the coalfields of eastern Ohio, stripping away dirt and rocks—overburden as it is called—from the shiny black seams of coal that lie anywhere from a few feet to a hundred feet beneath the surface of the earth.

Big Muskie and dozens of super machines like it have spearheaded a minor technological revolution in the mining industry. Surface mining—more commonly called stripping—is rapidly replacing underground digging as a method of choice for mining coal. Surface mining applies not only to coal, but to sand and gravel, quarried stone, phosphate rock and other mineral ores as well.

A national battle over the ecological consequences of surface mining has been brewing for several years now. On one side there are outraged citizens and environmental lobbies such as the Sierra Club and the Conservation Foundation. On the other are the coal companies, the United Mine Workers of America, and various trade associations and corporations with interests in surface mining.

The environmentalists want to muzzle Big Muskie and eliminate strip mining altogether—at least for coal. The National Coal Association brands that position "unrealistic and irresponsible," but concedes that some federal legislation—if it isn't too specific—might be in order. The Congress meanwhile is mulling over some 30 bills on the subject in appropriate House and Senate subcommittees.

Coal reserves

Almost half of the states produce coal in varying amounts, and total U.S. coal reserves are enormous. Current government estimates place domestic reserves at more than 3 trillion tons. The supplies are virtually inexhaustible. The U.S. Geological Survey (USGS) estimates that some 128 billion tons of coal in 27 states can be obtained by stripping. The U.S. Bureau of Mines says about 35% of that figure or 45 billion tons are "economically" strippable.

Strip mining is rapidly outpacing deep mining as a method for recovering coal. In 1965, total U.S. production of lignite and bituminous coal was slightly more than 512 million tons, of which about 180 million tons or 35% was produced by surface mining. The proportion of deep-mined to surface-mined coal fluctuated only slightly through 1969, when the figure was about 213 million tons (or 38% of the 560-million ton total).

Then in 1970, total coal production increased sharply to 603 million tons, according to the National Coal Association. That's a 42-million ton increase over the total for 1969. But the amount of deep-mined coal recovered in 1970 actually declined by 8 million tons. A record-setting 51 million tons of coal were mined by surface methods in 1970—44% of the nation's total. Thus, while total coal production in 1970 grew only 7.6% over the figure for 1969, the amount recovered by strip mining shot up a whopping 24%.

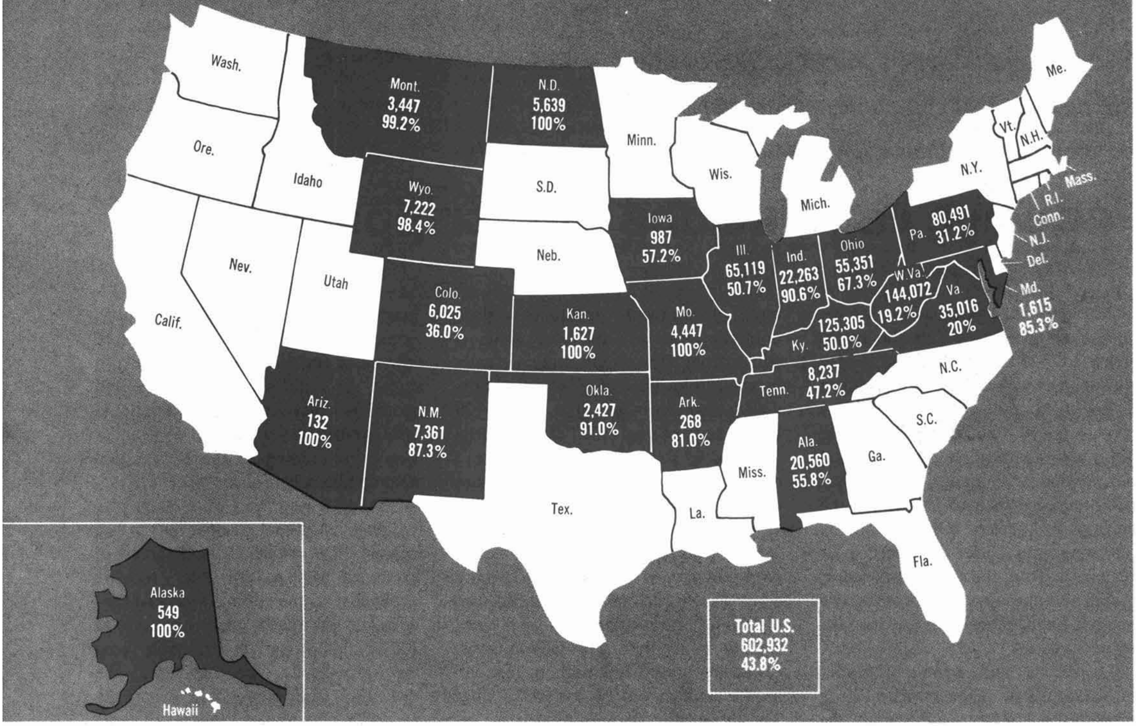
These statistics and others like them have the environmental lobbies on edge. For example, BuMines says that 77% of the country's economically strippable reserve lies in 13 states west of the Mississippi—an area where very little coal has ever been mined. In the past, it's been economically unsound to tap those vast reserves. But the situation is different now.

Emission limits on sulfur oxides are tightening, and electrical utilities are demanding ever greater quantities of low sulfur fuel. Seventy-five percent of all the coal that was strip-mined in 1970 was burned by electric utilities to produce about 34% of all the steam-generated electricity in this country. Some 80% of the nation's reserve of low-sulfur fuel lies beneath the western states. As utilities consume more and more low-sulfur coal, and as the national coal gasification program gets under way, strip mining in the West could assume colossal proportions.

The USGS estimates that some 4.4 billion tons of coal stripped by surface mining has disturbed land areas in excess of 2450 square miles—roughly equivalent to the surface area of Delaware. If all the available reserve of 128 billion tons of strippable coal was recovered, USGS estimates, the disturbed land area could eventually reach 71,000 square miles, an area roughly equivalent in size to the states of Pennsylvania and West Virginia.

Power shovel. *Machine scoops coal from seam exposed by removing soil*

Coal production and percentage obtained by strip mining in 1970 (thousands of short tons)



Reclaiming the land

Most of the controversy over surface mining eventually converges on the topic of reclamation. Both sides agree that some restoration and reclamation can be done. But the factions part company when it comes down to the nuts and bolts of how much is appropriate and who should set the standards. Both sides also believe that surface mining must be regulated, but beyond that there is little common ground.

Most conservation groups argue for outright bans on surface mining, and two bills [S. 1498 introduced by Gaylord Nelson (D.-Wis.) and H.R. 4556 introduced by Ken Hechler (D.-W.Va.)] would prohibit the opening of any new surface mines and phase out all established surface mining of coal after six months. Surface mining, the environmental lobbyists argue, ruins huge land areas and cannot be justified when other alternatives (chiefly deep mining) can satisfy the country's growing energy needs as well.

The coal companies, on the other hand, say that the answer to that dilemma is reclaiming the land. Edwin R. Phelps, president of the nation's number one coal producer, Peabody Coal Co., recently told the Senate Interior Committee that good reclamation of surface-mined land is possible. "I know," says Phelps, "because we are doing it."

Pennsylvania's U.S. Senator Richard S. Schweiker says that his state's legislation which requires restoration of strip-mined land to approximately the original contour, or terracing on steep terrain, "has virtually brought an end to the scarring of the landscape with open cuts and highwalls."

William Guckert, director of the Mine Reclamation Division of Pennsylvania's Department of Environmental Resources, concurs. Each year, he says, Pennsylvania returns in excess of 10,000 acres to approximate original contour or terracing. "Strip mining can and is being done in Pennsylvania without devastation of the landscape and water," Guckert says.

Any proposal to eliminate surface mining "is both unrealistic and irresponsible," according to Carl Bagge, President of the National Coal Association, "not only because a vital 44% of U.S. coal production is mined by surface methods, but because it ignores the fact that technology exists for effective reclamation of mined lands." More than 28% of the 1.5 trillion kW hours of electricity generated by the utilities in 1970—including the amount produced by the great hydroelectric dams—came from burning surface-mined coal, according to Bagge. Cutting off this supply of coal, he says, would mean that the utilities would have to come up with a substitute fuel from somewhere.

In view of the fact that atomic power has not yet developed sufficiently, and in the face of a domestic natural gas and fuel oil shortage, electric utilities would have to import fuel oil to meet their needs. Assuming fuel oil were available in sufficient quantities for import, Bagge contends, buying it would result in an additional $2.5 billion annual increase in the U.S. balance of payments deficit.

While Bagge doesn't argue that there's not sufficient coal that could be mined by underground methods, he says that to expect to replace surface-mined coal with deep-mined coal is "not realistic." Replacing the surface coal mined last year with deep-mined coal would require 132 additional deep mines, each with an annual capacity of 2 million tons, according to Bagge, necessitating a capital investment of $3.2–3.7 billion, three to five years before full production could be achieved, and an additional 78,000 trained miners.

"The coal industry would be required to virtually duplicate its present underground mine capacity, calling for an enormous capital investment, and at the same time be required to write off as a loss its existing investment in surface mining and reserves," Bagge warns. "To prohibit surface mining would have disastrous results for the nation and its constantly increasing need for energy."

The major argument for retaining strip mining is that it is cheaper, safer, and better than deep mining because it wastes less coal.

Peabody's Phelps admits that there are vast reserves that can be mined by the underground method, but notes there are "serious limits" on expansion of underground mining. Much of the U.S. coal reserve, Phelps says, "lies under strata too shallow, or too unstable, to support a roof safely so they cannot be recovered by underground methods."

In addition, according to Phelps, to open an underground mine requires at least three years. Underground mining is generally "more costly, less efficient, and more hazardous than surface mining." About half of the coal in an underground mine must be left to support the roof, Phelps says, but recovery of coal from surface mining "approaches 100%."

Real costs

The conservation groups don't quite see it that way. Strip mining is not cheaper, they argue, it's just that strippers don't count the real cost. The Conservation Foundation's Malcolm Baldwin says that coal obtained by strip mining is "extremely costly." Besides the costs to the strip operator and the consumer, some costs "are passed onto society as a whole," Baldwin says. While some costs, such as the damage to nearby homes from mudslides are measureable, according to Baldwin, others, such as the social effects of coal stripping, are impossible to calculate. "The difficulty of measuring such costs should not lead to the erroneous conclusion that they are insignificant; they are merely elusive."

Among the effects of strip mining most costly to society, Baldwin notes, are water pollution caused by acid leaching, siltation and erosion; flooding potential that may be increased by sediment which decreases carrying capacity of streams, destruction of fish and wildlife and destruction of flora; damage to personal property from blasting and slides, loss of aesthetic values, and more direct economic losses caused by erosion of the long-term tax base as stripped property is devalued.

Reclamation could help, according to Baldwin, but it is expensive. "Strippers rarely spend more than $300/acre on filling, although the few studies on restoring contour strip mines to their previous slope conditions indicate much higher costs," Baldwin says. One such study, he adds, shows that the cost of restoring a natural slope was $15.73 per linear foot of highwall or about $2700 per acre.

Hard economics aside, conservationists argue that aesthetic values must be duly considered. "To many persons, the scars left by strip mining in the form of naked spoil banks and highwalls, choked streams, and open trenches create mile after mile of unrelieved ugliness," the Conservation Foundation's Baldwin says.

Most of the bills before the Congress refer to unquantifiable considerations such as aesthetics and natural beauty. "I recognize the good intentions behind these terms, but they can be mischievous in effect," Peabody's Phelps says. "Beauty is indeed in the eye of the beholder and impossible to define. Nature created the Badlands of South Dakota and they were made a national monument, but if any surface miner duplicated them, even on a small scale, it would be called a national disgrace."

It seems almost certain that some form of national regulation for strip mining is in the offing. The reason most often given is that state regulation simply has not worked. Twenty-six states have laws regulating surface mining. Of the 23 coal-producing states, only four (Alaska, Arizona, Missouri, and New Mexico) do not regulate the coal strippers. But even Kentucky, West Virginia, and Pennsylvania—states which are often cited as models of tough regulations—still have difficulty regulating the strippers. There are two basic reasons for the failure of state regulations, according to the Sierra Club's Peter Borrelli. The first is lack of enforcement. "The feeble regulatory efforts of West Virginia and Kentucky are just no match for the immense political and economic power of the coal industry," Borrelli charges. "Lack of enforcement is less notorious in Pennsylvania, though quite prevalent."

The second is that laws specify the steps to be taken instead of results to be achieved, he says. Thus while states may require performance bonds, grading, contouring, and planting, it's not good enough, Borrelli says. "Ultimately, no state holds the strip mine operator accountable for the condition of the land he leaves, nor requires him to meet any proper standard of reclamation," he adds.

Federal regulation

If the Congress will not ban strip mining altogether—and the environmental groups are under no delusion that it will—the very least conservationists want is a series of tough federal regulations which limit the degree of slope that can be tackled by the strippers, restrict highwalls and the depth of overburden that can be removed, ban stripping near waterways, and provide for citizen suits.

The strippers, on the other hand, want no such specific regulations. They would prefer a law which would leave primary responsibility for regulation in the hands of the states, and would allow the federal government to intervene only if states are unable or unwilling to regulate effectively.

Of all the bills currently before Congress, S. 1176, "The Mined Area Protection Act of 1971," introduced by Senator Henry Jackson (D.-Wash.) and backed by the administration, would seem to be a model for the legislation likely to come. S. 1176 would regulate both surface and underground mining. The bill sets up broad guidelines and places administrative responsibility with the Department of Interior. Primary responsibility for regulating mining rests with the states, but provision is made for federal intervention in case states do not meet their obligations.

Just when such legislation is likely to come into effect is anybody's guess. But the environmental pressure groups will not let up in their lobbying efforts on Capitol Hill. Ironically perhaps, the strippers too are anxious for speedy congressional action. With the growing public outcry against strip mining in all forms, the major coal companies and labor unions are more anxious than ever for appropriate federal guidelines to follow. It is the fly-by-night operator, they charge, who cuts corners to compete and does not reclaim his land. Such irresponsible practices, they maintain, threaten the posture of the whole stripping industry by rankling public opinion. Unless these operators are brought under firm control, they reason, public outcry for a total ban on strip mining may be so loud that Congress will have to listen.

And an out-and-out ban on strip mining, they maintain, could be disastrous both for business and the economy of the nation. HMM

LEAD

feature

pollution and poisoning

High lead levels are dangerous to man, and ambient concentrations are presently rising

Stephen K. Hall, *Southern Illinois University, Edswardsville, Ill. 62025*

Lead has been mined and used by man for many years. Widespread early applications of lead are readily understood in light of its many desirable properties—relatively easily refined from natural ores, ductility, high resistance to corrosion, and other properties.

In both Greek and Roman culture, lead was used for manufacturing cooking utensils of the wealthy and in the lead pipes for the extensive plumbing systems of their homes. Studies indicate that Roman civilization deteriorated largely as a result of extensive lead poisoning (high incidence of infant mortality, mental retardation, and sterility) in the ruling class. This theory is supported by data showing a high lead concentration in the bones of their remains.

Of the nonferrous metals, lead is one of the most widely used in industry and everyday life. The annual consumption in the U.S. alone is well above one million tons. The storage battery industry is the largest consumer, about 40%, and the petroleum industry consumes about 20%, producing lead alkyls as gasoline additives. These 300,000 tons of lead are, of course, added directly into the ambient air. By contrast, only about 45% of the total lead consumed is recovered from metal products and batteries.

Today lead is an ubiquitous element present in food, water, and air. Lead aerosol is a common air contaminant. Dated samples of snow in northern Greenland indicate that up to 1750, there were about 20 μg of lead per ton of ice until the Industrial Revolution. By 1860, this had increased to 50 μg/ton. The proliferation of the automobile since World War II also resulted in sharp increases—in 1940, 80 μg; in 1950, 120 μg; and in 1965, 210 μg. In the past two decades, man's continuing use of lead has produced an environmental level far above that which would exist naturally, and this could have grave consequences on human health.

Sources of lead

Lead is a natural constituent of soil, water, vegetation, animal life, and air. Significant sources of naturally occurring lead include dust from soils and particles from volcanoes. In contrast to certain other metals such as mercury, lead in its elemental form is not a major source of poisoning.

In medieval times, the practice of "sweeting" wine with lead or lead acetate became a serious toxicological problem. Even today, alcoholic beverages of illicit origin are occasionally incriminated as the source of lead poisoning. Old automobile radiators are often used as the condenser component in illicit stills and contain enough solder to cause dangerous contamination of the "moonshine." Lead encephalopathy (disease of the brain), nephritis (disease of the kidneys) with gout, and other lead-related conditions have been reported in moonshine consumers.

Until the 1950's, most interior paints contained lead pigments which were a major source of childhood lead poisoning. Since then, lead oxide has been replaced by titanium dioxide. However, some old houses were painted countless times with leaded paint, and thick chips of leaded paint fall off as the walls and ceilings peel. Putty also contains lead and is even more likely to be found in substandard dwellings. Since children between the ages of one and four or five ingest nonfood particles of all types, about 8% of children in ghetto areas suffer from some degree of lead poisoning.

Another major lead source is earthenware pottery improperly glazed with lead. Large amounts of lead may be leached out of the glaze into certain foods. Today, man continues to pollute his environment with lead from other sources such as manufacturing, use of pesticides, incineration of refuse, and combustion of coal and leaded gasoline. Available data indicate that combustion of leaded gasoline is the major source of atmospheric lead in urban areas.

Atmospheric lead

Antiknock agents of lead alkyls, in the form of tetraethyllead (TEL) or tetramethyllead (TML), have been added to most gasoline since 1923. Their use rapidly became a cause for concern because lead intoxication and even death occurred among those occupationally exposed. In 1925, the U.S. Surgeon General appointed a committee to investigate possible public health hazards in the manufacture, distribution, or use of leaded gasoline. In the following year, the committee proposed a set of regulations which were concerned only with precautions in manufacture and distribution. The proposed regulations were adopted voluntarily by the petroleum industry.

About 1930, an attack on the significance of lead as a hazard to the general public began, but for the following 30 years, there was little interest in the potential environmental pollution problem of lead. Then in 1958, the Ethyl Corp. sought and was granted an increase in the concentration of lead in gasoline by the Surgeon General. Today, the amount of TEL ranges from 2 to 4 g/gal of gasoline.

A survey in 1964 indicated only 88 cases of TEL poisoning reported in the U.S. and Canada, subsequent to adoption of the regulations in 1926,

Uses of lead

Metal products
- cable covering
- solder
- caulking lead
- ammunition
- bearing metals
- sheet lead
- pipes
- type metal
- brass and bronze

Storage batteries

Chemicals
- tetraethyllead

Pigments

Miscellaneous
- weights
- galvanizing
- annealing
- shielding

and only 16 fatalities. This record is not bad, considering that several million tons of TEL have been manufactured and distributed since 1926.

Lead exhausted by automobiles originates in the antiknock fluid in the gasoline. The fluid contains lead alkyls and organic scavengers, ethylene dichloride, and dibromide, whose function is to combine with the lead to form inorganic lead salts, chiefly bromochloride, that enters into the atmosphere as part of the exhaust gases. Since only negligible amounts of the lead alkyls in the gasoline are exhausted directly into the atmosphere, it is unlikely that the health of the general public would be affected.

The amount of lead discharged into the atmosphere in exhaust gases varies, depending on driving conditions from about 25% to 75% of the lead intake in the fuel. At low speeds, the lead tends to be retained in the exhaust system and is discharged at some later period when the engine is run at greater speeds. The level of atmospheric lead varies directly with the volume of traffic and the size of the community. Los Angeles, with a population of more than 2.5 million, has the highest lead concentration of the communities studied, with an approximate mean of 5 $\mu g/m^3$ of air. Other urban communities with a population greater than 2 million have values of about 2.5 μg. Communities smaller than a million have a mean atmospheric concentration of about 2 μg, and communities with a population of less than 100,000 have a mean value of about 1.7 μg. The mean today is rising by as much as 5% per year, and week-long averages of 8 μg now occur in San Diego.

From the atmospheric precipitation samples collected by a nationwide network of 32 stations throughout the U.S., lead concentration is correlated with the amount of gasoline consumed in the area and the amount of lead in surface water supplies. Thus, any further rise in the dissemination of lead wastes into the environment can cause adverse effects on human health.

Lead absorption

Two major routes by which lead enters the human body are the alimentary and respiratory tracts. Absorption of inorganic lead through the skin is insignificant. Trace amounts of lead are found in normal daily diets. The mean dietary intake of lead for adult Americans is approximately 300 μg/day. Approximately 6–7% of the metal ingested is actually absorbed, but the percent absorption does not appear to be materially influenced by the amount of intake.

In addition to the dietary intake, lead absorption by the respiratory tract has been studied. The amount of lead absorbed from a given air concentration varies according to the particle size. Particles of approximately 1 μ or smaller will probably be retained by the lung, with up to 50% retained in the body, and the remaining portion expired with air. Particles larger than 2 μ impinge on the mucous lining of the airways, are swallowed, and are handled as though ingested by mouth.

About 75% of particulate lead in vehicle exhaust is less than 0.9 μ in mean diameter, a size easily retained by the lung. For example, an urban adult, breathing air containing 3 μg of lead and respiring about 15 m^3 of air per day, will absorb about 20–25 μg of lead from the respiratory tract. Roughly the same amount absorbed from a normal daily diet, this atmospheric lead contribution to the body approaches, and in some communities, even surpasses the contribution made by dietary intake.

Lead metabolism and effects

Under normal conditions, more than 90% of the lead retained in the body is in the skeleton. The amount of lead which is not retained in the body is excreted back into the gut in the bile and also excreted in urine, sweat, hair, and nails. Long-term exposure at some daily level of lead is potentially hazardous because lead is a highly cumulative poison. Under conditions of abnormally high calcium metabolism, such as feverish illness or during cortisone therapy, lead may be mobilized and a toxic amount released from the skeleton. Only a small fraction of the total bone lead need be mobilized to add an appreciable increment to the small soft tissue pool.

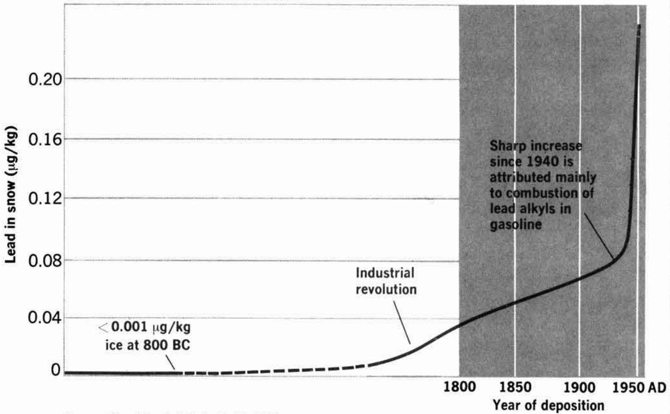
With the passage of time, absorbed lead becomes progressively more deeply buried in the bone matrix. This develops a potentially dangerous pool of exchangeable lead which can persist for months or even years. Acute lead poisoning can occur long after exposure to abnormal amounts of lead has ceased.

Lead poisoning results from very high levels of lead in the human body, particularly in the soft tissues. While in the soluble form, lead is both mobile and toxic, and most often affects the blood, kidneys, and nervous system.

The effect of excessive amounts of

Figure 1

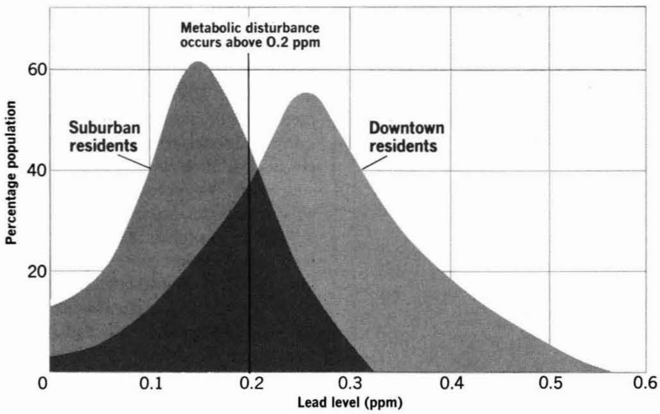
Lead content of Greenland snow layers continues to increase



Source: Chemistry in Britain, 7, 55, 1971

Figure 2

Lead levels[a] differ in suburban and downtown inhabitants



[a] Lead levels in blood of Philadelphia males 1961-2

Source: Chemistry in Britain, 7, 56, 1971

lead in the blood is anemia. The presence of stippled cells is characteristic of the blood of a patient with lead poisoning. Chronic nephritis, sometimes accompanied by gout, is a disease characterized by a scarring and shrinking of kidney tissues. In severe cases, it may lead to ultimate kidney failure.

The effects of lead on the central nervous system are seen in behavior problems characterized by convulsions or swelling of the brain. A single attack of acute encephalopathy can cause brain hemorrhage, mental retardation, and other permanent neurological injury. Similarly, repeated bouts of lead poisoning can also cause permanent brain damage ranging from subtle learning deficits to profound mental incompetence and epilepsy.

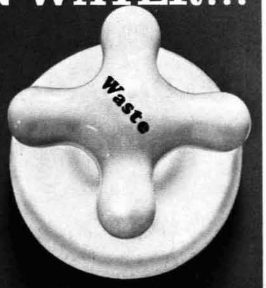
Chronic lead poisoning results from a slow buildup of lead over a period of years or the aftereffects of acute lead poisoning. Acute lead poisoning has easily recognizable symptoms, and if treatment is administered in time, permanent damage can be avoided. Chronic lead poisoning, however, without symptoms or with vague symptoms, is difficult to diagnose and may be recognized only after irreversible damage has been done.

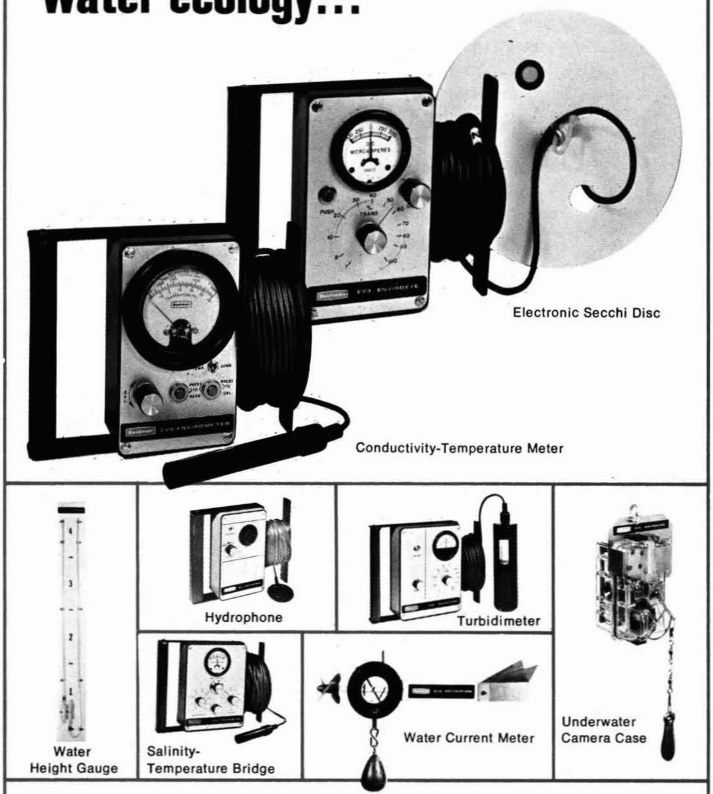
Childhood lead poisoning

Lead poisoning in children is primarily a metropolitan disease in preschool age children who live in deteriorated housing previously painted with thick layers of leaded paint. As they are converted into slum tenements, much of the leaded paint peels and crumbles and is readily available to a young child. A chip of paint about the size of an adult fingernail can contain between 50 and 100 mg of lead. A child swallowing a few small chips a day easily ingests beyond the tolerable adult lead intake.

Lead poisoning is more dangerous in children than adults. During the first few weeks of abnormal ingestion of lead, generally no symptoms appear. After about six weeks, minor symptoms such as decreased appetite, constipation, clumsiness, fatigue, irritability, lethargy, headache, abdominal pain, and sometimes vomiting occur. Repeated ingestion of lead can lead to intermittent drowsiness and stupor, more persistent and forceful vomiting, and convulsions. With more prolonged or intense ingestion, the disease can culminate in intractable convulsions and coma (the symptoms of encephalopathy) and sometimes sudden death.

The minimum blood concentration of lead below which it is most unlikely that poisoning will occur is 80 μg of lead per 100 ml of blood for adults. In children, however, the threshold should be much lower. Mild symptoms of lead poisoning have been found in children at 60–80 μg. As the blood–lead concentration rises above 80 μg, the risk of severe symptoms increases sharply. As many as 50,000 children in the United States today suffer from lead poisoning. Even though physical recovery is possible, brain damage and mental retardation often ensue, for the ages of one to four or five are critical years in the growth and development of the brain.





Lead poisoning control

The most frequently used lead poisoning treatment is to bind the soluble lead to chelating agents which remove lead ions from soft tissues and prevent deposition of lead on the surface of the red blood cells. With chelating agents, high lead levels in tissues can be rapidly reduced to levels approaching normal, and adverse metabolic effects can be promptly suppressed. However, if there is a large residue of lead in the stomach, chelates may encourage such rapid absorption of lead that death occurs. Chelates may also release lead already stored in the bones, causing further complications. Chelating agents frequently used to treat lead poisoning are calcium disodium ethylenediamine tetraacetate (EDTA), 2,3-dimercaptopropanol or British Anti-Lewisite (BAL), and *d*-penicillamine.

Before chelating agents were available to treat lead poisoning, about two thirds of all children with lead encephalopathy died. Now the mortality rate is less than 5%. Unfortunately, treatment has not substantially reduced brain damage and mental retardation in the survivors.

Among the various substances that man concentrates in his immediate environment, lead wastes have been accumulating rapidly during the last century. As far as is known, lead is not a trace metal essential to nutrition.

One must remember that lead absorbed in seemingly harmless trace quantities over a long period of time can accumulate to exceed the threshold level for potential poisoning and produce delayed toxic effects. Concentrations of lead in soft tissues as well as in bones continues to rise from birth through the fourth or fifth decade of life. Furthermore, concentrations are higher in the U. S. than in other parts of the world.

Normal concentrations of lead in adults are below 40 μg/100 ml of blood. The average concentration of lead in Americans is 27 μg. The question is whether this average is normal or whether it represents a serious increase beginning with adding TEL to gasoline and thereby reflecting documented increase in environmental lead. If this is so, then any further increase might well be dangerous. Unfortunately, there is no baseline with which to compare contemporary populations. Low level effects are yet to be recognized.

Since 50% of airborne lead can be absorbed from diet, hopefully, the amount of airborne lead will remain constant since automobile and oil companies have started to eliminate leaded gasoline. Some states have laws prohibiting leaded paints for interior painting. However, applying lead-free paint over old leaded paint does not solve the problem. When paint peels, the leaded paint again becomes available to the child. Old leaded paint must be removed from substandard housing. Where rehabilitation is impossible, urban redevelopment projects should replace substandard housing.

Present American industrial standards consider 200 $\mu g/m^3$ to be an acceptable level of occupational exposure. A known effect of chronic lead exposure among industrial workers is peripheral nerve disease, affecting primarily the motor nerves of the extremities, while symptoms of acute lead poisoning are strikingly absent. Federal and state governments are reponsible for instituting effective control measures in industry.

Whether or not lead concentrations measured are hazardous to human health, any further increase of lead in the environment will result in further concentration in some food chains, leading ultimately to toxic doses for man or for some other important organisms. Lead pollution, therefore, must be controlled.

Additional reading

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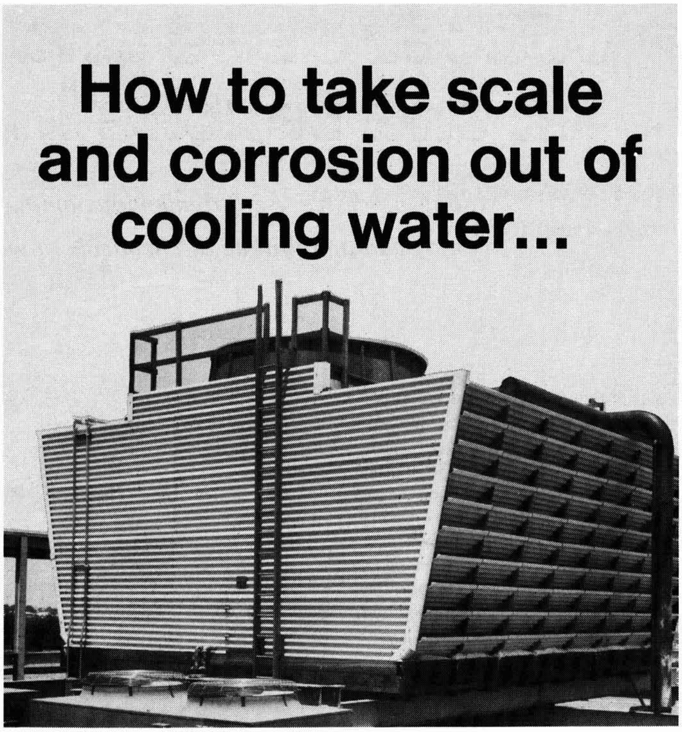
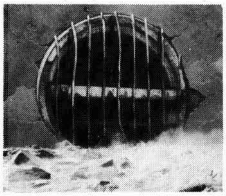
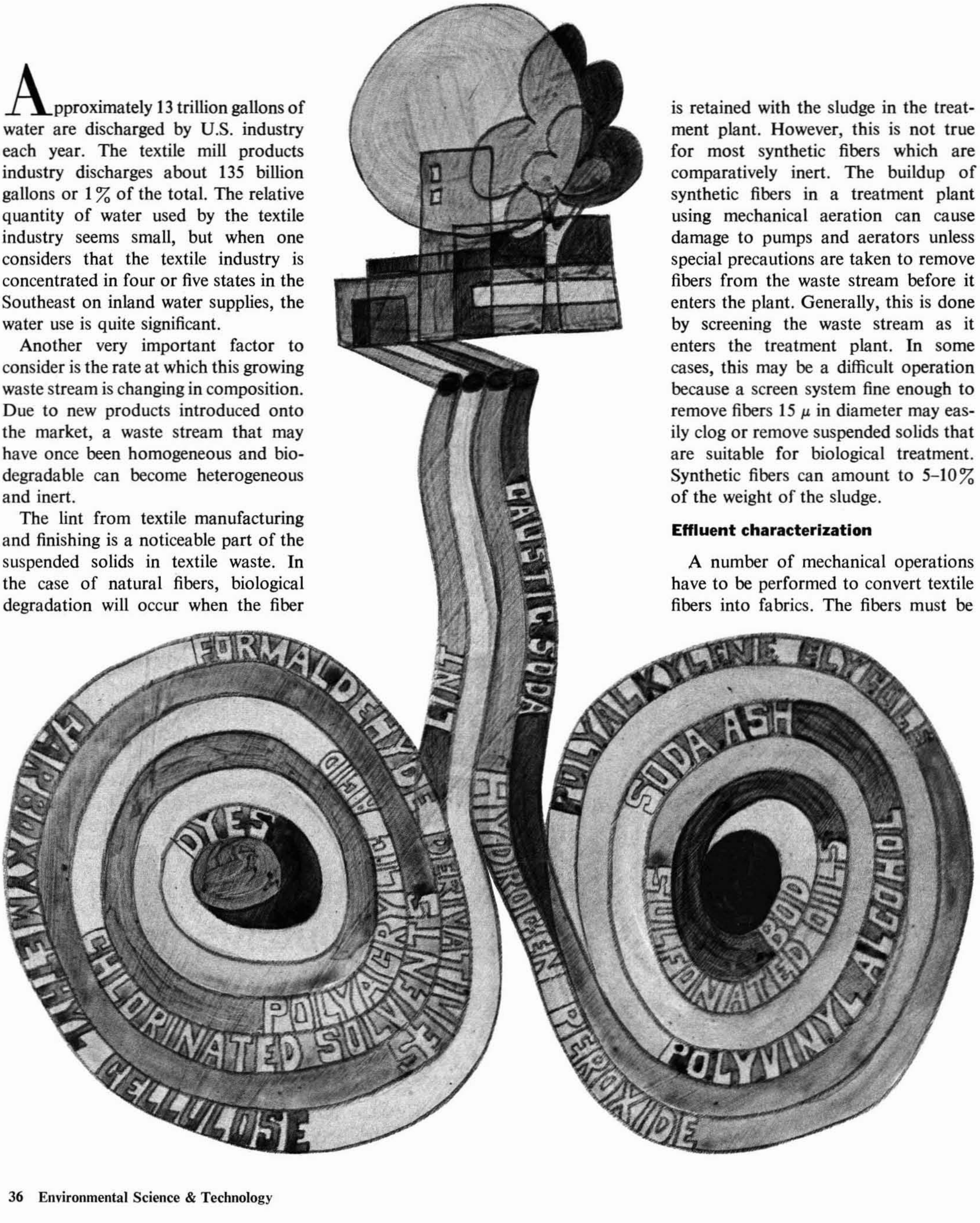




Water uses and wastes in the textile industry

Milling processes use a tremendous amount of water and may add a multitude of chemicals to waste streams



Approximately 13 trillion gallons of water are discharged by U.S. industry each year. The textile mill products industry discharges about 135 billion gallons or 1% of the total. The relative quantity of water used by the textile industry seems small, but when one considers that the textile industry is concentrated in four or five states in the Southeast on inland water supplies, the water use is quite significant.

Another very important factor to consider is the rate at which this growing waste stream is changing in composition. Due to new products introduced onto the market, a waste stream that may have once been homogeneous and biodegradable can become heterogeneous and inert.

The lint from textile manufacturing and finishing is a noticeable part of the suspended solids in textile waste. In the case of natural fibers, biological degradation will occur when the fiber is retained with the sludge in the treatment plant. However, this is not true for most synthetic fibers which are comparatively inert. The buildup of synthetic fibers in a treatment plant using mechanical aeration can cause damage to pumps and aerators unless special precautions are taken to remove fibers from the waste stream before it enters the plant. Generally, this is done by screening the waste stream as it enters the treatment plant. In some cases, this may be a difficult operation because a screen system fine enough to remove fibers 15 μ in diameter may easily clog or remove suspended solids that are suitable for biological treatment. Synthetic fibers can amount to 5–10% of the weight of the sludge.

Effluent characterization

A number of mechanical operations have to be performed to convert textile fibers into fabrics. The fibers must be

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combined into yarns and then the yarns into fabrics. After fabrics are manufactured, they are subjected to several wet processes collectively known as finishing, and it is in these finishing operations that the major waste effluents are produced.

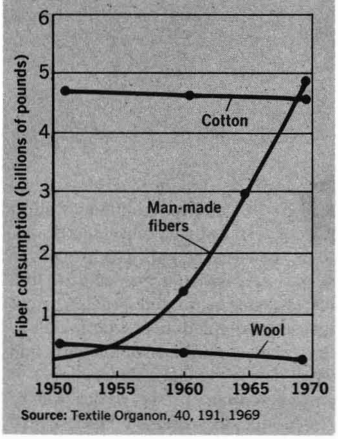
Cotton. The consumption of cotton fibers by textile mills in the United States exceeds that of any other single fiber (Figure 1). Slashing is the first process in which liquid treatment is involved. In this process, warp yarns are coated with "sizing" to give them abrasive resistance to withstand the pressures exerted on them during the weaving operation. The principal slashing polymer used before 1960 was starch which was easily degraded biologically and should present no problem to the conventional waste treatment plant other than BOD loading.

Development of many synthetic fibers in the 1950's and their use in blended fabrics created the need for new sizes which were more compatible with the hydrophobic fibers. Some of those which are still in use are polyvinyl alcohol (PVA), carboxymethyl cellulose (CMC), and polyacrylic acid.

If an average size concentration of 10% is assumed to be present on woven fabrics, which constitute 70% to 80% of the fabrics produced, approximately 400 million lb of size per year are currently entering textile finishing waste streams. Since PVA and CMC are resistant to biological degradation, conventional treatment methods would not be expected to alter their chemical structure. While the polymer may be partially removed from the waste water by adsorption on the sludge, it is questionable whether this is an effective method of treatment.

The operation of desizing removes the substance applied to the yarns in the slashing operation, by hydrolyzing the size into a soluble form. There are two methods of desizing—acid desizing and enzyme desizing. In acid desizing, the fabric is soaked in a solution of sulfuric acid, and in enzyme desizing, complex organic compounds produced from natural products or malt extracts are used to solubilize the size. Due to the unstable nature of these organic compounds, the whole bath must be discarded after each batch. Desizing contributes the largest BOD of all cotton finishing processes—about 45%.

Figure 1
Textile fiber consumption in the U. S.



Source: Textile Organon, 40, 191, 1969

Scouring follows desizing. In this process, cotton wax and other noncellulosic components of the cotton are removed by hot alkaline detergents or soap solutions. In most modern plants, scouring is done in conjunction with desizing rather than as a separate operation. Caustic soda and soda ash along with soaps and synthetic detergents and inorganic reagents are used to remove the noncellulosic impurities. The waste liquor will have a 0.3% alkaline concentration.

A few of the major chemical manufacturers are now offering solvent processes to the textile industry for scouring where little water is used. In these cases, nonflammable chlorinated solvents are used, and the projected solvent recovery is between 90% and 97%. However, nearly 1 ton of solvent per day per range will reach the atmosphere or waste stream.

Bleaching, the next process, removes the natural yellowish coloring of the cotton fiber and renders it white. The three bleaches most commonly used for cotton are sodium hypochlorite, hydrogen peroxide, and sodium chlorite. The bleaching process contributes the lowest BOD for cotton finishing.

Mercerization gives increased luster to cotton fabrics, but more importantly, imparts increased dye affinity and tensile strength to the fabric. The process uses sodium hydroxide, water, and an acid wash. The effluent from the overall process has a high pH and also a high alkalinity if the caustic material is not recovered. After mercerizing, the goods are sent to the dye house or color shop. The dyeing process is carried out in an aqueous bath with pH variations of 4 to 12.

In the color shop, the goods are printed with colored designs or patterns. The color is imparted to the fabric from rolling machines which contain the printing paste. This paste contains dye, thickener, hygroscopic substances, dyeing assistants, water, and other chemicals. The pollution load from the color shop comes mainly from the wash-down rinses (used to clean the equipment in the shop) and the cloth rinsings and is rather low in both volume and BOD. When a mill does both printing and dyeing, the BOD contribution of the combined processes is 17%, and the total BOD load comes from the process chemicals used.

Dyes have to be more and more

Table I. Pollution effects of cotton processing wastes

Process	*Wastes, ppm*		
	pH	BOD	Total solids
Slashing, sizing yarn	7.0–9.5	620–2,500	8,500–22,600
Desizing		1,700–5,200	16,000–32,000
Kiering	10–13	680–2,900	7,600–17,400
Scouring		50–110	
Bleaching (range)	8.5–9.6	90–1,700	2,300–14,400
Mercerizing	5.5–9.5	45–65	600–1,900
Dyeing:			
Aniline Black		40–55	600–1,200
Basic	6.0–7.5	100–200	500–800
Developed Colors	5–10	75–200	2,900–8,200
Direct	6.5–7.6	220–600	2,200–14,000
Naphthol	5–10	15–675	4,500–10,700
Sulfur	8–10	11–1,800	4,200–14,100
Vats	5–10	125–1,500	1,700–7,400

resistant to ozone, nitric oxides, light, hydrolysis, and other degradative environments to capture a valuable portion of the commercial market. It is not surprising, therefore, that studies on the biological degradation of dyestuffs yield negative results when dyes are designed to resist this type of treatment. The range of pollution loads of the various cotton textile wet-processing operations are listed in Table I.

Federal Water Pollution Control Administration estimates for BOD, suspended solids, total dissolved solids, and volume of waste water for 1970–82 are shown in Figure 2. The gradual decrease of the gross pollution load in coming years is based on these assumptions: new machinery, which tends to produce less pollution per unit of cloth due to water reuse and countercurrent flow designs; trends in process modification, new chemical manufacture, and better housekeeping will continue; a larger percentage of the wastes will be treated due to increased efficiency of treatment facilities; and increased state, local, and federal pressure.

Wool. Wool fiber consumption is the smallest of the three groups, and the trend seems to be toward less demand in the future on a percentage basis. Scouring is the first wet process that wool fibers receive. This process removes all the natural and acquired impurities from the woolen fibers. For every pound of scoured woolen fiber, 1 1/2 lb of waste impurities are produced; in other words, wool scouring produces one of the strongest industrial wastes in terms of BOD by contributing 55–75% of the total BOD load in wool finishing.

Depending on whether the fabric is classified as woolen or worsted, the remaining wet processes will vary. Burr picking and carbonizing are steps to remove any vegetable matter remaining in the wool after scouring and before dyeing.

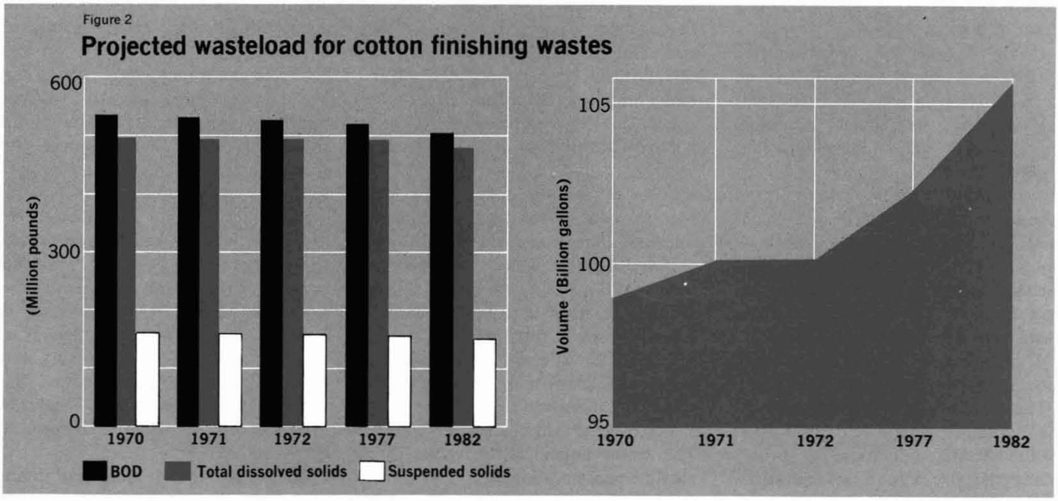
The volume of waste water generated by dyeing, either stock or piece goods, is large and highly colored, and many of the chemicals used are toxic. The BOD load is contributed by the process chemicals used, and represents 1–5% of the mill's total BOD load. Although the following mixing and oiling step does not contribute directly to the waste water volume, the oil finds its way into the waste stream through washing. The percentage contribution to total BOD load of this process varies with the type of oil used.

Fulling or felting is another operation that does not directly contribute to the waste stream, until the process chemicals are washed out of the fabric. It is estimated that 10–25% of the fulled cloth's weight is composed of process chemicals that will be washed out in this process and discarded.

Wool washing after fulling is the

Figure 2

Projected wasteload for cotton finishing wastes



second largest source of BOD, contributing 20–35% of the total. This process consumes 40,000–100,000 gal of water for each 1000 lb of wool fabric, and analyses show that wool, once thoroughly washed, will produce little or no BOD on being rewashed. Carbonizing the fabric or stock of fibers (with strong acid to remove cellulose impurities followed by a soda ash wash) contributes less than 1% of the total BOD load.

Wool is bleached if white fabric or very light shades of colored cloth are required; however, the amount of wool fabric bleached is rather small. With hydrogen peroxide and sulfur dioxide, bleaching the BOD contribution is usually less than 0.5%, and optical brighteners, which use organic compounds, contribute about 1% of the total BOD. In processing woolen fibers, five sources of pollution load exist—scouring, dyeing, washing after fulling, neutralizing after carbonizing, and bleaching with optical brighteners. The average values of the pollution load of each of these processes is shown in Table II. The waste water volume for woolen finishing wastes is shown in Figure 3.

Table II. Pollution loads of wool wet processes

Process	*pH*	*BOD, ppm*	*Total solids, ppm*
Scouring	9.0–10.4	30,000–40,000	1,129–64,448
Dyeing	4.8–8.0	380–2,200	3,855–8,315
Washing	7.3–10.3	4,000–11,455	4,830–19,267
Neutralization	1.9–9.0	28	1,241–4,830
Bleaching	6.0	390	908

Table III. Pollution load of synthetic wet fiber processes

Process	*Fiber*	*pH*	*BOD, ppm*	*Total solids, ppm*
Scour	Nylon	10.4	1360	1882
	Acrylic/modacrylic	9.7	2190	1874
	Polyester		500–800	
Scour & dye	Rayon	8.5	2832	3334
	Acetate	9.3	2000	1778
Dye	Nylon	8.4	368	641
	Acrylic/modacrylic	1.5–3.7	175–2000	833–1968
	Polyester		480–27,000	
Salt bath	Rayon	6.8	58	4890
Final scour	Acrylic/modacrylic	7.1	668	1191
	Polyester		650	

Synthetics. This category of textile fibers has two broad classifications: cellulosic and noncellulosic fibers. The two major cellulosic fibers are rayon and cellulose acetate; the major noncellulosic fibers are nylon, polyester, acrylics, and modacrylics. Different processes to produce synthetic fibers result in varying pollution loads (Table III).

The first process in which synthetic fibers are subjected to an aqueous treatment is stock dyeing (unless the fabric is to be piece dyed). When stock dyeing is used, the liquid waste discharge will vary from about 8 to 15 times the weight of the fibers dyed. Due to the low-moisture regain of the synthetic fiber, static electricity is a problem during processing. To minimize this problem, antistatic oils (polyvinyl alcohol, styrene-based resins, polyalkylene glycols, gelatin, polyacrylic acid, and polyvinyl acetate) are applied to the yarns and become a source of water

Figure 3

Projected wasteload for woolen finishing wastes

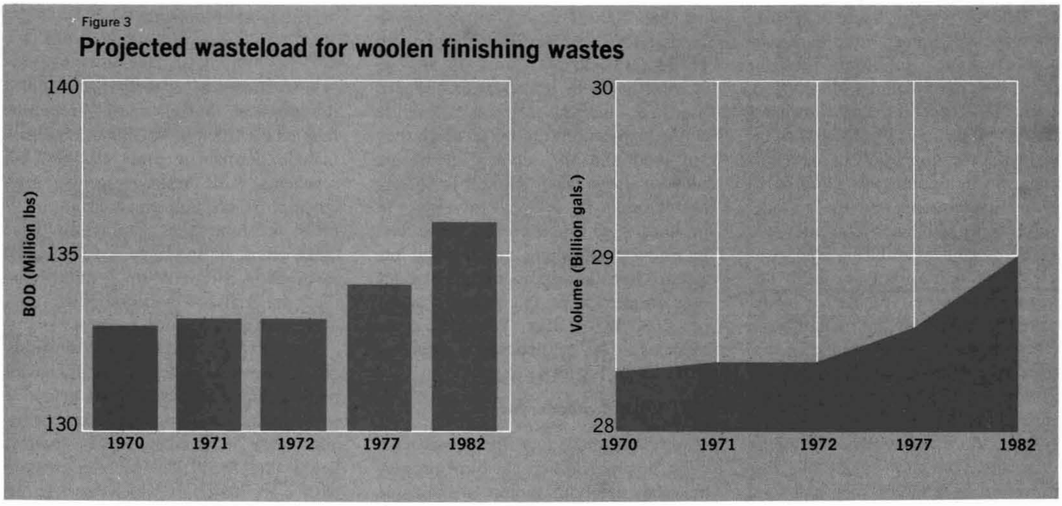
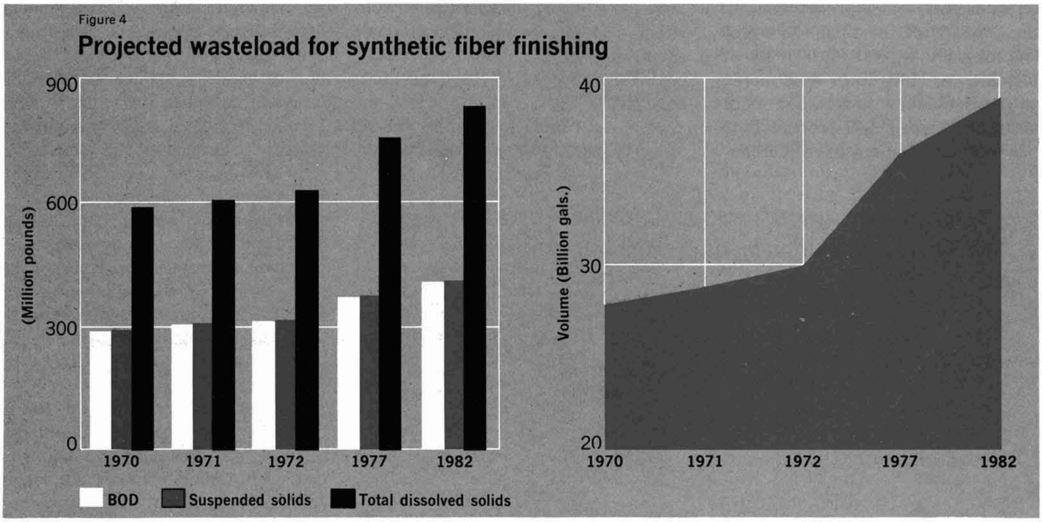


Figure 4

Projected wasteload for synthetic fiber finishing



pollution when they are removed from the fabrics during scouring.

Since the manufacture of synthetic fibers can be well controlled, chemical impurities are relatively absent in these fibers; and if synthetics are bleached, the process is not normally a source of organic or suspended solids pollution.

In finishing rayon, one of the synthetic fibers, scouring and dyeing are usually done concurrently in a single bath. If scouring and dyeing are the only finishing processes given rayon fabrics, an equalized effluent of 1445 ppm BOD and 2000–6000 ppm salt contained in approximately 5000 gal of water for each 1000 lb of fabric processed will be produced.

For acetate fibers, the wastes from scour and dye baths average 2000 ppm and 50 lb of BOD for each 1000 lb of acetate fabric. Typically, the bath contains antistatic lubricant desizing wastes, which contributes 40–50% of the BOD load; the sulfonated oil swelling agent, which accounts for 30–40% of the BOD load; the aliphatic ester swelling agent, which amounts to 10–20% of the BOD discharged; and the softener which has negligible BOD content.

These processes produce a composite waste of 666 ppm of BOD for each 1000 lb processed; the volume of water required to treat this amount of cloth averages 9000 gal. If bleaching is substituted for dyeing, the BOD of the discharge of the scouring and bleaching bath is approximately 750 ppm.

Nylon differs from other synthetics in that approximately 1% of the fiber dissolves when scoured. Soap and soda ash are used in the scouring process which averages 1360 ppm and 34 lb of BOD for each 1000 lb of cloth processed. The substances present in the bath contribute the following percentages to the total BOD of the bath; antistatic-sizing compound (40–50%), soap (40–50%), and fatty esters (10–20%).

When nylon is dyed, sulfonated oils are used as dye dispersants. These dye dispersants contribute practically all of the process's BOD, which amounts to an average of 600 ppm and 15 lb for each 1000 lb of cloth dyed. However, the BOD contribution of scouring is roughly 80%, the remaining BOD being contributed by the dyeing process.

Another group of synthetic fibers are the polyesters whose scour wastes average 500–800 ppm of BOD. Processing 1000 lb of polyester fabric will produce 15.5 lb of BOD of which 90% is contributed by antistatic compounds used for lubrication sizing. Because of the high concentrations at which they are used and the inherent high rate of BOD, the emulsifying and dissolving agents used in polyester dyeing will produce high BOD loads. The rinses in polyester finishing are usually low in BOD. But, the processing of polyester uses an average of 15,000 gal of water per 1000 lb of fiber. Projected gross wasteload for synthetic fiber finishing is shown in Figure 4.

Acrylics and modacrylics

Although these two fiber types have different physical and chemical properties, they are both subject to the same finishing techniques. The waste from the first scour averages 2190 ppm and 660 lb of BOD per 1000 lb of processed fiber. The chemical components of the bath are the antistatic compound, which accounts for 30–50% of the BOD, and the soaps used to accomplish this process. When using acid dyes, the dye baths average 175 ppm and 5.3 lb of BOD per 1000 lb of fabric, the total BOD load coming from the dye carriers.

The final scour averages 668 ppm and 20 lb of BOD for 1000 lb of cloth. This final scour is accomplished with synthetic detergents and pine oil, which together contribute practically all the BOD. The equalized discharges will have a BOD of 575 ppm and 120.9 lb in a volume of 25,000 gal of waste water for each 1000 lb of acrylic and modacrylic fabric processed.

Finishing

A treatment of a fabric that modifies its physical or chemical properties may be classified as finishing. Examples include permanent press finishes, oil repellents, soil release agents, low-crock polymers, abrasion-resistant polymers, fire retardants, lamination polymers, germicide and fungicide chemicals, to mention a few. A small number of these materials are biodegradable; however, most are not.

The polymers used for textile finishing are generally supplied to the finishing plant as emulsions which are sensitive to pH, salt, or agitation and may coagulate when they enter waste streams. Sewer lines may then become clogged with inert materials which have to be removed by hand. Although the bulk of the polymer emulsion can be coagulated and removed in a treatment plant, some of it remains emulsified and is not removed by biological treatment. For complete removal of the polymer emulsion, chemical treatment is sometimes necessary. However, this is an additional step which in itself could replace much of the need for biological treatment.

Most of the finishes used for wash and wear and permanent press fabrics are manufactured from urea, formaldehyde, melamine, and gloxal compounds. Some of these products are readily degradable by microbial action; others are not. The formaldehyde derivatives can react with themselves or other chemicals in the waste stream to form insoluble products that may be removed by sedimentation.

A class of finishing chemical that has come into prominence in recent years is fire retardants. Most of the commercial fire-retardant finishes are phosphorus- and nitrogen-containing compounds. One such compound, triaziridyl phosphine oxide (APO), could present a serious problem if it got into a natural stream. The chemical reactivity of APO would facilitate its hydrolysis in a waste stream and prevent the parent compound from reaching the discharge water of a treatment plant. Whether or not these initial hydrolysis products are toxic or harmful is not known. This points to the increasing need for the characterization of industrial waste.

In the future, waste streams from different processing operations will have to be isolated and treated by either chemical or biological methods. The choice of treatment will naturally depend on the composition of the stream. By using this approach, industry will have more latitude in choosing chemicals and processes for their inherent production advantages and not their effect on pollution.

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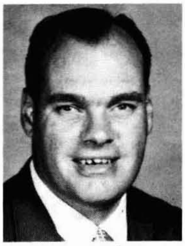

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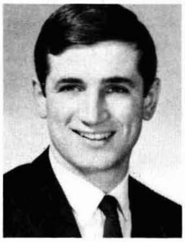

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Measurement of Suspended Solids Concentrations in Sewage by Use of a Depolarization Method

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■The depolarization of back-scattered polarization radiation was used to measure the concentration of suspended solids in sewage. The effect of such factors as variations in the particle size of the suspended solids, solids density, color of the samples, refractive index of the medium, sample flow, and coated optical windows of the sample cuvettes on the relationship between the degree of depolarization and suspended solid concentration was investigated. The results indicate that this relationship is unaffected by the above factors for a limited number of meaningful samples.

This investigation was undertaken to establish the feasibility of using depolarization of back-scattered polarized radiation for measuring the concentration of suspended solids in sewage systems.

Depolarization measurements on model hydrosol systems as described previously (Liskowitz, 1971) indicate that the degree of depolarization is dependent on the ratio of the refractive index of the solid to that of the medium, and to the volume concentration of particles in suspension. Correlation with the weight concentration of suspended solids can be obtained by measuring the density of the solids. Proper selection of the wavelength of incident radiation, so that it is comparable to, or smaller than, the size of the particles in the sewage samples, will significantly reduce the effect of particle size on the measurement. Adaptation of the depolarization technique for monitoring the amount of suspended solids in sewage requires that the effect on the degree of depolarization of variations in particle size of the suspended solids, solids density, color variations, and refractive index of the suspended medium be examined. The effects of flow rates and of coating cuvette windows with deposited solids are also considered.

Experimental

Source of Samples. Sewage samples from both the Middlesex County Sewerage Authority's plant (Sayreville, N. J.) (influent, effluent, activated-sludge pilot-plant effluent, and sludge from the clarifiers) and the Bernardsville, N. J., plant (effluent, influent, and activated sludge) were used in this investigation. These sources were selected to provide both industrial and domestic sewage, and to cover a wide range of suspended solids concentration from a few parts per million to 5000 ppm.

Depolarization Measurements. Initial depolarization measurements at a scattering angle of 170°, with (polychromatic) radiation from a mercury source, were performed on nonflowing sewage samples in a sample cuvette with a diameter of 11 cm. The laboratory instrument was assembled from components taken from a Brice Phoenix light-scattering photometer. The complete source unit (Figure 1) consisting of a type AH-3 mercury lamp, the iris diaphragm, the cylindrical lens, and the Polaroid polarizer was mounted on an optical bench containing two detector supports on which were fastened Brice Phoenix receiver units. The detector supports were set at back-scattering angles of 170° and the receiver units were directed at a point along the incident beam which corresponds to the center of the cylindrical sample cuvette. The width and height of the incident beam image at this point were 5 × 22 mm. Partitions separated the receivers and source units to prevent stray source radiation from interfering with the depolarization measurements. The degree of depolarization ($E_{\perp}/E_{\parallel}$) exhibited by the sewage samples was obtained by measuring $E_{\perp}$ (1/2 depolarized component) and $E_{\parallel}$ (polarized plus 1/2 depolarized component) simultaneously by use of two analyzers positioned in front of two 1P21 photomultipliers. All measurements were carried out in a darkened room.

The supposedly matched photomultipliers used in the laboratory suspended solids monitor were found to exhibit different responses to the same light intensity. This problem was overcome by regulating the power supplies to the photomultipliers so that they exhibited the same linear response to different levels of radiation.

The samples were continuously stirred during the measurement to maintain the solids in suspension. Without stirring, an immediate decrease in the degree of depolarization was observed as the particles settled.

A study of the rate of buildup of solids on optical surfaces was carried out by submerging four 1000-ml pyrex beakers in an activated sludge tank at the Bernardsville sewage treatment plant. Beakers were removed from the activated sludge tank after 42 hr, 6 days, 8 days, and 1 month. Depolarization measurements were performed on Middlesex influent by use of the surface of the beaker that contained the largest amount of deposited solids, and then by repeating these measurements on the same influent after the deposited solids were removed.

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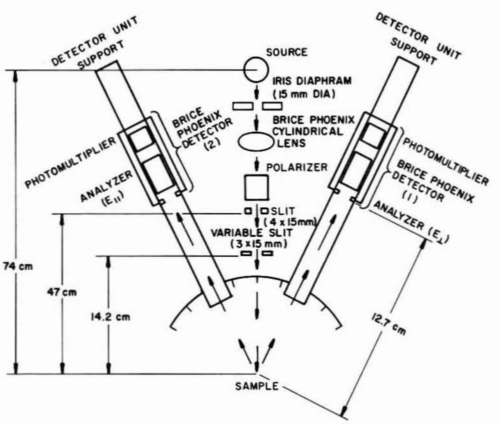

Figure 1. Schematic of instrumental arrangement for depolarization measurements at a back-scattering angle of 170°

Middlesex rather than Bernardsville influent was used in this study because the more concentrated Middlesex influent completely attenuated the incident beam within the beaker, and thus any reflection off the back surface of the beaker onto the detector was eliminated.

Because of the unevenness of the deposits on the beaker surface, only one detector was used for the depolarization measurements. The degree of depolarization, $E_\perp/E_\parallel$ was obtained by positioning the analyzer in front of the photomultiplier so that it first responded to $E_\perp$ and then to $E_\parallel$. All depolarization measurements were carried out by use of visible radiation and an optical path length of 5 cm because this optical path length coincides with the inner radius of the beakers. The intensity of the back-scattered radiation was determined because of its dependence on the amount of solids deposited on the surface of the beaker.

A gravity flow system was designed and built in the laboratory, and used for depolarization measurements on flowing sewage. The system consists of two 55-gal drums, one above the other. Opening a ball valve allows the fluid to flow from the upper to the lower drum through a clear 3-in. diam plastic test section. This diameter was selected to achieve as high a flow rate as possible with an optical path length which will permit accurate measurements of the degree of depolarization.

The velocity gradient at the test section was found to exhibit a linear decrease in velocity from 17.8 to 13.0 ft/sec in 5.5 sec, with tap water as the test liquid. The insertion of an orifice plate with a 1.187 in. diam below the test section was found to extend the time for the measurements from 5.5 to 50 sec. A constant flow rate of 1.8 ft/sec was observed during this period.

The depolarization measurements were performed initially on the nonflowing sample in the test section, with two detectors according to the procedure described earlier. Then the valve in the gravity flow system was opened and $E_\perp$ and $E_\parallel$ were continuously recorded as the sewage flowed from the upper to the lower reservoir. The degree of depolarization $E_\perp/E_\parallel$ was calculated at the end of the experiment.

Analyses of Samples. The gravimetric determination of the suspended solids was carried out by first filtering 100 ml of sewage samples through a 10μ membrane filter followed by a 0.3μ membrane filter. Both filters were then dried overnight under a slight vacuum at a temperature of 55°C, and weighed. The sum of the dried residues collected on the 10μ and 0.3μ membranes represents the weight of the suspended solids in the sample. A 0.3μ filter was used because the 0.3μ particles would also contribute significantly to the depolarization of the polarized incident radiation.

Dissolved Solids. The dissolved solids in the sewage samples were determined by bringing a known volume of the clear filtrate which passed through the 0.3μ membrane filter to dryness and weighing the resulting residue.

Refractive Index of Medium. Variations in the refractive index of the liquid medium in the sewage samples caused by changes in the concentration of dissolved solids may result in significant changes in the refractive index ratio. The refractive index of the medium was measured with a Brice Phoenix Model BP-1000V differential refractometer.

Density of the Suspended Solids. The density of the suspended solids in the sewage samples was measured with a density gradient column (Low and Richards, 1952) that ranged from 1.15 to about 1.72 grams/cc on a dry basis. This density gradient was obtained by the successive addition of aqueous sodium iodide solutions of decreasing density and allowing the column to equilibrate overnight. Fifty milliliters of sewage (plant influent) was then added slowly to the top of the column. The density distribution of the suspended solids was determined from their equilibrium position within the column. The density equivalent to each equilibrium position was defined by density standards which had reached equilibrium at various levels within the column.

Size Distribution. A Cahn no. 2800 particle sedimentation accessory was used to measure the size distribution. This accessory provides a continuous and automatic weighing of the different size fractions as they settle with time. A PDP-8 computer was programmed to provide the size distribution from data obtained with the Cahn accessory.

Results

Depolarization Measurement. The degree of depolarization was found to increase with suspended solids concentration regardless of whether the sewage samples were obtained from the Middlesex Sewerage Authority's treatment plant or the Bernardsville Sewage plant (Figure 2). The concentration

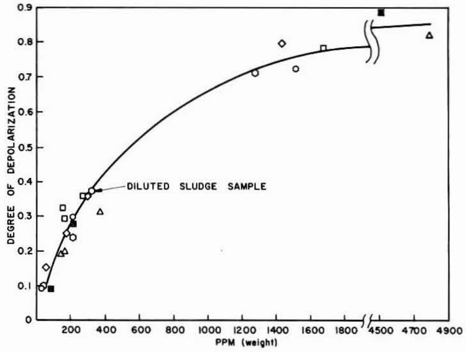

Figure 2. Degree of depolarization as a function of suspended solids. Wavelength of incident radiation = polychromatic light

Scattering angle = 170°
□ Middlesex samples collected 5/23/69
◇ Middlesex samples collected 5/27/69
○ Bernardsville samples collected 6/10/69
⬡ Bernardsville samples collected 6/13/69
△ Middlesex samples collected 6/17/69
⊠ Bernardsville samples collected 6/20/69

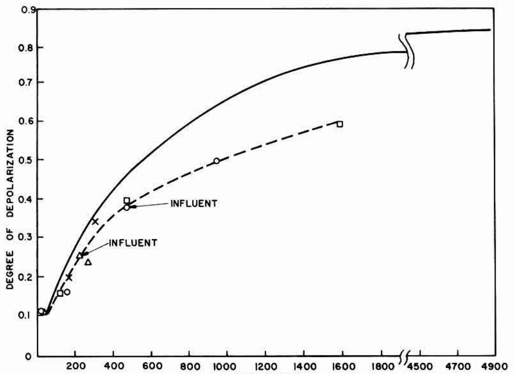

Figure 3. Degree of depolarization as a function of suspended solids for different optical path lengths

—— optical path length, 5.5 cm (reproduced from Figure 2)
- - - optical path length, 2.3 cm
○ Middlesex samples collected 7/10/69
△ Bernardsville samples collected 7/15/69
□ Middlesex samples collected 7/17/69
× Middlesex and Bernardsville samples collected 7/22/69

range covered in these experiments was from 30 to 4800 ppm. The suspended solids in the influent and effluent were from 30 to about 400 ppm, whereas the concentration in the sludge samples ranged from about 1300 to 4800 ppm.

The relationship between the degree of depolarization and concentration of suspended solids was found to be the same whether the sample was influent, effluent, or sludge. A Bernardsville activated-sludge sample diluted with effluent to reduce its solids concentration below 400 ppm exhibited the same degree of depolarization as influent and effluent samples with the same solids concentration (Figure 2). The Bernardsville plant effluent was used as a diluent because it contains low solids concentration (30 to 40 ppm), and it does not contain waste substances which may cause flocculation of the suspended solids in the sludge.

The sharpest increase in the degree of depolarization with concentration of suspended solid occurs below a concentration of about 1800 ppm (Figure 2), with polychromatic radiation and with the detectors at the incident beam directed at the center of the 11-cm-diam sample cell. Above 1800 ppm there is a more gradual increase in the degree of depolarization with concentration. At these high concentrations, complete scattering of the incident beam is observed before it reaches the center of the sample cell.

Reducing the optical path length for the depolarization measurements from 5.5 cm to 2.3 cm results in a more gradual increase in the degree of depolarization with concentrations below 1600 ppm (Figure 3). Because of the low concentration of suspended solids found in Middlesex and Bernardsville sludge samples during the period that measurements were carried out, the relationship between the degree of depolarization and concentration of suspended solids above 1600 ppm, with the shorter optical path lengths, was not examined.

The point scatter observed in Figure 2, especially at high suspended solids concentrations, is probably caused by imprecision of the gravimetric method of determining the suspended solids in the sewage rather than the lack of accuracy in the depolarization measurements. A check of the reproducibility of the gravimetric method showed a 16% variation in the results of separate determinations on the same influent sample.

Analysis of the Middlesex and Bernardsville influents indicated marked variations in the size distribution and density of the suspended solids particles (Table I). Sixty-eight percent of the particles in sample 1 was larger than 15μ, as opposed to only 54% in sample 2. The particle-size distribution of the suspended solids in sample 4 was somewhat similar to that found in sample 2, whereas the majority of the particles in sample 3 was smaller than 19μ. The solids in sample 1 separated into two layers in the density gradient column. The layers ranged from 1.20 to 1.40 grams/cc and from 1.50 to 1.59 grams/cc. The solids samples 2 and 4 formed single layers that ranged from 1.52 to 1.66 grams/cc. In comparison, the suspended solids in sample 3 formed a single layer that ranged from 1.14 to 1.39 grams/cc.

It is of interest to note that the degree of depolarization can be related to the weight concentration of suspended solids even though marked variations were observed in the density of the solids in the sewage samples. Earlier measurements on model hydrosols (Liskowitz, 1971) revealed that the degree of depolarization is related to the weight concentration of the solids when the density of the solids remains constant. The reason for the degree of depolarization being independent of the density of the particles for the case of the sewage samples is not clear at the present time.

Table I. Characterization of Influent Collected from Bernardsville and Middlesex Treatment Plants

Sample no.	Source	Date collected	Suspended solids, ppm	Dissolved solids, ppm	Density range, g/cc	Size distributions, % > μ
1	Middlesex	5/23/69	275	1733	1.20–1.40	13 > 54
					1.50–1.59	19 > 44
						68 > 15
2	Middlesex	5/27/69	300	1133	1.52–1.66	6 > 54
						15 > 54
						54 > 15
3	Middlesex	7/10/69	476	2236	1.14–1.39	10 > 36
						25 > 26
						38 > 19
4	Bernardsville	7/15/69	228	435	1.56–1.65	18 > 34
						43 > 24
						58 > 20

Table II. Optical Properties of Middlesex and Bernardsville Sewage

Sample	Source	Date collected	Total back-scattered radiation intensity, mV	Concn., ppm	Color of suspension
Effluent	Middlesex	6/17/69	9.97	165	Light brown
Influent	Middlesex	6/17/69	7.28	379	Dark brown
Sludge from clarifiers	Middlesex	6/17/69	10.83	4797	Dark brown
Effluent	Bernardsville	6/13/69	2.41	37	Clear
Influent	Bernardsville	6/13/69	6.43	206	White
Activated sludge	Bernardsville	6/13/69	1.79	1516	Black

The color variations in these sewage samples were quite marked. The influent, effluent, and sludge from the Middlesex plant range from light to dark brown, whereas the influent and effluent from Bernardsville range from white to clear, and the activated sludge was black. The wide range of color variations is indicated by the range of intensities of total back-scattered radiation (Table II), since color attenuates both the incident and scattered light.

The results of the refractive index measurements indicate that the contribution of the dissolved solids to the refractive index of the medium is small. A sample containing 1800 ppm of dissolved solids exhibited a refractive index difference of only 3.7×10^{-4} when compared to distilled water.

Effect of Solids Buildup on Optical Surfaces. A slow and irregular rate of buildup of solids was observed on the surface of the beakers submerged in the activated sludge tank at the Bernardsville sewerage plant. Six days were required before significant deposits were observed. These deposits were distributed unevenly, and covered only a small portion of the beaker's surface. The results of the depolarization and back-scattering intensity measurements on the Middlesex influent, in a beaker that was submerged for 42 hr, indicate that cleaning the beaker had no effect on either the degree of depolarization or the intensity of the total back-scattered radiation (Table III). However, when the beaker was submerged for six days, the intensity of back-scattered radiation, measured through the deposited solids, was reduced 7.5%. The degree of depolarization remained the same. This was also found to be the case for the beaker submerged for eight days. A 40.8% reduction in intensity of the back-scattered radiation was observed, whereas the degree of depolarization is unaffected by the deposited solids.

Visual examination of the beaker submerged for one month indicated less of a solids buildup than that on the beaker submerged for eight days, and the total back-scattered radiation was reduced only 9% by the deposits on the surface of the former, compared to 40.8% reduction in the eight-day case. The degree of depolarization was again unaffected by the solids buildup.

The low total back-scattered radiation from the influent in the beaker submerged for one month was the result of our reducing the width of the incident beam in the suspended solids monitor from 3 mm to 2 mm in anticipation of a large solids buildup on the beaker's surface. Depolarization studies with artificial deposits indicated that a large surface buildup could introduce an error in the measurement of the degree of depolarization. This arises because of the reflection of polarized light into the detector from the interface between the optical surface and the deposited solids. Reducing the width of the incident beam eliminated this problem.

Table III. The Effect of Solid Deposits on the Measurement of the Degree of Depolarizaton and Total Back-Scattered Intensity of Middlesex Influent

Date influent collected	Time beaker submerged	Degree of depolarization		% Change	Total back-scattered radiation, mV		% Change
		Before cleaning	After cleaning		Before cleaning	After cleaning	
8/19/69	42 hr	0.275	0.274	0	3.116	3.118	0
8/25/69	6 days	0.408	0.408	0	6.485	7.000	7.5
8/25/69	8 days	0.407	0.408	0	3.935	6.670	40.8
9/16/69	1 month	0.394	0.397	0	0.464	0.504	9.0

Table IV. Effect of Flow on the Measurement of the Degree of Depolarization

	With orifice			Without orifice		
$E_\perp/E_\parallel$ (static)	Time, sec	Flow rate, ft/sec	$E_\perp/E_\parallel$	Time, sec	Flow rate, ft/sec	$E_\perp/E_\parallel$
0.224	2	1.8	0.217	0	17.9	0.235
	30	1.8	0.209	1	17.1	0.213
	45	1.8	0.212	2	16.3	0.203
				3	15.5	0.210
				4	14.8	0.218
				5	14.0	0.230

Effect of Flow. A comparison of the results of depolarization measurements on static and on flowing sewage samples indicates that the degree of depolarization is unaffected by flow (Table IV). The slight variations in the degree of depolarization measured on the flowing samples results from the settling and mixing of the solids in the suspension as it flows from the upper reservoir of the gravity flow system into the test section.

Discussion

The depolarization method has been shown to be feasible for measuring suspended solid concentrations in the limited number of sewage samples examined. Suspended solids concentrations that range from a few parts per million to 5000 ppm by weight can be measured by use of the depolarization technique. The relationship between the degree of depolarization and concentration of suspended solids in sewage samples appears unaffected by the size distribution of the particles, density variations, source of samples (plant effluent, plant influent, sludge 100% domestic, or 50% industrial), color variations, and organisms and aggregates generally found in sludge samples. It may be that the degree of depolarization of back-scattered polarized radiation is the result of an averaging or cancellation of effects.

Acknowledgment

The authors wish to acknowledge the many helpful discussions with William Hodes and the assistance of R. L. Buckingham of the Bernardsville sewerage plant and R. A. Rowe and Sam Capano of the Middlesex County sewage treatment plant in collecting the sewage samples. We especially wish to thank Allyn Richardson for his guidance throughout this investigation.

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Development and Validation of a Generalized Mechanism for Photochemical Smog

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■ A detailed 81-step mechanism for the photooxidation kinetics of the propylene–NO_x–air system, based on consideration of the possible important reactions which might be occurring, is presented. From the detailed mechanism is deduced a general 15-step mechanism for photochemical smog formation. The flexibility of this mechanism lies in adjustable rate constants and stoichiometric coefficients, which are chosen according to the particular hydrocarbon and initial reactant ratios. The general mechanism is validated with smog chamber data on propylene, isobutylene, *n*-butane, and a mixture of propylene and *n*-butane. The general mechanism is also shown to simulate accurately the effect of CO on smog chamber photooxidation kinetics as well as the inhibitory effect of high initial concentrations of nitric oxide on the maximum concentration of ozone attained.

The formation of photochemical smog occurs by a complex series of reactions which is still not thoroughly understood. In recent years several reviews of atmospheric chemistry have appeared (Leighton, 1961; Wayne, 1962; Altshuller and Bufalini, 1965, 1971; Stephens, 1966; Haagen-Smit and Wayne, 1967; Johnston et al., 1970), and a number of kinetic mechanisms for photochemical smog have been proposed (Eschenroeder, 1969; Friedlander and Seinfeld, 1969; Westberg and Cohen, 1969; Behar, 1970; Wayne et al., 1970). In each case only limited success was achieved in matching predicted concentration-time behavior from the mechanism with experimental smog chamber data. It is clear, however, that a detailed understanding of the photochemical smog system will only be achieved by a combined study of smog chamber data and theoretical mechanisms.

In addition to elucidating the nature of the photochemical smog system, a kinetic mechanism will be a necessary component of an atmospheric simulation model, such as for the Los Angeles basin. Such urban atmospheric models, capable of simulating chemical reaction as well as convection and diffusion, will play an important role in assessing the effect of various emission control strategies on air quality. A kinetic mechanism for use in an atmospheric simulation model must obey some additional requirements. First, since a polluted urban atmosphere typically contains upward of 100 hydrocarbon species, the mechanism should be general enough to predict the behavior of a complex mixture of hydrocarbons. Second, since an atmospheric simulation model may consist of a set of partial differential equations, the kinetic mechanism must be as compact as possible to avoid excessive computing times in the numerical integration of the model.

Our objective in this paper is, thus, twofold. First, as a fundamental study of the photochemical smog reactions for a typical hydrocarbon species, we will formulate a detailed kinetic mechanism for the photooxidation of propylene in the presence of air, oxides of nitrogen, carbon monoxide, and water. Propylene was chosen because it has been widely studied in smog chambers and it exhibits behavior similar to the complex hydrocarbon mixture present in smog. The mechanism is deduced from a systematic analysis of the important possible reactions that could be occurring. Second, for use with an atmospheric simulation model, we will formulate a compact mechanism that has the flexibility of representing the behavior of a varied mixture of hydrocarbons. Both the detailed and the simplified mechanisms are integrated numeri-

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Table I. Reactions in the NO_x–O_2–CO–H_2O System

No.	Reaction	Rate constant	Ref.
1	$NO_2 + h\nu \longrightarrow NO + O$	$0.37\ min^{-1}$[a,d]	
2	$O + O_2 + M \longrightarrow O_3 + M$	$2.2 \times 10^{-5}\ ppm^{-2}\ min^{-1}$ $2.0 \times 10^{6}\ min^{-1}$[b]	Kaufman and Kelso (1967)
3	$O_3 + NO \longrightarrow NO_2 + O_2$	$22.5 \pm 2\ ppm^{-1}\ min^{-1}$ 21.8	Clyne et al. (1964)
4	$O_3 + NO_2 \longrightarrow NO_3 + O_2$	$0.049\ ppm^{-1}\ min^{-1}$	Ford et al. (1957)
5	$NO_3 + NO_2 \longrightarrow N_2O_5$	$858\ ppm^{-1}\ min^{-1}$	Altshuller and Bufalini (1965)
6	$N_2O_5 \longrightarrow NO_3 + NO_2$	$2.76\ min^{-1}$	Altshuller and Bufalini (1965)
7	$N_2O_5 + H_2O \longrightarrow 2\ HNO_3$	$0.75\ min^{-1}$[b]	
8	$NO_3 + NO_2 \longrightarrow NO + O_2 + NO_2$	$0.49\ ppm^{-1}\ min^{-1}$	Johnston et al. (1970)
9	$O + NO_2 \longrightarrow O_2 + NO$	$5150\ ppm^{-1}\ min^{-1}$	Altshuller and Bufalini (1965)
10	$NO_3 + NO \longrightarrow 2\ NO_2$	$1.40 \times 10^{5}\ ppm^{-1}\ min^{-1}$	Johnston et al. (1970)
11	$NO + NO_2 + H_2O \longrightarrow 2\ HNO_2$	$0.001\ ppm^{-1}\ min^{-1}$[c]	
12	$HNO_2 + h\nu \longrightarrow NO + OH\cdot$	$0.01\ min^{-1}$[a]	
13	$CO + OH\cdot \longrightarrow CO_2 + H\cdot$	$196\ ppm^{-1}\ min^{-1}$	Baulch et al. (1968)
14	$H\cdot + O_2 + M \longrightarrow HO_2\cdot + M$	very fast	
15	$HO_2\cdot + NO \longrightarrow NO_2 + OH\cdot$	$30\ ppm^{-1}\ min^{-1}$	Johnston et al. (1970)
16	$HO_2\cdot + NO_2 \longrightarrow HNO_2 + O_2$	$0.001\ ppm^{-1}\ min^{-1}$	
17	$OH\cdot + NO_2 + M \longrightarrow HNO_3 + M$	$1470\ ppm^{-1}\ min^{-1}$[c]	Johnston et al. (1970)
18	$OH\cdot + NO \longrightarrow HONO$	$10^{4}\ ppm^{-1}\ min^{-1}$	
19	$HO_2\cdot + HO_2\cdot \longrightarrow H_2O_2 + O_2$	$70\ ppm^{-1}\ min^{-1}$	

[a] Depends on the light intensity. The value shown is that used in the validation studies. [b] Pseudo-first-order value. [c] Pseudo-second-order value. [d] If no reference is cited, the values in column 2 were estimated by the authors.

cally and their predictions compared to available smog chamber data.

Rate constants for each of the possible reactions in smog formation are, unfortunately, not available. In fact, only for some of the more widely studied reactions are there rate constant values which have been measured. The flexibility in a proposed kinetic mechanism lies, therefore, in the adjustment of rate constants which have not been measured experimentally. We use this procedure in attempting to match mechanism predictions and experimental data as closely as possible.

We will not consider the role of oxides of sulfur or the generation of photochemical aerosols in this work. These aspects remain as topics of current investigation.

Detailed Propylene Mechanism

We now present a detailed kinetic mechanism for the photooxidation of propylene in the presence of air, NO, NO_2, CO, and H_2O. We have divided the reactions according to classes.

Reactions in the NO_x–O_2–CO–H_2O System. Table I presents the reactions in this class that are most important. Reactions 1–3 are the principal inorganic reactions in smog formation. However, the other reactions in Table I are important to describe some secondary effects. As the concentration of NO decreases, as a result of the overall oxidation of NO to NO_2 in the smog system, Reaction 4, even though much slower than 3, will convert small quantities of NO_2 to NO_3 in the latter stages of the reaction. NO_3 can then react with either NO_2 or NO (Reactions 5, 8, and 10), with rates depending on the relative abundance of NO_2 and NO, to form N_2O_5 or regenerate NO_2 and small amounts of NO. N_2O_5 can decompose (Reaction 6) or hydrolyze to nitric acid (Reaction 7). Reaction 7 can account for the formation of HNO_3 on the walls of smog chambers, often cited as the reason for the inability to obtain a nitrogen balance on the products in smog chambers, and also for formation of HNO_3 vapor in the atmosphere, which might eventually become incorporated in atmospheric aerosols in which high yields of nitrate products have been observed (Gay and Bufalini, 1969; Campion and Black, 1969; Hidy and Friedlander, 1970).

Recent smog chamber experiments have indicated that $OH\cdot$ radicals play a central role in photochemical smog. Reactions 11 and 12, although long recognized (Leighton, 1961), have only recently been suggested as a possible important source of $OH\cdot$ radicals in the smog system (Stedman et al., 1970). The $OH\cdot$ radical is a highly reactive species capable of reaction with hydrocarbons, CO, and aldehydes. CO, until recently, was ignored as a possible participant in the photochemical smog system because of its assumed low reactivity. However, a newly revised estimate of the activation energy of Reaction 13 indicates that the rate constant for this reaction is high enough to make it a possibly important reaction (Baulch et al., 1968; Dixon-Lewis et al., 1966). In addition, recent experiments reported by Holmes (1970), Westberg et al., (1971), and Stedman et al. (1970) have shown that CO accelerates the conversion of NO to NO_2 over the rate in the absence of CO. Also, when H_2O and CO are both present, the rate of conversion of NO to NO_2 is increased over that with only CO present. Although the experiments reported by Stedman et al. involved CO concentrations higher than those normally found in the atmosphere, recent unpublished work by Holmes (1971) has shown an accelerating effect of CO at concentrations as low as 10 ppm. Reaction 14 is very rapid so that 13 and 14 can be combined as

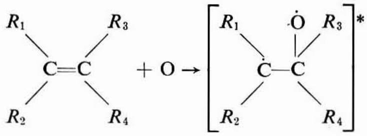
$$CO + OH\cdot \xrightarrow{O_2} CO_2 + HO_2\cdot$$

The net effect of Reactions 13–15 is to convert NO to NO_2 with no net loss of $OH\cdot$ radicals.

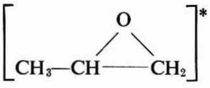
An extremely important conclusion arises from examination of Reactions 11–15, namely, that it is possible to convert NO to NO_2 in significant quantities in the absence of hydrocarbons (Wilson, 1971). Both CO and H_2O are required for this conversion in the absence of hydrocarbons. If H_2O is not present, HNO_2 cannot form, and the necessary $OH\cdot$ radicals are not produced. Finally, HNO_2 and HNO_3 can be formed from $OH\cdot$ and $HO_2\cdot$ reactions as in Reactions 16–18, and H_2O_2 from the HO_2–HO_2 recombination Reaction 19.

Oxidation of Propylene by O and O_3. The addition of a hydrocarbon such as propylene to the irradiated NO–NO_2–air system results in three well-known phenomena: the disappearance of hydrocarbon, a rapid and almost quantitative conversion of NO to NO_2, and the accumulation of a significant amount of O_3. Reactions 1–3 represent a cycle in which O_3 and NO are produced and consumed in equal quantities. If NO is converted to NO_2 by a path other than 3, for example, Reactions 13–15, then NO_2 and O_3 accumulate. In explaining the role of hydrocarbons in the conversion of NO to NO_2, we observed that a key step is the reaction between hydrocarbons and O and O_3. The reactions of C_3H_6 and O and O_3 and the subsequent reactions involving the free radicals formed are presented in Table II.

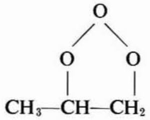
The elementary step of the olefin–atomic oxygen reaction is usually conceived as the addition of O to the double bond to form an activated complex,



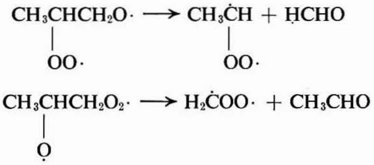
Cvetanovic (1956) found that the major products of the C_3H_6–O reaction in the absence of O_2 were propylene oxide, propionaldehyde, acetone, and CO. In a study of the C_3H_6–NO_x system, however, Altshuller et al. (1967) found formaldehyde and acetaldehyde as major products. Thus, one expects fragmentation rather than stabilization of the activated complex, resulting in Reactions 20 and 21, with 20 being the more likely. Altshuller et al. (1967) have suggested a third possibility, Reaction 22, involving an epoxide intermediate,



which would then react with O_2 rapidly to form a molozonide intermediate,



The formation of such an intermediate is also a likely initial step in Reactions 23 and 24. In Reactions 22–24, either of the O—O bonds of the molozonide intermediate may cleave to form unstable biradicals,



$$\underset{\textstyle OO\cdot}{CH_3CHCH_2O\cdot} \longrightarrow \underset{\textstyle OO\cdot}{CH_3\dot{C}H} + HCHO$$

$$\underset{\textstyle O\cdot}{CH_3CHCH_2O_2\cdot} \longrightarrow H_2\dot{C}OO\cdot + CH_3CHO$$

The biradical products can also be written as zwitterions, $CH_3\overset{+}{C}HOO^-$ and $H_2\overset{+}{C}OO^-$. The zwitterions can undergo a variety of decomposition reactions yielding methane, hydrogen, methanol, methyl formate, formic acid, and ketene (Leighton, 1961). Since each of these does not appear significantly as products in the C_3H_6–NO_x system, we have not included these reactions. The branching steps 25 and 28 have been included as representing a likely decomposition. Also the zwitterions can react with NO and NO_2 as in Reactions 26, 27, 29, and 30.

The $CH_3\cdot$ and $C_2H_5\cdot$ radicals formed in Reactions 20 and 21 readily add O_2 in Reactions 31 and 35 to form peroxymethyl and peroxyethyl radicals. The peroxyalkyl radicals then oxi-

Table II. Oxidation of Propylene by O and O_3

No.	Reaction	Rate constant	Ref.
20	$C_3H_6 + O \longrightarrow CH_3CH_2\cdot + CHO\cdot$	2925 ppm^{-1} min^{-1}	Range of values 3675–4410 ppm^{-1} min^{-1} Johnston et al. (1970)
21	$C_3H_6 + O \longrightarrow CH_3\cdot + CH_3\dot{C}O$	500 ppm^{-1} min^{-1}	
22	$C_3H_6 + O \xrightarrow{O_2} C_2H_4O_2 + HCHO$	250 ppm^{-1} min^{-1}	
23	$C_3H_6 + O_3 \longrightarrow C_2H_4O_2 + HCHO$	0.007 ppm^{-1} min^{-1}	Range of values 0.0091–0.0165 ppm^{-1} min^{-1} Johnston et al. (1970)
24	$C_3H_6 + O_3 \longrightarrow CH_3CHO + CH_2O_2$	0.007 ppm^{-1} min^{-1}	
25	$C_2H_4O_2 \longrightarrow CH_3O\cdot + CHO\cdot$	0.3 min^{-1}	
26	$C_2H_4O_2 + NO \longrightarrow CH_3CHO + NO_2$	3.0 ppm^{-1} min^{-1}	
27	$C_2H_4O_2 + NO_2 \longrightarrow CH_3CHO + NO_3$	0.1 ppm^{-1} min^{-1}	
28	$CH_2O_2 \longrightarrow OH\cdot + CHO\cdot$	0.3 min^{-1}	
29	$CH_2O_2 + NO \longrightarrow HCHO + NO_2$	3.0 ppm^{-1} min^{-1}	
30	$CH_2O_2 + NO_2 \longrightarrow HCHO + NO_3$	0.1 ppm^{-1} min^{-1}	
31	$CH_3\cdot + O_2 \longrightarrow CH_3O_2\cdot$	3×10^6 min^{-1}[a]	
32	$CH_3O_2\cdot + NO \longrightarrow CH_3O\cdot + NO_2$	6 ppm^{-1} min^{-1}	
33	$CH_3O\cdot + O_2 \longrightarrow HCHO + HO_2\cdot$	5.15×10^4 min^{-1}[a]	
34	$CH_3O\cdot + NO_2 + M \longrightarrow CH_3NO_3 + M$	16.2 ppm^{-1} min^{-1}[b]	
35	$CH_3CH_2\cdot + O_2 \longrightarrow CH_3CH_2O_2\cdot$	3×10^6 min^{-1}[a]	
36	$CH_3CH_2O_2\cdot + NO \longrightarrow NO_2 + CH_3CH_2O\cdot$	6 ppm^{-1} min^{-1}	
37	$CH_3CH_2O\cdot + O_2 \longrightarrow CH_3CHO + HO_2.$	5.15×10^4 min^{-1}[a]	
38	$CH_3CH_2O\cdot + NO_2 + M \longrightarrow CH_3CH_2NO_3 + M$	16.2 ppm^{-1} min^{-1}[b]	

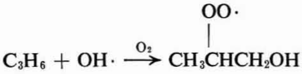
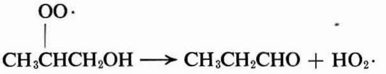
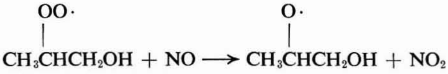
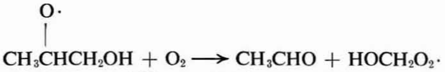
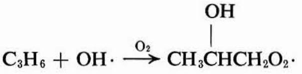
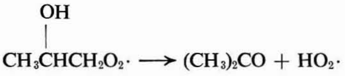
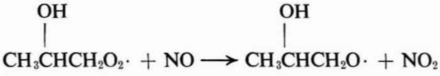
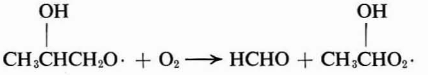
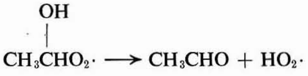
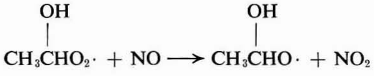
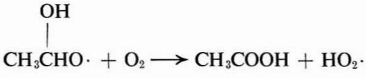
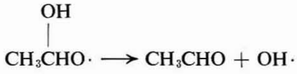
[a] Pseudo-first-order value. [b] Pseudo-second-order value.

dize NO to NO_2 (Reactions 32 and 36). These reactions are more likely than addition to NO to form the alkyl pernitrites, which are not observed as products in smog chambers. Another likely collision between peroxyalkyl radicals and O_2, postulated to form O_3, is endothermic and has not been included (Leighton, 1961).

Alkoxyl radicals which result from the oxidation of NO to NO_2 by peroxyalkyl radicals (Reactions 32 and 36), undergo reactions with O_2 (Reactions 33 and 37) in which hydrogen is abstracted. Alkoxyl radicals will also react with NO_2 forming alkyl nitrates (Reactions 34 and 38) which are observed as minor products in smog chambers.

Reaction of Propylene and OH·. Hydroxyl radicals will react significantly with olefins, as well as with aromatic and saturated hydrocarbons, especially the larger and branched members of the series. Two possible mechanisms for the C_3H_6–OH· reaction are presented in Table III. Because references are not generally available we have not included that column. The two mechanisms differ depending on the location of addition of OH· to the C_3H_6 molecule. The first mechanism (Reactions 39–45) is a result of addition of OH· to the number one carbon atom of C_3H_6. The peroxy radical formed in Reaction 39 can decompose (Reaction 40) or oxidize NO to NO_2 (Reaction 41). Reaction 40 might proceed by formation of a

Table III. Reaction of Propylene and OH·

No.	Reaction	Rate constant
	Mechanism 1	
39	 $C_3H_6 + OH\cdot \xrightarrow{O_2} CH_3\overset{OO\cdot}{C}HCH_2OH$	1.5×10^4 ppm^{-1} min^{-1}
40	 $CH_3\overset{OO\cdot}{C}HCH_2OH \longrightarrow CH_3CH_2CHO + HO_2\cdot$	0.001 min^{-1}
41	 $CH_3\overset{OO\cdot}{C}HCH_2OH + NO \longrightarrow CH_3\overset{O\cdot}{C}HCH_2OH + NO_2$	6 ppm^{-1} min^{-1}
42	 $CH_3\overset{O\cdot}{C}HCH_2OH + O_2 \longrightarrow CH_3CHO + HOCH_2O_2\cdot$	3000 $min^{-1\,a}$
43	$HOCH_2O_2\cdot + NO \longrightarrow HOCH_2O\cdot + NO_2$	4 ppm^{-1} min^{-1}
44	$HOCH_2O_2\cdot \longrightarrow HCHO + HO_2\cdot$	0.001 min^{-1}
45	$HOCH_2O\cdot \longrightarrow HCHO + OH\cdot$	3000 min^{-1}
	Mechanism 2	
46	 $C_3H_6 + OH\cdot \xrightarrow{O_2} CH_3\overset{OH}{C}HCH_2O_2\cdot$	10^4 ppm^{-1} min^{-1}
47	 $CH_3\overset{OH}{C}HCH_2O_2\cdot \longrightarrow (CH_3)_2CO + HO_2\cdot$	0.001 min^{-1}
48	 $CH_3\overset{OH}{C}HCH_2O_2\cdot + NO \longrightarrow CH_3\overset{OH}{C}HCH_2O\cdot + NO_2$	6 ppm^{-1} min^{-1}
49	 $CH_3\overset{OH}{C}HCH_2O\cdot + O_2 \longrightarrow HCHO + CH_3\overset{OH}{C}HO_2\cdot$	3000 $min^{-1\,a}$
50	 $CH_3\overset{OH}{C}HO_2\cdot \longrightarrow CH_3CHO + HO_2\cdot$	0.001 min^{-1}
51	 $CH_3\overset{OH}{C}HO_2\cdot + NO \longrightarrow CH_3\overset{OH}{C}HO\cdot + NO_2$	6 ppm^{-1} min^{-1}
52	 $CH_3\overset{OH}{C}HO\cdot + O_2 \longrightarrow CH_3COOH + HO_2\cdot$	1000 $min^{-1\,a}$
53	 $CH_3\overset{OH}{C}HO\cdot \longrightarrow CH_3CHO + OH\cdot$	2000 min^{-1}
	Mechanism 3	
54	$C_3H_6 + OH\cdot \longrightarrow CH_2{=}CHCH_2\cdot + H_2O$	5000 ppm^{-1} min^{-1}

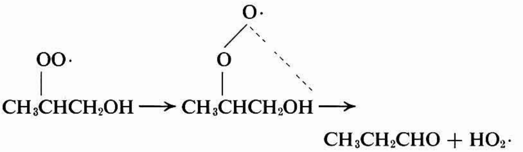
[a] Pseudo-first-order value.

Table IV. The Formation and Destruction of Pernitrates

No.	Reaction	Rate constant	Ref.
55	$CH_3\dot{C}O + O_2 \longrightarrow CH_3(CO)O_2\cdot$	3×10^{6} min^{-1}[a]	
56	$CH_3(CO)O_2\cdot + NO \longrightarrow CH_3(CO)O\cdot + NO_2$	8 ppm^{-1} min^{-1}	
57	$CH_3(CO)O\cdot + NO \longrightarrow CH_3\dot{C}O + NO_2$	0.1 ppm^{-1} min^{-1}	
58	$CH_3(CO)O_2\cdot + NO_2 \longrightarrow CH_3(CO)O_2NO_2$	2.0 ppm^{-1} min^{-1}	
59	$CH_3(CO)O\cdot \longrightarrow CH_3\cdot + CO_2$	0.0001 min^{-1}	
60	$CH_3(CO)O_2NO_2 + NO \longrightarrow CH_3(CO)O\cdot + 2\ NO_2$	0.16 ppm^{-1} min^{-1}	Schuck and Stephens (1969)
61	$CH_3(CO)O_2NO_2 + h\nu \longrightarrow CH_3(CO)O\cdot + NO_3$	0.01 min^{-1}[b]	
62	$CH_3O_2\cdot + NO_2 \longrightarrow CH_3O_2NO_2$	0.001 ppm^{-1} min^{-1}	
63	$CH_3O_2NO_2 + NO \longrightarrow CH_3O\cdot + 2\ NO_2$	0.1 ppm^{-1} min^{-1}	
64	$CH_3O_2NO_2 + h\nu \longrightarrow CH_3O\cdot + NO_3$	0.05 min^{-1}[b]	
65	$CH_3CH_2O_2\cdot + NO_2 \longrightarrow CH_3CH_2O_2NO_2$	0.001 ppm^{-1} min^{-1}	
66	$CH_3CH_2O_2NO_2 + NO \longrightarrow CH_3CH_2O\cdot + 2\ NO_2$	0.1 ppm^{-1} min^{-1}	
67	$CH_3CH_2O_2NO_2 + h\nu \longrightarrow CH_3CH_2O\cdot + NO_3$	0.05 min^{-1}[b]	

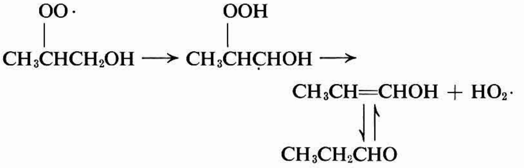
[a] Pseudo-first-order value. [b] Depends on the light intensity. The value shown is that used in the validation studies.

six-membered ring intermediate,



$$CH_3\overset{OO\cdot}{\overset{|}{C}}HCH_2OH \longrightarrow CH_3\overset{O\cdot}{\overset{O}{\overset{|}{C}}}HCH_2OH \longrightarrow CH_3CH_2CHO + HO_2\cdot$$

Alternatively, a secondary hydrogen could be abstracted, and $HO_2\cdot$ could split off forming the enol tautomer of propionaldehyde,



$$CH_3\overset{OO\cdot}{\overset{|}{C}}HCH_2OH \longrightarrow CH_3\overset{OOH}{\overset{|}{C}}H\underset{\cdot}{C}HOH \longrightarrow CH_3CH{=}CHOH + HO_2\cdot \rightleftharpoons CH_3CH_2CHO$$

Since not much propionaldehyde is observed as a product in propylene smog chamber experiments, Reaction 41 is probably more important than 40. The radical formed in 41 could decompose into acetaldehyde and a radical $HOCH_2\cdot$, which probably reacts readily with O_2 to yield $HOCH_2O_2\cdot$ (Reaction 42). This radical can react with NO to yield NO_2 (Reaction 43), or simply decompose to give formaldehyde and a hydroperoxyl radical.

The second mechanism (Reactions 46–53) results if the $OH\cdot$ adds to the number two carbon atom of C_3H_6. The steps are analogous to Reactions 39–45. Another likely possibility, Reaction 54, is the abstraction of a hydrogen atom from the number three carbon atom to form an allyl radical and water. The allyl radical has two equivalent resonance bond structures,

$$\cdot CH_2{-}CH{=}CH_2 \longleftrightarrow CH_2{=}CH{-}CH_2\cdot$$

and a resonance stabilization of 19 kcal/mol relative to $CH_3\cdot$ (Huyser, 1970). Employing bond energies at 298°K, $OH\cdot$ attack on the number one carbon atom

$$C_3H_6 + OH\cdot \longrightarrow CH_3\dot{C}HCH_2OH$$

has a $\Delta H = -22.3$ kcal/mol, compared to $\Delta H = -30.9$ kcal/mol for Reaction 54. In addition, 54 has a greater overall increase in entropy. Once formed, the allyl radical would probably react with O_2.

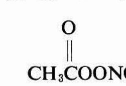
Peroxyalkyl radicals might also react with C_3H_6. Leighton (1961) suggests a direct addition forming a peroxide radical which could then react with O_2 regenerating a peroxyalkyl radical. Leighton also suggests that the intermediate might break at the double bond, forming an aldehyde or ketone and an oxy radical. This reaction would not be expected to be as rapid as the corresponding reaction with $OH\cdot$.

Oxidation of Propylene by Singlet Molecular Oxygen. It has been suggested that singlet molecular oxygen might be involved in atmospheric oxidation reactions (Pitts et al., 1969). Ackerman et al. (1970) estimated the rate constant for the $^1\Delta$ form of O_2–tetramethylethylene reaction to be about $10^8\ M^{-1}\ \mathrm{sec}^{-1}$. For singlet oxygen attack on propylene, the initial addition product would be a hydroperoxide,

$$CH_3CH{=}CH_2 + {}^1O_2 \longrightarrow CH_2{=}CHCH_2OOH$$

However, Herron and Huie (1970) have concluded that the oxidation of olefins by singlet molecular oxygen is less important than the reaction with atomic oxygen. Because of this uncertainty we have chosen to omit reactions involving singlet oxygen.

Formation and Destruction of Pernitrates. Pernitrates, especially peroxyacylnitrates (PAN's), have been shown to form in substantial quantities in smog chambers. Pernitrates are of the form $RO OO NO_2$, where R is an acyl group in the case of PAN's. The most common pernitrate in the propylene–NO_x system is peroxyacetylnitrate,



$$CH_3\overset{\overset{O}{\|}}{C}OONO_2.$$

This product begins to accumulate only after the NO is nearly depleted. The series of reactions related to pernitrate formation is shown in Table IV.

The formation of peroxyacetyl radicals (Reaction 55) is the initial step in the pernitrate chain reactions. The principal PAN-forming step is shown in Reaction 58. The delayed formation of PAN can be explained in at least two ways. The peroxyacetyl radical can participate in oxidation of NO to NO_2 (Reaction 56) when there is a substantial quantity of NO in the system. Reaction 56 would then compete with 58 until the NO disappears. The acetate radical formed in 56 can react further with NO, as in Reaction 57, or decompose into a methyl radical and CO_2 as in 59 (Leighton, 1961). The second explanation for the delayed appearance of PAN is its reaction

Table V. Aldehyde Decomposition Reactions

No.	Reaction	Rate constant	Ref.
68	$HCHO + h\nu \longrightarrow H\cdot + CHO\cdot$	3.3×10^{-5} min^{-1a}	Leighton (1961)
69	$HCHO + O \longrightarrow OH\cdot + CHO\cdot$	220 ppm^{-1} min^{-1}	Herron and Penzhorn (1969)
70	$HCHO + O_3 \longrightarrow OH\cdot + CHO\cdot + O_2$	2.45×10^{-5} ppm^{-1} min^{-1}	Leighton (1961)
71	$HCHO + OH\cdot \longrightarrow CHO\cdot + H_2O$	2.5×10^4 ppm^{-1} min^{-1}	
72	$CH_3CHO + h\nu \longrightarrow CH_3\cdot + CHO\cdot$	0.0036 min^{-1a}	Leighton (1961)
73	$CH_3CHO + O \longrightarrow CH_3\dot{C}O + OH\cdot$	294 ppm^{-1} min^{-1}	Leighton (1961)
74	$CH_3CHO + O_3 \longrightarrow CH_3\dot{C}O + OH\cdot + O_2$	0.0005 ppm^{-1} min^{-1}	Leighton (1961)
75	$CH_3CHO + OH\cdot \longrightarrow CH_3\dot{C}O + H_2O$	2.5×10^4 ppm^{-1} min^{-1}	

[a] Depends on the light intensity. The value shown is that used in the validation studies.

with NO, Reaction 60 (Schuck and Stephens, 1969). The rate constant for this reaction is high enough to prevent PAN from accumulating until the NO is almost completely converted to NO_2. Interestingly, Reaction 60 shows another means of converting NO to NO_2. The photolysis of PAN in Reaction 61 is also a possibility. Pitts (1970) has also recently reported that PAN reacts with water forming singlet oxygen as one of the products in a highly exothermic reaction. This step has not been included.

Although methyl and ethyl pernitrates are not reported as products in the propylene–NO_x system, formation of trace amounts can be described by Reactions 62–67.

Aldehyde Decomposition. It has been shown how aldehydes, especially HCHO and CH_3CHO, can be formed when propylene is oxidized. Reactions involving aldehyde decomposition are shown in Table V. Both HCHO and CH_3CHO undergo photodecomposition (Reactions 68 and 72). Oxygen atoms react with the aldehydes abstracting a hydrogen atom to form $OH\cdot$ and the corresponding acyl radical (Reactions 69 and 73). O_3 can also abstract hydrogen as in 70 and 74, and $OH\cdot$ reacts with aldehydes to give an acyl radical and water, as in 71 and 75.

Other Radical Reactions. Table VI summarizes some radical reactions which may play secondary roles in photochemical smog. We note that in smog chambers initially free of CO, small amounts have been observed to form. This is probably due primarily to Reaction 76. The possible peroxyformyl product of 76 is unstable and has not been observed in smog chambers.

Validation of the Detailed Mechanism

The validation consists of comparing the concentration-time results from the mechanism to those of an experimental run for the same initial conditions. The fit of the mechanism to the data is achieved by varying rate constants over ranges consistent with the expected order of magnitude for each reaction.

The experimental data used for propylene photooxidation were obtained from the Gulf Research Co. (Strickler, 1970). A comparison of the experimental data (solid line) and the detailed mechanism (dashed line) are presented in Figure 1 for the validation rate constants in Tables I–VI. The mechanism curves were generated by numerical integration of the rate equations for all of the species not in a pseudosteady state (all the nonradical species). By use of the numerical integration routine of Gear (1971), $3^1/_2$ hr of reaction time were simulated in 25 sec on an IBM 360/75.

Because of the large number of unknown rate constants, it is possible to fit the data in Figure 1 closely. Thus, we will not present a large series of comparisons of model predictions vs. data for the detailed mechanism. Perhaps the most important aspect of a detailed mechanism is to aid us in the formulation of a simplified version with far fewer steps and rate constants that gives comparable concentration-time predictions.

A Simplified Mechanism

As we have noted, in an urban atmospheric model it will be necessary to have a kinetic mechanism which not only describes the kinetics accurately over the concentration range of interest but also involves as few steps as possible to minimize computation time. Also, the mechanism should permit simulation of the behavior of a complex hydrocarbon mixture such as exists in the atmosphere. Therefore, it is necessary to achieve a balance between chemical detail and flexibility. In this section we propose a simplified mechanism for photochemical smog.

Simulations carried out with the detailed mechanism reveal that certain reactions are much more important than others. These conclusions are based on the results obtained by systematically varying rate constants and observing the changes in the concentration-time behavior. In addition, inspection of the mechanism shows that many reactions are of the same general type. For example, many free radical reactions can be classed according to the radical type. Thus, to obtain a simplified mechanism we should remove reactions of lesser importance,

Table VI. Other Radical Reactions

No.	Reaction	Rate constant
76	$CHO\cdot + O_2 \longrightarrow CO + HO_2\cdot$	5.15×10^5 min^{-1a}
77	$CHO\cdot + OH\cdot \longrightarrow CO + H_2O$	3.6×10^4 ppm^{-1} min^{-1}
78	$CH_3O\cdot + CH_3O\cdot \longrightarrow HCHO + CH_3OH$	3.6×10^5 ppm^{-1} min^{-1}
79	$CH_3CH_2O\cdot + CH_3CH_2O\cdot \longrightarrow CH_3CHO + CH_3CH_2OH$	3.6×10^5 ppm^{-1} min^{-1}
80	$CH_3(CO)O\cdot + CH_3O\cdot \longrightarrow HCHO + CH_3COOH$	3.6×10^5 ppm^{-1} min^{-1}
81	$CH_3(CO)O\cdot + CH_3CH_2O\cdot \longrightarrow CH_3CHO + CH_3COOH$	3.6×10^5 ppm^{-1} min^{-1}

[a] Pseudo-first-order value.

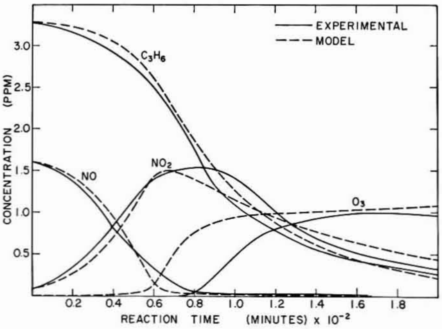


Figure 1. Comparison of experimental smog chamber concentrations and concentrations predicted by the detailed propylene mechanism

Data for propylene from Gulf Research Co.

combine reactions of similar type, and generalize the reactions involving hydrocarbons. The objective is a compact mechanism capable of accurate description of smog chamber results with different hydrocarbons by adjustment of flexible parameters.

To develop the mechanism let us consider the reaction classes discussed in relation to the propylene mechanism. First, in the NO_x–O_2–CO–H_2O system we will choose to include the following steps: Reactions 1–4, formation of nitric acid, formation and photolysis of nitrous acid, and reaction of CO and OH· radicals. We retain these features to be able to include the effect of water and CO in the simplified mechanism. Thus, the first 10 steps of the simplified mechanism are:

$$NO_2 + h\nu \xrightarrow{1'} NO + O$$

$$O + O_2 + M \xrightarrow{2'} O_3 + M$$

$$O_3 + NO \xrightarrow{3'} NO_2 + O_2$$

$$O_3 + NO_2 \xrightarrow{4'} NO_3 + O_2$$

$$NO_3 + NO_2 \xrightarrow[H_2O]{5'} 2\ HNO_3$$

$$NO + NO_2 \xrightarrow[H_2O]{6'} 2\ HNO_2$$

$$HNO_2 + h\nu \xrightarrow{7'} OH\cdot + NO$$

$$CO + OH\cdot \xrightarrow[O_2]{8'} CO_2 + HO_2\cdot$$

$$HO_2\cdot + NO \xrightarrow{9'} NO_2 + OH\cdot$$

$$HO_2\cdot + NO_2 \xrightarrow{10'} HNO_2 + O_2$$

Note that we have combined Reactions 5–7 as 5′. The rate constant of 5′ will be that of the rate-determining step 5. In view of the possible importance of HNO_2 as a source of OH· when water is present, Reactions 6′ and 7′ have been retained. In a dry system, Reactions 5′ and 6′ will not be included. Reaction 10′ is included to provide a path for $HO_2\cdot$ consumption when NO has been depleted.

Next we consider reactions involving hydrocarbons. We introduce a general hydrocarbon species, called HC, which may be taken to represent a single hydrocarbon or a complex mixture of hydrocarbons. If we neglect aldehydes, hydrocarbons present in smog can be divided according to olefins, aromatics, and paraffins. We will consider hydrocarbon attack by O, O_3, and OH·.

In the case of O attack on olefins the result is the production of two free radicals. For example, the products of O attack on three common olefins are:

ethylene	$CH_3\cdot + H\dot{C}O$
propylene	$CH_3\cdot + CH_3\dot{C}O$ or $C_2H_5\cdot + H\dot{C}O$
isobutylene	$(CH_3)_2CH\cdot + H\dot{C}O$ or $C_2H_5\cdot + CH_3\dot{C}O$

Oxygen atom attack on aromatics in some cases can be as fast as for olefins (Leighton, 1961). The products of the initial aromatic–O reaction are not well-known. Among the products that have been observed from the reaction chain initiated by O attack on aromatics are peroxides, acids, and alcohols (Eventova and Prytkova, 1960; Kemula and Grabowska, 1960). The reaction with paraffins is much slower, the most probable step being hydrogen abstraction (Leighton, 1961),

$$RH + O \longrightarrow R\cdot + OH\cdot$$

Thus, the result of O attack on hydrocarbons is branching, generally to form two free radicals. We will write this step in the general mechanism as

$$HC + O \xrightarrow{11'} \alpha RO_2\cdot$$

where $RO_2\cdot$ is a lumped radical species (in general, a peroxyalkyl or peroxyacyl radical) and α is the stoichiometric coefficient—i.e., the number of such radicals produced by this reaction.

Consider now O_3 attack on hydrocarbons. For O_3 attack on olefins the initial products are an aldehyde and a zwitterion. The number of free radicals formed depends on the subsequent zwitterion reaction. For three common olefins, the result of O_3 attack is:

ethylene	$HCHO + CH_2O_2$
propylene	$HCHO + C_2H_4O_2$ or $CH_3CHO + CH_2O_2$
isobutylene	$HCHO + (CH_3)_2CO_2$ or $(CH_3)_2CO + CH_2O_2$

The reactions between O_3 and alkanes and aromatics are slow and can probably be neglected. Summarizing the general hydrocarbon–O_3 reaction, we can write the general step

$$HC + O_3 \xrightarrow{12'} \beta RO_2\cdot + \gamma RCHO$$

where β and γ are stoichiometric coefficients to be determined by the particular hydrocarbon mix.

Next we consider the general hydrocarbon–OH· reaction. We have proposed three possible mechanisms for the propylene–OH· reaction. In the first two, aldehydes and free radicals are the products, and in the third, the chain reaction is terminated by allyl radical and water formation.

The alkane–OH· reaction has been recently considered by Greiner (1970). The principal products from the hydrogen abstraction are a free radical and water. We might also expect that the branched aromatic–OH· reaction would yield products similar to those of the alkane–OH· reaction.

Combining each of these possible steps we can propose the general hydrocarbon–OH· step,

$$HC + OH\cdot \xrightarrow{13'} \delta RO_2\cdot + \epsilon RCHO$$

where the stoichiometric coefficients δ and ϵ are determined by the hydrocarbon mix. Since aldehyde formation only occurs for olefins and possibly aromatics (Heuss and Glasson, 1968), ϵ will be less than one.

The remaining reactions in the simplified mechanism describe the oxidation of NO to NO_2 by peroxy radicals and the formation of PAN,

$$RO_2\cdot + NO \xrightarrow{14'} NO_2 + \theta OH\cdot$$

$$RO_2\cdot + NO_2 \xrightarrow{15'} \text{PAN}$$

It is important to note that if CO and H_2O are present we treat $HO_2\cdot$ and $RO_2\cdot$ as separate species. If CO and H_2O are not present, we consider only the single species $RO_2\cdot$, which includes $HO_2\cdot$ within it, since Reactions 5′–10′ are omitted. In that case, θ is the fractional product of $OH\cdot$ from Reaction 14′—i.e., the fraction of $HO_2\cdot$ in the total lumped radical species $RO_2\cdot$.

Many reactions have not been included, for example, the formation of organic nitrates (which can presumably be included in Reaction 15′), reactions involving PAN decomposition (of secondary importance), aldehyde decomposition (can be treated by adjustment of γ and ϵ) and radical-radical recombination (of secondary importance).

The simplified mechanism consists of Reactions 1′–15′ and includes the following species: NO, NO_2, O_3, HC, O, NO_3, $OH\cdot$, $HO_2\cdot$, $RO_2\cdot$, HNO_2, HNO_3, RCHO, PAN. Differential equations are required for the first four; steady-state relations are written for the next six, and the last three represent products.

Validation of the Simplified Mechanism

In the validation of the simplified mechanism we will consider smog chamber data for the following hydrocarbons:

- Propylene (Strickler, 1970; Wayne et al., 1969)
- Isobutylene in the presence and absence of CO (Westberg et al., 1971)
- *n*-Butane in the presence and absence of CO (Wilson, 1971)
- Propylene and *n*-butane (Wilson, 1971)

These experiments were selected to test the mechanism on both olefins and paraffins, on the effect of different initial reactant ratios, and on the effect of CO.

Let us first discuss the generalized stoichiometric coefficients in the mechanism. Of prime importance is α, the chain-branching factor in the HC–O reaction. In the early stages of reaction, the HC–O reaction is critical in determining the rate of oxidation of NO to NO_2. The peak O_3 level will depend on how much of the NO is oxidized before the hydrocarbon is consumed. We have found that α should, in some cases, not be taken as constant but rather as a function of the NO to HC ratio throughout the course of the reaction. Large NO to HC ratios apparently affect the chain length, and since α governs the chain length directly, it is convenient to reflect this by allowing α to depend on the NO to HC ratio as it changes with time. This dependence should follow the general behavior of a plot of peak O_3 concentration vs. initial NO to HC ratio.

The generalized coefficients δ ($RO_2\cdot$ from the HC–$OH\cdot$ reaction) and θ($OH\cdot$ from the $RO_2\cdot$–NO reaction) are important in simulating the effect of CO. Since $OH\cdot$ attacks both HC and CO and since the products of both reactions are radical species capable of oxidizing one NO to NO_2 ($HO_2\cdot$ in the former case and $RO_2\cdot$ in the latter), it is necessary that the number of $HO_2\cdot$ radicals formed in the CO–$OH\cdot$ reaction (always equal to one) be greater than the number of $RO_2\cdot$ radicals formed in the HC–$OH\cdot$ reaction in the presence of CO. If $\delta\theta > 1$, CO would effectively inhibit the rate of NO oxidation because CO would be scavenging $OH\cdot$ radicals from a reaction with HC capable of generating more radicals able to oxidize NO than the single $HO_2\cdot$ formed in the CO–$OH\cdot$ reaction. This can also be seen by examining the differential equation for NO. The terms governing the contribution to the NO oxidation rate from the HC–$OH\cdot$ and CO–$OH\cdot$ reaction both have the quantity $(1 - \delta\theta)$ in the denominator. If $\delta\theta > 1$, the sign of $d[NO]/dt$ will be positive rather than negative. Also, since the term governing the effect of CO has [CO] in the denominator, if $\delta\theta > 1$, CO will inhibit rather than accelerate the oxidation of NO.

Propylene Experiments. The propylene data used are shown in Figures 2 and 3. The data in Figure 2 are the same as in Figure 1 (Strickler, 1970). The data in Figure 3 have been presented by Wayne et al. (1970) from the California Air Resources Board. The photolysis rate for each experiment is $k_1 = 0.37\ \text{min}^{-1}$.

Both simulations, shown by the dashed curves, were made with the following rate constants:

$k_1' = 0.37$
$k_2' = 2.76 \times 10^6$
$k_3' = 21.8$
$k_4' = 0.006$
$k_5' = 0.1$
$k_6' = 0.0025$
$k_7' = 0.005$
$k_8' = 200$
$k_9' = 1800$
$k_{10}' = 10$
$k_{11}' = 5 \times 10^4$
$k_{12}' = 0.0075$
$k_{13}' = 1000$
$k_{14}' = 1800$
$k_{15}' = 10$

The initial conditions for Figures 2 and 3 are: $[C_3H_6]_0 = 3.29$, $[NO_2]_0 = 0.088$, $[NO]_0 = 1.612$ and $[C_3H_6]_0 = 1.0$, $[NO_2]_0 =$

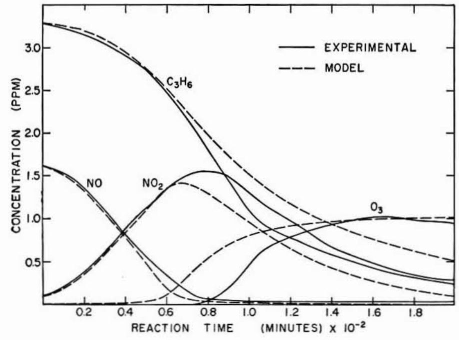


Figure 2. Comparison of experimental smog chamber concentrations and concentrations predicted by the simplified mechanism

Data for propylene from Gulf Research Co.

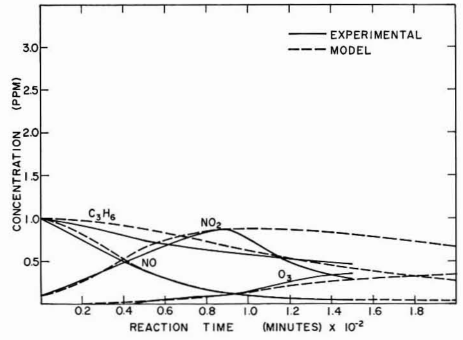


Figure 3. Comparison of experimental smog chamber concentrations and concentrations predicted by the simplified mechanism

Data for propylene from the California Air Resources Board

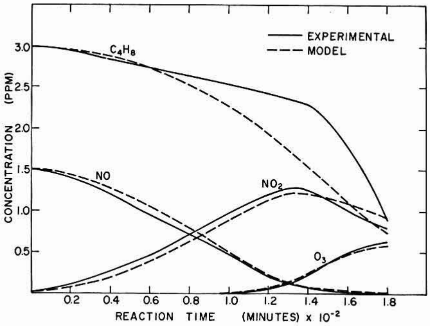


Figure 4. Comparison of experimental smog chamber concentrations and concentrations predicted by the simplified mechanism

Data for isobutylene from Westberg et al. (1971)
Initial concentration of carbon monoxide = 0 ppm

0.1, $[NO]_0 = 1.0$, respectively. Each 3-hr simulation was carried out in 3 sec by use of the routine of Gear (1971). Because of the generalized nature of the 15-step mechanism, the "rate constants" for the reactions are more a quantitative expression of the relative importance of classes of reactions than a reflection of the actual rate constants. Consequently, the rate constants for the 15-step mechanism are not identical to those in Tables I-VI, particularly k_{10}'–k_{15}'. This feature is a necessary, if undesirable, feature of a mechanism which sacrifices details of chemical reality for conciseness. Similarly, the stoichiometric coefficients must be viewed only qualitatively as true stoichiometric coefficients. Following the dependence of peak O_3 on the NO to HC ratio for ratios from 0.25 to 1 reported by Altshuller et al. (1967), α was determined as

$$\alpha = \begin{cases} 2.45 & [NO]/[HC] < 0.25 \\ 9.8\,\dfrac{[NO]}{[HC]} & 0.25 < [NO]/[HC] < 1 \end{cases}$$

For $[NO]/[HC] < 0.25$, $\alpha = 2.45$ ensures that a minimum number of free radicals are generated, even when [NO] is very low. For $[NO]/[HC] > 1$, although we did not have validation data for this range, we would expect α to decrease in accordance with the peak O_3 for such ratios. The values of 2.45 and 9.8 have no significance other than the fact that they give good validation for the experiments shown. The value of β was set at 1.7. The values of δ and θ were set at 0.8 and 0.02, respectively. γ and ϵ were not needed since we did not compute the concentration of aldehydes.

Isobutylene Experiments. Next we consider the isobutylene experiments reported by Westberg et al. (1971) in the presence and absence of CO. Figure 4 presents concentration-time behavior for the following initial conditions: $[C_4H_8]_0 = 3$, $[NO_2]_0 = 0.04$, $[NO]_0 = 1.5$, $[CO]_0 = 0$, and $k_1' = 0.355$ min^{-1}. Figure 5 shows concentration-time behavior for the same initial conditions except $[CO]_0 = 100$ ppm. The purpose of these trials is to examine the performance of the simplified model for another hydrocarbon and for the effect of CO.

Because isobutylene and propylene are both terminal olefins of similar reactivity, α was kept the same as for the propylene runs. The rate constants and stoichimetric coefficients are the same as for propylene except:

$k_1' = 0.355$
$k_{11}' = 3.1 \times 10^4$
$k_{12}' = 0.017$
$k_{13}' = 10^4$

$\beta = 1.9$
$\delta = 0.2$
$\theta = 0.22$

The model results are shown in Figures 4 and 5 by the dashed lines. In the actual experiments, the NO_2 peaks 32 min sooner when 100 ppm CO is present initially (104 min vs. 136 min). In the simulation, the NO_2 also peaks 32 min sooner with 100 ppm CO (105 min vs. 137 min). The model also predicts the more rapid oxidation of isobutylene and accelerated accumulation of O_3 when CO is present.

***n*-Butane Experiments.** We now consider the photooxidation of *n*-butane in the presence and absence of CO, as reported by Wilson (1971). The experimental results in Figure 6 have $[C_4H_{10}]_0 = 3.05$ ppm, $[NO_2]_0 = 0.106$ ppm, $[CO]_0 = 0$, and $k_1' = 0.4$ min^{-1}. For the results in Figure 7, $[C_4H_{10}]_0 = 3.25$ ppm, $[NO_2]_0 = 0.106$ ppm, $[NO]_0 = 0.50$ ppm, $[CO]_0 = 100$ ppm, and $k_1' = 0.4$ min^{-1}. In both cases the initial NO_x to C_4H_{10} ratio is about 1:5. The rate constants and stoichiometric coefficients were the same as propylene with the following exceptions: $k_1' = 0.4$, $k_6' = 0.004$, $k_{11}' = 2000$, $k_{12}' = 0.001$, $k_{13}' = 6000$, $\alpha = 5$, $\beta = 0.5$, $\delta = 1.2$, and $\theta = 0.61$. Note that a constant value of α was used because of the lower reactivity of *n*-butane.

Although O_3 does not react with *n*-butane, we use a nonzero k_{12}' because olefins are probably some of the first stable products formed after O and OH· attack on butane. Some possible reaction schemes for olefin formation are

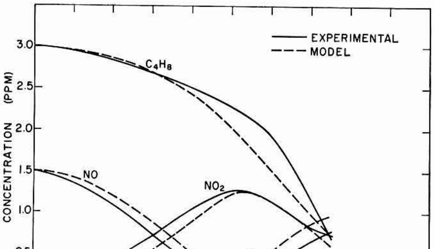


Figure 5. Comparison of experimental smog chamber concentrations and concentrations predicted by the simplified mechanism

Data for isobutylene from Westberg et al. (1971)
Initial concentration of carbon monoxide = 100 ppm

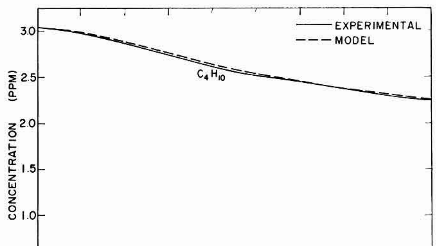


Figure 6. Comparison of experimental smog chamber concentrations and concentrations predicted by the simplified mechanism

Data for *n*-butane from Wilson (1971)
Initial concentration of carbon monoxide = 0 ppm

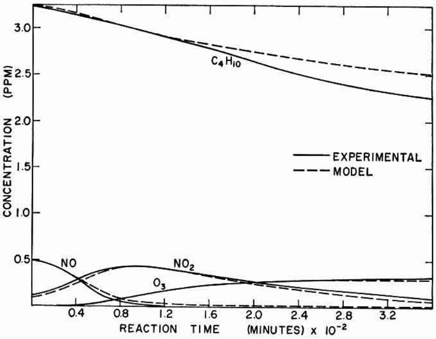


Figure 7. Comparison of experimental smog chamber concentrations and concentrations predicted by the simplified mechanism

Data for *n*-butane from Wilson (1971)
Initial concentration of carbon monoxide = 100 ppm

$$C_4H_{10} + O \longrightarrow C_4H_9\cdot + OH\cdot$$

$$C_4H_{10} + OH\cdot \longrightarrow C_4H_9\cdot + H_2O$$

$$CH_3CH_2CH_2CH_2\cdot \longrightarrow C_2H_5\cdot + CH_2{=}CH_2$$

$$CH_3CH_2\dot{C}HCH_3 + O_2 \longrightarrow (CH_3)_2C{=}CH_2 + HO_2\cdot$$

The formation of isobutylene in the butane oxidation may be evidenced by the fact that several products observed in the butane photoxidation—e.g., acetone and PAN (Altshuller, 1969)—are the same as those found in isobutylene photooxidation. The agreement between the model and the experimental results is quite close. It should be noted that the simulations in Figures 6 and 7 are for 6 hr.

Propylene and *n*-Butane Mixture. Next we consider the photooxidation of a mixture of propylene and *n*-butane carried out by Wilson (1971). The initial conditions for the experiment are $[C_3H_6]_0 = 0.56$ ppm, $[C_4H_{10}]_0 = 3.4$ ppm, $[NO_2]_0 = 0.098$ ppm, $[NO]_0 = 0.48$ ppm, $[CO]_0 = 0$, and $k_1' = 0.4$ min^{-1}. Thus, $[NO_x]_0/[C_3H_6]_0 \simeq 1$. The rate constants and stoichiometric coefficients are determined as a linear combination of those for pure propylene and *n*-butane, where proportionality is given by the initial concentration fraction of each in the mixture. α was set at the constant value of 3.0, with $\beta = 0.67$, $\delta = 1.2$, and $\theta = 0.53$. This method of using a linear combination of the pure hydrocarbon rate constants is similar in nature to the combined-rate approach used by Glasson and Tuesday (1971). They reported that the combined-rate approach predicted a greater oxidation rate than was observed experimentally, and we found the same phenomenon. Changing k_{15}' from the combined rate value of 96 to 45, we obtained the results shown by the dashed curves in Figure 8. Aside from this one change, the model effectively predicts the behavior of this mixture with rate constants as average values based on the initial hydrocarbon fractions.

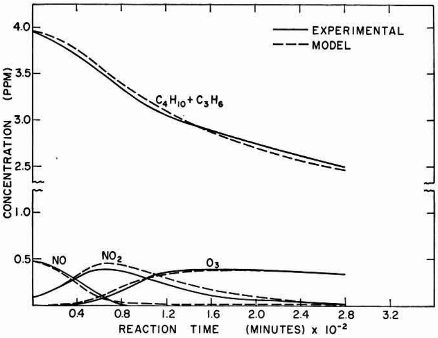


Figure 8. Comparison of experimental smog chamber concentrations and concentrations predicted by the simplified mechanism

Data for propylene and *n*-butane from Wilson (1971)

NO_x Inhibition. Finally, we consider the effect of initial reactant ratios on the maximum O_3 concentration attained during the course of the photooxidation. Extensive experimental results reported in the literature indicate that after a certain point, increasing the initial concentration of NO_x will result in a decreasing in the maximum concentration of O_3 reached (Glasson and Tuesday, 1970). In some cases, smog chamber results have been presented in the form of O_3 concentration after a fixed time of irradiation vs. initial concentration of NO_x at a fixed initial hydrocarbon concentration. Information of this type is useless unless the initial NO_x concentration is known in terms of both NO and NO_2. This is because the time to the NO_2 peak and time at which O_3 appears are dependent on the individual concentrations of NO and NO_2, as well as the total NO_x concentration. We can demonstrate this point quite simply. We have run two cases, in each of which $[HC]_0{:}[NO_x]_0 = 2{:}1.1$. In the first case, the NO_x was composed of 0.1 ppm NO_2 and 1.0 ppm NO, while in the second case the NO_x was composed of 0.4 ppm NO_2 and 0.7 ppm NO. In the first case the NO_2 peaked at 94 min while in the second, it peaked at 57 min. Although the concentration of O_3 ultimately reached about the same maximum level in both cases, after 2 hr the two concentrations were 0.424 and 0.634 ppm, respectively. The peak O_3 formation rate defined and reported by Glasson and Tuesday (1970) as $[O_3]$ max/2 $t_{1/2}$, where $t_{1/2}$ is the time for the formation of one-half of the peak O_3 concentration is also highly dependent on the initial mix of NO and NO_2. The above points are illustrated in Table VII, in which the simulated results of three runs in which $[NO_x]_0$ was kept constant but the individual $[NO]_0$ was varied are reported. It is clear from Table VII that if smog chamber data are reported in terms of the quantities in either of the last two columns, both the initial NO and NO_2 concentrations must be reported.

One of the key requirements that a simplified mechanism for photochemical smog must satisfy is that it demonstrates the inhibitory effect of NO on the maximum concentration of O_3. Altshuller et al. (1967) have reported results on the oxidant level as a function of $[NO_x]_0$ at fixed $[C_3H_6]_0$. Even though the individual $[NO]_0$ and $[NO_2]_0$ were not reported, the irradiation time for each run was 6 hr, ensuring that the peak O_3 level had been reached. Their results are shown by the solid curve in Figure 9. We note a sharp inhibition at $[NO_x]_0$ greater than about 3 ppm for $[C_3H_6]_0 = 2$ ppm. We have simulated these runs using the general 15-step mechanism with $[NO_2]_0 = 0.1$ ppm, the results of which are shown by the dashed curve in Figure 9. It is important to realize that NO inhibition is reflected in the model by the choice of α, so that Figure 9 really

Table VII. Effect of Initial NO and NO_2 Concentrations on the Time of Appearance of O_3

$[C_3H_6]_0 = 2$ ppm, $[NO_x]_0 = 1.1$ ppm

$[NO_2]_0$	$[NO]_0$	$[O_3]_{max}$	$t_{1/2}$, min	$[O_3]$, 2 hr	$[O_3]_{max}/2\ t_{1/2}$
0.05	1.05	0.734	127	0.311	2.89×10^{-3}
0.10	1.00	0.741	113	0.424	3.28×10^{-3}
0.40	0.70	0.789	77	0.634	5.12×10^{-3}

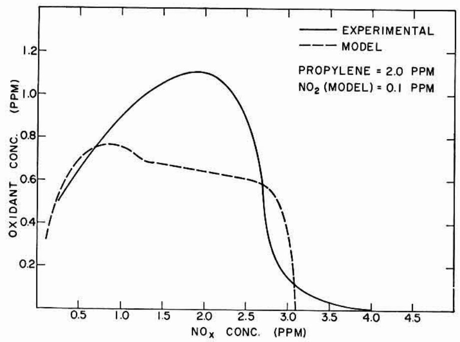


Figure 9. Effect of initial NO_x concentration on peak oxidant concentration.

Experimental curve from Altshuller et al. (1967). Model curve based on assumed initial NO_2 concentration of 0.1 ppm

only shows that the choice of α is consistent with observed behavior.

Summary

The validation experiments lend strong support to the approach of using a generalized mechanism consisting of a small number of reactions and parameters for mathematical modeling of photochemical smog kinetics. We must stress that the simplified mechanism presented is by no means a unique model for smog formation. Indeed, other mechanisms may also be capable of matching experimental smog chamber data by proper choice of parameters. The mechanism we have developed represents a compact generalized scheme, in which we have strived to retain certain elements of chemical reality. It does not appear that at this point we can suggest firm rules for the selection of rate constants and stoichiometric coefficients. These must be determined by fitting the model to the sets of data available.

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A Numerical Method for Computing Equilibria in Aqueous Chemical Systems

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■ A general purpose computer program especially adapted to the study of acid–base and coordinative interactions and dissolution and precipitation in aqueous systems has been developed. The program uses the stability constant approach and the Newton-Raphson method for digital computation of equilibria. It is able to handle numerous species and to find the equilibrium set of solids. Gas phases are considered to be at constant partial pressures. The method is explained by use of the aqueous iron(III)–calcium–carbonate–phosphate system as an example. An application of the program to a system of 788 soluble species, 83 possible solids, and one gas-phase component is given as an illustration.

Equilibrium models can be very useful for understanding the various processes—dissolution and precipitation, oxidation and reduction, acid–base and coordinative interactions—which govern the chemical composition of natural waters (Stumm and Morgan, 1970). A classical example of such an equilibrium model is the seawater model of Sillén (1961).

Typically, these models require the computation of equilibrium compositions for systems containing numerous species distributed among an aqueous phase, a gas phase, and several solid phases. For any given model, the temperature and the pressure can generally be taken as constants. Exchange of matter with the surroundings being neglected and ideality being assumed, the thermodynamic treatment of such closed systems is straightforward (Denbigh, 1966), and the equilibrium composition is given by the minimum of the Gibbs free energy function or, equivalently, by the mass action laws, both subject to the constraints of the mole balance conditions.

We have been interested in developing a general purpose computer program especially adapted to solving these types of chemical equilibrium problems. Two main choices have to be made in the development of such a program: First, the choice of a notation that will allow the description of the system in algebraic terms and the setting up of the equations; second, the choice of a method to solve the equilibrium problem.

Every possible kind of notation has been proposed in the literature from the most particular one which identifies every chemical species under a special symbol, to the most general one where elements of multidimensional tensors represent the species and their formulas. Because our prime interest is with coordination processes we have chosen to differentiate between metals (M), ligands (L), and complexes (C). Since acid–base interactions are of special interest to us, the proton has been given a special symbol (H). Gas and solid phases interact with the soluble species in a fairly similar way and they are given a single symbolic representation (S). We feel that this notation is general enough to allow the treatment of most of the systems we are interested in and that it is particular enough to facilitate the translation of a particular chemical problem into a general algebraic one. The metals and the ligands are thus logically taken as the components of the system and this division of the components into two families allows an unusually compact description of the system in a tableau form. This compactness is important in enabling a large number of species (up to a few thousand) to be handled.

To solve the chemical equilibrium problem, two principal techniques can be distinguished. First, the so-called equilibrium constant approach which consists of solving the set of nonlinear equations provided by the mass law and the mole balance equations. This method was pioneered by such workers as Brinkley (1947), and its most prominent application to aqueous systems is the Haltafall program developed by Sillén and his co-workers (Ingri et al., 1967). The second technique was first proposed by Dantzig and co-workers (White et al., 1958) and consists of directly minimizing the Gibbs free energy function subject to the constraints of the mole balance equations. This method was applied to large multiphasic systems by Shapiro (1964). A fairly complete review of the two methods has been given by Zeleznik and Gordon (1968).

We have chosen to use the equilibrium constant approach. The determining factor in choosing this method was that it allows reduction of the number of principal variables. In our case, for example, the concentrations of the complexes can be expressed as a function of the free metal and free ligand concentrations by the mass law equations, and the problem is thus reduced to finding this set of free metal and free ligand concentrations that will satisfy the mole balance conditions. This is done by use of the Newton-Raphson method for systems of nonlinear equations.

As can be seen, our method is just the application of well-known principles to a particular class of problems. Our goal is simply to present what we have found to be an efficient and reliable tool for solving a fairly general and important class of chemical equilibrium problems in order to help others develop similar tools.

By use of examples, the notation and the systematic setting-up of the equations, both in the absence and in the presence of solids, will be presented. An iterative procedure to find the equilibrium solid phases will then be shown. An abridged description of the program will finally be given, followed by an example demonstrating the possibilities of the method.

Description of the System

To derive a general method of computation one has to choose some systematic notation that will describe the chemical system in algebraic terms. The notation that we have chosen differentiates metals and ligands and represents the chemical system in a tableau form. For example, the iron(III)–calcium–carbonate–phosphate system in water is represented in Figure 1. The values in parentheses are the logarithms of the concentration stability constants for formation of aqueous

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Metals	Ligands: CO_3^{2-}		PO_4^{3-}		OH^-	
Ca^{2+}	$CaCO_3$	(1.95)	$CaHPO_4$	(12.6)	$CaOH^+$	(0.9)
	$CaHCO_3^+$	(10.58)				
	$CaCO_3(s)$	(−7.0)	$Ca_5(PO_4)_3OH(s)$	(−51.5)	$Ca(OH)_2(s)$	(−4.9)
Fe^{3+}	No important complex or solid known		$FeHPO_4^+$	(18.0)	$FeOH^{2+}$	(11.3)
					$Fe(OH)_2^+$	(22.0)
					$Fe(OH)_4^-$	(31.0)
			$FePO_4(s)$	(−23.0)	$Fe(OH)_3(s)$	(−36.0)
H^+	HCO_3^-	(9.6)	HPO_4^{2-}	(11.8)	Water	
	H_2CO_3	(15.4)	$H_2PO_4^-$	(18.5)		
	$CO_2(g)$	(−17.0)	H_3PO_4	(20.4)		

Figure 1. Tableau representation for the iron(III)–Ca^{2+}–CO_3^{2-}–PO_4^{3-} system in water

Equilibrium constant (0.5*M* ionic medium) for formation of aqueous species and for dissolution of solids and gases are given in parentheses, as the logarithm

species from their components and for the dissolution of solid or gaseous species. The stability constants used here and in the other examples in this paper apply to a constant ionic medium of 0.5*M*. They have been selected mainly from the compilations of Sillén and Martell (1964), Ringbom (1963), and Garrels and Christ (1965). When experimental values for 0.5*M* ionic medium were not available, approximate values were obtained by applying Ringbom's ionic strength corrections (Ringbom, 1963). Our equilibrium constant values are not intended to be critical selections; applications to specific problems will require critical examination of the appropriate thermodynamic data for particular solid phases and aqueous species.

The choice of independent components is, of course, partly arbitrary. For example, either carbonate (CO_3^{2-}) or bicarbonate (HCO_3^-) could be chosen as a component, but both of them could not be chosen at the same time if the proton (H^+) is also to be a component; (CO_3^{2-}), (HCO_3^-), and (H^+) are not independent. We have chosen the least-protonated forms of the ligands and the unhydrolyzed forms of the metals as the components of the system.

The advantage of such a presentation is twofold: It allows a compact writing of large systems, and it has a pedagogic and practical value in pointing out the possible complex formations. The main disadvantage of the presentation is that it is not completely general: Unless special provision is made, no complex involving two different metals or two different ligands can be considered. Because H^+ and OH^- often react with another metal or ligand in complex formation, the general complex formula we use does allow this possibility. A metal M_i and a ligand L_j can form a complex C_{ijk} of the form

$$C_{ijk} \equiv (M_i)_\alpha (L_j)_\beta (\mathrm{H})_\gamma$$

where *i* is an index specifying the metal, *j* is an index specifying the ligand, *k* is an index specifying the different M_i–L_j complexes in an arbitrary order, α (in fact, α_{ijk}) is the stoichiometric coefficient of the metal in the formula of C_{ijk}, β (in fact, β_{ijk}) is the stoichiometric coefficient of the ligand in the formula of C_{ijk}, and γ (in fact, γ_{ijk}) is the stoichiometric coefficient of the hydrogen ion, H^+, or hydroxide ion, OH^-, in the formula of C_{ijk}. For H^+ in the complex $\gamma > 0$; for OH^- in the complex $\gamma < 0$; so that the formula of C_{ijk} may also be:

$$C_{ijk} \equiv (M_i)_\alpha (L_j)_\beta (\mathrm{OH})_{-\gamma}$$

Then, with the appropriate definition of the stability constant K_{ijk}, one can always write the mass action law:

$$[C_{ijk}] = K_{ijk} \cdot [M_i]^\alpha \cdot [L_j]^\beta \cdot [\mathrm{H}]^\gamma \tag{1}$$

This contains implicitly the result $[\mathrm{OH}] = K_w/[\mathrm{H}]$ in case $\gamma_{ijk} < 0$.

It should be pointed out that with this notation H^+ is identified at the same time both as H and conventionally as the last metal, M_3, in our example (Figure 2).

In the same way, the solids can be described by

$$S_{ij} \equiv (M_i)_\delta (L_j)_\eta (\mathrm{H})_\lambda$$

or

$$S_{ij} \equiv (M_i)_\delta (L_j)_\eta (\mathrm{OH})_{-\lambda}$$

where δ, η, λ (in fact, δ_{ij}, η_{ij}, λ_{ij}) have definitions similar to those of α, β, γ.

	L_1	L_2	$L_3(=\mathrm{OH})$
M_1	$C_{111} \equiv (M_1)(L_1)$ $C_{112} \equiv (M_1)(L_1)(\mathrm{H})$ $S_{11} \equiv (M_1)(L_1)$	$C_{121} \equiv (M_1)(L_2)(\mathrm{H})$ $S_{12} \equiv (M_1)_5(L_2)_3(\mathrm{OH})$	$C_{131} \equiv (M_1)(L_3)$ $S_{13} \equiv (M_1)(L_3)_2$
M_2		$C_{221} \equiv (M_2)(L_2)(\mathrm{H})$ $S_{22} \equiv (M_2)(L_2)$	$C_{231} \equiv (M_2)(L_3)$ $C_{232} \equiv (M_2)(L_3)_2$ $C_{233} \equiv (M_2)(L_3)_4$ $S_{23} \equiv (M_2)(L_3)_3$
$M_3(=\mathrm{H})$	$C_{311} \equiv (M_3)(L_1)$ $C_{312} \equiv (M_3)_2(L_1)$ $S_{31} \equiv (M_3)_2(L_1)$	$C_{321} \equiv (M_3)(L_2)$ $C_{322} \equiv (M_3)_2(L_2)$ $C_{323} \equiv (M_3)_3(L_2)$	

Figure 2. General representation (aqueous species, solids, and gas) of the system of Figure 1 in terms of metals M_i, ligands L_j, H ions, and OH ions

It should be noted that this notation does not allow the formation of two different solids involving a metal and a ligand (there is no third index). This is being modified in newer versions of the program.

There is no computational reason to differentiate between solids and components of gas phases at constant partial pressure since in both cases we can write the solubility equation in the general form:

$$k = [M_i]^{\delta} \cdot [L_j]^{\eta} \cdot [\mathrm{H}]^{\lambda} \qquad (2)$$

where k (in fact, k_{ij}) is corrected by the right power of K_w in case $\lambda < 0$ and contains the partial pressure in case we are dealing with a gas phase. Consequently both solid and gas phase components will be referred to by the letter S.

Now Figure 1 can be rewritten in general terms, as shown in Figure 2.

In this tableau the three-dimensional arrays of numbers K, α, β, γ and the two-dimensional arrays k, δ, η, λ completely describe the general chemical properties of the system. Figure 3 shows these eight arrays of numbers.

To be able to solve a problem we need as many equations as we have unknowns. It is convenient to consider the concentrations of the complexes as secondary unknowns given from the principal unknowns M_i, L_j, and H by Equation 1. We thus need an equation for every metal ($\neq$H), for every ligand ($\neq$OH), and for the proton. These equations are given by the particular conditions of the system in different cases.

Case Where No Solid is Present. Let us first suppose that in our example the system has been made by adding 10^{-6} mole of ferric phosphate ($FePO_4$), 10^{-4} mole of calcium hydroxide, $Ca(OH)_2$, and 10^{-3} mole of carbon dioxide (CO_2) in 1 liter of water. Suppose also that we know that no solid phase is present and that we study the equilibrium before the gas phase has had time to form. We can then write down the mole balance equation for each metal ($\neq$H) and each ligand ($\neq$OH).

$$M_1\text{: } 10^{-4} = [M_1] + [C_{111}] + [C_{112}] + [C_{121}] + [C_{131}] \qquad (3.1)$$

$$M_2\text{: } 10^{-6} = [M_2] + [C_{221}] + [C_{231}] + [C_{232}] + [C_{233}] \qquad (3.2)$$

$$L_1\text{: } 10^{-3} = [L_1] + [C_{111}] + [C_{112}] + [C_{131}] + [C_{312}] \qquad (3.3)$$

$$L_2\text{: } 10^{-6} = [L_2] + [C_{121}] + [C_{221}] + [C_{321}] + [C_{322}] + [C_{323}] \qquad (3.4)$$

In general,

$$+\log K = \begin{array}{|c|c|c|} \hline \begin{matrix}1.95\\10.58\end{matrix} & 12.6 & 0.9 \\ \hline & 18.0 & \begin{matrix}11.3\\22.0\\31.0\end{matrix} \\ \hline \begin{matrix}9.6\\15.4\end{matrix} & \begin{matrix}11.8\\18.5\\20.4\end{matrix} & \\ \hline \end{array} \qquad \alpha = \begin{array}{|c|c|c|} \hline \begin{matrix}1\\1\end{matrix} & 1 & 1 \\ \hline & 1 & \begin{matrix}1\\1\\1\end{matrix} \\ \hline \begin{matrix}1\\2\end{matrix} & \begin{matrix}1\\2\\3\end{matrix} & \\ \hline \end{array}$$

$$\beta = \begin{array}{|c|c|c|} \hline \begin{matrix}1\\1\end{matrix} & 1 & 1 \\ \hline & 1 & \begin{matrix}1\\2\\4\end{matrix} \\ \hline \begin{matrix}1\\1\end{matrix} & \begin{matrix}1\\1\\1\end{matrix} & \\ \hline \end{array} \qquad \gamma = \begin{array}{|c|c|c|} \hline \begin{matrix}0\\1\end{matrix} & 1 & 0 \\ \hline & 1 & \begin{matrix}0\\0\\0\end{matrix} \\ \hline \begin{matrix}0\\0\end{matrix} & \begin{matrix}0\\0\\0\end{matrix} & \\ \hline \end{array}$$

$$-\log k = \begin{array}{|c|c|c|} \hline 7.0 & 37.8^{a} & 4.9 \\ \hline & 23.0 & 36.0 \\ \hline 20.5^{b} & & \\ \hline \end{array} \quad \delta = \begin{array}{|c|c|c|} \hline 1 & 5 & 1 \\ \hline & 1 & 1 \\ \hline 2 & & \\ \hline \end{array} \quad \eta = \begin{array}{|c|c|c|} \hline 1 & 3 & 2 \\ \hline & 1 & 3 \\ \hline 1 & & \\ \hline \end{array} \quad \lambda = \begin{array}{|c|c|c|} \hline 0 & -1 & 0 \\ \hline & 0 & 0 \\ \hline 0 & & \\ \hline \end{array}$$

Figure 3. The arrays of stability constants and stoichiometric coefficients required to describe the iron(III)–Ca^{2+}–CO_3^{2-}–PO_4^{3-} system in water

[a] Computed for $K_w = 10^{-13.7}$. [b] Computed for $p_{CO_2} = 10^{-3.5}$ atm

$$TOTM_i = [M_i] + \sum_{j,k} \alpha_{ijk} \cdot [C_{ijk}] \text{ (sum on line } i \text{ of Figure 2)}$$

$$TOTL_j = [L_j] + \sum_{i,k} \beta_{ijk}[C_{ijk}] \text{ (sum on column } j \text{ of Figure 2)} \qquad (3)$$

where $TOTM_i$ and $TOTL_j$ are the analytical or total concentrations of the metal M_i and the ligand L_j, respectively.

We need one more equation for (H); different cases can be entertained. First, we might know the pH either because we have measured it experimentally or because we have imposed it—practically or conceptually—by adding a buffer which has no interaction (other than through the proton concentration) with the chemicals we are interested in. In this case the problem is trivial: (H) is fixed (pH = 5.21 in our example) and we do not need any other equation. If the pH is not known, we have to compute it by using either the electroneutrality or the proton condition. These two equations are known to be mathematically (not computationally) equivalent and can be deduced from each other by combination with the mole balances (Equations 3). For the electroneutrality condition to be written, we need to include the charges of each metal and each ligand in the data and then to compute the charge of every complex. The electroneutrality equation also has the computational disadvantage that for any salt present in high concentration and essentially free, we will add and subtract the concentrations of the cations and anions, respectively, in such a way as to create a round-off error that might not be negligible.

For these reasons we have judged it preferable to use the proton condition:

$$\sum \text{“acids” put into the system} - \sum \text{“bases” put into the system} = \sum \text{all species containing } H^+ - \sum \text{all species containing } OH^-$$

This equation comes from the conservation equations of H^+ and OH^- and from the fact that for any proton produced by the dissociation of water there is a corresponding hydroxide ion produced.

The definitions of “acids” and “bases” are, of course, relative to our choice of metals and ligands—e.g., if $CO_3^{2-} \equiv L_1$ then HCO_3^- (HL_1) and CO_2 (H_2L_1) are acids; if $CO_2 \equiv L_1$ then HCO_3^- (OHL_1) and CO_3^{2-} [$(OH)_2L_1$] are bases.

With our notation, the proton condition can be written in the general form:

$$TOTH = [\mathrm{H}] - [\mathrm{OH}] + \sum_{\substack{\text{last row}\\ j,k}} \alpha_{ijk}[C_{ijk}] - \sum_{\substack{\text{last column}\\ i,k}} \beta_{ijk}[C_{ijk}] + \sum_{i,j,k} \gamma_{ijk}[C_{ijk}] \qquad (4)$$

$TOTH$ is an input into the problem whose value will correspond to the experimental base-neutralizing capacity (respective acid-neutralizing capacity) of the system if the components are written in their least-protonated (respective most protonated) form. If only neutral components are chosen, the proton condition is strictly identical to the electroneutrality condition. In our example, if $CO_3^{2-} \equiv L_1$ and $Ca(OH)_2 \equiv M_1$ then $TOTH$ = base-neutralizing capacity; if $CO_3 \equiv L_1$ and $Ca^{2+} \equiv M_1$ then $TOTH$ = acid-neutralizing capacity. Since in this case our choice is mixed ($CO_3^{2-} \equiv L_1$ and $Ca^{2+} \equiv M_1$) $TOTH$ has no direct experimental meaning.

In our particular example the proton condition is written:

$$TOTH = [\mathrm{H}] - [\mathrm{OH}] + [C_{311}] + 2[C_{312}] + [C_{321}] + 2[C_{322}] + 3[C_{323}] - [C_{131}] - [C_{231}] - 2[C_{232}] - 4[C_{233}] + [C_{112}] + [C_{121}] + [C_{221}] \qquad (4.1)$$

Table I. Successive Computed Solutions for the Equilibrium Values of Free Metals and Ligands for an Iron(III)-Ca^{2+}-CO_3^{2-}-PO_4^{3-} System under Conditions Where No Solid Forms and H_2CO_3 Is Considered a Nonvolatile Species

Components: $[FePO_4]_T = 10^{-6}M$; $[Ca(OH)_2]_T = 10^{-4}M$; $[CO_2]_T = 10^{-3}M$. The equilibrium composition is computed with sufficient accuracy by the tenth iteration

Iteration no.	$[M_1]$	$[M_2]$	$[L_1]$	$[L_2]$	[H]
0	1.00×10^{-8}	1.00×10^{-8}	1.00×10^{-8}	1.00×10^{-8}	1.00×10^{-8}
1	1.00×10^{-5}	4.90×10^{-12}	2.43×10^{-5}	2.89×10^{-10}	1.00×10^{-8}
2	9.89×10^{-5}	2.59×10^{-12}	1.80×10^{-5}	7.12×10^{-11}	1.26×10^{-8}
3	9.90×10^{-5}	6.30×10^{-12}	1.80×10^{-6}	2.61×10^{-11}	2.80×10^{-8}
4	9.92×10^{-5}	1.39×10^{-10}	1.80×10^{-7}	2.61×10^{-12}	3.36×10^{-7}
5	9.98×10^{-5}	3.87×10^{-9}	1.80×10^{-8}	2.61×10^{-13}	5.02×10^{-6}
6	9.98×10^{-5}	9.66×10^{-10}	8.06×10^{-9}	2.61×10^{-14}	5.64×10^{-6}
7	9.98×10^{-5}	1.88×10^{-10}	8.42×10^{-9}	4.79×10^{-15}	6.17×10^{-6}
8	9.98×10^{-5}	5.94×10^{-12}	8.46×10^{-9}	8.13×10^{-15}	6.11×10^{-6}
9	9.98×10^{-5}	9.33×10^{-12}	8.46×10^{-9}	8.19×10^{-15}	6.11×10^{-6}
10	9.98×10^{-5}	9.33×10^{-12}	8.46×10^{-9}	8.19×10^{-15}	6.11×10^{-6}

where $TOTH = 2[CO_2]_T - 2[Ca(OH)_2]_T = 2 \times 10^{-3} - 2 \times 10^{-4} = 1.8 \times 10^{-3}$.

Equations 3 and 4 completely define the system once the secondary variables have been replaced by their values (Equation 1). To solve this system of nonlinear equations we have used a slightly modified Newton-Raphson method. This involves writing the general expressions of the derivatives of Equations 3 and 4 with respect to the principal variables (M_i), (L_j), and (H). It is a simple matter; the expressions are given in the Appendix. The Newton-Raphson method starts from an initial guess and improves it by use of the iterative procedure

$$\bar{X}_{n+1} = \bar{X}_n - J_n^{-1}\bar{Y}_n$$

Where $\bar{X}_n$ is the approximation of the solution vector $\bar{X}$ in the system $\bar{Y}(\bar{X}) = 0$ at the nth iteration and $\bar{X}_{n+1}$ is its improvement at the next iteration. J is the Jacobian matrix of the system. $\bar{Y}_n$ is $\bar{Y}(\bar{X}_n)$ and J_n is $J(\bar{X}_n)$. For details see, for example, Isaacson and Keller (1966).

To avoid the convergence toward a negative solution we have slightly modified this iterative procedure and developed the empirical rule to simply divide by 10 any concentration that the Newton-Raphson iteration would make negative—i.e., if $X_{n+1}^i < 0$ take instead $(X_{n+1}^i)' = X_n^i/10$. This "trick" seems to work well. Table I shows how the solution of our particular example [$10^{-6}M$ $FePO_4$; $10^{-4}M$ $Ca(OH)_2$; $10^{-3}M$ CO_2] was found, starting with the initial guess that each free metal and each free ligand concentration was $10^{-8}M$ at equilibrium.

At the tenth iteration the values were judged to verify the equations satisfactorily. Specifically: $|$right-hand side of Eq. 3 $-$ left-hand side of Eq. 3$| \leq 10^{-5} \times$ left-hand side, Eq. 3 and a similar condition for Equation 4. The negative logarithm of the concentrations of every species at equilibrium is shown in Figure 4.

Case Where Known Solid Phases or Gas-Phase Components at Fixed Partial Pressure Are Present. In continuing to work on our iron(III)-calcium-carbonate-phosphate system, suppose that the particular conditions are: $p_{CO_2} = 3 \times 10^{-4}$ atm; $[Ca_5(PO_4)_3OH]_T = 2 \times 10^{-3}M$; $[FePO_4]_T = 10^{-3}M$; $[H_3PO_4]_T = 3 \times 10^{-3}M$; and if we know that the solid phases $Ca_5OH(PO_4)_3$, S_{12}, and $FePO_4$, S_{22}, are present at equilibrium, then Equations 1 defining the secondary variables, $[C_{ij}]$, are still the same. Defining $[S_{ij}]$ as the number of moles of solid S_{ij} or gas S_{ij} per liter of solution (a bizarre but convenient definition), we can write the mole balance equations:

$$M_1: TOTM_1 = 5\,[S_{12}] + (\text{rhs, Equation 3.1}) \quad (5.1)$$

$$M_2: TOTM_2 = [S_{22}] + (\text{rhs, Equation 3.2}) \quad (5.2)$$

$$L_1: TOTL_1 = [S_{31}] + (\text{rhs, Equation 3.3}) \quad (5.3)$$

$$L_2: TOTL_2 = 3[S_{12}] + [S_{22}] + (\text{rhs, Equation 3.4}) \quad (5.4)$$

and the proton condition:

$$\text{H}: TOT\text{H} = -[S_{12}] + 2[S_{31}] + (\text{rhs, 4.1}) \quad (6.1)$$

The general Equations 5 and 6 are easily written similarly to 3 and 4:

	$pL_1 = 8.07$	$pL_2 = 14.09$	$pL_3 = 8.49$
$pM_1 = 4.00$	$pC_{111} = 10.12$ $pC_{112} = 6.71$	$pC_{121} = 10.70$	$pC_{131} = 11.59$
$pM_2 = 11.03$		$pC_{221} = 12.33$	$pC_{231} = 8.22$ $pC_{232} = 6.01$ $pC_{233} = 13.99$
$pM_3 = 5.21$	$pC_{311} = 3.68$ $pC_{312} = 3.10$	$pC_{321} = 7.50$ $pC_{322} = 6.01$ $pC_{323} = 9.33$	

Figure 4. Results of equilibrium computation for an iron(III)-Ca^{2+}-CO_3^{2-}-PO_4^{3-} system in absence of solid or gas phases

The tableau gives the negative logarithm (p[ ]) of each metal ion, ligand, protonated ligand, and complex at equilibrium

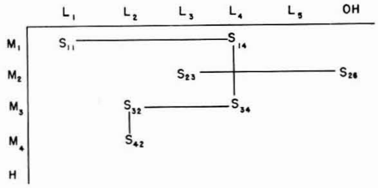

Figure 5. Examples of "connected" solids

S_{23}, S_{26} are connected; S_{32}, S_{42} are connected; S_{11}, S_{42} are also connected

There are two families of connected solids: $\begin{cases} S_{23}, S_{26} \\ S_{11}, S_{14}, S_{34}, S_{32}, S_{42} \end{cases}$

$$\left.\begin{aligned} TOTM_i &= [M_i] + \sum_j \delta_{ij}[S_{ij}] + \sum_{j,k} \alpha_{ijk}[C_{ijk}] \\ TOTL_j &= [L_j] + \sum_i \eta_{ij}[S_{ij}] + \sum_{i,k} \beta_{ijk}[C_{ijk}] \end{aligned}\right\} \quad (5)$$

$$TOTH = [H] - [OH] + \sum_{\substack{\text{last row} \\ j}} \delta_{ij}[S_{ij}] + \sum_{\substack{\text{last row} \\ jk}} \alpha_{ijk}[C_{ijk}] - \sum_{\substack{\text{last column} \\ i}} \eta_{ij}[S_{ij}] - \sum_{\substack{\text{last column} \\ i,k}} \beta_{ijk}[C_{ijk}] + \sum_{ij} \lambda_{ij}[S_{ij}] + \sum_{ijk} \gamma_{ijk}[C_{ijk}] \quad (6)$$

Let us come back to our example. Not knowing what the value of $[CO_2(g)]_T$ is, we can take it to be some sufficiently large number, say $[CO_2]_T = 0.1M$; then

$$TOTM_1 = 5[Ca_5(PO_4)_3OH]_T = 10^{-2}M$$

$$TOTM_2 = [FePO_4]_T = 10^{-3}M$$

$$TOTL_1 = [CO_2]_T = 10^{-1}M$$

$$TOTL_2 = 3[Ca_5(PO_4)_3OH]_T + [FePO_4]_T + [H_3PO_4]_T = 10^{-2}M$$

$$TOTH = -[Ca_5(PO_4)_3OH]_T + 2[CO_2]_T + 3[H_2PO_4]_T = 2.07 \times 10^{-1}M$$

We have introduced three new unknowns $[S_{12}]$, $[S_{21}]$, $[S_{31}]$; correspondingly, we can write three new equations of the type 2:

$$S_{12}: [M_1]^5[L_2]^3[H]^{-1} = 10^{-37.8} \quad (2.1)$$

$$S_{22}: [M_2][L_2] = 10^{-23.0} \quad (2.2)$$

$$S_{31}: [H]^2[L_1] = 10^{-20.5} \quad (2.3)$$

Rather than to solve this new system with the new unknowns $[S_{ij}]$ (which are, in fact, only formally defined), we have chosen to eliminate systematically those unknowns and thus to reduce the number of equations.

We shall say that solids are connected whenever they share a common metal or a common ligand. We shall also say that solids are connected whenever they are connected to a common solid (Figure 5).

Whenever we have a family of connected solids, we can arbitrarily select a principal variable among the metals and the ligands involved in such a family and, using Equations 2, define the other metals and ligands involved as secondary variables. For example, choosing (H) and (L_2) as principal variables in our system, we get:

$$\text{from (2.3)}: [L_1] = 10^{-20.5} \cdot [H]^{-2} \quad (7.1)$$

$$\text{from (2.2)}: [M_2] = 10^{-23.0} \cdot [L_2]^{-1} \quad (7.2)$$

$$\text{from (2.1)}: [M_1] = 10^{-37.8} \cdot [L_2]^{-3/5}[H]^{+1/5} \quad (7.3)$$

In general:

$$[\text{secondary variable}] = \mu \cdot [\text{principal variable}]^{\nu} \cdot [H]^{\nu^1} \quad (7)$$

For simplicity [H] is always chosen as a principal variable and the coefficients μ, ν, and ν' can be computed on a systematic basis. It can be easily verified that the coefficients ν and ν' so defined for each new secondary variable are those that will eliminate the $[S_{ij}]$ from Equations 5 and 6:

$$(\text{equation with } [S_{ij}] \text{ eliminated}) = (\text{equation of principal variable}) + \sum \nu \cdot (\text{equation of connected secondary variable}) \left[+ \sum \nu' \,(\text{equation of any secondary variable}) \atop \text{only for proton condition} \right] \quad (8)$$

In our example:

Equation 5.4 − 3/5(5.1) − (5.2) gives:

$$TOTL_2 - 3/5\, TOTM_1 - TOTM_2 = (\text{rhs}, 3.4) - 3/5(\text{rhs}, 3.1) - (\text{rhs}, 3.2) \quad (8.1)$$

and

Equation 6.1 + 1/5(5.1) − 2(5.3) gives:

$$TOTH + 1/5 TOTM_1 - 2TOTL_1 = (\text{rhs}, 4.1) + 1/5(\text{rhs}, 3.1) - 2(\text{rhs}, 3.3) \quad (8.2)$$

We then have two equations (8.1 and 8.2) and two principal

	$pL_1 = 9.63$	$pL_2 = 10.01$	$pL_3 = 8.27$
$pM_1 = 2.64$	$pC_{111} = 10.32$ $pC_{112} = 7.12$	$pC_{121} = 5.48$	$pC_{131} = 10.00$
$pM_2 = 12.99$		$pC_{221} = 10.43$	$pC_{231} = 9.96$ $pC_{232} = 7.53$ $pC_{233} = 15.07$
$pM_3 = 5.43$	$pC_{311} = 5.46$ $pC_{312} = 5.09$	$pC_{321} = 3.64$ $pC_{322} = 2.37$ $pC_{333} = 5.90$	

Figure 6. Equilibrium composition of the aqueous phase of the iron(III)–Ca^{2+}–CO_3^{2-}–PO_4^{3-} system with $p_{CO_2} = 3 \times 10^{-4}$ atm and with $Ca_5OH(PO_4)_3$(s) and $FePO_4$(s) existing at equilibrium

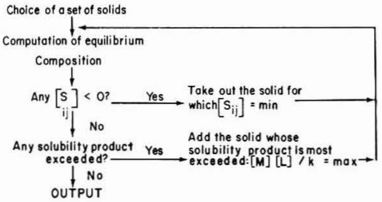

Figure 7. Routine for modifying the existing set of solids in a system at each stage in the computation

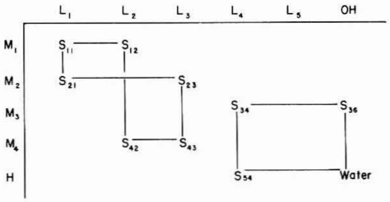

Figure 8. Examples of "closed" families of connected solids

S_{11}, S_{12}, S_{42}, S_{43}, S_{23}, S_{21}, S_{11} is a "closed" family of connected solids. S_{36}, S_{34}, S_{54} is also a "closed" family of connected solids since H and OH are not independent. (Water $\equiv S_{56}$)

unknowns (H and L_2). The secondary unknowns are given by Equations 1 and 7. The derivatives of those equations with respect to the principal variables are easily computed from the derivatives of Equations 3 and 4 (see Appendix). The Newton-Raphson method can then be used as before and Table II shows how the solution of our example ($p_{CO_2} = 3 \times 10^{-4}$ atm; $2 \times 10^{-3} M$ apatite; $10^{-3} M$ $FePO_4$; $3 \times 10^{-3} M$ H_3PO_4) was found starting with the initial guess that every free metal and every free ligand were $10^{-8} M$ at equilibrium (in fact, only [H] and [L_2] are important since the others are computed as secondary variables).

At the tenth iteration, the values were judged to verify the equations satisfactorily. The negative logarithms of the concentrations of every species at equilibrium are shown in Figure 6.

Case Where the Solid Phases Present Are Unknown. It is not always possible to know, a priori, which solid phases are actually present at equilibrium; we might guess that a solid is present while it is in fact completely dissolved at equilibrium or, reciprocally, we might not foresee the precipitation of a certain solid. In the first of those cases the system of equations has a solution that corresponds to a negative [S_{ij}]. On the other hand, if we have not foreseen the presence of a solid that does exist at equilibrium, the set of concentrations that solves the problem simply exceeds the corresponding solubility product. In either of those cases a solution can be computed on which the chosen set of solids can be tested. One can then modify this choice and start a new computation. This process is repeated until, hopefully, the right set of solids is found. The following diagram shows how our program modifies the set of solids after each computation. Other ways are, of course, possible; this one seems to work well (Figure 7).

We have chosen to "precipitate" and "dissolve" solids one by one to change the system as little as possible and to use the solution of the preceding computation as a good guess to start the new one. We have also chosen to "dissolve" solids before "precipitating" them to avoid the creation of a "closed" family of connected solids (Figure 8).

Such families are defined by

$$\text{"number of metals"} + \text{"number of ligands"} \leq \text{"number of solids"}$$

and they can be shown to be, in general, impossible merely by applying the Gibbs phase rule. In the example of Figure 8 the coefficients λ are all supposed to be zero. If the pH is arbitrarily fixed one needs an additional degree of freedom and the examples are valid even with nonzero λ coefficients.

The scheme of Figure 7 works only for solids and no provision has been made in the program to compute equilibrium of gas phases at constant volume. It is thus important to impose a sufficiently high total concentration of the known gas-phase components to avoid trouble with the "dissolving" routine. Figure 9 shows how the scheme of Figure 7 worked in the example previously treated ($p_{CO_2} = 3 \times 10^{-4}$ atm; $2 \times 10^{-3} M$ apatite; $10^{-3} M$ $FePO_4$; $3 \times 10^{-3} M$ H_3PO_4) where the solids S_{11}, $CaCO_3$, and S_{23}, $Fe(OH)_3$, were imposed instead of S_{12} and S_{22}.

These numbers at iteration 25 are, of course, identical to those found before (Table II). Cv means that the program converged at that iteration—i.e., the values on that line are the mathematical solution of the system when the corresponding solids are imposed up to that point. For example, at the third iteration, S_{11} and S_{23} are imposed; at the 20th iteration, S_{12}, S_{22}, and S_{23} are imposed.

Iteration no.	[M_1]	[M_2]	[L_1]	[L_2]	[H]
0	3.16×10^{-3}	1.26×10^{-19}	3.16×10^{-5}	1.00×10^{-8}	1.00×10^{-8}
3 (cv)	9.44×10^{-3}	6.50×10^{-19}	1.06×10^{-5}	8.00×10^{-7}	1.73×10^{-8}
	Solid S_{11} "dissolves"				
6 (cv)	9.41×10^{-3}	7.56×10^{-19}	9.57×10^{-6}	7.58×10^{-7}	1.82×10^{-8}
	Solid S_{12} "precipitates"				
14 (cv)	3.01×10^{-3}	1.63×10^{-11}	1.23×10^{-10}	6.88×10^{-11}	5.06×10^{-6}
	Solid S_{22} "precipitates"				
20 (cv)	4.78×10^{-4}	1.48×10^{-14}	1.32×10^{-8}	6.77×10^{-10}	4.89×10^{-7}
	Solid S_{23} "dissolves"				
25 (cv)	2.30×10^{-3}	1.03×10^{-13}	2.33×10^{-10}	9.67×10^{-11}	3.68×10^{-6}

Figure 9. Illustration of successive modifications of solids in an iron(III)–Ca^{2+}–CO_3^{2-}–PO_4^{3-} system where an initially imposed set of solids was not the equilibrium set [same conditions as in Table II except that the solids $CaCO_3$ (s) and $Fe(OH)_3$ (s) were imposed at the outset of the computation]

At the 25th iteration the correct set of solids has been formed and the equilibrium composition is attained

Table II. Successive Computed Solutions for the Equilibrium Values of Free Metals and Ligands in an Iron(III)–Ca^{2+}–CO_3^{2-}–PO_4^{3-} System Where p_{CO_2} Is Fixed and the Phases $Ca_5OH(PO_4)_3$ (s) and $FePO_4$(s) Are at Equilibrium

Components: $[Ca_5OH(PO_4)_3]_T = 2 \times 10^{-3}M$; $[FePO_4]_T = 10^{-3}M$; $[H_3PO_4]_T = 3 \times 10^{-3}M$; $p_{CO_2} = 3 \times 10^{-4}$ atm. The equilibrium composition is computed with sufficient accuracy by the tenth iteration.

Iteration no.	$[M_1]$	$[M_2]$	$[L_1]$	$[L_2]$	[H]
0	4.36×10^{-5}	1.00×10^{-15}	3.16×10^{-5}	1.00×10^{-8}	1.00×10^{-8}
1	1.02×10^{-5}	4.99×10^{-17}	9.90×10^{-7}	2.00×10^{-7}	5.65×10^{-8}
2	5.38×10^{-5}	4.99×10^{-16}	6.01×10^{-8}	2.00×10^{-8}	2.29×10^{-7}
3	2.77×10^{-4}	4.99×10^{-15}	4.61×10^{-9}	2.00×10^{-9}	8.28×10^{-7}
4	1.41×10^{-3}	4.99×10^{-14}	3.97×10^{-10}	2.00×10^{-10}	2.82×10^{-6}
5	5.54×10^{-3}	4.41×10^{-13}	2.15×10^{-10}	2.26×10^{-11}	3.83×10^{-6}
6	3.83×10^{-3}	1.94×10^{-13}	6.29×10^{-11}	5.14×10^{-11}	7.09×10^{-6}
7	2.62×10^{-3}	1.30×10^{-13}	2.47×10^{-10}	7.71×10^{-11}	3.58×10^{-6}
8	2.35×10^{-3}	1.06×10^{-13}	2.22×10^{-10}	9.43×10^{-11}	3.78×10^{-6}
9	2.30×10^{-3}	1.03×10^{-13}	2.33×10^{-10}	9.67×10^{-11}	3.68×10^{-6}
10	2.30×10^{-3}	1.03×10^{-13}	2.33×10^{-10}	9.67×10^{-11}	3.68×10^{-6}

Description of the Program. The program is written in FORTRAN and is usually run on an IBM 360/75 computer. It is made up of 11 principal subroutines organized in the following way (Figure 10):

INMAT is a subroutine that reads the data: general stoichiometric and thermodynamic data; special conditions of the problem; total concentrations of metals and ligands, pH, or *TOT*H; guesses for the free concentrations of metals and ligands and chosen sets of solids.

SOLIDO finds out if any solid is present; scans the tableau for families of connected solids; defines the principal and secondary variables; and computes the coefficients μ, ν, and ν'.

MLINSO computes the secondary variables M and L (other than C) in function of the principal variables using μ, ν, and ν'.

XCYZ computes the secondary variables, C, the mole balance equations for each metal and ligand ($\neq$H or OH) and their derivatives with respect to every metal and ligand. By computing a mole balance equation, we mean finding the actual numerical difference between the sum of the concentrations of the soluble species and the imposed analytical (total) concentration of the same component. In the same way the derivatives are the numerical values obtained by replacing the concentrations by their molar values in the formal algebraic formulas of the derivatives.

SUBPH computes the proton condition equation, its derivatives with respect to every metal and ligand, and the derivatives of all the equations with respect to H.

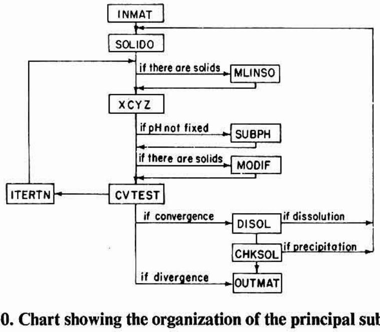

Figure 10. Chart showing the organization of the principal subroutines of the computer program

MODIF modifies the equations in accordance with our choice of principal and secondary variables—i.e., eliminates the $[S_{ij}]$. It also modifies the derivatives accordingly.

CVTEST verifies that the number of iterations does not exceed any arbitrary number and checks whether or not the equations are satisfied within an arbitrary precision.

ITERTN performs the Newton-Raphson iteration using a Gaussian elimination without iterative improvement to solve the system of linear equations: $J_n(\bar{X}_n - \bar{X}_{n+1}) = \bar{Y}_n$.

DISOL computes the amount of every solid precipitated and verifies that none is negative. In case some are negative, the least-probable solid ($[S_{ij}]$ = minimum) is no longer imposed and the computation is restarted.

CHKSOL verifies that no solubility product has been exceeded. In case some are exceeded, the solid for which the driving force is greatest $[([M_i][L_j])/K_{ij}$ = maximum$]$ is imposed and the computation is restarted.

OUTMAT prints the output. Metals, ligands, and complexes are printed in a matrix form.

Example of Computation. The following example shows the application of the program to an equilibrium computation involving 20 metals (+H), 31 ligands (+OH), 738 complexes, 83 possible solids, and one gas-phase component. Pressure, temperature, ionic strength, pH, and oxidation–reduction state are all taken to be constant. Table III gives the list of the metals and the ligands (and their identifying numbers) involved with their imposed analytical (total) concentrations.

Such an example can be seen to have some of the characteristics of certain well-known natural systems. The first guesses for the free metal and the free ligand concentrations were all taken to be $10^{-8}M$. The chosen set of solids at the start of the computation and its subsequent modifications by the program are shown in Figure 11.

The final result was found at the 56th iteration. Figure 12 gives the tableau of the thermodynamic data and has been deposited with the American Chemical Society Microfilm Depository Service. Table IV gives the computed equilibrium concentrations.

It is worthwhile to note that the whole computation took a little less than 60 sec. Equilibrium solutions at other pH's were also computed with this result as a starting guess; it takes about 35 iterations to go from one pH to the next one, say 8 to 9. The computation was also made without fixing the pH. *TOT*H = $-0.83M$, found in the first computation, was im-

Table III. List of Metal Ions and Ligands (Identified by Number) and Their Total Concentrations (Solid, Aqueous, and Gas Phases) in a Hypothetical Model System of 20 Metals and 31 Ligands[a]

Metals						Ligands								
1	Ca^{2+}	$10^{-1.0}$	11	Cd^{2+}	$10^{-6.0}$	1	CO_3^{2-}	$10^{-0.5}$	11	$P_3O_{10}^{-5}$	$10^{-8.0}$	21	DIP	$10^{-7.0}$
2	Mg^{2+}	$10^{-1.2}$	12	Zn^{2+}	$10^{-3.0}$	2	SO_4^{-2}	$10^{-1.5}$	12	$SiO_2(OH)_2^{2-}$	$10^{-0.01}$	22	SUSAL	$10^{-7.0}$
3	Sr^{2+}	$10^{-2.7}$	13	Ni^{2+}	$10^{-6.0}$	3	Cl^-	$10^{-0.3}$	13	$S_2O_3^{2-}$	$10^{-7.0}$	23	GLY	$10^{-6.0}$
4	K^+	$10^{-2.0}$	14	Hg^{2+}	$10^{-6.0}$	4	F^-	$10^{-2.0}$	14	AC	$10^{-6.3}$	24	GLUT	$10^{-6.0}$
5	Na^+	$10^{-0.3}$	15	Pb^{3+}	$10^{-7.0}$	5	Br^-	$10^{-3.0}$	15	ACAC	$10^{-7.0}$	25	PIC	$10^{-6.3}$
6	Fe^{3+}	$10^{-1.0}$	16	Co^{2+}	$10^{-7.0}$	6	I^-	$10^{-6.0}$	16	CIT	$10^{-6.0}$	26	NTA	$10^{-7.0}$
7	Fe^{2+}	$10^{-8.0}$	17	Co^{3+}	$10^{-4.0}$	7	NH_3	$10^{-6.0}$	17	OX	$10^{-5.7}$	27	EDTA	$10^{-7.3}$
8	Mn^{2+}	$10^{-7.0}$	18	Ag^+	$10^{-7.0}$	8	S^{2-}	$10^{-8.0}$	18	SAL	$10^{-6.3}$	28	DCTA	$10^{-7.3}$
9	Cu^{2+}	$10^{-3.5}$	19	Cr^{3+}	$10^{-4.0}$	9	PO_4^{3-}	$10^{-3.0}$	19	TART	$10^{-6.0}$	29	CYST	$10^{-8.0}$
10	Ba^{2+}	$10^{-3.0}$	20	Al^{3+}	$10^{-0.01}$	10	$P_2O_7^{4-}$	$10^{-7.0}$	20	EN	$10^{-7.0}$	30	NOC	$10^{-8.0}$
												31	PHTH	$10^{-7.3}$

[a] The equilibrium computation for this system involves 738 complexes and 83 possible solids. There is one gas-phase component, CO_2. Pressure, temperature, ionic strength, pH, and oxidation–reduction state are all assumed to be constant. Fixed pH = 8; fixed $p_{CO_2} = 10^{-3.5}$ atm; ionic strength $\simeq 0.5M$.

AC = acetate
ACAC = acetylacetone
CIT = citrate
OX = oxalate
SAL = salicylate
TART = tartrate
EN = ethylenediamine
DIP = dipyridyl
SUSAL = sulfosalicylate
GLY = glycine
GLUT = glutamate
PIC = picolinate
NTA = nitriloatriacetate
EDTA = ethylenediaminetetraacetate
DCTA = 1,2-diaminocyclohexane-tetraacetate
CYST = cysteine
NOC = nocardamine (desferri-ferrioxamine)
PHTH = phthalate

posed and the result (identical to Table IV) was obtained in 52 iterations ($10^{-8}M$ being the systematic first guess and the correct set of solids having been imposed). The storage space needed for the program itself is about 50,000 bytes while it takes about 90,000 bytes to store the data. In all the examples we have taken a systematic guess of $10^{-8}M$ for every free concentration, not because we could not find a better one, but to show that the domain of convergence is rather large in general.

The program has now been extensively tested on numerous small and large systems and we have been able to converge toward the solution in each case. The program is being currently modified to handle variations in the ionic strength and oxidation–reduction reactions.

To vary the ionic strength, two sets of equilibrium constants are stored, one at $I = 0.0M$, the other one at $I = 0.5M$. An interpolation routine allows computation of the set of constants corresponding to an intermediate ionic strength. An iterative technique looping on the whole program is envisaged to correct the equilibrium constants to the computed ionic strength of the system.

Iteration no.		
0	First guesses: all free concentrations = 10^{-8} M Chosen set of solids: S_{1-1}, S_{1-9}, S_{3-1}, S_{6-32}, S_{10-2}, S_{12-12}, S_{13-1}, S_{14-8}, S_{17-32}, S_{20-12}, S_{20-32}, S_{21-1} [CO_2 (g)]	
31	S_{13-1}	dissolves
39	S_{1-4}	precipitates
42	S_{19-32}	precipitates
45	S_{3-2}	precipitates
49	S_{3-1}	dissolves
53	S_{9-1}	precipitates
56	Found set of solid: S_{1-1}, S_{1-4}, S_{1-9}, S_{3-2}, S_{6-32}, S_{9-1}, S_{10-2}, S_{12-12}, S_{14-8}, S_{17-32}, S_{19-32}, S_{20-12}, S_{20-32}, S_{21-1} [CO_2 (g)]. See solution Table IV	

Figure 11. Successive modifications of sets of solids in a 20-metal, 31-ligand model system

After 56 iterations an equilibrium set of 13 solids [+CO_2 (g)] is found

The redox reactions are handled in several ways. One way involves the use of optional complexes ($NO_3^- \equiv NH_3 + 3\,H_2O - 9H^+ - 8e^-$), or optional solids ($MnO_2 \equiv Mn^{2+} + 4\,OH^- - 2e - 2H_2O$) whose equilibrium constants are given as a function of the $p\epsilon$ of the system. Another way is to define new secondary variables ($[Fe^{2+}] = k[e^-][Fe^{3+}]$) much in the same way it has been shown for solids. The existing subroutines MLINSO and MODIF are used to handle these.

Appendix

DERIVATIVES OF THE MOLE BALANCE EQUATIONS

$$\text{Let } YM_i = [M_i] + \sum_{j,k} \alpha[C_{ijk}] - TOTM_i \; (= 0 \text{ from Eq. 3})$$

$$YL_j = [L_j] + \sum_{i,k} \beta[C_{ijk}] - TOTL_j \; (= 0 \text{ from Eq. 3})$$

$$YH = [\mathrm{H}] - [\mathrm{OH}] + \sum_{\substack{\text{last row}\\ j,k}} \alpha[C_{ijk}] - \sum_{\substack{\text{last column}\\ i,k}} \beta[C_{ijk}] + \sum_{i,j,k} \gamma[C_{ijk}] - TOT\mathrm{H} \; (= 0 \text{ from Eq. 4})$$

By use of Equation 1: $[C_{ijk}] = K_{ijk}[M_i]^\alpha[L_j]^\beta[\mathrm{H}]^\gamma$ it follows:

$$\frac{\partial YM_i}{\partial[M_k]} = 0 \text{ for } i \neq k$$

$$\frac{\partial YL_j}{\partial[L_k]} = 0 \text{ for } j \neq k$$

$$\frac{\partial YM_i}{\partial[M_i]} = 1 + \sum_{j,k} \alpha^2[C_{ijk}]/[M_i]$$

$$\frac{\partial YL_j}{\partial[L_j]} = 1 + \sum_{i,k} \beta^2[C_{ijk}]/[L_j]$$

$$\frac{\partial YM_i}{\partial[L_j]} = \sum_{k} \alpha\beta[C_{ijk}]/[L_j]$$

Table IV. Equilibrium Composition of the

Concentrations of metals, ligands, and complexes are given as negative logarithms. The values for the complexes are the sums of the com

		Ligands	CO_3^{2-}	SO_4^{2-}	Cl^-	F^-	Br^-	I^-	NH_3	S^{2-}	PO_4^{3-}	$P_2O_7^{4-}$	$P_3O_{10}^{5-}$	SiO_2-$(OH)_2^{2-}$	$S_2O_3^{2-}$	AC
		Total concn	0.5	1.5	0.3	2.0	3.0	6.0	6.0	8.0	3.0	7.0	8.0	0.01	7.0	6.3
Metals		Free concn	4.50	2.00	0.30	3.65	3.00	6.05	7.23	32.55	11.10	10.43	12.43	10.60	15.75	6.37
Ca^{2+}	1.0	2.50	4.33(s)	3.30		5.65(s)			9.93		9.00(s)	7.93	9.53		17.45	8.37
Mg^{2+}	1.2	1.28	3.17	1.99		3.63			8.31		7.98	7.12	8.02		16.33	7.15
Sr^{2+}	2.7	4.20		(s)							10.88	11.33	12.58		19.04	10.17
K^+	2.0	2.01		3.52								10.15	11.65		17.35	
Na^+	0.3	0.31	4.11	2.11								8.04	9.94		15.95	
Fe^{3+}	1.0	18.90		18.48	18.39	16.83	22.20	23.65			20.00	23.13		15.50	32.65	21.87
Fe^{2+}	8.0	8.95		9.75	8.85				14.78							12.12
Mn^{2+}	7.0	7.57	9.07	8.37	7.17				14.00		12.47	14.41			22.52	13.44
Cu^{2+}	3.5	7.90	7.59(s)	8.70	8.50	10.75	10.40		9.23		13.40	11.63	13.03			12.57
Ba^{2+}	3.0	8.00		(s)								13.83	14.13		22.54	13.97
Cd^{2+}	6.0	8.28	10.78	9.09	6.00	11.43	9.68	11.93	12.91		17.38	11.52	12.52		21.23	13.65
Zn^{2+}	3.0	6.80		7.60	6.27	9.65	10.40		11.73			8.51	12.34	(s)	21.35	11.87
Ni^{2+}	6.0	6.34		7.15	6.84	9.39	9.44		10.77			10.98			21.09	12.01
Hg^{2+}	6.0	20.05		20.71	6.06	22.70	8.65	8.35	17.00	32.15(s)		18.79			7.00	
Pb^{2+}	7.0	9.19		9.69	7.01		11.09	13.97				24.76			19.83	13.66
Co^{2+}	7.0	7.25		7.85	7.75		10.35		12.48				13.08		22.10	12.52
Co^{3+}	4.0	26.70				25.78			26.51							
Ag^+	7.0	14.75		16.25	9.87		13.35	7.00	18.58	30.50					22.20	20.72
Cr^{3+}	4.0	13.20		12.20		12.29										
Al^{3+}	0.01	15.30		15.86		10.84								(s)		
H^+		8.00	2.90(g)	8.20		8.75			6.03	27.92	7.28	9.93	12.53	4.48	22.45	9.77

[a] $-\log$ (moles solid per liter of solution): $CaCO_3$, 1.05; CaF_2, 2.32; $Ca_5(PO_4)_3OH$, 3.48; $SrSO_4$, 2.72; $Fe(OH)_3$, 1.00; $Cu_2CO_3(OH)_2$, 3.80; $BaSO_4$, 3.00;

$$\frac{\partial YL_j}{\partial[M_i]} = \sum_k \alpha\beta[C_{ijk}]/[M_i]$$

$$\frac{\partial YM_i}{\partial[\mathrm{H}]} = \sum_{j,k} \alpha\gamma[C_{ijk}]/[\mathrm{H}] - \sum_{\substack{\text{last column}\\ k}} \alpha\beta[C_{ijk}]/[\mathrm{H}]$$

$$\frac{\partial YH}{\partial[M_i]} = \sum_{j,k} \alpha\gamma[C_{ijk}]/[M_i] - \sum_{\substack{\text{last column}\\ k}} \alpha\beta[C_{ijk}]/[M_i]$$

$$\frac{\partial YL_j}{\partial[\mathrm{H}]} = \sum_{i,k} \beta\gamma[C_{ijk}]/[\mathrm{H}] + \sum_{\substack{\text{last row}\\ k}} \alpha\beta[C_{ijk}]/[\mathrm{H}]$$

$$\frac{\partial YH}{\partial[L_j]} = \sum_{i,k} \beta\gamma[C_{ijk}]/[L_j] + \sum_{\substack{\text{last row}\\ k}} \alpha\beta[C_{ijk}]/[L_j]$$

$$\frac{\partial YH}{\partial[\mathrm{H}]} = 1 + [\mathrm{OH}]/[\mathrm{H}] + \sum_{ijk} \gamma^2[C_{ijk}]/[\mathrm{H}] + \sum_{\substack{\text{last row}\\ j,k}} \alpha^2[C_{ijk}]/[\mathrm{H}] + \sum_{\substack{\text{last column}\\ i,k}} \beta^2[C_{ijk}]/[\mathrm{H}]$$

Whenever a solid S_{ij} precipitates, a new secondary variable is defined according to Equation 7; say

$$[M_i] = \mu[L_j]^{\nu}[\mathrm{H}]^{\nu'}$$

Then the derivatives are modified in the following way:

$$\text{new}\ \frac{\partial YM \text{ or } \partial YL}{\partial[L_j]} = \text{old}\ \frac{\partial YM \text{ or } \partial YL}{\partial[L_j]} + \nu\,\frac{[M_i]}{[L_j]}\,\frac{\partial YM \text{ or } \partial YL}{\partial[M_i]}$$

$$\text{new}\ \frac{\partial YM \text{ or } \partial YL}{\partial[\mathrm{H}]} = \text{old}\ \frac{\partial YM \text{ or } \partial YL}{[\partial \mathrm{H}]} + \nu'\,\frac{[M_i]}{[\mathrm{H}]}\,\frac{\partial YM \text{ or } \partial YL}{\partial[M_i]}$$

Furthermore, since the equations are modified according to Equation 8; say

$$\text{new } YL_j = \text{old } YL_j + \nu \cdot YM_i$$

$$\text{new } YH = \text{old } YH + \nu' \cdot YM_i$$

(YM_i will be discarded in the rest of the computation.)

We have to modify the derivatives further:

$$\text{new}\ \frac{\partial YL_j}{\partial[M] \text{ or } \partial[L]} = \text{old}\ \frac{\partial YL_j}{\partial[M] \text{ or } \partial[L]} + \nu \cdot \frac{\partial YM_i}{\partial[M] \text{ or } \partial[L]}$$

$$\text{new}\ \frac{\partial YH}{\partial[M] \text{ or } \partial[L]} = \text{old}\ \frac{\partial YH}{\partial[M] \text{ or } \partial[L]} + \nu' \frac{\partial YM_i}{\partial[M] \text{ or } \partial[L]}$$

It should be noted that the order in which those modifications are made is not indifferent for $\frac{\partial YL_j}{\partial[L_j]}$ or $\frac{\partial YH}{\partial[\mathrm{H}]}$; the order shown here is the correct one.

Acknowledgment

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Aqueous Solution Phase for the Model System

plexes of a particular metal and ligand. (s) indicates that a solid exists at equilibrium,[a] and (g) indicates the gas phase component $(CO)_2$

ACAC	CIT	OX	SAL	TART	EN	DIP	SUSAL	GLY	GLUT	PIC	NTA	EDTA	DCTA	CYST	NOC	PHTH	OH
7.0	6.0	5.7	6.3	6.0	7.0	7.0	7.0	6.0	6.0	6.3	7.0	7.3	7.3	8.0	8.0	7.3	
8.96	16.32	6.94	11.80	6.30	9.83	7.97	10.60	7.83	7.75	7.45	12.28	19.59	20.88	16.13	21.65	7.35	5.70
	7.32	6.44		7.10				9.73	8.85	8.15	8.38	11.39	10.88		12.85	8.25	7.30
7.04	6.81	5.82		6.38	10.71	8.76		8.12	7.13	6.54	8.16	14.18	11.86		8.94		4.88
	9.72	9.73						11.43	10.54	9.95	11.47	15.19	15.07		13.95		9.30
											10.98	18.20					
18.40	10.22	17.75	13.95				14.69	16.73	14.55		10.60	12.51	10.44	19.95	8.05		8.30(s)
13.21	9.77		14.15		14.48	12.52	13.65	12.88	12.60	11.51	12.42	14.24	11.63	14.07			8.15
12.72	12.49	11.80	13.47		14.70	13.04	12.97	13.40	12.52	11.44	12.45	13.16	11.65	20.09	17.31		10.07
9.06	6.22	10.33	9.10	11.00	7.15	7.77	9.00	7.47	8.22	7.24	7.43	8.69	7.48		14.90	12.15	8.20
	29.92	13.72	19.49	12.79				15.43	14.44	13.76	15.57	19.79	20.85			13.85	13.30
13.84	12.08	12.32	14.49	11.78	12.61	11.76	14.19	11.72	11.63	11.15	10.46	11.38	9.97		21.06	13.14	9.68
11.16	11.72	10.04	11.70	10.70	10.93	9.37	11.30	9.37	9.55	8.96	8.58	9.89	8.98	13.02	16.25	11.95	8.69
9.80	8.35	9.18	11.14		8.47	7.18	10.55	8.37	8.59	7.00	7.32	7.33	7.82	19.79	15.79	11.59	7.44
					16.32			16.19		19.25	16.73	17.78	16.63	8.30			
13.95	12.26			11.69		14.16		11.92		12.05	9.67	10.78	10.37	13.01		13.14	8.68
11.21	26.77	10.69	12.25	11.45	11.17	9.52	11.85	10.38	10.40	9.01	9.03	10.54	9.23	14.27	17.09	17.95	8.05
					9.29							10.29					(s)
	30.72	19.29			19.88	23.89		19.28		18.82		27.04					18.55
		14.64					14.20					8.84					6.30(s)
16.14	6.72	18.17	13.10				12.91				12.78	16.39	17.80				7.50(s)
8.16	8.32	10.94	6.30	10.20	7.86		7.00	6.03	6.05	10.06	10.48	17.29	18.07	13.08	17.65	10.25	

$ZnSiO_3$, 3.00; HgS, 8.00; $Co(OH)_3$, 4.00; $Cr(OH)_3$, 4.00; $Al_2Si_2O_6(OH)_2$, 0.31; $Al(OH)_3$, 2.99

Nomenclature

C_{ijk} = complex k formed by reaction of M_i with L_j
H = hydrogen ion
J = Jacobian matrix of the system
k_{ij} = dissociation constant for the solid S_{ij} (corrected for ionic strength)
K_w = ion product of water
L_j = ligand j
M_i = metal i
OH = hydroxide ion
$p[\ ]$ = negative logarithms of the concentrations
S_{ij} = solid formed by reaction of M_i with L_j
$TOTM$, $TOTL$ = analytical (total) concentrations of metals and ligands in all phases of the system, respectively
$[\bar{Y}(\bar{X}) = 0]$ = general system of equations to be solved

GREEK LETTERS

α_{ijk} = stoichiometric coefficient of M_i in C_{ijk}
β_{ijk} = stoichiometric coefficient of L_j in C_{ijk}
γ_{ijk} = stoichiometric coefficient of H or OH in C_{ijk}
δ_{ij} = stoichiometric coefficient of M_i in S_{ij}
η_{ij} = stoichiometric coefficient of L_i in S_{ij}
λ_{ij} = stoichiometric coefficient of H or OH in S_{ij}
μ,ν,ν' = constants defined in text

SYMBOLS

$[\ ]$ = concentrations
$[\ ]_T$ = number of moles of a substance used to make up the system, per liter of solution
$\equiv$ = defines the formulas (distinct from $=$)

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Gaseous Bromine and Particulate Lead, Vanadium, and Bromine in a Polluted Atmosphere

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■ Atmospheric gaseous bromine and particulate lead, vanadium, and bromine were collected simultaneously in Cambridge, Mass., with activated charcoal and membrane filters. This study showed a significant fraction of bromine in the polluted atmosphere exists in the gaseous phase. Concentrations of gaseous bromine ranged from 0.12–0.45 $\mu g/m^3$; particulate bromine, 0.12–0.94 $\mu g/m^3$; and particulate vanadium, 0.08–1.32 $\mu g/m^3$ as determined by neutron activation analysis. Lead concentrations varied from 0.4–3.7 $\mu g/m^3$ as determined by atomic absorption spectroscopy. All particulate species showed significant correlation with each other, indicating that their interrelationships in the atmosphere can be explained largely by meteorological conditions. However, the correlation of Pb with both particulate Br and total Br was exceptionally good since Pb and Br come from the same source. Despite this, results indicate the atmospheric concentrations of Br are less than suspected from the amounts of Br added to gasoline in ethyl fluid. The lower atmospheric Br concentration may be explained by different residence times for Br and Pb or that some Br exists in a chemical form not collected by filtration or activated charcoal adsorption.

There is presently no information available on the concentration of gaseous bromine in a polluted atmosphere. Concentrations of gaseous bromine have been estimated in the marine atmosphere in Hawaii by Duce et al. (1965) with a crude potassium carbonate bubbler and filter arrangement. Their results showed a possible gaseous bromine concentration of 0.008–0.040 $\mu g/m^3$ for the unpolluted marine atmosphere. Recent measurements of gaseous bromine in Hawaii by Moyers (1970) are the most trustworthy for the marine atmosphere and average 0.050 ± 0.015 $\mu g/m^3$. The concentration of particulate bromine at the same location reported by Moyers (1970) is 0.009 ± 0.003 $\mu g/m^3$. In urban areas, particulate bromine is a major pollutant resulting from the combustion of ethyl fluid in gasoline. Lininger et al. (1966), Winchester et al. (1967), and Loucks (1969) have indicated the role of particulate bromine in pollution. The possible production of gaseous bromine by oxidation of particulate bromine by ozone and other chemical oxidants or by photochemical processes was suggested by Winchester et al. (1967). Pierrard (1969) has shown that lead bromochloride particles suspended in carbon tetrachloride do release bromine by the photochemical oxidation of bromide. However, the quantity and importance of gaseous bromine in a polluted or unpolluted atmosphere have largely remained unknown.

The concentration of gaseous bromine is related to the concentration of lead in the aerosols either as a source or as a possible reactive sink. The concentration of lead in polluted air has been studied extensively by many investigators. The extent of lead pollution, as well as the toxicity of this element, was discussed in detail by Patterson (1965). Measurements of the lead concentration of Cambridge, Mass., air have been made by the U.S. Public Health Service (1962, 1968) and other investigators.

To explain correlation of particulate lead and bromine in the atmosphere, simultaneous measuring of a metallic element with an entirely different source is important. For comparison, vanadium, whose primary source in polluted air is the combustion of residual fuel oils in power plants (Zoller and Gordon, 1970), was also measured. Vanadium has been found in rather high concentrations in Cambridge by Zoller and Gordon (1970). The vanadium concentration in the Boston area has been shown to be among the highest in the nation by Larsen (1964). Vanadium has also been measured by the U.S. Public Health Service (1962, 1968) at a few locations, although the analytical technique employed was not sensitive enough to obtain concentrations unless the level of vanadium was extremely high. Some measurements of the vanadium content of polluted air in other regions were made by Stocks et al. (1961) in England, and Brar et al. (1969) in Chicago by neutron activation analysis.

Experimental

Atmospheric particulate samples were collected on both type EH and HA Millipore filters (47 mm) with a vacuum pump on the roof of the Arthur A. Noyes Nuclear Chemistry Center at the Massachusetts Institute of Technology, Cambridge, Mass., during September 1969. The filter blank correction for the elements measured (V, Pb, and Br) was less than 5% for all samples. Gaseous bromine samples were collected on clean activated charcoal during the same period as the particulate matter. The gas collector consisted of an electrostatic precipitator, which removed the particulate matter, followed by a 2-gram bed of precleaned activated charcoal. The charcoal was precleaned by heating to 750 °C for two weeks in a vacuum of approximately 10^{-5} cm Hg. This procedure reduced the Br blank in the charcoal to approximately 15 ppb. The charcoal samples were analyzed for bromine by neutron activation analysis with the method developed by Moyers

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(1970). Following a 20-min irradiation with neutrons, the sample (charcoal) was agitated in a hot $1M$ sodium hydroxide solution containing a few drops of a 5% sodium hypochlorite solution and bromate carrier. After acidifying, the bromate carrier was slowly reduced to bromide by the dropwise addition of $0.5M$ $Na_2S_2O_5$. This allowed the radioactive bromine to exchange with the carrier. This procedure has been shown by Moyers (1970) to remove better than 95% of the bromine activity. The slurry was filtered and bromine was chemically separated from the filtrate by the method of Duce and Winchester (1965) before beta counting.

The particulate samples were analyzed by three methods, two involving thermal neutron activation analysis and the third, atomic absorption. Each filter was divided in half and both sections were sealed into clean polyethylene envelopes for neutron irradiation in the MIT Nuclear Reactor (flux $\Phi_{Th} \simeq 2.3 \times 10^{13}$ n/cm²/sec). Vanadium was measured nondestructively by a slight modification of the method used by Zoller and Gordon (1970). γ-Ray spectra were taken with a high-resolution Ge(Li) detector with a full width at half maximum (FWHM) of 2.5 KeV for the 1.332 MeV line of ^{60}Co. The pulses for the detector and amplifier system were fed into a 4096 channel pulse height analyzer where the γ-ray spectra were accumulated for 2-min intervals. Alternate spectra of standards and of the sample were accumulated and stored on magnetic tape for later computer analysis. The filters were set aside to allow decay of the induced radioactivity before subsequent lead analysis by atomic absorption. The second portion of the filter was irradiated with neutrons for 20 min and then agitated in a hot $1M$ sodium hydroxide solution containing carrier bromide. Subsequent chemical separation of the bromine fraction by a procedure similar to that of Duce and Winchester (1965), followed by gross beta counting, allowed the determination of the particulate bromine concentration. The counting was done on a low-background anticoincidence proportional counter in conjunction with an automatic sample changer and timer.

For the lead analysis, the filters were agitated with $0.1M$ HNO_3 for 15 min in an ultrasonic bath. The samples were then centrifuged and the wash solution decanted before analysis. This procedure has been shown by Jernigan (1969) to remove essentially all pollution lead from the filters. The analyses were performed with a Perkin-Elmer 303 atomic absorption spectrophotometer. It should be noted that in a polluted atmosphere such as Cambridge, only a few cubic meters of air need be sampled to obtain accurate results with the sensitive analytical methods described here.

The values reported in this paper for all particulate species have analytical uncertainties of ±10%. The reliability of the gaseous Br concentrations is somewhat less certain. The electrostatic precipitator can possibly change the gaseous Br concentration by either ionizing and thus collecting the gaseous bromine before it reaches the charcoal or by releasing gaseous Br from the particulate bromine (this is probably due to the formation of Br_2 by the oxidation of particulate bromide). Various field tests were conducted to determine how the electrostatic precipitator might alter the gaseous bromine concentrations. These tests indicated that the precipitator's effect on the gaseous bromine concentrations was variable but that the measured concentrations were good to ±20%.

Results and Discussion

The results of the analyses are given in Table I. The concentration range observed for lead, 0.39–3.7 μg/m³, is close to that observed by the U.S. Public Health Service (1962, 1968) for Cambridge, Mass. The vanadium concentrations range between 0.080–1.32 μg/m³ and are in agreement with results obtained by other investigators for the polluted Cambridge atmosphere (Zoller and Gordon, 1970; Larsen, 1964; U.S. Public Health Service, 1962, 1968). The particulate bromine concentrations vary from 0.12 to 0.94 μg/m³ and are also within the range of previous particulate Br measurements in Cambridge (Lininger et al., 1966; Zoller and Gordon, 1970). The gaseous bromine concentrations are, in most cases, approximately equal to the particulate Br concentrations. The particulate Br concentrations in Cambridge are from 10 to 100 times the concentrations generally observed in marine air in Hawaii (Duce et al., 1965, 1967; Moyers, 1970), whereas the gaseous Br in Cambridge is only two to six times the concentration found in Hawaii (Moyers, 1970). This indicates that the sea may possibly contribute a significant fraction of the gaseous Br present in Cambridge air when pollution levels are low.

During the early part of the sampling period (samples 1–5), the weather was characterized by weak westerly winds and a strong temperature inversion, giving poor visibility and generally little mixing of air masses due to a stationary front north of the Boston area. The latter part of the sampling period (samples 6–11) consisted of clear days with good

Table I. Lead, Vanadium, and Bromine Concentrations in the Atmosphere of Cambridge, Mass.

Sample no.	Collection date, 1969	Time, EST	Meteorological conditions	Pb[a], μg/m³	V[a], μg/m³	Particulate[a] Br, μg/m³	Gaseous[b] Br, μg/m³	Total Br, μg/m³
1	9/2	1000–1800	Weak westerly	2.04	0.68	. . .	. . .	. . .
2	9/3	0630–1130	winds, strong	2.31	0.95	0.60	0.21	0.81
3	9/4	0645–1145	temperature in-	3.32	1.12	0.80	0.16	0.96
4	9/4	1200–1630	version, low	3.70	1.32	0.69	0.45	1.14
5	9/4–5	1645–0530	visibility	3.30	0.48	0.94	0.22	1.16
6	9/5	0530–1545	Brisk easterly	0.68 ± 0.10	0.09	0.17	0.28	0.45
7	9/15	1240–1900	winds, no	1.33 ± 0.20	0.16	0.19	. . .	. . .
8	9/15–16	1900–0550	clouds, good	0.45 ± 0.10	0.08	0.13	0.15	0.28
9	9/16	0550–1620	visibility	1.84	0.15	0.39	0.15	0.54
10	9/16	1620–2340		1.66 ± 0.25	0.21	0.32	0.19	0.51
11	9/16–17	2340–0540		0.39 ± 0.10	0.19	0.12	0.12	0.24

[a] All values reported have analytical uncertainties of ±10% unless otherwise indicated.
[b] Values have analytical uncertainties of ±20%.

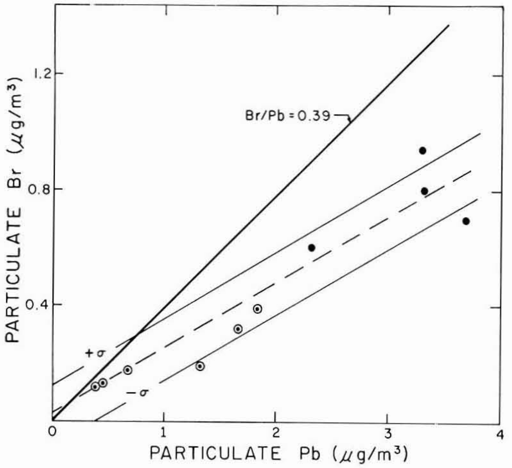

Figure 1. Variation of the particulate bromine concentration with changing particulate lead concentration in Cambridge, Mass.

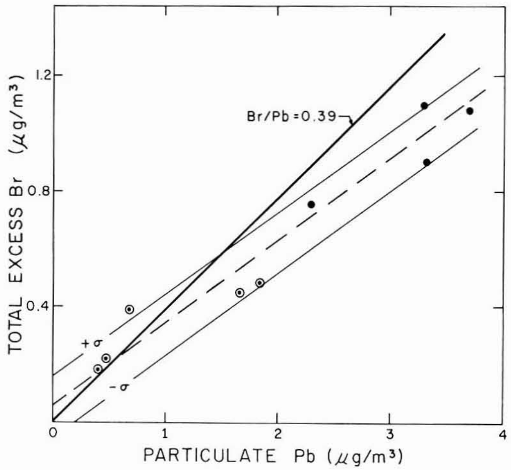

Figure 2. Variation of the total excess bromine concentration (gaseous plus particulate less background) with changing particulate lead concentration in Cambridge, Mass.

visibility and brisk easterly winds off the ocean. The results of the analyses for lead, vanadium, and particulate Br show consistently higher concentrations for the first five samples than the latter six samples, supporting a pollution (or at least continental) source for these elements. Since the sampling site was located near the center of the Boston metropolitan community, the "cleaner" ocean air from the Atlantic Ocean always picked up some pollutants before we were able to obtain samples.

Correlation coefficients between the various elemental pairs have been calculated and are presented in Table II. The correlations between the particulate species (Pb, V, and particulate Br) are all high indicating that to a large extent the individual particulate matter concentrations are controlled by gross meteorological parameters. The highest correlation coefficient of 0.95 between particulate Pb and particulate Br strongly indicates that these elements have a common source. Gaseous bromine shows essentially no correlation with the particulate species.

The particulate bromine concentration vs. lead concentration found in this work is plotted in Figure 1. In Figure 1, those samples collected during the period of high pollution and weak westerly winds are plotted as solid circles while the samples collected during the period of low pollution and easterly winds are indicated by open circles. The solid line on the plot refers to the ethyl fluid ratio of Br:Pb = 0.39 which represents equimolar concentrations of Pb and Br in the ethyl fluid (Ter Haar, 1971) and is in good agreement with the results presented by Lininger et al. (1966) and Winchester et al. (1967). The slope of the least-squares regression line to the data points is less than 0.39 indicating a possible loss of bromine to the gas phase, as previously suggested. The regression line does go through the origin, however, strongly supporting the argument that particulate bromine and lead are from the same source.

Examination of the total Br:Pb ratio for these data shows: (1) samples collected during periods of high lead and bromine concentrations still have total Br:Pb ratios less than the ethyl fluid value of 0.39, and (2) samples collected during periods of low lead and bromine concentrations have total Br:Pb ratios greater than the ethyl fluid value. That the Br:Pb ratio exceeds the ethyl fluid ratio during periods of little pollution can probably be explained by a nonpollution bromine source. Moyers (1970) has shown that unpolluted marine air in Hawaii contains approximately 0.06 μg/m³ of bromine (gas plus particulate). If this value is assumed to be the natural background bromine concentration of Cambridge air, then a relationship can be obtained between total pollution bromine and lead. This relationship is presented in Figure 2 where particulate lead is plotted vs. total excess bromine. Total excess bromine is obtained by subtracting the background bromine value of 0.06 μg/m³ from the observed value of total bromine. The correlation coefficient for the regression line plotted in Figure 2 is 0.96. In Figure 2, it can be seen that the total excess Br:Pb ratio is still less than the ethyl fluid value. The positive intercept on Figure 2 cannot be regarded as significantly different from zero, owing to the small number of samples and the analytical uncertainties for these data. The most significant observation from Figure 2 is that the ratio of total Br:Pb is statistically different from the ethyl fluid ratio (at least at higher pollution levels).

There are several factors which complicate an attempted mass balance of this type. The total Br:Pb ratio in fresh automobile exhaust has never been shown to be equal to the ratio in gasoline. The amount of Br retained in the exhaust and lubricating system is unknown, although it would be expected to be less than Pb due to the generally greater volatility of Br compounds. If, however, unequal production of atmospheric

Table II. Correlation Coefficients

	Particulate Pb	Particulate V	Particulate Br	Gaseous Br
Particulate Pb	. . .	0.83	0.95	0.51
Particulate V		. . .	0.75	0.56
Particulate Br			. . .	0.34
Gaseous Br				. . .

Pb and Br did occur in this manner, it should cause the Br:Pb ratio to be greater than the value in gasoline, not less.

Hurn (1968) states that approximately 20% of the hydrocarbons emitted to the atmosphere by automobiles come from the evaporation of gasoline from the gas tank. This process would also be expected to add tetraethyl lead and ethylene bromide to the atmosphere. However, the vapor pressures of these two substances at 40°C are approximately 1 and 29 mm Hg, respectively. Since these two species are present in approximately equimolar concentration in gasoline, any possible vaporization into the atmosphere would again result in a total Br:Pb ratio higher than that in gasoline.

A further complication arises concerning the atmospheric residence times of the various species. To accurately compare the ratio of total Br/Pb in the atmosphere with that in its suspected source, gasoline, the atmospheric residence time for particulate Pb and total Br must be the same. However, it is unlikely that the gaseous bromine has the same lifetime in polluted air as particulate lead and bromine. If the gaseous bromine has a shorter residence time than the particulate lead and bromine, the value for total excess bromine, compared to the particulate lead, would be too low and the total excess Br:Pb ratio would be less than the ethyl fluid ratio of 0.39, as is found in this work.

That the total excess Br:Pb ratio in air is less than the ethyl fluid value can also be explained by the possibility that our collection procedure discriminates against some form of bromine. This factor requires additional attention before it can be ruled out. Coconut shell activated charcoal (which was used in this work) generally has good retentive properties for Br_2, HBr, and bromo-organic compounds. Additional information concerning the various chemical species of atmospheric bromine is necessary before it is possible to comment further on a bromine discrimination by the collection procedure.

Conclusions

Gaseous bromine concentrations in the atmosphere of Cambridge, Mass., are approximately equal to particulate bromine concentrations and are two to six times the concentration found in unpolluted marine air. The total excess Br:Pb ratio in Cambridge approaches the Br:Pb ratio of 0.39 in gasoline but is still below this value on days of heavy air pollution. One possible explanation for the total excess Br:Pb ratio being less than the ethyl fluid ratio is that the gaseous and particulate species have different atmospheric residence times. Another possibility is that the collection procedure used for this work discriminates against a particular form of atmospheric bromine.

These preliminary results indicate that a significant portion of the bromine produced by the combustion of leaded gasoline can be released to the gaseous phase with the gaseous bromine concentration being between 20 and 70% of the total bromine concentration. It must be emphasized, however, that these data are obtained from a small number of samples collected in a single location with only limited changes of meteorological conditions. To understand the cycle of bromine in a polluted atmosphere, it is necessary to obtain many more samples under different meteorological conditions and in different locations. Further studies of these problems are under way in our laboratory.

Acknowledgment

We would like to thank Joan Moyers who assisted in the bromine analyses. We are also grateful to the reactor staff and the Department of Chemistry at the Massachusetts Institute of Technology for providing space for atmospheric sample analyses, and the reactor staff at the Rhode Island Nuclear Science Center for providing space and facilities for study of the gaseous bromine collection technique.

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CORRECTION

EFFECT OF PEROXYACETYL NITRATE (PAN) IN VIVO ON TOBACCO LEAF POLYSACCHARIDE SYNTHETIC PATHWAY ENZYMES

On page 623 of this article by L. Ordin, M. J. Garber, J. I. Kindinger, S. A. Whitmore, L. C. Greve, and O. C. Taylor [ENVIRON. SCI. TECHNOL., **5** (7), 623 (1971)], in the first column, line 19 should read "0.7 nmole of UDP-glucose-^{14}C" instead of "0.7 μmole." Also, in Table II on the same page, the column heading should be changed to: "nmoles of substrate converted/min/mg protein" instead of μmoles of substrate."

Photooxidation of Sulfur Dioxide

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■ Rate constants for the quenching of excited triplet sulfur dioxide molecules with the atmospheric gases were determined with the aim of delineating the mechanism of the photooxidation of SO_2 in the atmosphere. The triplet species were excited directly by the absorption of a 3828.8 Å laser light pulse within the "forbidden" $SO_2(^1A_1) \rightarrow SO_2(^3B_1)$ band. The data gave the following new estimates for the triplet sulfur dioxide quenching rate constants (liters/mole-sec) at 25°C: N_2 $(8.5 \pm 1.0) \times 10^7$; O_2 $(9.6 \pm 0.5) \times 10^7$; H_2O $(8.9 \pm 1.2) \times 10^8$; Ar $(5.2 \pm 0.5) \times 10^7$; He $(6.8 \pm 0.7) \times 10^7$; Xe $(7.1 \pm 1.1) \times 10^7$; CO_2 $(1.14 \pm 0.07) \times 10^8$; O_3 $(1.10 \pm 0.12) \times 10^9$; NO $(7.4 \pm 0.3) \times 10^{10}$. These and other recent rate data and absorption data for SO_2 were used to estimate the maximum rate of homogeneous photooxidation of sulfur dioxide in the atmosphere. At a solar zenith angle of 20° and 50% relative humidity (rH), the theoretical maximum rate is 1.9% per hour.

Interest in the sulfur dioxide removal mechanisms in the atmosphere remains high among atmospheric scientists. There is substantial evidence that health hazards are associated with urban atmospheres containing moderately low levels of sulfur dioxide (above 0.2 ppm), and that these harmful effects are apparently enhanced when there are significant levels of suspended particulates (U. S. Dept. Health, Education and Welfare, 1969). However, there is now little evidence as to the chemical nature of the active species responsible for these effects. The detailed mechanism of sulfur dioxide oxidation remains unclear. For examples, see the recent reviews of Altshuller and Bufalini (1965), Cadle and Allen (1970), Katz (1970), Urone and Schroeder (1969). The majority of existing evidence suggests that a major fraction of the sulfur dioxide is ultimately converted to sulfuric acid and sulfate salts, but the intermediate species involved and the reaction paths which lead to these products are open to question. The relatively slow rates of photooxidation of sulfur dioxide in air exposed to sunlight (Gerhard and Johnstone, 1955; Hall, 1953) and the demonstrated catalytic influence of certain solids and moisture on the rate of SO_2 oxidation (Foster, 1969; Johnstone and Coughanowr, 1958; Johnstone and Moll, 1960; Junge and Ryan, 1958; Matteson et al., 1969; van den Heuval and Mason, 1963) have led to the common belief that heterogeneous paths for SO_2 oxidation probably far outweigh the homogeneous modes. Although this conclusion may prove to be true for certain atmospheric conditions, it is by no means established today. There is a real question as to the availability of sufficient reactive metallic oxide, catalyst particles, and acid-neutralizing compounds in many atmospheres to promote SO_2 removal at the observed rates. The most compelling argument which has favored the importance of the heterogeneous removal processes has been the apparent lack of alternative homogeneous reactions of sufficient rate which might be invoked. It now appears to us that there are several such possible processes which are open for sunlight-irradiated atmospheres, but these remain quantitatively unevaluated. Our approach to this problem is based on the hypothesis that it is more realistic to evaluate the contributions from these homogeneous processes and arrive indirectly at the contribution of the heterogeneous modes than to establish unambiguously and directly the importance of heterogeneous paths in the real atmospheres.

In this report we describe the first stage of our study of the possible homogeneous paths of SO_2 removal operative in the atmosphere: the photooxidation of SO_2. Quantitative information on the theoretical maximum rates of photochemical oxidation of SO_2 in the atmosphere is presented; we have utilized the results of the most recent studies of SO_2 photochemistry and new data presented here on the rate constants for the quenching reactions of excited SO_2 with atmospheric gases. These data should prove useful in determining the importance of alternative homogeneous or heterogeneous removal mechanisms for specific atmospheric systems.

Reactions of the Excited States of Sulfur Dioxide

During the past few years several independent quantitative studies of the photochemistry of sulfur dioxide have appeared (Cehelnik et al., 1971; Collier et al., 1970; Jackson and Calvert, 1971; Mettee, 1968, 1969; Okuda et al., 1969; Otsuka and Calvert, 1971; Rao and Calvert, 1970; Rao et al., 1969a, 1969b; Sidebottom et al., 1971a, 1971b; Strickler and Howell, 1968; Timmons, 1970). From these studies has emerged new information which relates directly to the mechanism of the photooxidation of SO_2 in the atmosphere. A brief review of these results is in order here.

The major sunlight absorption of sulfur dioxide occurs within the relatively strong band which extends from 3400 to 2400 Å (see Figure 1a). Absorption within this band results initially in the generation of an electronically excited singlet state in SO_2. Presumably this excited species is the $SO_2(^1B_1)$ state, although its spectroscopic assignment is still uncertain (see Herzberg, 1966). In this work we symbolize this state as: $^1SO_2$.

$$SO_2 + h\nu(3400\text{–}2900\ \text{Å}) \rightarrow {}^1SO_2 \qquad \text{(I)}$$

A second, "forbidden" absorption region of SO_2, of much lower extinction, extends from 4000 to 3400 Å; see Figure 1b. The absorption of sunlight within this region results in the direct excitation of SO_2 to an electronically excited triplet species, $SO_2(^3B_1)$ (Brand et al., 1970; Merer, 1963). We will symbolize this state as: $^3SO_2$.

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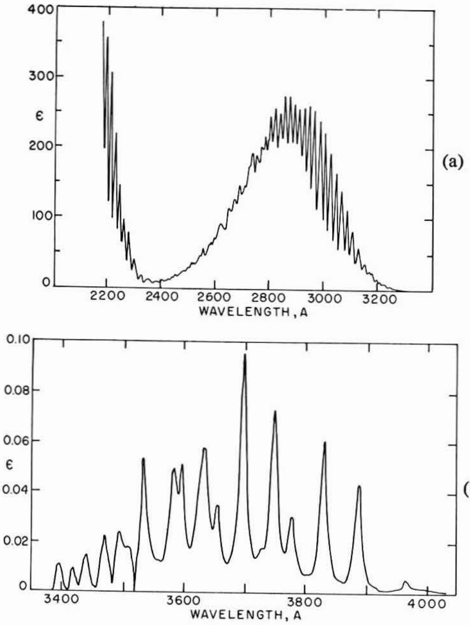

Figure 1. The extinction coefficients of sulfur dioxide gas in the first allowed band (1a) and the "forbidden" band (1b); $\epsilon = [\log_{10}(I_0/I)]/cl$ (liter/mole-cm)

$$SO_2 + h\nu(4000\text{–}3400\ \text{Å}) \rightarrow {}^3SO_2 \qquad \text{(II)}$$

When the sulfur dioxide is excited within the 2400–3400 Å region, both the $^1SO_2$ and the $^3SO_2$ states are ultimately populated as evidenced by the emission which can be observed from both of these states. The mechanism of the populating and deactivating steps can be summarized well in terms of the following reaction scheme:

$$^1SO_2 + SO_2 \rightarrow (2\ SO_2) \qquad \text{(1a)}$$
$$\rightarrow {}^3SO_2 + SO_2 \qquad \text{(2a)}$$
$$^1SO_2 + M \rightarrow SO_2 + M \qquad \text{(1b)}$$
$$\rightarrow {}^3SO_2 + M \qquad \text{(2b)}$$
$$^1SO_2 \rightarrow SO_2 + h\nu_f \qquad \text{(3)}$$
$$\rightarrow SO_2 \qquad \text{(4)}$$
$$\rightarrow {}^3SO_2 \qquad \text{(5)}$$
$$^3SO_2 \rightarrow SO_2 + h\nu_p \qquad \text{(6)}$$
$$\rightarrow SO_2 \qquad \text{(7)}$$
$$^3SO_2 + SO_2 \rightarrow SO_3 + SO \qquad \text{(8a)}$$
$$\rightarrow 2\ SO_2 \qquad \text{(8b)}$$
$$^3SO_2 + M \rightarrow \text{products} \qquad \text{(9a)}$$
$$\rightarrow SO_2 + M \qquad \text{(9b)}$$

M represents some molecule other than SO_2. From the available rate constant data it can be shown that the fast reactions 1b and 2b are the only important decay modes for the $^1SO_2$ species formed within the lower atmosphere. About 9% of the $^1SO_2$-deactivating collisions with SO_2 results in generation of $^3SO_2$ molecules in Reaction 2a. The preliminary results of Horowitz and Calvert (1971) show that the $^1SO_2$ deactivating collisions with N_2 and cyclohexane create $^3SO_2$ with somewhat lower efficiency. These and other recent studies from our group suggest that to a first approximation we can assume that $k_{2_b}/(k_{1_b} + k_{2_b}) \leq 0.09$, where M is N_2, O_2, and H_2O.

Compelling evidence of Okuda et al. (1969) suggests that the major, if not the exclusive, chemically reactive entity in the photochemistry of pure sulfur dioxide is the $^3SO_2$ molecule. Apparently little or no overall chemical change results from the excited singlet species, and its major role in the photochemistry of SO_2 is its part in the generation of triplets by the intersystem crossing reactions (2a,b). Recent studies of the excited SO_2 reactions with the paraffinic hydrocarbons (Badcock et al., 1971; Timmons, 1970), the olefinic hydrocarbons (Sidebottom et al., 1971a) and carbon monoxide (Jackson and Calvert, 1971) are consistent with the hypothesis of $^3SO_2$ being the major chemically active species in these systems also. A new nonemitting triplet (SO_2^{**}) species has been postulated by Cehelnik et al., 1971, in their explanation of product rates from SO_2–CO and SO_2–C_2F_4 irradiated mixtures. They suggest that photochemically induced O-atom transfer reactions of the SO_2^{**} species are important in these systems: $SO_2^{**} + CO \rightarrow SO + CO_2$; $SO_2^{**} + C_2F_4 \rightarrow SO + CF_2O + CF_2$. The extent of the involvement of a nonemitting triplet even in these highly exothermic oxygen atom transfer reactions remains open to question. Furthermore, the analogous O-atom transfer reaction to molecular oxygen must be unimportant in the atmosphere since the possible reaction, $SO_2^{**} + O_2 \rightarrow SO + O_3$, is highly endothermic ($\Delta H \cong 30$ kcal/mole). From all of the evidence at hand it appears to us that the rate data which would be most pertinent to our quantitative consideration of the photochemical reactions of excited sulfur dioxide in the atmosphere are the rate constants for the triplet sulfur dioxide reactions with the various atmospheric components. We report these determinations in the present work.

$^3SO_2$-Quenching Reactions of the Atmospheric Components

In this study we have carried out experiments in which the $^3SO_2$ molecules were excited directly by absorption of a laser pulse of 3828.8 Å light within the "forbidden" $SO_2 \rightarrow {}^3SO_2$ band. The experimental methods have been described pre-

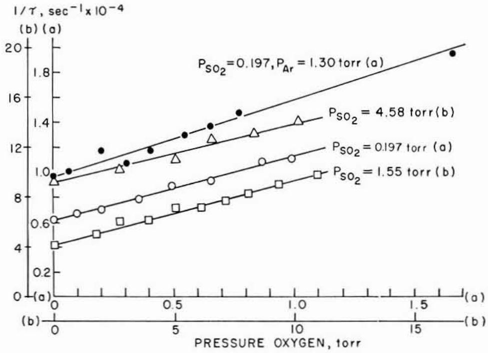

Figure 2. The quenching of $^3SO_2$ by oxygen gas; Stern-Volmer plots of the data for the pressures of SO_2 indicated

Note that the scale for the ordinates and abscissas for the lines labeled (b) is 10 times that for those labeled (a)

Table I. Summary of Quenching Rate Constant Data for Sulfur Dioxide Triplet Molecules with Various Atmospheric Components and Common Atmospheric Contaminants at 25 °C

Compound	Parameters of Stern-Volmer plots[a]		k_9, liter/mole-sec $\times 10^{-8}$
	Intercept, $\text{sec}^{-1} \times 10^{-4}$	Slope, $(\text{mm-sec})^{-1} \times 10^{-4}$	
Nitrogen	4.19 ± 0.36	0.458 ± 0.051	0.85 ± 0.10
Oxygen[b]	1) 0.611 ± 0.020	1) 0.516 ± 0.036	1) 0.96 ± 0.07
	2) 0.955 ± 0.061	2) 0.622 ± 0.135	2) 1.16 ± 0.25
	3) 4.14 ± 0.38	3) 0.515 ± 0.059	3) 0.96 ± 0.11
	4) 9.18 ± 0.57	4) 0.463 ± 0.089	4) 0.86 ± 0.16
			Wtd. av.: 0.96 ± 0.05
Water	4.34 ± 0.39	4.78 ± 0.63	8.9 ± 1.2
Argon	4.30 ± 0.37	0.280 ± 0.029	0.52 ± 0.05
Helium	3.92 ± 0.63	0.365 ± 0.035	0.68 ± 0.07
Xenon	3.83 ± 0.86	0.381 ± 0.058	0.71 ± 0.11
Carbon monoxide	. . .	. . .	0.84 ± 0.04[c]
Carbon dioxide	4.53 ± 0.29	0.614 ± 0.039	1.14 ± 0.07
Nitric oxide	4.19 ± 0.33	399 ± 18	741 ± 33
Ozone	3.77 ± 0.43	5.93 ± 0.62	11.0 ± 1.2
Sulfur dioxide	. . .	. . .	3.9 ± 0.1[d]
Methane	. . .	. . .	1.16 ± 0.16[e]
Propane	. . .	. . .	5.11 ± 0.58[e]
Propylene	. . .	. . .	850 ± 87[f]
Cis-2-butene	. . .	. . .	1340 ± 98[f]

[a] Derived from the least-squares treatment of the $1/\tau$ vs. pressure of reactant plots in Figures 2–4; the error limits reported are the 95% confidence limits (twice the standard deviation).

[b] The four independent estimates of the rate constant for the $^3SO_2$-quenching by O_2 are from runs at various SO_2 and Ar pressures: (1) $P_{SO_2} = 0.197$ torr, (2) $P_{SO_2} = 0.197$, $P_{Ar} = 1.30$ torr, (3) $P_{SO_2} = 1.55$ torr, (4) $P_{SO_2} = 4.58$ torr.

[c] Data from Jackson and Calvert (1971).

[d] Data from Sidebottom et al. (1971b).

[e] Data from Badcock et al. (1971).

[f] Data from Sidebottom et al. (1971a).

viously by Sidebottom et al. From the measured phosphorescence intensities as a function of time, the $^3SO_2$ lifetimes were determined in experiments at 25° and at varied pressures of the common atmospheric gases and impurities. In theory, the lifetimes (τ) of the $^3SO_2$ species should be described by relation A:

$$1/\tau = k_6 + k_7 + (k_{8_a} + k_{8_b})[SO_2] + (k_{9_a} + k_{9_b})[M] \quad \text{(A)}$$

In experiments at a fixed $[SO_2]$, the slope of the plot of $1/\tau$ vs. $[M]$, the concentration of added atmospheric component gas, should give $k_9 = k_{9_a} + k_{9_b}$. The data for a series of experiments with different O_2–SO_2–Ar mixtures are plotted in Figure 2; data from SO_2 mixtures with O_3, H_2O, CO_2, N_2, and Ar are shown in Figure 3, and those with *cis*-2-butene and NO in Figure 4. In each case the theoretically expected linear form of the plots is seen. The slopes of these lines give the estimates of the rate constants, $k_9 = k_{9_a} + k_{9_b}$, which are summarized in Table I.

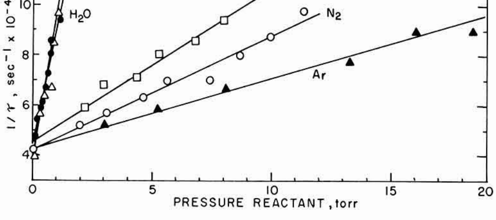

Figure 3. The quenching of $^3SO_2$ by various components of the atmosphere

Stern-Volmer plots of the reciprocal of the $^3SO_2$ lifetimes at 25 °C vs. the pressure of the reactant; $P_{SO_2} = 1.55$ torr

There are some interesting and unexpected observations related to the quenching efficiencies of the different atmospheric components which should be made. Completely unexpected was the significant rate of $^3SO_2$ quenching by N_2, Ar, and the other rare gases; with these species a chemical reaction with the $^3SO_2$ molecule is highly unlikely. These data cannot be attributed to impurity quenching, and they point to the importance of some type of physical quenching in these cases. The rate constants for N_2, O_2, CO, CO_2, CH_4, and the rare gases are all very similar [$k_9 = (0.68\text{–}1.2) \times 10^8$ liters/mole-sec]. The rate constant for $^3SO_2$-quenching by H_2O ($k_9 = 8.9 \times 10^8$) and O_3 ($k_9 = 11.0 \times 10^8$ liters/mole-sec) is about a factor of 10 higher than those of the major atmospheric gases. That for the paraffinic hydrocarbons increases with the ease of C—H bond rupture in the hydrocarbon molecule (Badcock et al., 1971); for example, with methane, $k_9 = 1.2 \times 10^8$ while for propane, $k_9 = 5.1 \times 10^8$ liters/mole-sec. A truly remarkable increase in quenching constant is found for hydrocarbons containing double bonds (Sidebottom et al., 1971a); for example, for *cis*-2-butene, $k_9 = 1.3 \times 10^{11}$, and for propylene, $k_9 = 0.85 \times 10^{11}$ liter/mole-sec. Nitric oxide also shows a large quenching facility with $k_9 = 0.74 \times 10^{11}$ liter/mole-sec. The rate constants for $^3SO_2$ quenching by olefinic hydrocarbons and nitric oxide are near the collision number ($\sim 2 \times 10^{11}$ liters/mole-sec).

In terms of these findings one notes that the atmospheric reactions of electronically excited SO_2 must be estimated in relation to the fraction of $^3SO_2$ which is quenched by the

Table II. Percentage of Triplet Sulfur Dioxide Quenching by Various Atmospheric Components at 25°C, 1 Atmosphere Pressure

Component	Relative humidity, 25°C 0%	50%	100%
Nitrogen	76.1	65.4	57.1
Oxygen	23.4	20.0	17.5
Argon	0.5	0.5	0.4
Water	0.0	14.2	24.5

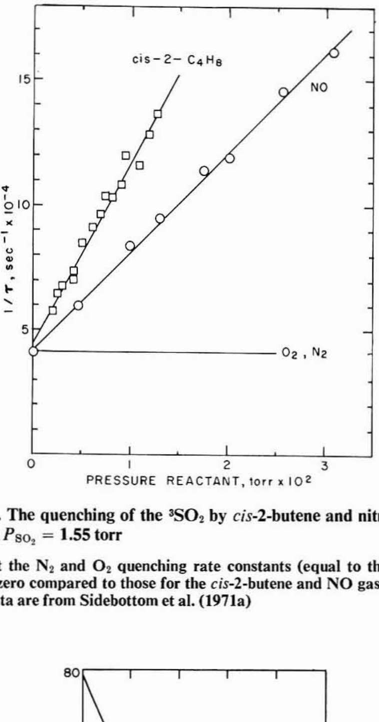

Figure 4. The quenching of the $^3SO_2$ by *cis*-2-butene and nitric oxide at 25°C; P_{SO_2} = 1.55 torr

Note that the N_2 and O_2 quenching rate constants (equal to the slopes) are near zero compared to those for the *cis*-2-butene and NO gases; *cis*-2-butene data are from Sidebottom et al. (1971a)

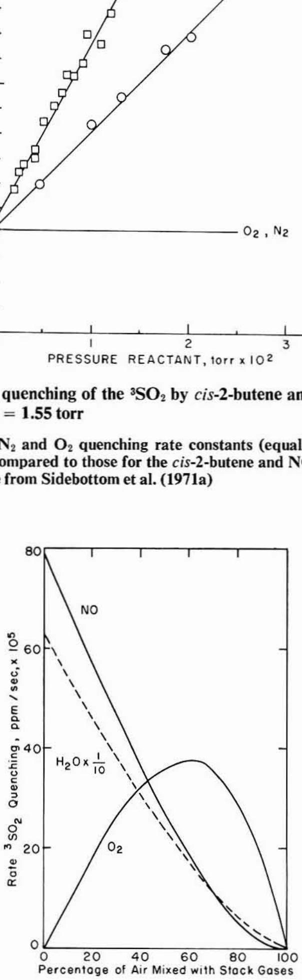

Figure 5. Theoretical rates of triplet sulfur dioxide quenching for typical stack gas effluent from the combustion of sulfur-bearing fuel oil (~1%) as a function of the extent of mixing with air

Initial concentrations: [SO_2] = 600 ppm; [NO] = 200 ppm; [N_2] = 7.47 × 10^5 ppm; [H_2O] = 1.31 × 10^5 ppm; [CO_2] = 1.21 × 10^5 ppm; [O_2] = 0.00 ppm; the air with which the stack gases is mixed is assumed to be at 50% rH; the solar zenith angle is taken as 40°

specific atmospheric components. In the previous quantitative considerations of sulfur dioxide atmospheric photochemistry (for example, see Leighton, 1961), it had been assumed that oxygen was the dominant, if not the only, quencher of excited SO_2 molecules in the atmosphere. It is evident from the present work that this approach will lead to a serious error. In Table II we can compare the percentage of $^3SO_2$ quenching by the various atmospheric components at 25° and 1 atmosphere pressure. Note that the quenching by oxygen varies from 23.4% for dry air to 17.5% for air at 100% relative humidity (rH). About 25% of the $^3SO_2$ species is quenched by the relatively few water molecules present in the atmosphere for the high humidity condition. Because of the abnormally high quenching rate constant for the olefinic hydrocarbons, about one or two excited SO_2 molecules out of 10^4 can react with olefin even though the olefin is present at only the parts per hundred million level. The marked influence of SO_2 on aerosol formation in photochemical smog simulation experiments (see Prager et al., 1960; Renzetti and Doyle, 1960) may be due to this reaction, at least in part.

Rates of Sunlight Absorption by Sulfur Dioxide

In the previous estimates of the rates of excited SO_2 molecule formation in sunlight made by Leighton (1961), the contribution due to the absorption within the "forbidden" singlet-triplet band of SO_2 was neglected. From the knowledge of SO_2 photochemistry available in 1961, this was a reasonable approach. However, as we noted previously the rate of $^3SO_2$ formation will be the important factor for SO_2 photoreactions. Although the absorption by SO_2 within the 2900–3400 Å region is much larger than that from the 3400–4000 Å band, both the intensity of the solar energy and the efficiency of triplet formation are significantly lower in the 2900–3400 Å region than that in the 3400–4000 Å band. Thus, the contribution of $^3SO_2$ formation in sunlight for the "forbidden" band should be considered. Using Leighton's estimate of the actinic irradiance in the lower atmosphere and our extinction data of Figure 1, we have estimated the rates of sunlight absorption by SO_2 and the rate of $^3SO_2$ generation for sunlight absorption within both bands of SO_2 (Table III). Note that although the maximum absorption in the forbidden band is less than 0.03% of that in the first allowed band, the rate of $^3SO_2$ generation from the "forbidden" band compared to that for the more intense, allowed absorption band, ranges from 3.3 to 20% for solar zenith angles of 0° to 80°. Obviously, one cannot neglect the "forbidden" band in quantitative considerations of sunlight-induced photoreactions of SO_2. The total rates of $^3SO_2$ formation are summarized in the last column of Table III for various solar zenith angles.

Rates of Excited Sulfur Dioxide Reactions in the Atmosphere

Our estimated rates of $^3SO_2$ generation in sunlight can be combined with the quenching rate constants reported here to estimate the theoretical maximum rates of the homogeneous, direct photooxidation of SO_2 in sunlight; see Table IV. These are maximum rates for two reasons: The efficiency for intersystem crossing, $k_{2_b}/(k_{1_b} + k_{2_b})$, may be somewhat less where $M = N_2, O_2$, and H_2O than for $M = SO_2$. Physical quenching of SO_2 by O_2 may occur as well as the chemical quenching reaction; this seems highly likely since the quenching of the $^3SO_2$ by O_2 is only 13% greater than that for N_2 for which chemical quenching is not possible.

It is important to recognize the fact that in previous quantitative work (Hall, 1953; McQuigg and Allen, 1970; Warneck, 1968) the quantum yields of SO_3 product or SO_2 removal in

Table III. Estimated Rates of Absorption of Solar Radiation by Sulfur Dioxide[a]

Solar zenith angle, z	First allowed band (2900–3300 Å), sec^{-1} ($\times 10^{-4}$)	"Forbidden" band (3400–4000 Å), sec^{-1} ($\times 10^{-6}$)	Total rate of absorption, k_a sec^{-1} ($\times 10^{-4}$)	$\frac{\text{Rate } ^3SO_2(1b)^b}{\text{Rate } ^3SO_2(1a)}$	Total rate $^3SO_2$ formation	
					sec^{-1} ($\times 10^{-5}$)	hr^{-1} ($\times 10^{-2}$)
0°	3.16	0.95	3.17	0.033	2.94	10.6
20°	2.86	0.91	2.87	0.036	2.66	9.6
40°	1.99	0.80	2.00	0.044	1.87	6.7
60°	0.73	0.57	0.74	0.087	0.71	2.6
80°	0.093	0.17	0.095	0.20	0.10	0.36

[a] Estimates of the actinic irradiance in the lower atmosphere were taken from the Table 8 of Leighton (1961), page 29.

[b] Estimated taking the quantum yield of intersystem crossing of excited singlet sulfur dioxide, $k_{2b}/(k_{1b} + k_{2b}) = 0.09$, the value for $^1SO_2$–SO_2 collisions. The ratio represents the relative rate of generation of triplet sulfur dioxide molecules by absorption which occurs within the "forbidden" triplet-singlet band (Figure 1) to that generated by absorption within the first allowed absorption band (Figure 1a).

SO_2–O_2 mixture photolyses were determined by using mixtures in which the dominant quenching reaction was 8a, involving the SO_2 molecules, not the quenching Reaction 9 involving the O_2 molecules. Thus in a 50% mixture of SO_2 in O_2, 80% of the $^3SO_2$ quenching is by SO_2 molecules. Obviously, one cannot extrapolate such quantum yield data directly to the real atmosphere and expect a meaningful prediction of the SO_2 photooxidation rates. There are at present no reliable data of which we are aware that allows an estimate of $k_{9_a}/(k_{9_a} + k_{9_b})$ ratio. We are continuing work to evaluate this quantity.

It is instructive to compare our estimated maximum rates of homogeneous photooxidation of SO_2 with those observed experimentally in simulated and real atmospheres. Mixtures of SO_2 in pure air irradiated in natural sunlight show rates of SO_2 photooxidation of about 0.1% per hour (Gerhard and Johnstone, 1955; confirmed by Urone et al., 1968). Comparison of this result with our theoretical maximum rates suggests that chemical quenching of excited SO_2 (Reaction 9a) occurs in only about 5% of the total of the quenching collisions with O_2. The preliminary results of McQuigg and Allen (1970) are also qualitatively consistent with this view; they found the quantum yield of SO_2-removal in SO_2–O_2 mixtures to be $(7.2 \pm 1.4) \times 10^{-3}$ at 3130 Å. Our data suggest that the theoretical maximum quantum yield of SO_2-removal is about 18×10^{-3} for O_2-rich mixtures with SO_2 irradiated at 3130 Å. Katz (1950) estimated the rate of conversion of SO_2 to SO_3 (and H_2SO_4) in the atmosphere of Sudbury, Ontario; he found a rate of about 2.1% per hour. Although this checks well with our estimated maximum theoretical rate of photooxidation (see Table IV), the agreement is probably fortuitous since additional reaction paths for SO_2 were probably operative in the polluted air employed in these studies. The relatively enormous rates of SO_2 conversion observed by Shirai et al. (1962), 11.7% per min, found in an industrial area near Tokyo, suggest the importance of alternative efficient paths for SO_2 conversion under these circumstances. Gartrell et al. (1963) reported conversions of 6% per hour (70% rH) and 30% per hour (100% rH) in SO_2 emissions from a coal-burning power plant. Again, one must invoke other mechanisms than homogeneous photooxidation to account for these rates. Foster has rationalized well these rates in terms of the heterogeneous, catalytic oxidation of SO_2 on iron salt containing dusts in the power plant effluent. It should be noted, however, that there are alternative homogeneous reactions which may play an important part in SO_2 removal in NO_x and NO_x–*R*H-polluted atmospheres. See the discussion on next page.

Under certain conditions in polluted atmospheres the extensive quenching of excited SO_2 may occur by other than O_2 and N_2. For example, during the early stages of the dilution of power plant stack gases by air, the photochemically excited SO_2 species in the gases will be quenched in large part by NO and H_2O vapor. Consider the case of a stack gas with a composition typical of that observed in burning of 1% sulfur-containing fuel oil: $[SO_2] = 600$ ppm; $[NO] = 200$ ppm in the N_2, H_2O, CO_2-exhausted mixture. Shown in Figure 5 are the expected rates of $^3SO_2$ quenching by NO, H_2O, and O_2 in the sunlight-irradiated stack gas for different compositions which result from the mixing of the stack gas with air. For simplicity we have assumed that no water condensation occurs. Note the relatively large rates of quenching of $^3SO_2$ by H_2O and NO for these conditions. Gale (1968) has observed an acceleration of the SO_2 removal rate with increasing humidity in his SO_2 photooxidation studies. One can account for this effect in terms of our rate constant data if the net result of H_2O–$^3SO_2$ quenching interactions results in SO_2 removal, and if only about 14% of the $^3SO_2$–O_2 quenching interactions results in oxidation of SO_2. It is not known now what chemical effects, if any, result from the $^3SO_2$–NO and $^3SO_2$–H_2O quenching encounters. It is possible that some new chemical species are created in these cases. If the H_2O quenching collisions with $^3SO_2$ lead to the ultimate removal of SO_2, then the theoretical maximum rates of removal of SO_2,

Table IV. Estimated Theoretical Maximum Rates of Direct Photooxidation of Sulfur Dioxide in the Atmosphere[a]

Solar zenith angle, z	Theoretical maximum rate of the homogeneous, direct SO_2 photooxidation in sunlight[b]					
	$sec^{-1} \times 10^6$			$hr^{-1} \times 10^2$		
	rH: 0%	50%	100%	0%	50%	100%
0°	6.9	5.9	5.1	2.4	2.1	1.8
20°	6.3	5.3	4.7	2.3	1.9	1.7
40°	4.4	3.7	3.3	1.6	1.3	1.2
60°	1.7	1.4	1.2	0.61	0.50	0.43
80°	0.23	0.20	0.18	0.083	0.072	0.065

[a] Estimates of the actinic irradiance in the lower atmosphere were taken from the Table 8 of Leighton (1961), page 29.

[b] Calculated from the theoretical rate of triplet sulfur dioxide formation (Table III data) and the fraction of the $^3SO_2$ quenching collisions which occur with oxygen molecules at the level present in the atmosphere (Table II); it has been assumed that there is no oxidation which results from the $^1SO_2$–O_2 quenching collisions; the maximum rate refers to the $^3SO_2$ reaction with O_2 only; if the H_2O quenching collisions also result in SO_2 removal, then the maximum total rate of removal of SO_2 at 50% and 100% rH should be multiplied by 1.71 and 2.40, respectively.

given in Table IV should be multiplied by 1.71 and 2.40 for the conditions of 50% and 100% rH, respectively. Further work is necessary to delineate the nature of the mechanism of $^3SO_2$ quenching by H_2O and NO molecules.

Detailed Mechanism of SO_2 Photooxidation

Blacet (1952) first suggested a possible mechanism for SO_2 photooxidation. He recognized that the photodissociation of SO_2 ($SO_2 + h\nu \rightarrow SO + O$) was energetically possible only at wavelengths less than 2180 Å which are absent in sunlight in the lower atmosphere. He suggested that an electronically excited sulfur dioxide molecule (SO_2*) would react with oxygen to generate the intermediate SO_4 species (Reaction 10). It was proposed that in air SO_4 would generate SO_3 and ozone by Reaction 11.

$$SO_2^* + O_2 \rightarrow SO_4 \quad (10)$$

$$SO_4 + O_2 \rightarrow SO_3 + O_3 \quad (11)$$

This mechanism has been rather generally employed since its proposal (Altshuller and Bufalini, 1965; Gerhard and Johnstone, 1955; Hall, 1953; Katz, 1970; Urone and Schroeder, 1969). To our knowledge there has been no direct or indirect experimental evidence for the occurrence of Reactions 10 and 11. Specifically, SO_4 has not been identified as a transient in these systems. Also, ozone formation has never been shown to accompany SO_2 photooxidation, although adequate tests for this have not been made. In fact, evidence obtained in this work brings into serious question the occurrence of this simple reaction scheme. In terms of our present knowledge we would involve the triplet sulfur dioxide molecule in Reaction 10. With the conservation of electron spin, $^3SO_2$ would react with $O_2(^3\Sigma_g^-)$ ground-state molecules to give an energy-rich, singlet $SO_4\ddagger$ species, Reaction 12. The lifetime of the very simple SO_4 molecule should be short since it has few degrees of freedom in which it might share the excess vibrational energy. Unless some vibrational energy is removed in a collision with other molecules (Reaction 17), it should dissociate in an early vibration. There are several alternative dissociation modes which are energetically possible, Reactions 13–16.

$$^3SO_2 + O_2(^3\Sigma_g^-) \rightarrow SO_4\ddagger \quad (12)$$

$$SO_4\ddagger \rightarrow {}^3SO_2 + O_2(^3\Sigma_g^-) \quad (13)$$

$$\rightarrow SO_2 + O_2(^3\Sigma_g^-) \quad (14)$$

$$\rightarrow SO_2 + O_2(^1\Sigma_g^+, {}^1\Delta_g) \quad (15)$$

$$\rightarrow SO_3 + O(^3P) \quad (16)$$

$$SO_4\ddagger + M \rightarrow SO_4 + M \quad (17)$$

$$SO_4 + O_2 \rightarrow SO_3 + O_3 \quad (18)$$

Reactions 14 and 16 require a spin inversion and would be expected to be less important than 13 and 15. If only the sequence 12, 13, 17, and 18 were important in this system then one would expect that the experimentally observed $^3SO_2$ quenching constant for oxygen would be dependent on the total pressure of the mixture, at least in the low pressure range. We have checked for this dependence in the series of runs using SO_2, O_2, and Ar gas mixtures over the pressure range from 0.2 to 14.8 torr. Note the data of Figure 2 and Table I. The slopes of the $1/\tau$ vs. P_{O_2} plots, which are equal to the quenching rate constant, are equal within the experimental error for all pressures employed. Hence, the simple sequence of reactions commonly accepted in the description of SO_2 photooxidation are probably not correct in detail, and alternative mechanisms should be considered.

The interaction of $^3SO_2$ and O_2 may generate SO_2 and one of the low-lying electronically excited states of oxygen ($^1\Sigma_g^+$, $^1\Delta_g$), either by the sequence 12 and 15 or directly by energy transfer in 19.

$$^3SO_2 + O_2(^3\Sigma_g^-) \rightarrow SO_2 + O_2(^1\Sigma_g^+, {}^1\Delta_g) \quad (19)$$

This path is the analog to the organic triplet molecule generation of singlet oxygen which has been proposed by Pitts (1969) as a possible atmospheric reaction. If we attempt to explain SO_2 photooxidation in the atmosphere through the occurrence of Reaction 15 or 19, then we must require that the $O_2(^1\Sigma_g^+, {}^1\Delta_g)$ states encounter SO_2 in the environment and oxidize it efficiently. This oxidation could proceed by one of the following paths:

$$O_2(^1\Sigma_g^+) + SO_2 \longrightarrow SO_3 + O(^3P) \quad (20)$$

$$\xrightarrow{(+M)} SO_4 \quad (21)$$

$$O_2(^1\Delta_g) + SO_2 \longrightarrow SO_3 + O(^3P) \quad (22)$$

$$\xrightarrow{(+M)} SO_4 \quad (23)$$

Reaction 20 is energetically possible ($\Delta H = -1.4$ kcal/mole) as are 21 and 23, but 22 must be unimportant for atmospheric conditions since it is highly endothermic ($\Delta H = +13.6$ kcal/mole). Although 20 could be important in laboratory experiments at relative high SO_2/O_2 ratios, it can not be important for atmospheric conditions; the $O_2(^1\Sigma_g^+)$ state will be deactivated (Reaction 24) to the $O_2(^1\Delta_g)$ state within the first few hundred collisions with O_2, N_2, and H_2O in the dilute SO_2 mixture of the atmosphere:

$$O_2(^1\Sigma_g^+) + (O_2, N_2, H_2O) \rightarrow O_2(^1\Delta_g) + (O_2, N_2, H_2O) \quad (24)$$

The chance for a significant number of $O_2(^1\Sigma_g^+)$–SO_2 encounters in the atmosphere with resultant oxidation of SO_2 is negligible. Among the energy transfer mechanisms, 15, 19–23, only Reaction 23 remains as a possible source of SO_2 photooxidation in the atmosphere. The rate constant for the quenching of $O_2(^1\Delta_g)$ by SO_2 is not now available, but it is a reasonable assumption that it is no larger than that of the fastest known quenching reaction of $O_2(^1\Delta_g)$, the reaction with tetramethylethylene ($k = 1.8 \times 10^6$ liters/mole-sec; Hollinden and Timmons, 1970). If Reaction 23 is to be significant it must compete successfully with $O_2(^1\Delta_g)$ deactivation by the major components of the atmosphere, Reaction 25:

$$O_2(^1\Delta_g) + (O_2, N_2, H_2O) \rightarrow O_2(^3\Sigma_g^-) + (O_2, N_2, H_2O) \quad (25)$$

From Clark and Waynes's data (1969) for these reactions, it can be shown that SO_2 at 0.2 ppm (in an atmosphere at 50% rH) could react with a maximum of only 1 in every 1400 of the $O_2(^1\Delta_g)$ molecules formed. The actual efficiency of the reaction probably will be much lower than this estimated maximum. Although electronically excited O_2 may be formed in Reaction 15 or 19 in irradiated atmospheres containing SO_2, one must conclude that the significant involvement of these molecules in SO_2 photooxidation seems highly improbable. The final test must await proper experimental evidence concerning this alternative.

Only Reactions 12 and 16 remain among those we have considered as potentially important mechanisms for SO_2 photooxidation. Alternatively, the sequence could be replaced by the equivalent O-atom transfer Reaction 26 in which the SO_4 species exists only as a transition state for the reaction.

$$^3SO_2 + O_2 \rightarrow SO_3 + O(^3P) \qquad (26)$$

Reaction 26 is rather exothermic ($\Delta H = -37.6$ kcal/mole), and it should have a relatively low activation energy. Of course it follows the second-order kinetics demanded by our experimental observations. In terms of this mechanism the relative smallness of the rate constant for $^3SO_2$ quenching by O_2 ($k_9 = 9.6 \times 10^7$ liters/mole-sec) could result from a relatively low preexponential factor expected in theory to be associated with the spin forbidden character of this reaction. The spin allowed reaction, $^3SO_2 + O_2(^3\Sigma_g^-) \rightarrow SO_3 + O(^1D)$, must be unimportant for atmospheric conditions since it is endothermic by 7.8 kcal/mole.

The dominant fate of $O(^3P)$ formed in Reaction 26 would be O_3 formation in the atmosphere. Thus, if our preferred mechanism is correct, then O_3 formation is expected to accompany the SO_2 photooxidation. This hypothesis, also common to the Blacet mechanism, has not been tested adequately as yet. However, one must keep this possible complication in mind in the study of the SO_2 photooxidation. Analytical techniques must be employed which allow SO_2, SO_3 (H_2SO_4), and O_3 determinations without interference from one another. Obviously, methods based on the iodide oxidation, triiodide reduction, or ultraviolet absorption do not seem to be appropriate choices. We are continuing our work to delineate better the detailed mechanism of the SO_2 photooxidation.

Alternative Homogeneous Removal Mechanisms for SO_2 in the Polluted Atmospheres

We conclude from the present work that a maximum rate of SO_2 removal of about 2% per hour is expected from the homogeneous photooxidation of SO_2 in the atmosphere. Of course this is much lower than the rates of SO_2 removal observed in many polluted atmospheres. However, we would recommend caution in the acceptance of the contention that the "excess" rate is entirely attributable to heterogeneous SO_2 reaction paths. Several investigators have reported that SO_2 is removed much more rapidly when irradiated in NO_2-containing air mixtures than when SO_2 alone is present in the air (for example, Gale, 1968; Katz, 1970; Renzetti and Doyle, 1960; and Wilson and Levy, 1970). The importance of heterogeneous catalytic paths for SO_2 removal is highly unlikely in these cases. However, there are numerous homogeneous paths for SO_2 removal which exist at least in theory when NO, NO_2, and hydrocarbon impurities are present with the SO_2. For example, at the relatively high NO and SO_2 concentrations present in many stack gases, significant NO_2 levels may develop as the stack gases mix with air; this will occur through the reaction, $2\,NO + O_2 \rightarrow 2\,NO_2$, which is usually unimportant at the low ambient levels of NO found in the atmosphere. The NO_2 developed will lead to the photochemical generation of O-atoms during the daylight hours ($NO_2 + h\nu \rightarrow NO + O$). At the very low levels of SO_2 found in the usual polluted atmospheres, the relatively slow Reaction 27 cannot compete with the Reaction 28:

$$O + SO_2 + M \rightarrow SO_3 + M \qquad (27)$$

$$O + O_2 + M \rightarrow O_3 + M \qquad (28)$$

However, the $[SO_2]/[O_2]$ ratios in the stack gases remain well above those commonly encountered in ambient urban air until extensive dilution of the stack gases occurs. A significant rate of homogeneous oxidation of SO_2 can occur by this mechanism for certain conditions expected in stack plumes.

There are many other reactions which may be important for SO_2 removal in NO_x-RH-containing atmospheres. Among these are the following:

$$NO_3 + SO_2 \rightarrow SO_3 + NO_2 \qquad (29)$$

$$RO_2 + SO_2 \rightarrow RO + SO_3 \qquad (30)$$

$$R(RO, RO_2) + SO_2 \rightarrow RSO_2(ROSO_2, RO_2SO_2) \qquad (31)$$

Each of these reactions is considerably exothermic: $\Delta H_{29} = -32$; $\Delta H_{30} = -19$ for $R = $ H, -30 for $R = CH_3$; $\Delta H_{31} = -25$ for $R = CH_3$ (Busfield et al., 1961); they should be of reasonably low activation energy and have fairly high preexponential factors. The preliminary studies of Gall et al. (1971) show that Reaction 31 is fast. In the real atmospheres containing NO_x-RH impurities, the theoretically expected levels of HO, RO, HO_2, and RO_2 suggest that the Reactions 30 and 31 involving SO_2 could compete significantly with other reactions of the HO, RO, HO_2, and RO_2 species. The evaluation of these potentially important homogeneous removal paths for SO_2 is now in progress in our laboratories and will be reported later.

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COMMUNICATION

Proton Activation Analysis for Trace Elements

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■ Trace element concentrations in water samples have been determined from analysis of γ-ray spectra produced by bombarding the samples with a 4-MeV proton beam from a Van de Graaff accelerator. Concentration levels in the parts per billion range for most light elements $Z \lesssim 25$ seem to be detectable. Some measured representative values are: P, 28 ppb; N, 190 ppb; S, 37 ppb; F and Na, 0.1–1.0 ppb.

The method of identifying trace isotopes from their X-ray and γ-ray spectra is proving to be very sensitive (*Bull. Amer. Phys. Soc.*, 1971; Johansson et al., 1970). Both kinds of spectra are generated when a several million-electron-volt (MeV) beam of charged particles, impinging upon a thin layer of material, strips off atomic electrons and collides with atomic nuclei. The X-rays are produced from the de-excitation of the excited atoms, while the γ-rays come from the excited nuclei. Whereas X-ray analysis is currently feasible for elements with a charge greater than 11, the γ-ray technique is better suited for the lighter elements (*Bull. Amer. Phys. Soc.*, 1971).

This paper will describe some measurements of trace element concentrations in a water solution by use of proton-induced reactions and γ-ray detection—proton activation analysis.

In this work, a Van de Graaff accelerator is used to produce a proton beam at a well-defined energy equal to the resonance energy of a specific strong nuclear reaction. Generally, the strongest reactions are inelastic proton scattering followed by

Table I. Detectable Concentration Levels in Light Elements

Reaction	E_p (MeV)	Γ (keV)	Estimate of lowest detectable concentration levels, ppb
^{7}Li$(p,p'\gamma)$	1.03	168	0.1–1.0^a
^{9}Be(p,p',γ)	0.991	89	0.1–1.0
^{9}Be(p,α,γ)	2.567	40	0.1–1.0
^{11}B$(p,p'\gamma)$	2.664	48	3
^{13}C(p,γ)	1.747	0.075	200
^{14}N(p,p',γ)	...	...	...
^{15}N(p,α,γ)	0.899	2.2	190^a
^{16}O(α,α)	3.045	8.0	...
^{18}O(p,p',γ)	0.846	40.0	500
^{19}F(p,α,γ)	0.874	5.0	0.1–1.0^a
^{20}Ne			
^{23}Na(p,α,γ)	1.327	2.8	0.1–1.0^a
^{23}Na(p,p',γ)	1.458	7.5	0.1–1.0^a
^{24}Mg(p,p',γ)	2.400	0.47	0.1–1.0
	2.930	50.0	0.1–1.0^a
^{27}Al(p,α,γ)	1.365	1.1	31^a
^{28}Si(p,γ)	1.652	53.0	10
^{28}Si$(p,p'\gamma)$	3.58	95	15^a
^{31}P(p,α,γ)	3.102	20.0	22^a
^{32}S(p,p',γ)	3.096	0.34	37^a
^{35}Cl(p,α,γ)	2.808	...	50

[a] Measured values.

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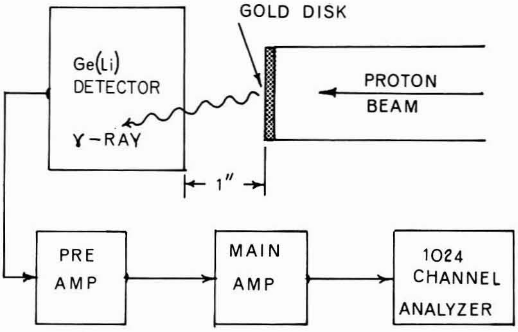

Figure 1. A proton beam impinges on the target material which has been evaporated on a gold disk

Some of the emerging γ-rays are stopped in the Ge(Li) detector producing electrical signals which, after amplification, are pulse-height analyzed.

γ-ray emission, (*p*,*p*′,γ) or proton absorption followed by α- and γ-ray emission, (*p*,α,γ).

The resonance energy and width for these reactions have been well-established and are listed in Table I; the lowest detectable concentration levels presently measured from a matrix of standard solutions or estimated from cross-section data appear there as well.

Target Preparation

A standard solution was prepared by dissolving the following salts into 100 ml of distilled water: 7.1 mg of $NaNO_3$, 3.2 mg of Na_2SO_4, and 4.2 mg of $Na_2HPO_4 \cdot 7H_2O$, (corresponding to 52.3 ppm NO_3, 21.6 ppm SO_4, and 15.3 ppm PO_4, respectively). Several drops of the solution were placed on a clean gold disk and allowed to evaporate leaving a nonuniform residue. These disks were used as the target in some runs. Data were also taken with uniformly thin targets which were made by placing the water drops in a tantalum boat in an evaporator and then heating the residue to ~1000°C with the gold disk suspended over the tantalum. In either case, the protons going through the target material lose about 2 keV of energy as determined by the measured width of a narrow (<1 keV) resonance.

Electronic and Physical Setup

The proton beam was stopped by the gold disk (Figure 1) and the γ-rays were detected by a lithium-drifted germanium solid-state detector (ORTEC Catalog 1002, Oak Ridge, Tenn.) [Ge(Li)]. Signal pulses from the Ge(Li) were amplified, shaped, and then stored in a 1024-channel pulse-height analyzer. A ^{60}Co source was used to calibrate the γ-ray energy spectra.

Phosphorus

The $^{31}P(p,\alpha,\gamma)^{28}Si^*$(1.78 MeV) reaction was used to detect phosphorus at a proton energy equal to the resonance energy at E_p = 3.102 MeV. The target was bombarded with a beam of 2 μA for 50 min. The γ-ray spectrum is shown in Figure 2.

If we assume that a phosphorus peak twice the size of the statistical fluctuation in the background could be measured—i.e., equal to $2\sqrt{N}$, where N is the average number of counts in a background channel—then it is possible to detect a peak 550 times smaller than the one shown here, which would correspond to a concentration level of 28 ppb. If the γ-rays from sulfur were not present, the background near the phosphorus peak would have been less, lowering the detectable concentration level to 22 ppb.

The factor which limits the minimum concentrations detectable by this method is the γ-ray background due to the other trace elements. One can minimize this effect by using a very thin target, but one for which the proton energy loss will be no less than the energy resolution of the proton beam: about 2 keV. If the background has a sharp minimum within the half-width of the resonance (20 keV in this case), it would be advantageous to collect data there.

Nitrogen

Of the possible reactions with nitrogen, the largest resonance occurs with the ^{15}N isotope (only 0.37% of the naturally occurring abundance). The reaction used was $^{15}N(p,\alpha,\gamma)^{12}C^*$-(4.43 MeV) at a proton energy of 0.899 MeV. The target was bombarded for 1 hr at 15 μA. Figure 3 shows the γ-ray spectrum. The broadening of the γ-ray peaks is due to Doppler effects and the kinematics of the reaction. Because of the small (0.37%) isotopic abundance of ^{15}N, the lower limit of nitrogen detection was 190 ppb. The possibility of using a $^{14}N(p,p',\gamma)$ reaction to improve on this value is being investigated.

Sulfur

The sulfur from Na_2SO_4 in the standard solution was detected at a proton energy of 3.096 MeV. A beam intensity of 1

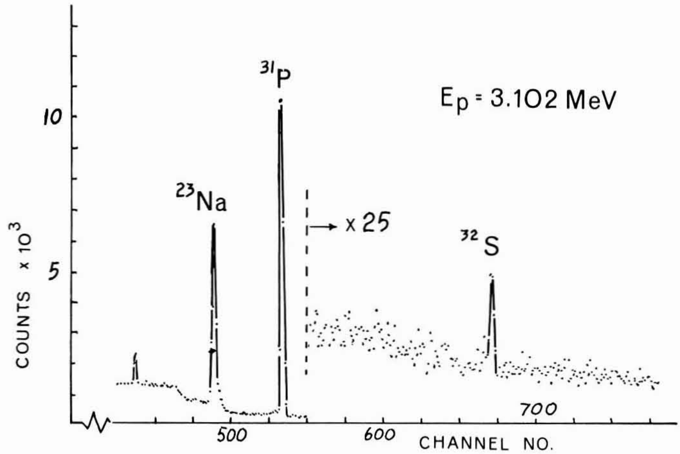

Figure 2. γ-Ray spectrum at the resonance energy of a $^{31}P(p,\alpha,\gamma)$ $^{28}Si^*$(1.78 MeV) reaction. Also shown are $^{23}Na(p,\alpha,\gamma)$ and $^{32}S(p,p,\gamma)$ γ-ray peaks

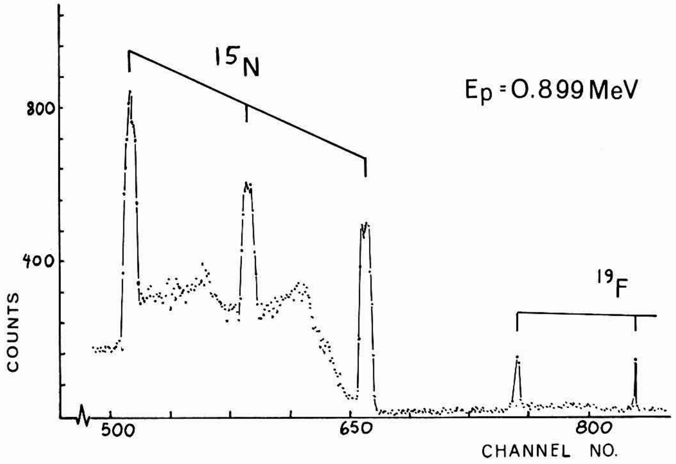

Figure 3. γ-Ray spectrum at the resonance energy of a $^{15}N(p,\alpha,\gamma)$ $^{12}C^*(4.43$ MeV) reaction. Also shown are two of the three $^{19}F(p,\alpha,\gamma)$ peaks (the detection mechanism of these higher energy γ-rays produces three peaks)

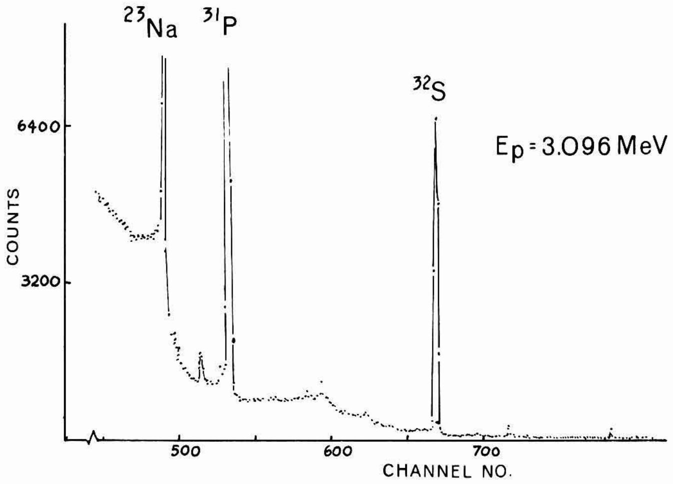

Figure 4. γ-Ray spectrum at the resonance energy of a $^{32}S(p,p',\gamma)$ reaction

μA for 2 hr on a target made from a few drops of water was used. The lower limit of detection extracted from the data in the spectrum shown in Figure 4 was 37 ppb.

Fluorine and Sodium

Large γ-ray yields from F and Na were also observed and these elements could be detected in the 0.1–1.0-ppb range. In fact, for the resonances near 3.0 MeV, the intense γ-ray flux from the $^{23}Na(p,\alpha,\gamma)$ and $^{23}Na(p,p',\gamma)$ reactions limited the beam current, thereby precluding faster collection times.

Application to Air Samples

The standard bubbler used in the West and Gaeke (1956) SO_2 detection method pumps 300 liters of air through 50 ml of solution. This corresponds to a gain in solution-to-air concentration of 8—i.e., 10 ppb in air corresponds to 80 ppb in solution, based on 100% efficiency in the scrubber. A convenient scrubber to use is hydrogen peroxide which oxidizes the sulfur dioxide to sulfuric acid. Adding sodium chloride converts the H_2SO_4 to Na_2SO_4 and HCl, and the Na_2SO_4 can then be evaporated onto a gold disk. The same procedure can be used to prepare a nitrogen target from NO_2 since,

$$2\,NO_2 + H_2O_2 \rightarrow 2\,HNO_3$$

and

$$HNO_3 + NaCl \rightarrow NaNO_3 + HCl$$

Future plans include determining the ultimate sensitivity of this technique for the elements listed in Table I from measurements first on standard solutions, then on actual samples of water and air.

Acknowledgment

We would like to thank R. L. Middaugh for making many helpful suggestions.

Literature Cited

Bull. Amer. Phys. Soc., **16,** 545 (1971), Abstracts DJ-4, DJ-5.
Johansson, T. B., Akselsson, R., Johansson, S. A. E., *Nucl. Instrum. Methods*, **84,** 141–3 (1970).
West, P. W., Gaeke, G. C., *Anal. Chem.*, **28,** 1916 (1956).

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industry trends

Basic Sciences Inc., (Bethel, Conn.) has completed acquisition of the United Corp. (Topeka, Kan.) for an undisclosed amount of Basic's common stock. Basic Science makes mobile thin-walled incinerators. United makes commercial air pollution control incinerators.

Resources Conservation Co. (RCC) (Seattle, Wash.) has signed an eight-year contract with Caneel Bay Plantation to produce freshwater from seawater for the Virgin Island resort. RCC will build and deliver the 60,000-gpd desalination plant by mid 1972.

The California Filter Co. (CALFILCO) will design an automatic demineralizer system for Carolina Power and Light's Brunswick Nuclear Station, Southport, N.C. The demineralizer will supply makeup water for two 820-MW boiling water reactors.

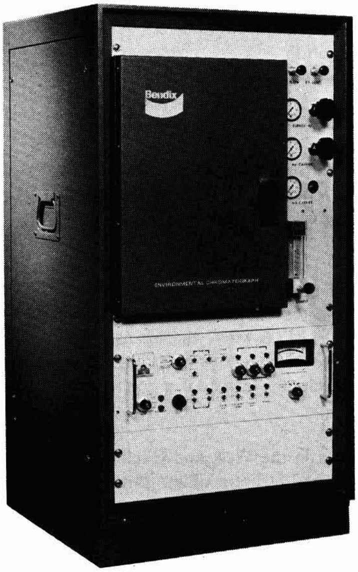
Earth Satellite Corp. (EarthSat), Washington D.C., has received a contract from the New Jersey Department of Environmental Protection for the mapping of 450 square miles of wetlands using aerial color infrared photography.

Westinghouse subsidiary C&C/Bohrer, Inc., has received a $1.6-million contract to build a waste treatment plant at Cabo Rojo, Puerto Rico. The contract also calls for improvement of water transmission lines in parts of Puerto Rico. The Cabo Rojo facility will process 700,000 gpd. Work will be complete by September 1972.

Wisely and Ham, a South Pasadena, Calif. engineering consulting firm, has received a contract from the Department of Housing and Urban Development (HUD) to prepare the first comprehensive manual dealing with noise abatement and land use planning around airports. Bolt, Beranek and Newman, an acoustical engineering firm, will consult with Wisely and Ham on the project.

Zurn Industries' Zurn Foundation is sponsoring two environmental fellowships at Cornell University's College of Engineering. The fellowships will be used to support two research projects. One is directed toward improvement of automatic control methods for water treatment systems. The other will investigate problems of air-water interaction on lakes and in the lower atmosphere.

Heil Process Equipment Corp. has expanded its international marketing program by signing licensing agreements with 3 foreign companies. Toyo Rubber Industries Ltd., Osaka, Japan; Ateliers Belges Reunis, Familleureux, Belgium; and Maskell Productions Ltd., Auckland, New Zealand have been authorized to manufacture some of Heil's proprietary equipment.

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Vibrating screen

Eighteen-in. circular screen separator is useful for laboratory, pilot plant, or low-capacity production runs. Model permits accurate scale-up for high-capacity applications. Kason Corp. **61**

Water quality monitor

Mark II Water Quality Analyzer gives in-situ, five-parameter profile for fresh- or saltwater to depths of 100 meters. Monitor analyzes for pH, temperature, depth, conductivity, and dissolved oxygen. Unit is portable but can be installed for unattended permanent monitoring. Martek **62**

Lead detection kit

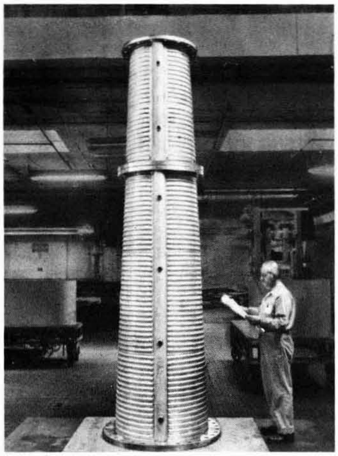
Kit relies on selective extraction of dissolved lead into an organic phase and colorimetric detection of metal in appropriately prepared samples. Results are semiquantitative. Koslow Scientific Co. **63**

Polyelectrolyte

New cationic polyelectrolyte, which is unaffected by chlorine or permanganate, meets Environmental Protection Agency's criteria for safe use in potable water supplies. Cat-Floc B is equally effective in treating industrial wastes. Calgon Corp. **64**

Thermal oxidizer

Asphalt fume thermal oxidizer boasts air preheater which saves 40% in fuel costs. Unit can be attached to existing asphalt exhaust systems. UIP Engineered Products Corp. **65**



Heat transfer surfaces

New series of Panelcoil heat transfer surfaces optimize gas temperatures for pollution control systems. Surfaces are formed into ducts or stacks and may be fabricated in bank assembly forms for use within ducts or stacks. Dean Products, Inc. **66**

Diffractometer

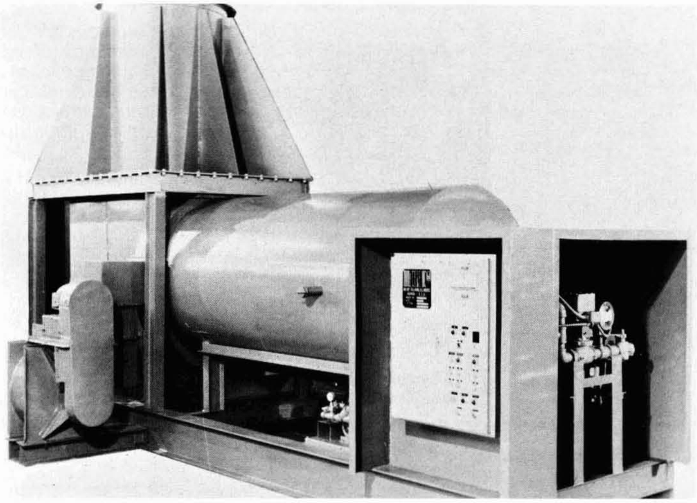
Speediffrax nondispersive X-ray fluorescence and diffraction system is applicable to monitoring of trace metals as well as lead, mercury, cadmium, and selenium. New approach to X-ray diffraction allows growth of all diffraction peaks simultaneously. Nuclear Equipment Corp. **68**

Particle counter

Particle counter is portable unit designed to monitor airborne particulate matter on a continuous mode. Lower limit is particle size of $0.5\ \mu$ and unit measures concentrations as high as 10 million particles/ft^3. Climet Instruments **69**

Water analyzer

Multianalyzer is really three instruments in one. Unit accepts two sensors, permitting continuous dual input of dissolved oxygen plus either pH, relative mV, or specific ion with digital readout and simultaneous chart recording of two parameters. Weston and Stack, Inc. **70**



Liquid incinerator

Thermal system disposes of low- and high-viscosity waste liquids, aqueous liquids, solvents, sludges, or two noncompatible streams fed simultaneously by exchanging energy from high- to low-energy waste streams and using the energy to minimize operation costs. Capacity is 10–1000 gph. Scrubber is available. Brulé Incinerators **67**

Chart editor

Easy-to-use device allows better holding and handling of strip charts for reading or editing. Full roll of chart paper can be inserted and manually advanced throughout its length for working on specific sections. Nuclear Supply and Service Co. 71

Chlorinator

Advance direct cylinder-mounted, gas chlorinator needs no additional power or water pressure for operation. Unit is designed for emergency or standby use in water treatment plants or for remote areas where vacuum feed-type chlorinators would be impractical. Capital Controls Co. 72

Organic vapor analyzer

Portable organic vapor analyzer detects and measures hazardous gases in trace quantities in ambient air. Unit uses hydrogen flame ionization detector to measure organics in presence of inorganics. Century Systems Corp. 73

NO analyzer

Nitric oxide analyzer is designed to monitor trace concentrations of gas continuously in ambient air. New design eliminates need for reagents, metering pumps, fragile glass contactors, and several other complex components previously needed. Unit operates on principle of galvanic coulometry. Beckman Instruments, Inc. 74

SO_2 analyzer

Lightweight, portable SO_2 monitor gives precise readout in 60 sec. Self-calibrating unit uses wet chemistry method coupled with solid state electronics for rapid results on direct-reading, dual scale meter. Research Appliance Co. 75

Air purifier

Type AAV self-contained air purification module has nominal air-handling capacity of 100 cfm. Unit can handle up to three filter units with selection including roughing type dust filters, HEPA filters, activated charcoal, or special adsorbing filters for low molecular weight gases. Barnebey-Cheney 76

Aeration control

Automatic continuous dissolved oxygen analyzer/controller allows maximum BOD removal efficiency. Unit features heavy duty DO probe which can be located in any part of the waste stream. Delta Scientific Corp. 77

new literature

Sludge conditioning. New Booklet tells how to use Dow Chemical's Purifloc to condition sludges. Applications, advantages, and laboratory evaluations are covered as well as various sludge-handling techniques. Dow Chemical Co. **91**

Pneumatic systems. Literature describes heavy-duty, negative-pressure pneumatic waste collection systems. Brochure describes installations and advantages in both new and old structures. ECI Air-Flyte Corp. **92**

Bibliography. Collection of Rand Corp. publications on environmental questions is available in newly compiled bibliography from West Coast think tank. Rand Corp. **93**

Water standards. Technical folder tells of research to establish absolute turbidity of pure water in Formazin Turbidity Units. Hach Chemical Co. **94**

Management guide. New Booklet describes systems available for air and water pollution and solid waste disposal. Monsanto Enviro-Chem Systems, Inc. **95**

Gas detection. Bulletin lists units for analyzing and detecting gases, liquids, and vapors. Includes combustible gas meters, oxygen and thermal conductivity analyzers, nondispersive infrared, hydrogen flame ionization and process chromatographs. Mine Safety Appliance Co. **96**

Reagents. Catalog/price schedule offers concise listing of reagents, accessories, and equipment for air pollution analysis. Research Appliance Co. **97**

Waste water. Booklet gives practical six-step approach to solving industrial waste water pollution problems and describes modular solutions to a variety of liquid waste problems such as phenols, oily water, meat packing, liquor, toxic metals, and refining wastes. Fram Corp. **98**

Trace metals. Eight-page brochure describes multiple anodic stripping analyzer for detecting trace metal pollutants. Environmental Sciences Associates, Inc. **99**

Sampler. Technical bulletin describes sampler that can be programmed on a flow and/or time basis to provide accurate records of fluids. BIF SaniTrol, Inc. **100**

Tertiary treatment. Information on tertiary waste water treatment is contained in literature from company which built the world's first tertiary sewage treatment plant. California Filter Co. **101**

Methods guide. Comprehensive listing of more than 200 current analytical methods involving company's 27 sensing electrodes. Full specs of electrode capabilities are included. Orion Research Inc. **102**

Metal finishing. "Environmental Quality for Metal Finishing Exhausts" is four-page summary which defines common contaminant loading, and presents data tables on such topics as mist generation in various plating processes, solution concentrations, operating temperatures, and other parameters of interest in pollution control. Tri-Mer Corp. **103**

Analysis service. Four-page booklet describes effluent analysis services offered to clients in the United States. Routine analyses include BOD, COD, heavy metals, and pesticides. Nalco Chemical Co. **104**

Combined treatment. Bulletin describes Rex Satellite Plants for treatment of combined sewer/storm water overflows. Rex Chainbelt, Inc. **105**

Apparatus. Catalog lists equipment for analyzing environmental pollutants. Emphasis is on glassware, but chemicals and other test equipment are also listed. Tudor Scientific Glass Co. **106**

Engineering expertise. Release describes engineering capabilities, products, and services of pollution control firm. Peabody Engineering 107

Instruments. Catalog lists instruments for pollution monitoring. Includes price list and equipment specs. National Environmental Instruments, Inc. 108

Grit removal. Bulletin describes Hydrogritter system for grit removal and gives plant sizing methods and data tables. Envirotech 109

Sewage treatment. Brochure describes package of plans and operational data for manufacturing and installing extended aeration, domestic sewage treatment system for commercial use. Stanley M. Strine Design Associates, Inc. 110

Wet grinder. Literature describes compact wet grinding waste disintegrator which requires no accessories for installation. Available with five different inlet fittings to suit various connection requirements. BIF SaniTrol, Inc. 111

Air filter. Data sheet details operating data on industrial air filters. Cyclonic dust separation combined with filtration through felted tubes produces 99.9+% efficiency. Hart-Carter Co. 112

Sludge disposal. Booklet describes "Solidfixation" systems which convert sludge, liquid, or semisolid pollutants into inert landfill. Applications are cited for dissolved metals, tars, oils, and other residues as well as radioactive wastes. Conservall, Inc. 113

Reverse osmosis. Booklet describes water treatment using reverse osmosis and gives details of company's Helical Tubular Segment which provides key to system's simplicity and efficiency. Philco-Ford Corp. 114

Controls. Bulletin describes expanded line of automatic valve controls including cage-trim-type valves, globe valves, cryogenic valves, throttling ball valves, and valve positioners. ITT Hammel-Dahl. 115

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The nation's first recycling day brought together leaders in government, education, industry, and communities. Full texts of sessions and general addresses are given. ■

Inadvertent Climate Modification. xxi + 308 pages. M. I. T. Press, 50 Ames St., Cambridge, Mass. 02142. 1971. $2.95, paper.

Thirty scientists from 14 countries participated in the 1971 Study of Man's Impact on Climate. Provides an overview for the lay reader and detailed assessments of present knowledge about specific problem areas. Follows the 1970 Study of Critical Environmental Problems (SCEP). ■

Water—1970. viii + 610 pages. American Institute of Chemical Engineers, 345 E. 47th St., New York, N.Y. 10017. 1971. $15, paper.

Presents most of the papers given at 1970 meetings of AIChE. Nearly every phase of water pollution technology is treated in these 90 papers. Valuable for libraries, colleges, and industrial and municipal researchers. ■

Trees and Forests in an Urbanizing Environment. Silas Little, John H. Noyes, Eds. 168 pages. Cooperative Extension Service, Rm. 204, Holdsworth Hall, University of Massachusetts, Amherst, Mass. 01002. 1971. $3.00, paper.

Proceedings of a symposium on this subject. Covers how trees modify urban climate, reduce air pollution, and abate noise; how trees can be used in urban landscapes; and research needs. ■

Man and Ecosphere. viii + 307 pages. W. H. Freeman & Co., 660 Market St., San Francisco, Calif. 94104. 1971. $11, hard cover.

Suitable supplemental reading for courses in environmental studies. Twenty seven articles from *Scientific American* have been organized into an integrated book on the history of man's relationship with his environment. ■

The Great American Forest. Rutherford Platt. xii + 271. Prentice-Hall, Inc., Englewood Cliffs, N.J. 07631. 1971. $2.95, paper.

Introduces the reader to the threatened and dwindling forests. Explains "what forests mean to this country and why they should be preserved," according to *Saturday Review*. ■

Pollution: A Selected Bibliography of U.S. Government Publications on Air, Water, and Land Pollution, 1965–1970. Louis Kiraldi, Janet L. Burke. Institute of Public Affairs, Western Michigan University, Kalamazoo, Mich. 49001. 1971. $3.00.

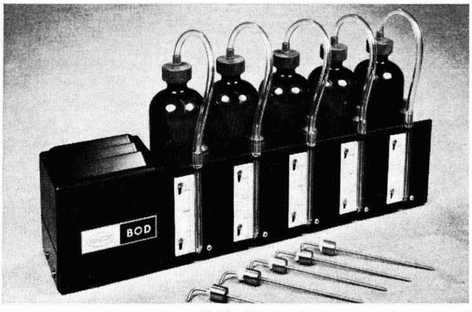
Geared to help students, researchers, and persons anywhere who are interested in the problems of pollution. ■

Effective Technology for Recycling Metal. National Association of Secondary Materials Industries, Inc., 330 Madison Ave., New York, N.Y. 10017. 1971. $7.50.

First technical manual of its kind, says NASMI. Deals with technology and research in metals recycling and air pollution control technology. Based on NASMI workshops. ■

Sulfur and SO_2 Developments. 157 pages. American Institute of Chemical Engineers, 345 E. 47th St., New York, N.Y. 10017. 1971. $12.

Technical manual spanning two major concerns of industries employing sulfur and sulfuric acid: economics of supply and manufacture and the need to improve control of sulfur dioxide emissions and sulfur-bearing wastes. Contains 27 articles. ■



Impingement of Man on the Oceans. Donald W. Hood, Ed. x + 738 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, N.Y. 10016. 1971. $24.95, hard cover.

Discusses the problems of ocean pollution on a broad scale. This is the "first single volume to place the vital subject of world ocean pollution in survey perspective," say the publishers. ■

As We Live and Breathe: The Challenge of Our Environment. Gilbert M. Grosvenor, Ed. 239 pages. National Geographic Society, Washington, D.C. 20036. 1971. $4.95, hard cover.

The National Geographic Society's new book is produced by eight authors who present a biography of America's environment, its ills, and the efforts to cure and protect it. Contains 323 color photographs. ■

Integrated Experimental Ecology. Heinz Ellenberg, Ed. xx + 214 pages. Springer-Verlag New York, Inc., 175 Fifth Ave., New York, N.Y. 10010. 1971. $16.80, hard cover.

Report on research begun in 1966 and still continuing. Scientists representing a variety of disciplines are working on the practical possibilities of the analysis of ecosystems. ■

Combustion-Generated Air Pollution. Ernest S. Starkman, Ed. v + 335 pages. Plenum Publishing Corp., 227 W. 17th St., New York, N.Y. 10011. 1971. $14.50, hard cover.

Covers fundamentals of combustion and combustion systems; performance of combustion systems; effects of air pollution on health, vegetation, and weather; detection and analysis of pollution; and legal and administrative controls. Based on a short course held at the University of California. ■

Toward a Rational Power Policy: Energy, Politics, and Pollution. Neil Fabricant, Robert M. Hallman. vi + 292 pages. George Braziller, Inc., One Park Ave., New York, N.Y. 10016. 1971. $3.95, paper.

A report by the Environmental Protection Administration of New York City. Prompted by the controversy over Consolidated Edison's proposed expansion at Astoria, Queens and by a request from the Temporary State Commission on the environmental impact of major public utility facilities. ■

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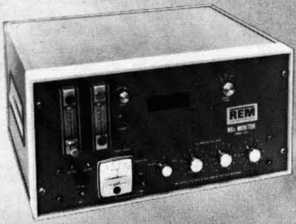

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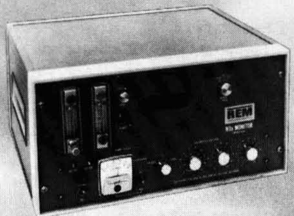

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January 17-21
American Society for Testing and Materials
ASTM Committee Meeting
Ft. Lauderdale, Fla.
Session on water. Contact: Hank Hamilton, ASTM, 1916 Race St., Philadelphia, Pa. 19103

January 24-26
Cooling Tower Institute
New Orleans, La.
Deals with cooling tower operations and related areas. Contact: CTI, 3003 Yale, Houston, Tex. 77018

January 24-28
American Society of Civil Engineers
National Water Resources Engineering Meeting
Atlanta, Ga.
Government, industry, and university spokesmen discuss the nation's increasingly important water problems. Contact: American Society of Civil Engineers, United Engineering Center, 345 East 47 St., New York, N.Y. 10017

January 25-27
American Society of Mechanical Engineers and others
Annual Reliability and Maintainability Symposium
San Francisco, Calif.
Merged meeting with the Institute of Environmental Sciences and others. Write: C. M. Bird, Publicity Chairman, IBM Corp., Dept. 942, 8600 N. Astronaut Blvd., Cape Kennedy, Fla. 32920

January 27
American Society of Heating, Refrigerating and Air Conditioning Engineers
Semiannual Meeting
New Orleans, La.
Symposium on control of particulate emissions. Contact: N. A. LaCourte, Secretary, ASHRAE, 345 E. 47 St., New York, N.Y. 10017

January 31-February 1
Southern California Chapter of the American Statistical Association
Symposium on the Application of Statistical Techniques to the Analysis of Environmental Problems
Los Angeles, Calif.
Fee: $35–40. Attempts to solve environmental problems combining environmental expertise with statistical analysis. Contact: Max Astrachan, Department of Management Science, San Fernando Valley State College, 18111 Nordhoff St., Northridge, Calif. 91324

January 31-February 2
Cornell University and EPA
Agricultural Waste Management Conference
Syracuse, N.Y.
Presents latest research that can be used to solve or alleviate environmental pollution from agricultural wastes. Contact: Department of Agricultural Engineering, 207 Riley-Robb Hall, Cornell University, Ithaca, N.Y. 14850

February 5-7
Water Resources Congress
1972 Annual Meeting of the Water Resources Congress
St. Louis, Mo.
Held in conjunction with the U.S. Marine Exposition. Contact: Water Resources Congress, 1130 17th St., N.W., Washington, D.C. 20036

February 9-10
Ill. EPA and Dept. of Civil Engineering, Univ. of Ill.
14th Water Quality Conference
Urbana, Ill.
"Groundwater Quality and Treatment" is conference title. Write: V. L. Snoeyink, Assistant Professor of Sanitary Engineering, 3230 Civil Engineering Bldg., Univ. of Ill., Urbana, Ill. 61801

February 12-17
Engineering Foundation
Recycle Implementation Conference
Pacific Grove, Calif.
Idea exchange on the subject of recycle among persons concerned with the solid waste field. Fee: $150. Details: Engineering Foundation, 345 E. 47 St., New York, N.Y. 10017

February 14
The Sports Foundation, Inc.
Gold Metal Awards Program for Water Pollution Control
Chicago, Ill.
Since 1968, awards are made annually to members of American industry who have made outstanding achievements in pollution control. Contact: The Sports Foundation, Inc., 717 N. Michigan Ave., Chicago, Ill. 60611

February 14-15
MTS Coastal Zone Management Committee
Tools for Coastal Zone Management Conference
Washington, D.C.
Contact: Marine Technology Society, 1730 M St., N.W., Washington, D.C. 20036

February 14-16
Technical Association of the Pulp and Paper Industry
57th Annual Meeting
New York, N.Y.
Write: M. J. Williams, TAPPI, 360 Lexington Ave., New York, N.Y. 10017

February 19
Gannon College
Systems Approach to Noise in the Urban Community Seminar
Erie, Pa.
Contact: Institute for Community Development, Gannon College, Erie, Pa. 16500

February 20-23
American Institute of Chemical Engineers
AIChE 71st National Meeting
Dallas, Tex.
Many sessions on various phases of pollution control. Contact: R. S. Schechter, Dept. of Chem. Eng., Univ. of Texas, Austin, Tex. 78712

February 21-22
Environmental Protection Agency and Clemson University
Coastal Zone Pollution Management Symposium
Charleston, S.C.
Focuses attention of regional, state, and local agencies on water quality problems in the coastal zone. Write: Billy L. Edge, Co-Director, Coastal Zone Pollution Management, Rhodes Engineering Research Center, Clemson Univ., Clemson, S.C. 29631

March 5-9
Society of Toxicology
1972 Annual Scientific Meeting
Williamsburg, Va.
For additional information, Robert A. Scala, Esso Research and Engineering Co., P.O. Box 45, Linden, N.J. 07036

March 11
Gannon College
Literature of the Environmental Crises Seminar
Erie, Pa.
Contact: Institute for Community Development, Gannon College, Erie, Pa. 16500

March 14-15
American Gas Association and others
GATE-SwRI Energy Conservation Forum
San Antonio, Tex.
Will consider conservation and ways of producing more energy. Write: Jack Wolfe, GATE Information Center, Southwest Research Institute, 8500 Culebra Rd., San Antonio, Tex. 78284

March 14-16

U.S. Bureau of Mines and IIT Research Institute

Third Mineral Waste Utilization Symposium

Chicago, Ill.

Registration accepted on an as-received basis. For details: Murray A. Schwartz, Symposium Chairman, IIT Research Institute, 10 W. 35 St., Chicago, Ill. 60616

March 16-20

National Association of Secondary Materials Industries

59th Annual Convention

Los Angeles, Calif.

Theme "National Leadership for the Recycling Industries." Contact: NASMI, 330 Madison Ave., New York, N.Y. 10017

March 20-24

Ohio State University

Midwest Workshop in Environmental Science

Columbus, Ohio

Contact: John Lindamood, Dept. of Food Science and Nutrition, Ohio State University, Columbus, Ohio 43210

March 21-23

Environmental Protection Agency and University of Houston

National Conference on Control of Hazardous Material Spills

Houston, Tex.

Write: H. Nugent Myrick, Associate Professor of Civil and Environmental Engineering, University of Houston, 3801 Cullen Blvd., Houston, Tex. 77004

March 26-28

Environmental Mutagen Society

1972 Meeting

Cherry Hill, N.J.

Write: Warren Nichols, Program Committee Chairman, Environmental Mutagen Society, Dept. of Cytogenetics, Institute for Medical Research, Copewood St., Camden, N.J. 08103

April 10-12

North Carolina State University and others

Fourth Annual Air Pollution Workshop

Raleigh, N.C.

Program presents current and future goals concerning research on the effects of air pollution on vegetation and ways of communicating these goals between and among scientists and program planners at governmental levels. Contact: William A. Feder, Suburban Experiment Station, Univ. of Massachusetts—Waltham, 240 Beaver St., Waltham, Mass. 02154

(*continued on page 92*)

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The International Association
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JERUSALEM, ISRAEL

JUNE 18-23, 1972

The Conference Technical Program will consist of ninety scientific papers chosen by panels of the leading international experts on the latest research developments in the field of water pollution control. In addition, there will be thirteen Workshop Sessions which will be of interest to the widest possible range of practising engineers, administrators and research scientists.

The Conference program will feature:

1. Problems of Developing Countries and Arid Zones
2. Wastewater Re-use and Reclamation
3. Low Cost Wastewater Treatment Systems
4. Tertiary and Advanced Treatment Methods

Included as well will be sessions on water quality management; wastewater treatment; lake and river pollution; marine disposal and pollution control; industrial wastes; sludge handling and disposal; disinfection; control of pathogenic bacteria and viruses; odor and insect nuisance control; pond systems; analytical methods and monitoring techniques; automation and water quality criteria, and the administration and management of water pollution control programs. Authors and titles of all scientihc papers will be announced at a later date.

The International Water Quality Exhibition

The International Water Quality Exhibition will be held in Jerusalem at the conference hall. The Exhibition will cover the following subjects: Water and Wastewater Treatment Processes; Supplies and Chemicals; Water Quality Monitoring Equipment; Scientific and Laboratory Equipment; Technical and Scientific Books and Publications; Consulting Engineering Services; International and National Agencies.

General information concerning the Conference and Exhibition may be obtained from the Israel Host Committee, P.O.B. 16271, Tel-Aviv.

REGISTRATION FORM

Please return the Registration Form to the Organizing Committee, The 6th International Conference on Water Pollution Research, P.O.B. 16271, Tel-Aviv, Israel

PLEASE TYPE OR PRINT

Surname.......................... First Name........................

Address..

Business Affiliation............. Title or Position......................

Registration fee per person:

	Before* April 1, 1971	After April 1, 1971
Participants	\$50.—	\$60.—
Accompanying persons	\$25.—	\$25.—

I wish to attend the 6th International Conference on Water Pollution Research and will be accompanied by......persons. I enclose \$......in payment of registration fees. Please have checks or drafts payable to the 6th International Conference on Water Pollution Research. The official bank of the Conference is the Bank Leumi le-Israel B.M., Kikar Malchei Israel Branch, Tel-Aviv.

Date.......................... Signature..........................

* Only registration forms accompanied by the registration fee of \$50.— postmarked before April 1, 1972 will benefit from the low pre-Conference registration fee rate.

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B-grade	6.60 to 7.40	9.10 to 10.80

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In the opinion of Bond Counsel, interest on the Bonds is exempt under existing laws from all present Federal income taxes (except for interest on any Bond for any period during which the Bond is held by a person who is a substantial user of the project or a related person). A ruling to that effect has been received from the Internal Revenue Service. In addition, in the opinion of Bond Counsel, interest on the Bonds is exempt from taxation in the State of Alabama.

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International Paper Company

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Principal and semi-annual interest (December 1 and June 1), with the first coupon due June 1, 1972, are payable at the principal office of either the Trustee, The First National Bank of Mobile, Mobile, Alabama, or at the Bankers Trust Company, New York, N. Y. The Bonds will be coupon bonds in denomination of $5,000 registrable as to principal only and fully registered Bonds in the denomination of $5,000 each or in multiples thereof, and may be interchanged. The Bonds are subject to redemption prior to maturity as more fully described in the Official Statement.

Amount	Maturity	Interest Rate	Price	Amount	Maturity	Interest Rate	Price
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320,000	1975	3¾	100	375,000	1979	4.70	100
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345,000	1977	4¼	100	410,000	1981	4.90	100

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MEETING GUIDE (continued)

Courses

January 24–25
George Washington University
Solid Waste Management for Hospitals
Washington, D.C.

Fee: $125. For details: J. E. Mansfield, Director of Continuing Engineering Education Program, The George Washington University, Washington, D.C. 20006

February 22–24
American Water Works Association
Emergency Planning Short Course
San Mateo, Calif.

Designed to enable water utility managers to plan for disasters and minimize damage and continue utility operations. Contact: Director of Education, AWWA, 2 Park Avenue, New York, N.Y. 10016

March 4, 11, and 14
California State College
Statistical and Probability Analysis of Hydrologic Systems Short Course
Los Angeles, Calif.

Designed for engineers, hydrologists, and geophysicists. Contact: Office of Community Services, California State College, 5151 State College Drive, Los Angeles, Calif. 90032

March 6–7
USDA Graduate School
Policy Issue Seminar on the Quality of the Environment
Washington, D.C.

Will discuss environmental degradation and why it occurs or can occur in the future. Nominations due before Feb. 21. Fee: $95. Write: Dee W. Henderson, Suite 265, National Press Bldg., 529 14th St., N.W., Washington, D.C. 20004

March 7–9
University of California Extension
San Francisco Bay–Delta Water Quality Short Course.
Berkeley, Calif.

Fee: $125. Focuses on research, regulations, waste management practices, and control policies for water quality enhancement. Contact: Continuing Education in Engineering, University of California Extension, 2223 Fulton St., Berkeley, Calif. 94720

Harvard School of Public Health
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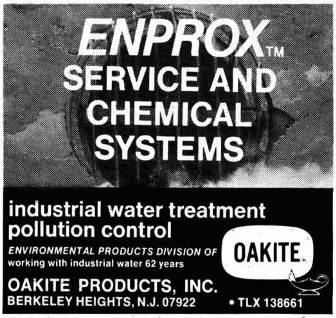

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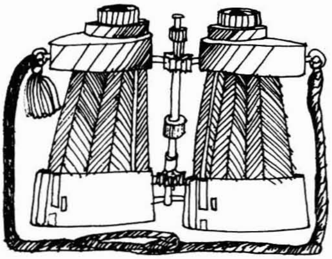

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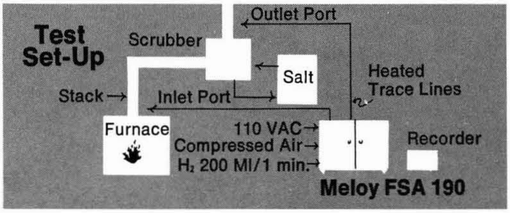
MELOY FSA 190 FLUE GAS MONITOR

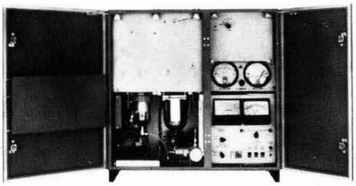
VS.

INFRA-RED DISPERSION ANALYZER



Assignment: Monitor stack wet scrubber emissions

	FSA 190	**IR Analyzer**
Response:	**30 sec.**	**Hours**
Interference:	**None**	**Positive & Negative**
Moisture in gas:	**No problem-overcome by trace line engineering**	**Problem-Requires condensers and sample conditioning**



Test was conducted in on-stream Field Test installation. Results of similar Field Tests of FSA 190 in low sulfur coal fired boilers, Kraft process, black liquor fired boilers, and oil fired boilers are available for your review. Contact the Marketing Director, Meloy Laboratories, Instruments & Systems Division.

The superior performance of the FSA 190 and other Meloy Air Pollution Measurement Instruments is due to the use of Flame Photometric Detector (U.S. Pat. 3,489,498) which utilizes the photometric detection of the 394 mu-centered band emitted by sulfur containing compounds in a hydrogen-rich air flame.

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