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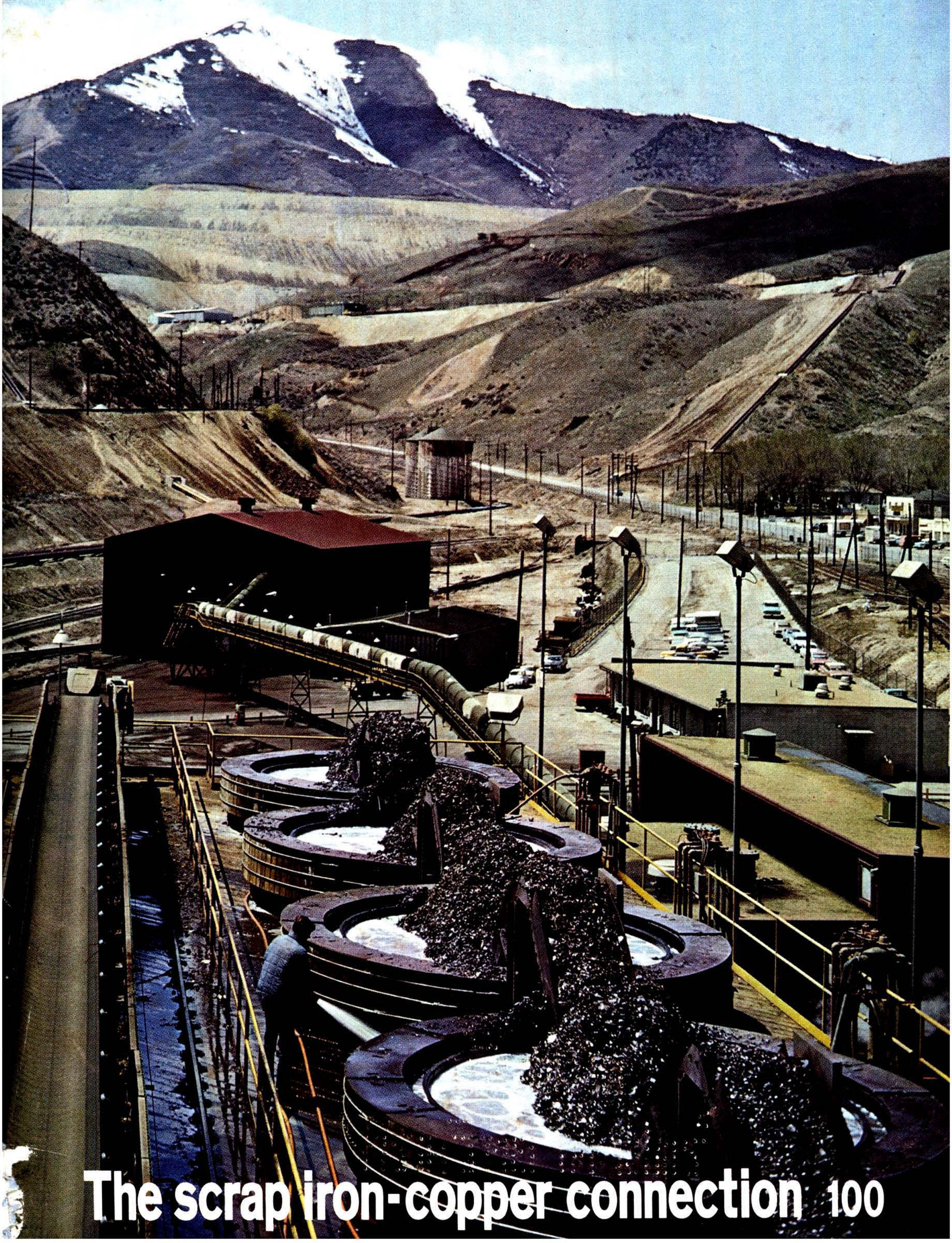

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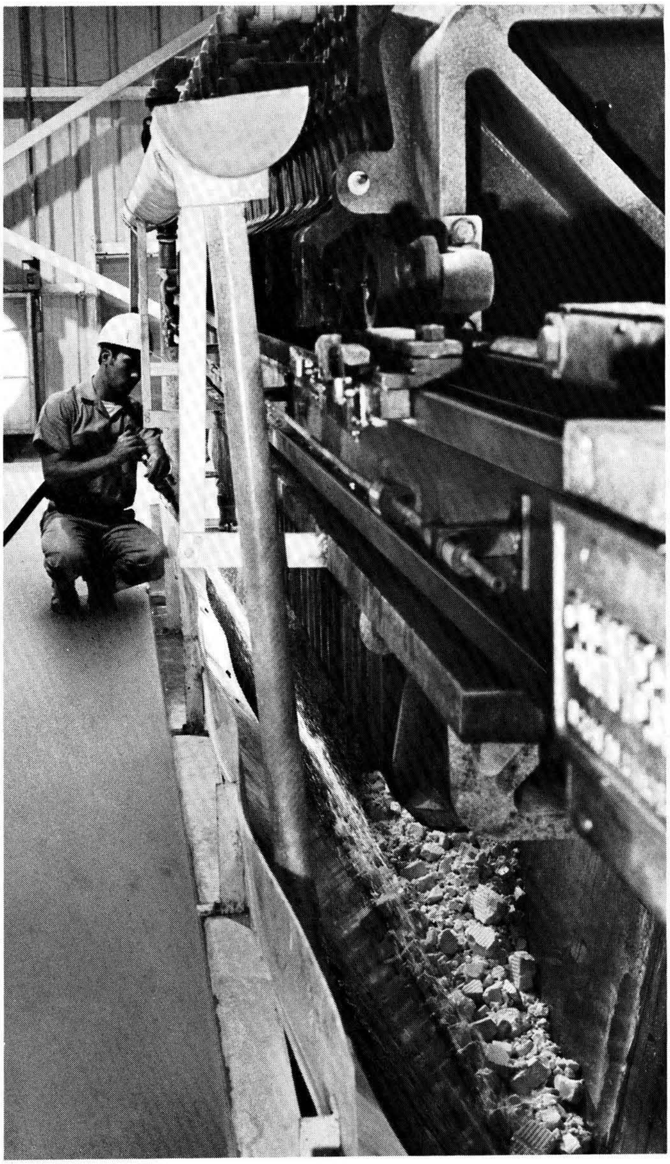

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Volume 7, Number 2, February 1973

ESTHAG 7(2) 83-172 (1973)

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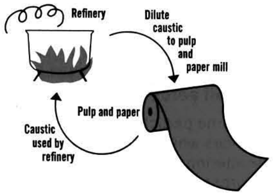

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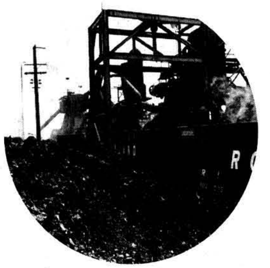

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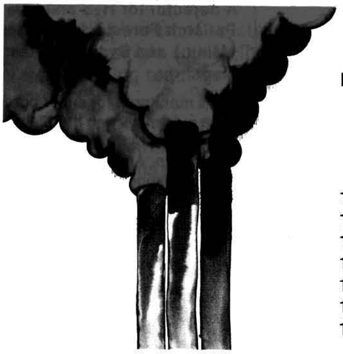

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RESEARCH BRIEFS

California Institute of Technology's Mitchell, Simmonds, and Shair report on oil spill identification with microencapsulated compounds 121

Five to 10 million tons of oil are added each year to the world's oceans through accidental spillage and intentional discharge. A technique has been developed, based on tagging with Freon-13, that permits identification of oil slicks up to one month after a spill.

Persiani and Shelby, a team at GTE Laboratories (Bayside, N.Y.), tell of nondestructive monitoring technique for monitoring fuel oil contaminants 125

Commercial heating oil may contain contaminants that not only pollute the air, but also impair the efficiency of fuel burners when deposition on the impellers takes place. An analytical method is described that compares favorably with other methods. The limits of detection are 10 ppm for vanadium, 500 ppm for sulfur, and 100 ppm for sodium.

GM Corp. Research Laboratories Klimisch and Taylor detail the role of ammonia formation in catalyst selection for NO reduction 127

Nitrogen oxides in auto exhaust can be rendered harmless by conversion to other forms of nitrogen, such as ammonia. Various combinations of metal catalysts (nickel, copper, platinum, palladium, ruthenium) were evaluated for their effect on product formation. Ruthenium is unusual in that it can perform both ammonia decomposition and reduction activity.

Buchauer of Rutgers—The State University (N.J.)—summarizes soil and vegetation contamination effects near a zinc smelter 131

Palmerton, Pa., is the site of two smelters which are sources of metal oxide fumes. Metals have been deposited in soil, plants, and trees in the vicinity of the smelters, the greatest amounts (90%) being found in the top 15 cm of soil and in vegetation closest (within 2 km) to the smelters, for example, 4500 ppm zinc and 70 ppm cadmium in tree foliage.

Canadian Department of the Environment spokesman, Oliver of the Inland Waters Directorate, finds heavy metals in Ottawa and Rideau River sediments 135

Paper mills, a sewage plant, and an area previously used as a river snow dump contribute to the metal content of river sediment in the vicinity of Ottawa. Sediment near paper mills contained an average of 2.2 ppm mercury. A sediment sample near the sewage plant contained (in ppm) Pb 390, Hg 2.3, Zn 846, Cu 236, Ni 71, and Co 128. The high levels of lead, 336 and 1344 ppm, found near the former river snow dump is probably from snow containing lead from auto exhaust.

Kennedy of the Rohm and Haas Co. discusses the treatment of effluent from the manufacture of chlorinated pesticides with an amberlite resin 138

Pesticide manufacturing plants can be the source of pollutant waste effluents. A polymer is described on which chlorinated pesticides are adsorbed, and later recovered. The operating costs are less than those when activated carbon is used.

Cooper, Byers, and Davis at Pennsylvania State University measure laser light backscattering humidity for salt aerosols 142

Airborne particle concentration is often determined by devices which illuminate the particles and measure their light-scattering ability. Humidity alters backscattering from hygroscopic aerosols. NaCl, KCl, and NaBr particles scatter more than twice as much light when humidified than they do when dry.

Univ. of Minn. Mechanical Engineering Department's Berglund and Liu report on the generation of monodisperse aerosol standards 147

Aerosol standards are needed for fundamental research and calibration of sampling and measuring instruments. The generator described can produce particles (0.5–50 μ) from various solid and liquid materials, such as methylene blue and sodium chloride. These particles are both monodisperse and measurable, unlike those provided by conventional generators.

A detector for H_2S and SO_2 is evaluated by Greer of Potlatch Forests, Inc. Paper and Paperboard Research (Minn.) and Bydalek of the Univ. of Minn. Chemistry Dept. 153

Air is monitored for sulfur compounds in the vicinity of a kraft pulp mill using the Melpar detector. The detector is less sensitive at higher sulfur masses (>70 ng) due to self-absorption. An equation is given which defines the optimum working range of the detector (0–60 ng) where maximum sensitivity is obtained.

Credits: 93, Alberta Government Photograph; 95, Ray Rakow; 97, 98, Leonard Soned; 100 (right), 101, Kennecott's Don Green; 104, Crane Co.; 106, Ed Loureiro; 118, Monsanto Enviro-Chem Systems, Inc.

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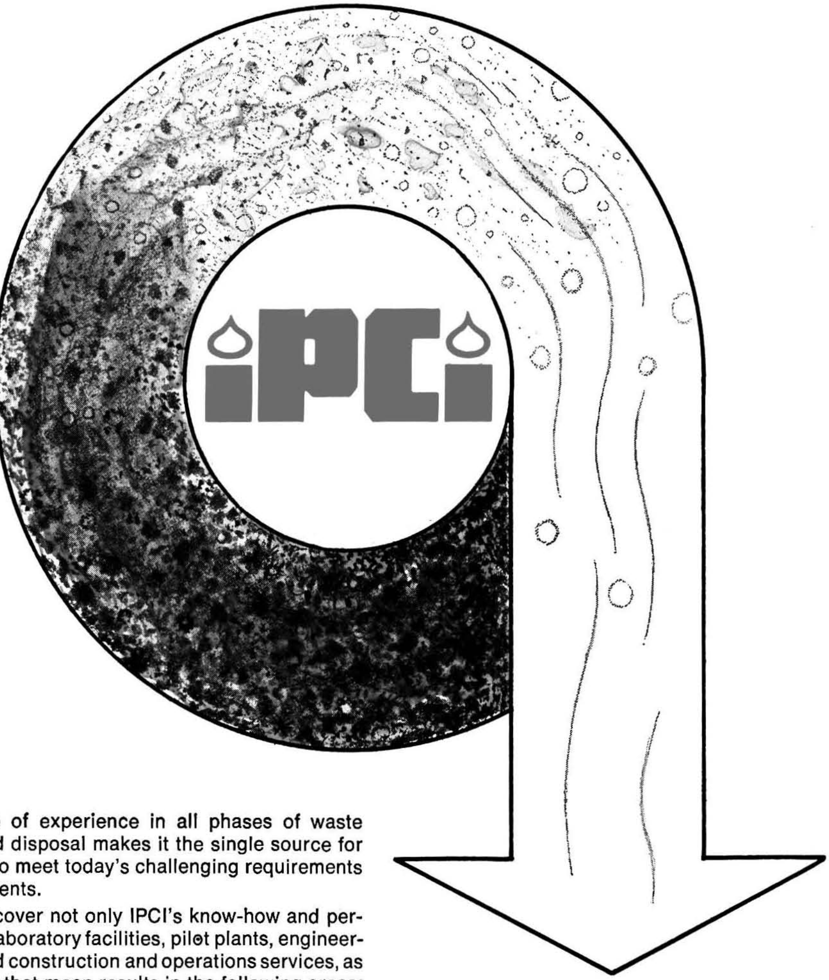

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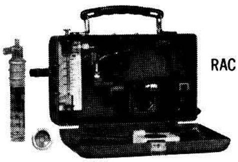
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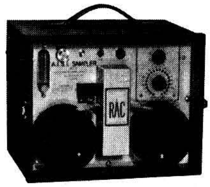
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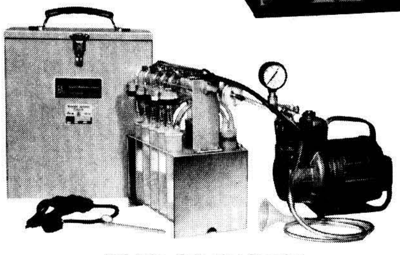
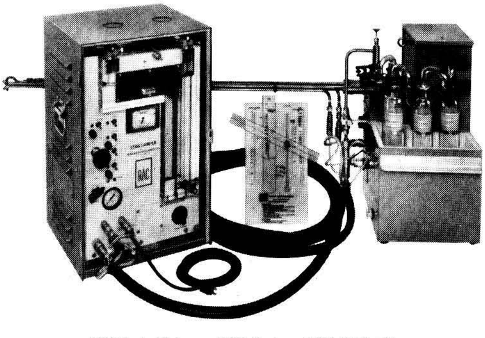

RAC 5-Gas Collecting Sampler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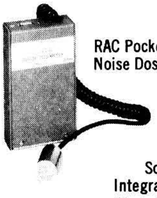
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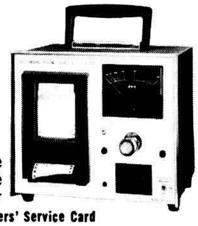
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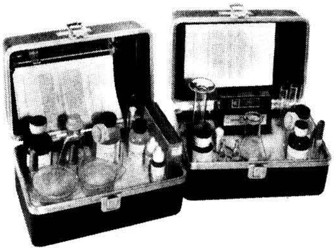
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For author's guide and editorial policy, see June 1972 issue, page 523 or write Norma Yess, Manuscript Reviewing Office.

In each paper with more than one author, the name of the author to whom inquiries should be addressed carries a numbered footnote reference.

A sometimes renewable challenge

Early last month, Congress started a clean new slate, ideally for a better state of the union and understandably for a cleaner environment. Once again the Congress will be faced with environmental issues—energy, strip mining, land use, and solid waste. Some of them have been addressed by earlier sessions, but the list also includes power plant siting, toxic chemicals, just to mention a few.

Part of its responsibility is, of course, the writing of new environmental protection laws to safeguard our vital resources, but another, perhaps more important charge —or at least ES&T thinks so—is the oversight of existing environmental laws to ensure that congressional intent is, in fact, carried out and now thwarted by the pressures of the federal bureaucracy.

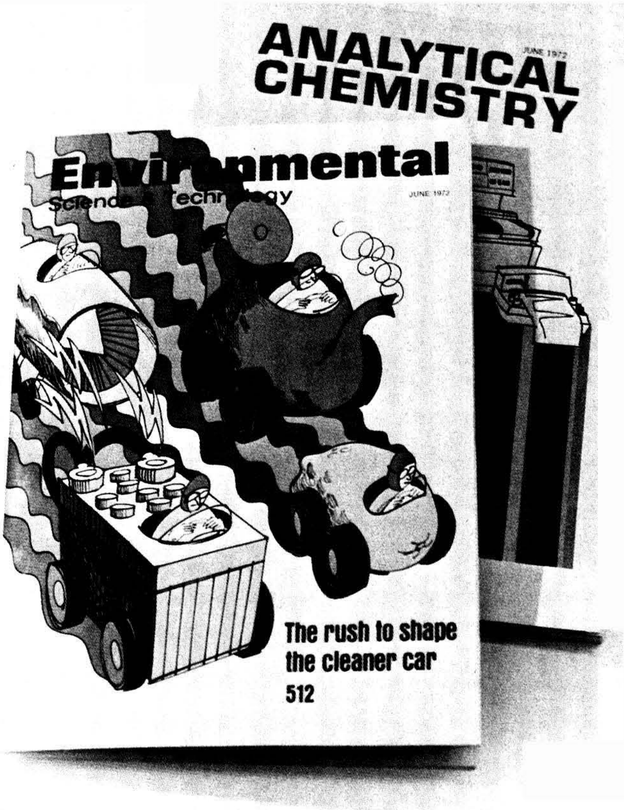
ES&T anticipates attention to and action on so-called remaining environmental issues that have not been addressed at the national level. But looking back over the years at earlier clean air legislative attempts, clean water tries, and improved solid waste management practices, there is a distinct observation that ideally much is promised, yet little is actually achieved—hence, the renewable aspect of all cleanup laws.

Take a look at the myriad laws under which the fledgling Environmental Protection Agency operates. Is it too early to think in terms of codification of all existing environmental laws? Who needs more legislation that will expire in a few years if its intent is thwarted? How many more pieces of renewable legislation do we need?

Don't misunderstand us. We commend Congress not only on its early start of the session but on its early hearings for the land use proposals now awaiting national attention. We also look forward to inroads on reorganization of committees, changes in the seniority system, and congressional procedure.

In all candor, we commend its past efforts. Our very best wishes are extended for this session of Congress. Only by keeping communication lines open can there be progress, however slight it might appear at times.

Stanton S Miller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The rush to shape the cleaner car
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LETTERS

Thermal processing

Dear Sir: In general, I feel that my opinions as conveyed in the article "Hard road ahead for city incinerators" (ES&T, November 1972, p 992) are not really accurate. For example, I do believe that pyrolysis has considerable potential in the *future* as a newly applied processing technique in the solid waste management field. However, I do not feel that the technique has been adequately demonstrated from technical and economic standpoints at this time. I also don't believe that "thermal processing is the wave of the future," as you have stated.

The fact is that I firmly believe that there just isn't a panacea available or on the horizon which is going to make solid waste disappear or magically become a valuable asset to communities. As a nation, we certainly need to strive for improved technological developments and conservation of our resources. However, we also need to adopt a sense of realism directed to the solution of today's problems with available technology in parallel with efforts for the future, such as resource recovery and improved technology.

So I'm really for a balanced approach to the problem which does not eliminate viable options such as conventional incinerators—which I believe can be designed and operated in an environmentally acceptable manner. I was impressed with the article entitled, "Incineration: Environmental Whipping Boy?" by William Harrington, which appeared in the February 1972 issue of the *APWA Reporter* and which I feel concisely presented some of the misunderstandings and unrealistic demands being made on incinerator facilities.

John T. Talty, Director
Processing and Disposal Division
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

Computer models

Dear Sir: In our opinion, excessive claims may well have been made about the usefulness and validation of the current EXPLOR model for stimulating air pollution described in the December 1972 issue (page 1071).

The California freeway air pollution measurements referred to were derived from a project being conducted by the California Division of Highways with sponsorship of the Federal Highway Administration and collaboration of the Los Angeles County Air Pollution County District, the California Air Resource Board, and the Environmental Protection Agency.

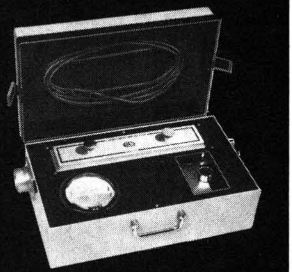
Sampling for air quality on this project has been very limited. The fragmentary results which come from only a few time periods and locations are only a small fraction of the data the investigators and the contracting organization consider desirable for adequate model validation. Measurements involving more and varied highway sites and a much larger sampling of meteorological and traffic conditions will be available in the future on this and other projects; then validation of all the various highway air pollution analytical models should be more feasible.

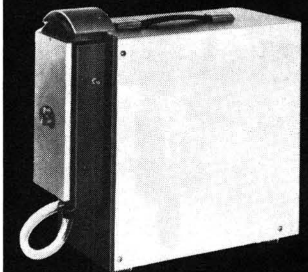
Howard A. Jongedyk
Federal Highway Administration
Washington, D.C. 20591

EPA technical views

Dear Sir: I want to assure you that at EPA we feel the public has a right to be informed about the Agency's activities on a timely basis. Publications such as yours play a valuable role in providing information about our efforts to deal with environmental problems. It is our responsibility to see that you get the information you need.

Regarding your charge (October 1972 editorial) that technical expertise at EPA is "buried under stifling layers of nontechnical bureaucrats and political appointees," I think the best answer lies in the type of person administering EPA technical programs. Dr. Stanley M. Greenfield, Assistant Administrator for Research and Monitoring, received his doctorate in meteorology from UCLA, is the author of 35 technical papers in his field, serves on a committee ~~of~~ the National Academy of Sciences, and received an award for his research from the American Meteorological Society. Dr. Robert L. Sansom, Assistant Administrator for Air and Water Programs, was both a Fulbright Fellow and Rhodes Scholar and holds a Doctorate in Economics from Oxford. Sheldon Meyers, Director of the Office of Federal Activities, holds degrees in marine engineering, mechanical engineering, and business administration, and has extensive experience administering re-





search and technical programs. None of these men fits your description of "nontechnical bureaucrats and political appointees."

Incidentally, I was interested to find in the same issue of your magazine containing the critical editorial, two articles by EPA technical personnel describing the technical basis for decisions in air standards. I hope this will help reassure your readers that EPA scientists and engineers are an extremely important part of the Agency's decision-making process.

William D. Ruckelshaus
Administrator
Environmental Protection Agency
Washington, D.C.

Hard road for incinerators

Dear Sir: The thrust of the article in the November 1972 issue (page 992) appears to judge the performance of obsolete incinerators built since 1920, many of which have little or no air pollution control devices, lack resource recovery features and modern combustion systems, plus an assumption that acceptable landfill sites are available to all communities.

We submit that one cannot judge the performance of modern incinerators by citing the number of obsolete incinerators which have been closed down or are operating inefficiently, any more than one can judge the performance of modern industry by referencing obsolete plants or systems. The author failed to recognize that modern incinerators can be good neighbors as experienced in the major cities of Europe where environmentally acceptable incinerators are operating in residential areas and reclaiming a substantial amount of energy from the incineration process.

Contrary to the statement that the City of Chicago is ". . . having trouble finding a market for steam. . .," please be advised that the City has been selling steam produced by burning refuse at the Southwest Incinerator for the last eight years and has had no difficulty in finding customers for the steam at the new Northwest Incinerator. Many industries look with favor toward purchasing a guaranteed supply of steam from a source which meets current air quality standards, rather than attempting to solve the equipment and personnel costs associated with manufacturing steam.

The City of Chicago has never held to the position that incineration is the only solution to the solid waste disposal problem and in the past has actively sought new and improved alternatives, and will continue to do so in the future.

Milton Pikarsky
Department of Public Works
Chicago, Ill. 60602

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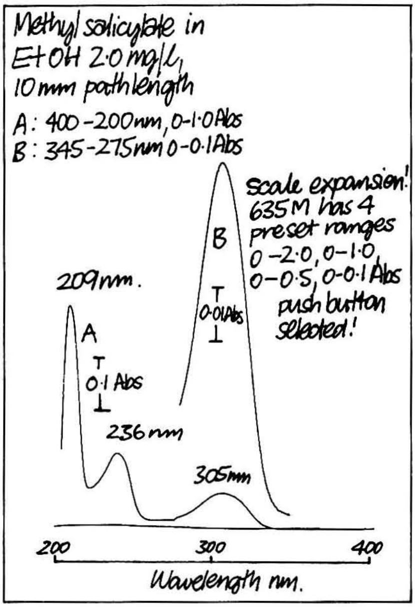

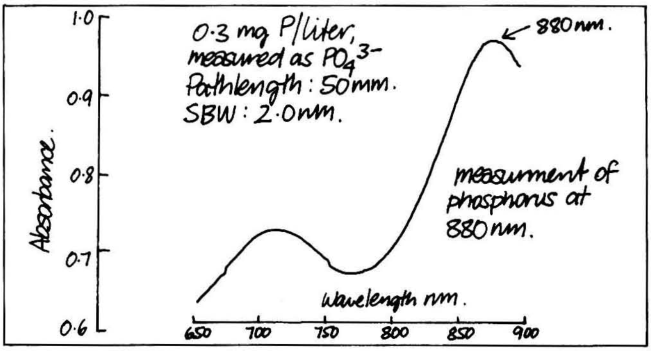

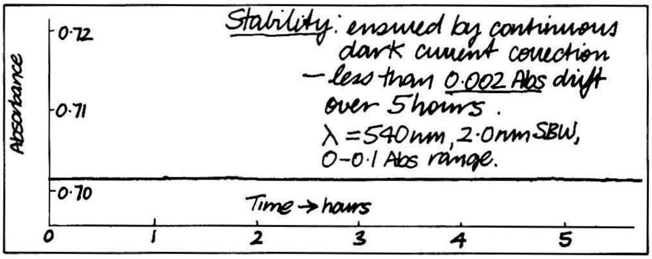

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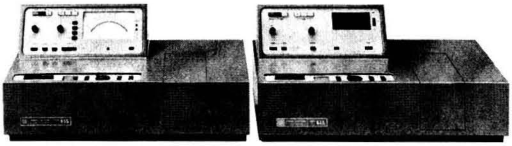

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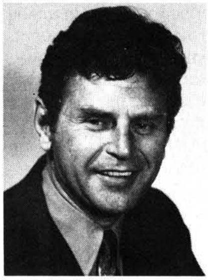
CURRENTS

INTERNATIONAL

In Alberta, Canada, a winter works program is under way. It's costing the provincial government $1 million. Dubbed PEP (Priority Employment Program), the program will generate 36,000 man-days of work on environmental projects, according to W. J. Yurko, Minister of the Environment. All told, there are 52 projects; the government is funding the entire cost of 25 and half the cost of the remaining 27. A majority of them deal with the clearing of reservoirs and river channels and erosion control.


Minister of the Environment Yurko

WASHINGTON

EPA opens ninth research lab, flexes its new legislative muscle on noise and pesticides, and says that applicants for waste water discharge permits who already have filed a Refuse Act permit need not reapply on the new form. It also says there is $34 million for research, development, and demonstration for the remainder of fiscal 1973.

- The new research lab at Corvallis, Ore., is one of the National Environmental Research Centers (NERC). Named the National Ecological Research Laboratory and headed by A. F. Bartsch, the ninth lab is the first to be engaged in the study of air pollution effects and is dedicated to study of terrestrial ecosystems. The other eight NERC perform research on water pollution.
- Its noise program has been moved internally, to the Office of Categorical Programs, so that the agency can discharge its responsibilities under the new law. The program is still headed by Alvin Meyer, now a deputy assistant administrator under David Dominick.
- Flexing its muscle under the new pesticides law, EPA impounded 64,000 lb of allegedly nonregistered and mislabeled DDT. It's the first action to be taken under this law (against H. D. Cannon and Sons, Inc. of Bridgeville, Del.) and was not related to the June 12 EPA order banning most uses of DDT which became effective at the end of 1972.

Navy affirms its cleanup commitment with a multimillion dollar four-year program. Its Naval Civil Engineer Laboratory (NCEL) at Port Hueneme, Calif., is developing, in cooperation with 53 leading manufacturers, a system for in-harbor oil spills. Arthur Widawsky heads the program which is subdivided into containment, removal, storage and transfer, and separation. Their evaluation includes 23 booms, 26 removal devices, 9 storage and transfer units, and 16 oil/water separators. Some 400 million gal. of oil are spilled in all waters (ocean, lakes, etc.) from sea-going vessels, according to one estimate, but the Navy only contributes a minute fraction of the total. During the first six months of 1972, the Navy reported 176 spills totaling 12,500 gal.

Congress is faced once again with a raft of environmental proposals. Sen. Henry Jackson (D.-Wash.) is seeking early action on six environmental subjects—land-use planning, strip mining, public land laws, expansion of water-based recreation lands, and Youth Conservation Corps and Wilderness Areas. The architect of the NEPA law and chairman of the Senate Interior and Insular Affairs Committee, Sen. Jackson says "The leadership in both the House and the Senate are committed to practical and progressive steps to end the degradation of our nation's air, water, and land. Much has been done—yet, much remains to be done."

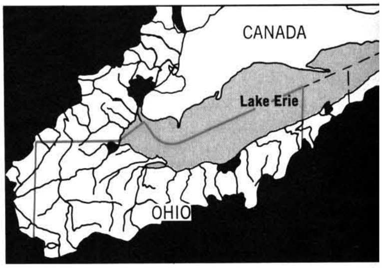

Senator Jackson

TVA has a model for national action and is backing air cleanup to the tune of $130 million. In its 39th annual report, the TVA's Board of Directors finds that planned industrial growth is helping to disperse population in the Tennessee Valley—a fact which is counter to the national pattern. The report finds that "80% of the region's new industrial jobs and over two thirds of all nonfarm employment opportunities are being created outside the major metropolitan centers." As part of TVA's program to improve control of fly ash from its coal-burning plants, electrostatic precipitators are being installed at its Colbert, Allen, John Sevier, and Johnsonville plants. In aggregate, the devices cost $41.3 million.

Keeping up its environmental guard, Environmental Defense Fund (EDF) late last year petitioned the Federal Aviation Administration for information on civilian supersonic jet aircraft—specifically, data on sonic boom, airport noise, emissions, and fuel consumption for both prototype and production models of the Anglo-French "Concorde" and the Soviet TU-144.

STATES

Ohio's EPA has named Lake Erie as its top water cleanup priority. Governor John Gilligan and EPA director Ira Whitman recently created a strike force on water quality improvement in interstate and international waters with principal emphasis on Lake Erie. More than 9900 square miles of its drainage basin is located in Ohio, and by December 1973, every Ohio municipality discharging 1 mgd or more of waste water must have phosphorus removal facilities in operation in its sewage treatment plants.

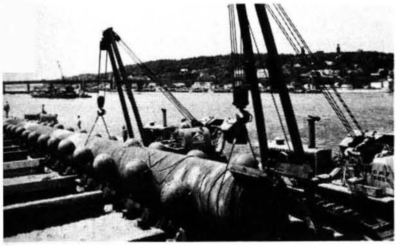


CURRENTS

Under OSHA requirements, three state occupational safety and health plans have been approved. At the beginning of this year, Montana, Oregon, and South Carolina plans were approved, leaving the remaining 47 state plans to be approved before the end of fiscal year 1973.

Mandatory installation of NO_x exhaust control devices on 1966–70 model year passenger cars, pickup trucks, and other vehicles under 6000 lb gross weight begins this month in California. Through June, NO_x control devices will be required upon change of ownership and registration. Starting in July, the second phase of the program will get under way with the installation schedule being based on license plate numbers. This installation will be completed by April 1974, and each vehicle must have a window sticker indicating that the device is installed or the vehicle is exempt. California's Highway Patrol will enforce the program, and stickers will be issued by vehicle inspection and installation stations.

A 48-in. sewage outfall pipe is being constructed in Monmouth County, N.J.; it should be completed this year. The $3 million outfall pipe will extend 4000 ft into the Atlantic Ocean. There, in more than 35 ft of water, it will discharge thoroughly treated effluent through a 640-ft-long diffuser, according to the Monmouth County Bayshore Outfall Authority. The diffuser will have 80 horizontal ports and will discharge the effluent in alternate directions. The outfall pipe is part of Monmouth County's $14 million Master Sewage Plan, which will tie more than a dozen communities within 121 square miles into the system. Initial flow from the outfall is projected at 4.5 mgd; its ultimate capacity will be 28 mgd.



N.J. sewage outfall pipe

Detroit, Mich., has purchased six scrubbers as part of a massive $591 million effort to clean up Lake Erie. The scrubbers—from Combustion Equipment Associates, Inc. (New York, N.Y.)—will cool and clean exhaust gases from six furnaces which will burn sewage sludge that now goes into the lake. The Detroit incineration system will be the largest ever built in the U.S. Each scrubber will cool and clean up to 185,000 acfm of exhaust gases which will contain less than 0.20 lb of solids/1000 lb of gas when discharged into the atmosphere. There will be no plumes since the gases will be cooled below the saturation point.

Great Falls, Mont., is the 33rd community now operating or planning magnetic separation to reclaim steel cans and other ferrous metals from municipal solid waste for recycling. Scheduled for start-up in mid 1973, this operation will salvage more than 30 million steel cans annually from household and industrial refuse.

Last month, Alexandria, Va., began a mandatory trial program of recycling which could save the city $50,000 each year. For a four-month period, all residents are required to separate newspapers and magazines from their trash. The city picks up the paper every other week and sells it to a recycling plant.

The Minnesota Pollution Control Agency has approved a $3 million plan for Reserve Mining Co. (Silver Bay, Minn.) to reduce air pollution from Reserve's taconite processing plant by 85–99% by March 1975. The plant now emits about 100 tons daily of particulate matter from its stacks. This agreement, however, has no bearing on Reserve's daily disposal of 67,000 tons of taconite tailings into Lake Superior.

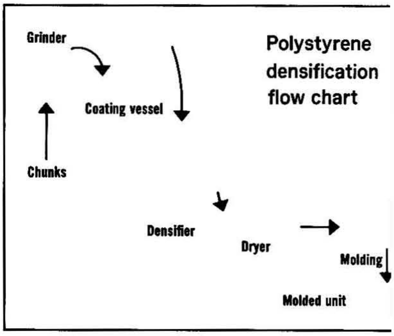
Pennsylvania's Department of Environmental Resources is suing U.S. Steel in a $518,000 civil suit for violating state water quality standards. Based on samples taken by inspectors patrolling the Monongahela and Allegheny Rivers, the suit involves eight plants along the Monongehela and alleges 94 violations from 40 different outfalls. It also alleges that the company never obtained a discharge permit from the state for almost half of the outfalls and that discharges from the others were in violation of the industry's permit requirements.

TECHNOLOGY

Ammonia leaching may be the answer to The Anaconda Company's prayer for a way to clean up its copper smelter emissions and comply with a tough Montana air quality standard. Full details of the process will not be available pending patent issuance, but the process looks roughly like this: regular copper concentrate from milled sulfide ore progresses sequentially through low-pressure and low-temperature vats where ammonia is used to leach copper from the ore. Copper in the leachate is then separated by liquid ion exchange and recovered by electrolysis. The hydrometallurgical process was tested by Anaconda in its labs near Tucson and is ready for full-scale testing at a new 36,000-tpy plant being built near the company's older, pyrometallurgical unit at Anaconda, Mont.

The process will probably make electrolytic grade copper with less capital cost and less operating cost than the old smelting method but the most important payoff will be in pollution control. Montana has not budged from its position that Anaconda must clean up its smelter to conform with tight standards that go into effect next June. Anaconda hopes that the fact that the company has sunk $22 million into R&D for the ammonia leaching process will convince the state to grant a variance while new facilities are being built. At press time, the variance issue was still unresolved.

Densification of scrap polystyrene foam makes it possible to recycle the hard-to-dispose-of plastic. Developed by Sinclair-Koppers Co., the process increases density by as much as sixtyfold. It uses the already existing low-pressure steam, water,



Polystyrene densification flow chart

and air available in most molding shops to turn the scrap into a higher density product which can then be reused or disposed of more easily than the low-density polystyrene. The scrap is ground, and the particles are coated with suitable antiagglomerating agents. Steam pressure in an autoclave collapses the cellular structure of the foam, and the volatile blowing agents escape. After air cooling, the scrap is sprayed with cold water and recovered.

Technology exchange was the hot topic of discussion at the close of the second United States–Japan Conference on sewage treatment technology. The Japanese proposed that a third such conference be held later in Japan. Headed by Japan's Takeshi Kubo, Director General of the department of sewerage and sewage purification, Ministry of Construction, and EPA's assistant administrator for Air and Water Programs, Robert Sansom, delegates from both countries discussed achievements and plans for the future. The delegations settled on a plan for exchanging technical personnel which would involve on-the-job training for Japanese engineers in American sewage treatment plants.

Ultraviolet curing of solventless inks speeds up production on can printing lines and eliminates air pollution. In operation since last summer, Continental Can Co. has unwrapped its new system, which uses a special ink based on acrylics that hardens under uv irradiation from mercury lamps. Continental Can says the inks cost about twice the amount of conventional inks, but curing time is cut to a second, from 15 min required by the conventional heating.

APPLICATIONS

Coliform bacteria survive up to five times longer in cold water than they do in more temperate climates, according to scientists at EPA's National Environmental Research Center (Corvallis, Ore.). Monitoring of the Tanana River near its confluence with the Chena River where it receives sewage from Fairbanks, Alaska, showed that coliforms persisted from Fairbanks' sewage as far as the Chena's confluence with the Yukon River, 210 miles downstream.

Radiation monitoring badges using borate-shielded plastic will screen out medically less significant low-energy neutrons but not more damaging high-energy neutrons, according to Lawrence Livermore Laboratory. The Boron-10–loaded plastic partially shields the commonly used copper and indium foils in badges and makes them more useful in personnel radiation dosimetry.

INDUSTRY

Du Pont's McCoy

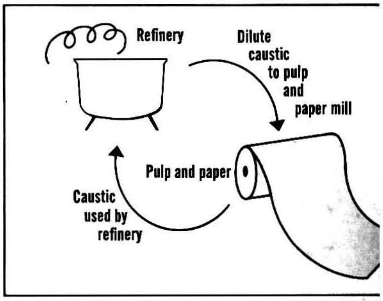
Meanwhile, DuPont President Charles McCoy says some short-term help in the impending natural gas shortage could come from industry. McCoy suggests industry fire its boilers whenever possible with less critical fuels. In a speech before the Economic Club of Detroit, McCoy also urged the government to gear the programs of 60 federal agencies concerned with energy, natural resources, and environmental protection toward a single national policy.

Net energy consumption in the U.S. will jump to 140 quadrillion Btu by the year 2000, from the current 57 quadrillion Btu level, according to a new energy report of the U.S. Department of the Interior. Since conversion losses will remain the same relative to generating capacity, gross energy consumption will rise to a projected 192 quadrillion Btu by 2000, from the current 69 quadrillion Btu level. The Interior study assumes a steady rate of population growth of about 1%, an annual growth rate for industrial production of about 5% until 1980, and a 4.4% growth rate thereafter. The report assumes major advances in coal gasification and breeder reactor technology which will ease the energy squeeze over the long haul.

Keene Corp. President Glenn Bailey has voiced his support of a recent General Accounting Office report criticizing the Environmental Protection Agency's lack of support for demonstrating new water pollution control technology. Bailey charged that there was an "incredible amount of misinformation" about water pollution and called EPA's approach to the problem "nonadventurous" and in the long run, "wasteful." "Municipal waste treatment in the U.S. is literally in the Dark Ages," Bailey says, adding that "if truly new technology were fostered and promoted with the full support of the federal government, we would be in a far better position today and in the future."

Foote Mineral Co. will close three marginal plants because of pollution control costs and has written off $9 million (about $4.50 per common share) during the last quarter of 1972. Foote's plants—Steubenville, Ohio (ferrochrome products); Wenatchee, Wash. (silicon metal); and Kimballton, Va. (lime)—will be shut down during 1973. Upgrading the plants to meet air quality standards would have cost about $8 million over the next two years. The expected profitability from the product lines would not justify the expenditures for pollution control, Foote says.

A Gulf refinery and a Weyerhaeuser pulp mill across the river from each other near Kamloops, British Columbia, are cooperating in an "ideal" solution to a pollution problem. Gulf uses caustic soda to scrub sour gas and has a disposal problem for the weakly alkaline scrubbing agent. Solution: Weyerhaeuser takes it and incorporates it into its sulfate pulping liquor, and the refinery buys its caustic from Weyerhaeuser.



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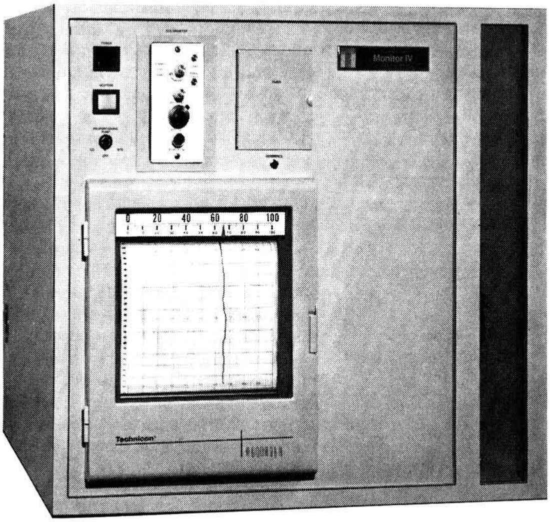

Monitor IV represents a new idea in continuous unattended in-plant monitoring of industrial wastewater. It satisfies the monitoring requirements of water quality surveillance. It monitors plant effluent at the source, tells what is happening *now,* not later...*before,* not after, effluents leave the plant.

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INTERVIEW

Peabody Galion's John McConnaughy

Who is responsible for the concept of Peabody Galion as a total environmental company? By analyzing the product line of the then-existing company, Hercules-Galion, we (mainly McConnaughy and A. J. Giglio, vice-president of corporate development) chose the environmental business as our base for growth. In terms of future development for the company, two product categories were singled out for growth potential, profitability, and a number of other factors. One was the refuse equipment business; the other was the fast food business. The refuse equipment business was used as the basis for future growth. Since refuse is, in essence, land pollution we decided not to look just at refuse equipment but to look at air, water, noise, and so on.

The first implementation of the concept was the acquisition of Peabody Engineering. The Peabody name was well recognized in the air pollution scrubbing business. In order to indicate the new direction, the company name was changed from Hercules-Galion, which was primarily known for garbage truck equipment. The name change was an external way of pointing out the expanded direction of the corporation. After getting into the air field, we moved into waste water treatment in July 1, 1970 and into the environmental services area last year.

Before coming to the company in 1969, I was with Westinghouse for seven years and then with Singer for about another seven in several positions, the first as controller of U.S. operations, then marketing director for the eastern half of the U.S., and before leaving, running Singer's European consumer business which hit about $400 million.

Do the four groups act autonomously? There is a president of each group, and although each group operates independently, they do some business with the other groups; but their number one assignment is to make their profit objectives individually as groups.

For example, when Peabody Galion was bidding on the Stamford, Conn., solid waste job which included a difficult incineration problem, the air group bid together with the solid wastes group. At the top level, the presidents of the groups get together to coordinate on problems, but it is important to note that the company does not force cooperation of its groups. Cooperation either happens naturally or it doesn't happen at all.

Recently, Philip Van Huffle became president of the air group; he replaced John Dunn who elected to retire but will do consulting work for the company. Within this air organization, there are three separate entities—Peabody Canada, Peabody U.S., and Peabody, London. Until recently, the three had been relatively separate. Each has its own leader, who in turn reports to Van Huffle, the new president who does the coordination and liaison within the group.

Varying degrees of cooperation are found within the groups. Again in the air group, for example, there is a great deal of cooperation between Peabody GCI in Paris with Peabody Roberg and Peabody Ltd. Each of the three reports to Peabody Ltd. in London; they have a lot of problems in common. Roberg and GCI distribute Peabody Ltd. products in France, Italy, and Scandinavia. In return, Peabody Ltd. will pick up their products and bid them in Canada, South Africa, and so on. It's a built-in working relationship.

ACQUISITIONS

What can you tell ES&T readers about acquisition strategy and organizational pains, if any? There are five things that Peabody Galion looks at. First, the acquisition must make conceptual sense, either from a product, marketing, or manufacturing standpoint. In this way, the acquisition ties in with something Peabody is trying to do. Let me give you an example. In the solid wastes management group, a company called DeWald was acquired on the West Coast. The acquisition was essentially a marketing strategy because Peabody was weak in terms of marketing its products there. The acquisition gave us immediate marketing capabilities plus two plants, one in Los Angeles, the other in San Francisco.

Second, the company has to be relatively well managed and doing well. Third, Peabody only believes in the friendly type of acquisition, where they want us and we want them. Four, we won't dilute our earnings for any reason. Last, Peabody takes a very hard look at the balance sheet.

What can you tell us about the more recent acquisition now known as the services group? The services group

At ease in his Manhattan office, John McConnaughy, Jr., is president of Peabody Galion Corp., a total environmental company that derives more than 70% of its revenue from balanced positions in all segments of pollution control—air, water, and solid waste, and testing services. The 42-year-old executive tells ES&T's Stan Miller how the individual groups were pulled together to make the corporate entity that the company is today. Since he joined the firm on May 1, 1969, Peabody Galion has showed that there is room for total pollution control companies in the U.S. clean-up operation; sales hit $134 million in 1972 as reported (year ending September 30), up from $90 million in 1971.

is regarded as an excellent opportunity for growth and profit. In the area of stack gas testing and water pollution testing it is very important to know what pollutants are going through a system before corrective control technologies are applied. One of our early mistakes on a pollution job was taking the customer's word for what was coming out of the plant. The reason that the controls were not working well was that what was going through the system was not well known. Terrible mistakes can be made by taking the customer's word and not knowing the parameters of moisture and temperature, for example, on air emissions. To make sure that a customer's pollution control problem is corrected, it is all-important to do the testing beforehand and make sure you know what to correct.

ES&T did an earlier interview with Stewart Udall and noted that he served on the board of directors for two years and came off in 1972. What influence did he exert? Most of the Peabody Galion directors, whether internal or external, were primarily businessmen and not environmentalists, if you will. The directors felt that it would be very helpful to have a conceptual input and to give the company an overview in the area of environment. Mr. Udall gave us his ideas in terms of what really was happening and what he felt was going to happen. While he was here, he was well worth having on the board.

What else does the service group do? The basic business of our Commercial Testing subsidiary is oriented toward the testing of coal as much as anything else. The fuel which goes into a combustion system is normally the source of most of the air pollutants. Knowing what is going in, one can design and fabricate efficient control equipment to handle it. Peabody has performed stack testing for Commonwealth Edison in Chicago and also has a long-term contract with Ontario Hydro. Our X-ray Engineering subsidiary performs nondestructive testing for nuclear-fueled utilities. They perform nondestructive testing to ensure that the equipment has no leaks and measures up to the requirements of the Atomic Energy Commission. Our Industrial Leasing subsidiary provides a capability for the other groups to provide financial backing arrangements for their customers. In many cases, Peabody is finding that the customer would rather pay so much each month or each year, than a lump sum.

Peabody Cactus, a recent acquisition, is our approach toward the petroleum industry. Cactus' major activity is the capping of abandoned wells and the recycling of used well tubing and casing for resale to the petroleum industry. Cactus charges a certain fee for the proper recapping of an abandoned well and the handling of the water and oils so that there is no pollution damage to groundwater and surface soils.

The newest acquisitions are Leonard S. Wegman Co.—the well-known consulting engineering firm in the solid waste area—and the Boston-based firm—Hayden, Harding & Buchanan—in the waste water treatment field, and the John L. Doré Co., a construction firm. The Wegman operation is included in the services group despite the fact that it concentrates on solid waste; we feel that its operation should not be tied in with solid waste equipment manufacture.

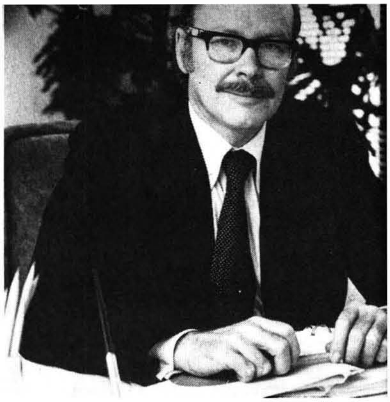
BUSINESS SPLIT

What is the breakdown of sales figures into products and services? Hardware equipment items account for 70% of total sales, services the remaining 30%. (The market splits within the various groups as shown in the box.) The industrial segment is normally a bit more profitable, particularly in the solid wastes area. The company plans to enlarge its solid waste activity in the municipal market as part of its natural growth.

What parcel of the recent water law does Peabody intend to carve out for itself? Under the law, water pollution controls will affect industry as well as municipalities. As such, it will impact on all entities in the water group plus some in the services group. Specifically, Peabody expects to provide consulting engineering services, water testing and analysis, hardware, and construction. A lot of testing will be required to prove that a certain effluent limitation has been achieved. Whatever the total expenditure of federal funds in the water area, the expenditure should bring about dramatic growth for the water group.

ACROSS-THE-BOARD

Why does a customer come to Peabody rather than to a company that specializes solely in air or water pollution controls or solid waste management? What attraction does the company offer the potential customer? We are not going to be all things to all people by any means. The attraction mainly is the customer knowing that he is dealing with someone he respects and who is working on his particular problem. Many times, the problem is much wider than the specific one the customer brings to Peabody. So the Peabody contact man might say, for example, you need to correct these related pollution control problems as well; let me bring some other groups in for a total answer to the problem. This is where the total environmental capability plays a very important role.



"If the administration really spends all the money in the new water law, we could be swamped with work."

Peabody Galion's McConnaughy

What is it that makes Peabody unique? The company is unique in that it is relatively more balanced than its competitors. Peabody has a broader scope and feels that there is more safety in balance, including a number of different types of balance —balance sheet vs. profit and loss; balanced positions in air, water, and land; and a balance between hardware (capital equipment) and consumables (services, fabric filter replacement bags, and chemicals). Overall, if one area is down, another is up.

MARKETING

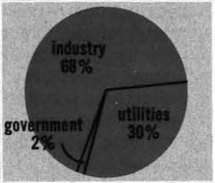
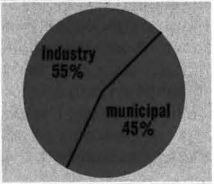
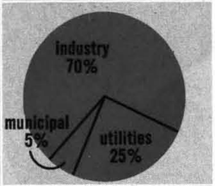
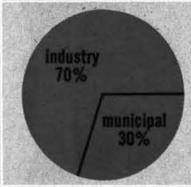
How does the company attract potential customers to the individual segments of its business? Is there an overall marketing function? Peabody has no formal marketing organization on a company-wide basis; generally, the marketing is done within an individual group. Each handles its own marketing activity; they vary in size, and it is difficult to say just what is marketing and what is engineering, particularly in the air group. Many of our engineers are, in essence, marketing experts who go out and sell the project while they are doing the engineering and so on. There is no standard approach. Quite often the customer brings the job directly to the competence within the company.

In the solid wastes area, the company recently introduced a new rear loader which is primarily aimed at municipal markets. The company is also in the business of transfer stations and has supplied equipment for 35 stations in different communities. The sales of these new product lines—stationary compactors and transfer stations—require different marketing direction from the sales of mobile types of equipment that have been historical. The marketing of two large SO_2 removal jobs in the air field is also quite different from the sale of normal combustion systems or off-the-shelf equipment products. In the latter case, we have moved away from agents and toward factory branches and in-house experts.

Where does the company concentrate its sales effort? In jargon, what piece of the cleanup action does Peabody hope to get? It varies with each group. The marketing must be cost effective for each individual segment or each individual business. Peabody is active in cost reduction projects; we are concerned with administrative costs of one kind or another, but when it comes to marketing organization, we feel that the local management has a much better idea of how to manage their products than we would here in New York.

Take the municipal business of Peabody Petersen, in the water group, which builds waste water treatment plants. They know where the jobs have been given out, and their marketing effort goes about getting the jobs. The president of the water group does not monitor the market in that particular case. Peabody Barnes, which manufactures pumps, has an entire marketing organization with regional managers, myriad agents of all kinds, factory representatives, and the lot. With Peabody Welles, which supplies specialty hardware including clarifiers, aerators, and filtration systems, again in the water group, sales are more oriented toward the engineer.

Peabody Galion, the environment company, at a glance
(all figures in millions of dollars)

	1972 sales	1971 sales	
Air pollution control group including Engineering (U.S. and Canada), Limited (London), Compower, Engineering (Power and Combustion), GCI (France), Roberg (Sweden), Gordon-Piatt and American Brattice Cloth	$33.0	$26.5	
Water resources group including Barnes, Welles, Hart, and Petersen	24.3	15.7	
Environmental services group including Commercial Testing and Engineering, X-ray Engineering, Ryan Instruments, Industrial Leasing, Cactus-Pipe,* Leonard S. Wegman Co.,* and Hayden, Harding & Buchanan*	24.8	7.4	
Solid wastes management group including DeWald and Rudco	22.0	16.6	
Truck equipment	17.5	14.9	
Others	12.4	9.2	
Totals	$134.0	$90.3	

*Recent acquisitions not included in 1972 sales figures
Figures do not include restatement

INNOVATION

What control technologies is Peabody backing that may well pay off in the future? Certainly, stationary compactors and transfer stations in the solid waste area. There is a line of air products aimed primarily at control of internal air in a plant. The device is relatively new in the industry and can be used to control solid particles such as smoke from welding fumes or aerosol particles such as those from lubricating liquids used on machine tools. The interest here is both from an air pollution control standpoint as well as an occupational health standpoint. The interest stems from the fact that if you can return clean air in the plant, you do not have to make up air from the outside. Peabody also expects to play a role in SO_2 absorption technology. We are now building a commercial plant (Detroit Edison) using limestone, and have test projects in magnesium oxide and citrate absorption.

When you ask about new products we can go on and on and on. A lot of them have fantastic potential; whether the potential is realized depends on many things in the marketplace, but Peabody Galion does not invest in an idea unless there is a very high potential that the idea will succeed. Peabody has an exclusive license for the sale of the Lugar fabric filters in the U.S. The filters are used in the glass and aluminum industries, for example. We also have a license for sale of the Lurgi radial flow wet scrubbers. Other items include an inerting system for oil tankers which snuffs out any spark that might cause a fire or explosion in the tanker, methanol combustion systems, and liquid waste incinerators. Last year, Peabody introduced 22 new products in the solid wastes area.

Each of the groups handles its own research and development to varying degrees. The air group has a separate research and development organization in Stamford, Conn.; the Ven-Kinetic air scrubber was a direct result of its research.

OUTLOOK

Copper industry uses much scrap iron

For every pound of copper produced by its dump and in-place leach operations the industry needs three pounds of scrap waste iron

Leaching of copper from its ore and subsequent recovery of the metal from solution by the cementation process is one of the oldest applications of hydrometallurgy. It dates back to the time of Agricola. It's a basic mining tool. In fact, partial or complete hydrometallurgical processes are used to extract all but six or seven of the 82 known metallic elements.

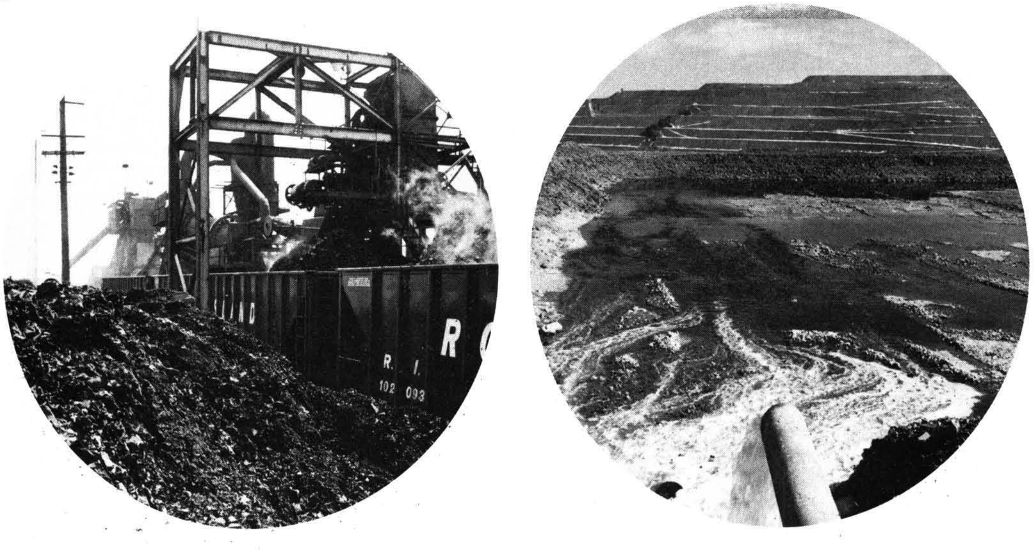
What is new with the cementation process is that it is gaining more and more of a foothold on copper production in the U.S. today. Last year, more than 10% of the copper found in this country was extracted by this process. That amounts to nearly 200,000 tons of the so-called precipitate copper.

Kennecott Copper Corp., an acknowledged leader in the field, produces more than half of the U.S. total of precipitate copper, amounting to 20% of Kennecott's total production. The Anaconda Company is second. Their precipitate copper production hit 42,000 tons in 1972—double the 1971 production figure of 21,000 tons. Together, these two big copper companies produce about 75% of the total.

There are several reasons why the copper industry is using the cementation process more and more. Ever increasingly strict environmental protection constraints make the roasting and smelting of copper-laden ores, at least as conventionally performed, less and less attractive. As expensive pollution control modifications are made on the conventional equipment, the hydrometallurgical process becomes increasingly competitive and therefore attractive. A more fundamental reason for wider practice of the process stems from the fact that the mine wastes which are too low in copper to justify conventional flotation techniques may often be leached and recovered by the cementation process.

How it works

Basically, in the cementation process the copper-laden solution is



The connections
Scrap steel cans (left) are shipped to copper mines (middle) where they are used to recover copper from low-grade ores (right)

contacted with metallic iron, usually in the form of waste scrap metal. A chemical reaction takes place, the net effect being that copper is precipitated from the solution as a red mud; the scrap iron is solubilized as an iron salt. After the basics, however, the technology has come a long way since acceptance of the cementation process by the industry more than 70 years ago.

Iron cementation in launders is the oldest and most common method of winning copper from its ore. A launder, 1000 ft long, 4 ft wide, and 4 ft deep, can process 1.25 million gallons per day of copper-bearing solutions. The launders ordinarily have a grizzly bottom with 1-in. openings to support the bed of scrap iron. To achieve a 90% recovery of the copper, a resident time for the solutions in the launders must be more than 1 hr.

Recently, Kennecott introduced the precipitation cone, a new cylindrical piece of equipment which handles the contact between the metal and the solution more efficiently. The cones are a more cost-effective way to practice the cementation process.

Other techniques include in-situ and hole-to-mine leaching. Perhaps the best example of in-situ leaching, involving a whole hillside, is being practiced by Ranchers Exploration and Development Co. Last March, its Old Reliable mine in Arizona was shattered with 2000 tons of high explosives. The mine contained some 4 million tons of 0.8% copper oxide ore in an area about 400 ft in diameter and 250 ft deep. The explosion resulted in the hillside being turned into a heap of copper oxide ore that is now being leached.

In hole-to-mine leaching, the leach solution of sulfuric acid percolates through 600 ft of material. It is being practiced at the Copper Cities mine at Miami, Ariz. In this case, the copper-bearing solutions at the lower level are pumped to the surface for recovery of the copper by the iron cementation process in open launders.

In fact, the surge of renewed interest in the use of the cementation process is attributed to Kennecott when the company started using the process at its largest mine at Bingham Canyon, Utah. Kennecott's Utah Copper Division precipitation plant, one of the largest of its kind, recovers additional traces of copper remaining in the overburden. Water is used to leach the tiny copper particles from the overburden, and the copper from the waters is precipitated from solution as a red mud. Approximately 4500 tons of this cement copper are recovered each month at this location and then shipped to the smelter for further processing.

Iron suppliers

For every pound of copper produced by the process, 3 pounds of scrap iron are needed. But the scrap iron must be of a certain type. The copper industry likes very thin—i.e., light gauge—shredded iron that is clean, meaning free of tin, coatings, and lacquers. Its requirements dovetail with many scrap steel can recycling plans, the caveat being that the tin must be removed.

Proler Steel Co. (Houston, Tex.) is one of about 15 suppliers of scrap steel to the copper industry. Without question, Proler is the largest supplier. A conservative estimate attributes 35–40% of the supply to Proler which has five plants—two in El Paso, Tex., and one each in Houston, Tex.; Chicago, Ill.; and Copperton, Utah. Much of its scrap for the copper industry comes from the El Paso and Copperton plants.

U.S. Copper production by the dump and in-place leach process

American Smelting and Refining Co. (ASARCO)—with only one operation at its Silver Bell mine, 35 miles northwest of Tucson, Ariz.

The Anaconda Company—with its largest operation at Butte, Mont., and another mine at Yerington, Nev.

Cities Service Co.—through its North American Chemicals and Metals Group one operation at its Copper Cities mine in Miami, Ariz.

Duval Corp., a subsidiary of Pennzoil United Corp.—three operations at its Esperanza mine at Tucson, Ariz., a copper-molybdenum mine at Mineral Park, Ariz., and a mine at Battle Mountain, Nev.

Inspiration Consolidated Copper Co.—five operations at its mines in Arizona—Black Copper, Live Oak, Ox Hide, Red Hill, and Thornton

Kennecott Copper Corp.—four operations, the largest at its Bingham Canyon mine, Utah; the second largest at its Santa Rita mine, New Mexico; and other operations at Ray, Ariz., and Ely, Nev.

Phelps Dodge Corp.—four operations, three at its mines (Morenci, Ajo, and Bisbee) in Arizona plus one at Tyrone, N.M.

Ranchers Exploration and Development Corp.—three operations at its Old Reliable mine in Ariz., its Blue Bird mine in Miami, Ariz., and its Old Mike mine in Winnemuca, Nev.

Copper companies without precipitate copper operations

Bagdad Copper Corp.—the company formerly produced precipitate copper but recently switched to an electrowinning operation

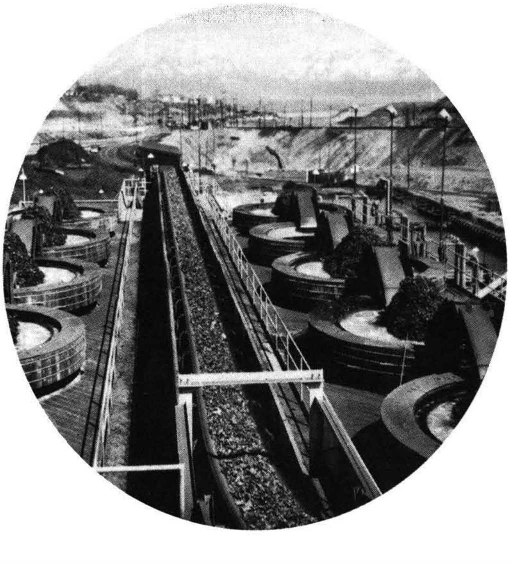
Magma Copper Co. (San Manuel, Ariz.)

Pima Mining Co. (Tucson, Ariz.)

White Pine Copper Co. (White Pine, Mich.)

Source: Bureau of Mines Minerals Yearbook

Proler supplies Kennecott, Anaconda, American Smelting and Refining Co., Inspiration Consolidated Copper Co., and Phelps Dodge. The company gets its scrap from different places including municipalities, and incinerator residues. At its plants, Proler uses magnetic separation followed by heat treatment of the scrap



which removes the coating, tin, labels, and lacquers. This operation is performed in a rotary kiln at about 1100°F. To shred the cans Proler uses a hammermill-type shredder of proprietary design with knives rather than hammers in the mill.

While Proler is the largest, L.A. By-Products is said to be the oldest company supplying scrap to the copper industry. L.A. By-Products did so back in 1926 and is credited with originating the use of steel cans for such a purpose. Although the extent to which this Los Angeles-based company supplies cans to the copper industry is a well-guarded secret, it is no secret that the company has operations today which separate steel cans from mixed urban refuse in three California communities—Sacramento, Martinez, and Oakland.

Other principal suppliers of scrap iron to the copper industry are Vulcan Materials Co. (Sandusky, Ohio) and M&T Chemicals Co. (Newark, N.J.), a wholly owned subsidiary of the American Can Co. The distinction between their operations and that of Proler is their recovery of tin. Both Vulcan and M&T recover the tin from the scrap steel before shipment to the copper industry.

Scrap tinplate sheeting wastes from can manufacturers, as well as steel cans for that matter, have about 0.8 wt % of tin. Vulcan has five detinning plants in operation today—in Gary, Ind.; Baltimore, Md.; Pittsburgh, Pa.; Newark, N.J.; and Los Angeles, Calif. What Vulcan and M&T share in common is that each detins essentially 100% new scrap—scrap from the can-manufacturing process, i.e., the trimmings from the can stamping operation. In their operations, the scrap steel is leached with a basic solution which dissolves the tin from the scrap; the tin is subsequently recovered electrolytically.

In some cases the steel is baled and returned to the steel industry; in others it is simply loaded on railcars for shipment to the copper industry. Overall, in the U.S. $\frac{5}{8}$ of the detinned steel supply goes to the copper industry; the remaining $\frac{3}{8}$ is returned to the steel industry.

Similar detinning operations are practiced by Wisconsin Metal & Chemicals Co. (Milwaukee, Wis.); National Metals (Phoenix, Ariz.); and McCloud Metals (Torrance, Calif.).

The connections

The extent to which individual suppliers ship detinned scrap iron, commonly referred to as precipitation iron to the copper industry, is difficult to come by. In general, however, Kennecott gets a main supply from Proler; Anaconda gets a main supply from Vulcan.

Cities operating steel can recovery systems

Amarillo, Tex. after incineration
Chicago, Ill. after incineration
Houston, Tex. dry separation at a transfer station
Los Gatos, Calif. after shredding, before incineration
Martinez (Contra Costa County), Calif. portable separator at landfill
Melrose Park, Ill. after incineration
Oakland, Calif. portable separator at landfill
Sacramento, Calif. portable separator at landfill
Stickney, Ill. after incineration
Tampa, Fla. after incineration

Cities planning steel can recovery systems

San Diego, Calif. after shredding
San Francisco, Calif. after shredding at transfer station
Scottsdale, Ariz. after shredding

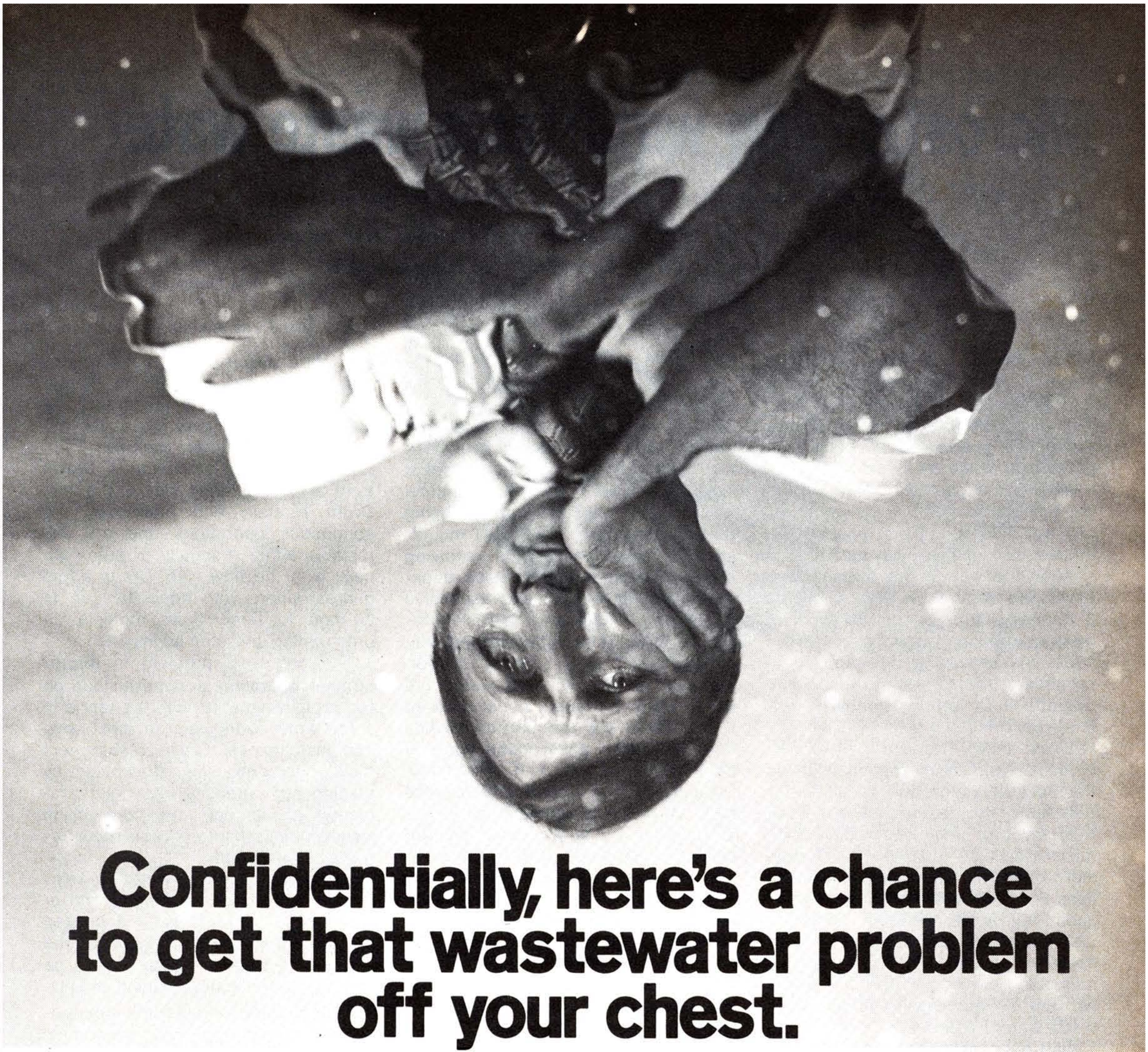
Source: American Iron and Steel Institute

The fact that the copper industry uses between 2.5 and 3 pounds of scrap steel for every pound of cement copper that it produces means that, on an annual basis, 800,000 tons of scrap iron are needed to produce 200,000 tons of cement copper.

Copper statistics from the Bureau of Mines Minerals Yearbook report that the production of copper from dump and in-place leaching, which is largely recovered by precipitation with iron, was 165,000 tons in 1969, 172,000 tons in 1970, and 154,500 tons in 1971. The '70 and '71 figures reflect 10% of the total mine output according to the yearbook. Although '72 figures were not available at press time, copper industry leaders corroborate the fact that their practices of dump and in-place leaching operations are definitely on the increase.

Other sources

Steel cans may be causing a waste disposal problem in your community, but in this age of resource recovery a number of cities are operating steel can recovery systems and others are planning such operations, according to the recent report from the American Iron and Steel Institute, "Progress Report on Recycling." Last year alone, cities sent more than 700 million scrap cans to copper mines, presumably via the supplier connections. These cities recognize that the copper industry is a market for their cans. SSM



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Mr. B. Q. Welder, Environmental Group, Calgon Corp.
P.O. Box 1346, Pittsburgh, Pa. 15230

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Name________________ Title________________

Company________________________________

Address________________________________

City____________ State________ Zip________

Telephone Number________________________

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Microstraining water and waste water

Invented during WW II, microstrainers are now marketed for effluent polishing as well as preliminary treatment of raw waste water

Microstraining, a form of simple filtration, was invented in England during World War II to remove fibers from the effluent of a munitions plant. The process was simple—intercepting solids by direct screening—and was accomplished by mounting a fine wire cloth on the periphery of a revolving drum and passing the effluent through the revolving drum.

After the war, microstraining was developed commercially by Glenfield & Kennedy Ltd., London, England for treating drinking water supplies. In 1950, microstraining was applied to secondary treated sewage effluent to upgrade it to tertiary standards (effluent polishing).

Since then, Crane Co. (King of Prussia, Pa.), an international firm in the field of water and waste water treatment, has acquired Glenfield & Kennedy Ltd. and further developed microstraining technology. Today, more than 600 microstrainer installations filter two billion gallons of water each day in 32 different countries (300 microstrainers are operating in operating in the U.S.). It's used for municipal drinking water treatment as well as municipal and industrial waste water treatment.

Only six companies in the U.S. produce microstraining equipment. It's really a different type of process—not quite sewage treatment and not quite water treatment. It can supersede waste treatment processes or can complement them by effluent polishing (tertiary treatment).

How it works

By definition, filtration is a process to separate solids from liquids by passing the liquid through a network of wires, threads, or other porous membranes, or through porous beds of granular material, such as sand. As the liquid passes through the filter material, certain sizes of solids are directly intercepted by the medium itself and indirectly arrested by solids already held or matted on the medium.

When the process is performed without the aid of chemical or biological controls, it is called simple filtration. Using chemical controls results in the equivalent of rapid sand filtration; biological controls lead to the equivalent of low sand filtration.

Microstraining clarifies liquids by filtering the greatest possible amount of suspended solids, especially microscopic solids. Crane Co. uses a specially woven 316 stainless steel wire cloth (with apertures ranging from 60 down to 23 microns) mounted on the periphery of a revolving drum arranged for continuous backwashing. Stainless steel is expensive but more durable and corrosion resistant. "We have experimented with plastic cloth," says E. W. J. Diaper, manager of the municipal water and waste water treatment department of Crane Co., "but the plastic strands tend to stretch and reduce filtration efficiency."

Enclosed in a reinforced concrete tank, the drum is submerged in flowing water to approximately three fourths of its depth. Raw water enters through the open upstream end of the drum and flows radially outward through the microfabric which intercepts suspended solids. The pressure from the difference in the water level (head loss) between the inside and outside of the drum (see illustration) pushes the water through the drum. The mat, created as the solids build up on the microfabric, will trap many particles smaller than the aperture size of the mesh.

The intercepted solids are carried upward on the fabric on the inside of the drum beneath a row of wash water jets spanning the full width of the fabric. From there, these wastes are flushed into a receiving hopper on the hollow axle of the drum. The solids move by gravity out of the microstrainer for ultimate disposal.

Water for backwashing is drawn from the downstream side of the unit. Drum rotation and backwash are continuous operations and are adjustable either manually or automatically with the flow rate. Crane offers microstrainers with capacities up to 30 mgd; for larger flows, multiple microstraining units can be installed.

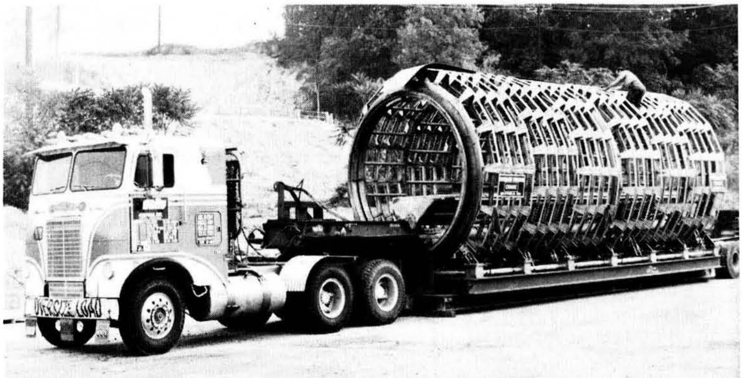
The only real problem in microstrainer operation is slime buildup on the drum which "blinds" the fabric in some water works and in most sewage installations. Crane researchers have overcome this drawback by placing high-intensity ultraviolet irradiation equipment over the drum which inhibits bacterial and other organic slime growth.

If the incoming raw water contains iron or manganese, a film of iron or manganese oxide may be deposited on the microfabric. However, the corrosion-resistant drum can be cleaned by an inhibited acid cleanser.

Municipal applications

Water supplies which are virtually free of color and extraneous matter may be distributed for consumption after being microstrained and sterilized. Also, in the municipal water treatment field, microstraining can be used to clarify water prior to sand fil-

World's largest. *This microstrainer, now operating in Chicago, treats 15 mgd*



tration, explains Diaper. Microstraining reduces the load on the plant, reduces wash water requirements, maintains plant capacity under overload conditions, increases output to meet high demands, reduces the amount of chemicals used and resulting sludges, and is economical to operate. In 1960 a microstrainer was installed in Denver, Colo., to treat 100 mgd of drinking water for Denver residents.

In municipal waste water treatment, microstraining can be applied to the final filtration or polishing of sewage effluent. Remaining suspended solids and BOD can be reduced by 90%. There are now 56 microstrainer installations in the U.S. in operation or under construction which treat sewage or industrial effluents.

Chicago's North Side Sewage Treatment Plant at Skokie, Ill., also employs a microstrainer—the largest one in the world. In fact, the 10 × 30-ft drum treats 15 mgd, reducing the suspended solids from 18 to 5 ppm. To increase capacity, the periphery of the microstrainer drum was corrugated (making it equivalent to a 50-ft-long drum).

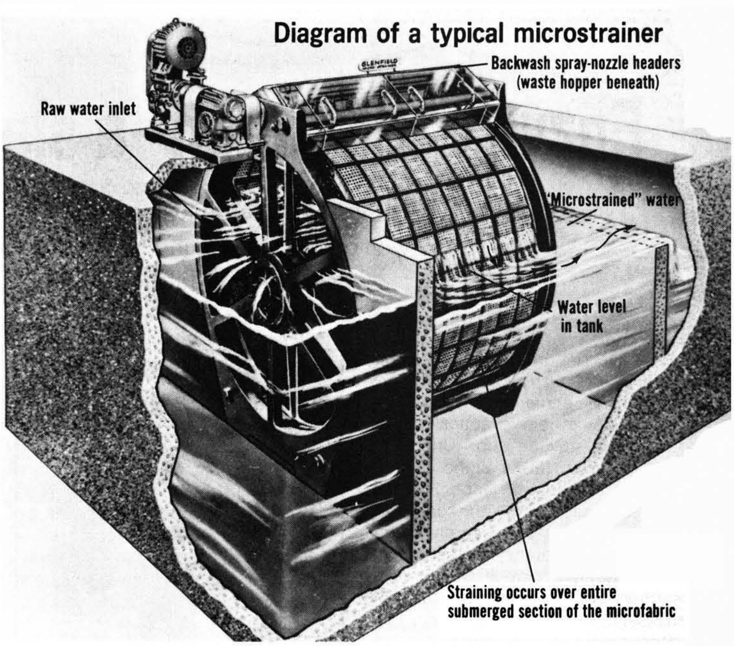
Two Pittsburgh, Pa., suburbs are operating microstrainers for tertiary treatment of municipal sewage effluent. Similar units are in operation or under construction in Michigan, Ohio, Illinois, Florida, Massachusetts, New York, Tennessee, Maryland, Kentucky, Minnesota, North Carolina, Pennsylvania, and New Jersey. Microstrainers being considered for Euclid, Ohio, will have a twofold purpose. In dry weather, sewage effluent will undergo tertiary treatment, and, during wet weather storm flows, the storm sewer overflow will be microstrained. This new method of treatment is being considered by other cities.

Industrial applications

Microstrainers are also used to treat industrial water supplies. One of the first installations in the U.S. (1957) was used by the Anaconda Co. in Montana to protect high-pressure pumps used in the hydraulic debarking of logs. In Thurso, B.C. (Canada), a redesigned water system using microstrainers for a paper mill reduced total water costs by 2.5¢/1000 gal. with an annual savings of $45,000 per year in chemicals.

In Port Alice, B.C., two units remove microorganisms (Copepoda) and organic debris from up to 20 mgd of lake water supply for a paper mill. The shrimp-like crustacea caused discoloration in the stock prior to installation of the microstraining equipment in 1957.

Diagram of a typical microstrainer



About a year ago a paper mill in Turners Falls, Mass., installed a microstrainer that removes 80% of the suspended solids and BOD from paper and board mill effluent. Since no chemical additive is needed in the treatment, the reclaimed material can be returned directly to the process. Normally, these solids are concentrated to approximately 2% of the total filter flow. When heavier loads are anticipated, the microstrainer is operated downstream of the primary clarifier.

Expansion to other fields

Crane Co. researchers are now looking to nutrient removal applications for the microstrainer. Results thus far show that by using ferric chloride as a chemical coagulant, microstrainers can remove 60 and 90% of the phosphorus from treated effluent. A pilot plant operation at a distillery is testing algae removal from the water supply for the plant. The microstrainer removes 96% of the algae—a record which even beats the sand filter used for the same purpose.

"We're even using the microstrainer to remove oil from water," continues Crane's Diaper. "We've applied for a patent on this process." After water with an oil content of 200 ppm passes through the microstrainer, the discharged water only contains 2 ppm oil.

A growing application for the microstrainer is treating storm sewer overflows. Crane Co. was awarded a government contract several years ago to operate a small microstrainer on storm sewer overflows in Philadelphia, Pa. The 800-ppm suspended solids in the storm discharge was reduced to 40 ppm with a very high flow rate—45 gal./min/ft^2. "I think the microstrainer stands head and shoulders above other forms of treatment for versatility, simplicity, and economy," summarizes Diaper.

The competition

Microstraining is in direct competition with sand filtration. Although sand filters can remove a few parts per million more of suspended solids, microstrainers have several inherent advantages.

Total installation and operating costs for microstrainers are about 1.5¢ per 1000 gallons for a 10-mgd plant which compares favorably with other tertiary treatment methods. For example, sand filtration runs about 4¢ per 1000 gallons, and carbon absorption has a price tag of 8¢ per 1000 gallons.

Also, these microstrainers require only about one third the space that sand filters need, and land is often at a premium. Sand filters often require additional equipment for proper operation: holding tanks to ensure constant flow into the filter and pumping equipment to lift the incoming water for the necessary 10-ft head loss for sand filter operation. Besides adjusting to effluent flow and requiring only 6–18 in. head loss, microstrainer characteristics include instantaneous startup and continuous filtration. CKL

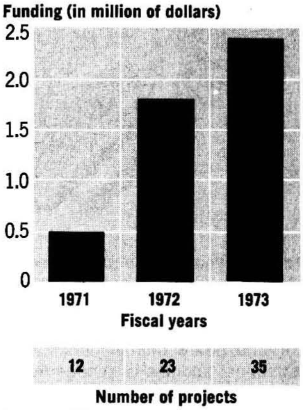
Enzyme utilization—a sleeping giant

Use of immobilized and regenerable enzymes may well one day solve industrial processing and waste water treatment problems

Enzymes are in. The three Nobel prizes in chemistry last year were awarded for earlier studies on enzyme systems, but practical things are in the making too. Under its RANN program (ES&T, June 1972, p 508), the National Science Foundation has funded, over the past few years, a number of research grants to learn what role enzyme technology may or may not play in waste water treatment and advanced industrial processing.

Henry Bungay III, program manager for the NSF/RANN program on advanced industrial processing, says that the areas of emphasis are enzyme technology and extractive metallurgy. On leave of absence from Clemson University (South Carolina), Bungay managed the program for all of calendar year 1972. Last month, he became vice-president–technical director of Worthington Biochemical Corp. (Freehold, N.J.). He says that the whole new thing in enzyme technology is the use of immobilized enzymes to do a job that otherwise would have to be done by chemical or other biological processes. One way to think of an immobilized enzyme is to regard it as one with a handle. By putting on the handle, the enzyme can be used again and again in unit processing operations. And in Bungay's word, the goal of the enzyme technology program, or any other NSF/RANN program for that matter, is "to carry forth the research to the 'proof of concept' stage."

Enzyme technology program at a glance



At this point, Bungay says that NSF has three grants that relate in one way or another to waste water treatment. At the University of Pennsylvania (Philadelphia), work by biochemist Kendall Pye and engineer Arthur Humphrey which was initiated as one of the 1971 grants, is paving the way for enzyme technology which might be used for the treatment of concentrated phenolic wastes or, more immediately possible, this technology may find use as a polishing treatment step to remove phenols from waste water. In this way, it would help ameliorate the odor and taste problems in drinking water.

Changes. Incoming manager George Tsao (left) takes over from Bungay

Two other projects which got underway as 1972 grants are also showing promise in the waste water treatment category. At the University of Virginia (Charlottesville), Donald Kirwan and his team of investigators are finding that enzymes (specifically, lysozyme) can be used to kill viruses in drinking water, but an immediate payoff is not foreseeable. In their work, they find that the enzyme is only useful for one week, and before the technique could be applied by potential users such as municipal drinking water plants, the enzyme would have to be stable for much longer periods of time.

Economical destruction of pathogenic viruses in water is an engineering problem; the common practice of chlorination is only a partial solution. Nevertheless, Kirwan and his group are also looking at the use of proteolytic enzymes such as trypsin to destroy viruses along with the adsorption of virus particles on conducting electrodes which carry sufficient current to degrade the viruses.

At Ohio State University (Columbus), G. P. Royer uses enzymes to treat food plant wastes. The enzymes are used to break down these materials, but Royer finds that when the wastes are overtreated, they become resistant to further microbial attack. So, optimum conditions are being sought by this team of investigators.

How it works

Everyone is familiar with the fact that enzymes are used in hydrolytic processes, such as the degrading of cellulose wastes and the making of cheeses. But what everyone doesn't realize is that immobilized enzymes are hot news. Despite the fact that an enzyme was immobilized for the first time in the '50's by Katchalski, research on enzyme utilization has come a long way since then and could perhaps pay off in the industrial processing area in the next few years.

In another case, enzymes are used to synthesize materials, to convert (in a sense) a relatively abundant and inexpensive chemical commodity to a more desirable product. Usually, this reaction occurs in a routine exothermic reaction.

Enzymes can also be used to oxidize or reduce materials. And herein lies the hot news on the use of immobilized enzymes. The oxidation of phenol by the University of Pa. team is a specific case. In this oxidation, or for that matter any oxidation or reduction process, there is a transport of electrons. What must happen before a phenol molecule is oxidized is that an electron must be transferred to an enzyme cofactor. Before another phenol molecule is oxidized by the enzyme another molecule of cofactor is needed.

Regeneration is the key

So, regeneration of the enzyme cofactor is the key, and the University of Pennsylvania team may well be on the threshold of success in this regeneration process. This is precisely what they are so excited about.

Based on enzymatic processing, phenol sensor which can detect phenol in the ppb range has been developed by the team over the past year.

Then, too, enzyme technology may be used one day in the area of synthetic manufacturing processing. Bungay says there are eight research teams looking at this aspect of the new technology; 30 teams are aiming toward industrial processes, but most are spontaneous, hydrolytic, or rearrangement processes. For example, an industrial process based on an oxidation-reduction scheme by enzymes might be handled more easily and more economically than by unit-processing operations. In a sense, an inexpensive raw material might be either oxidized or reduced to a more desirable industrial product by enzymes.

At Rutgers, one of six research teams is looking at the oxidation of glucose to gluconic acid. Another team at Tulane works on the oxidation of alcohol to acetic acid. At the University of San Diego, the well-known biochemist Martin Kamen and his group are looking at ways to introduce hydroxyl and keto groups into the steroid nucleus. The latter reaction also involves an oxidation step and again another cofactor enzyme.

An M.I.T. group under D. I. C. Wang is also working on some cofactor enzymes. In their work, adenosine triphosphate (ATP) is the cofactor. They are interested in the synthesis of gramicidin S, a peptide antibiotic. At Louisiana State University, George Guilbault is working on the inhibition of more than 30 different enzymes by 21 pesticides. His team is finding that enzyme inhibition can be used in the design of sensors for the pesticides (similar in concept to the Univ. of Pa. sensor for phenols).

Now the LSU area of investigation is being expanded to include enzyme inhibitions due to materials other than pesticides—materials such as cyanide and hydrocarbons. Eventually, they hope to develop fluorescent assay procedures using enzymes attached to solid surfaces.

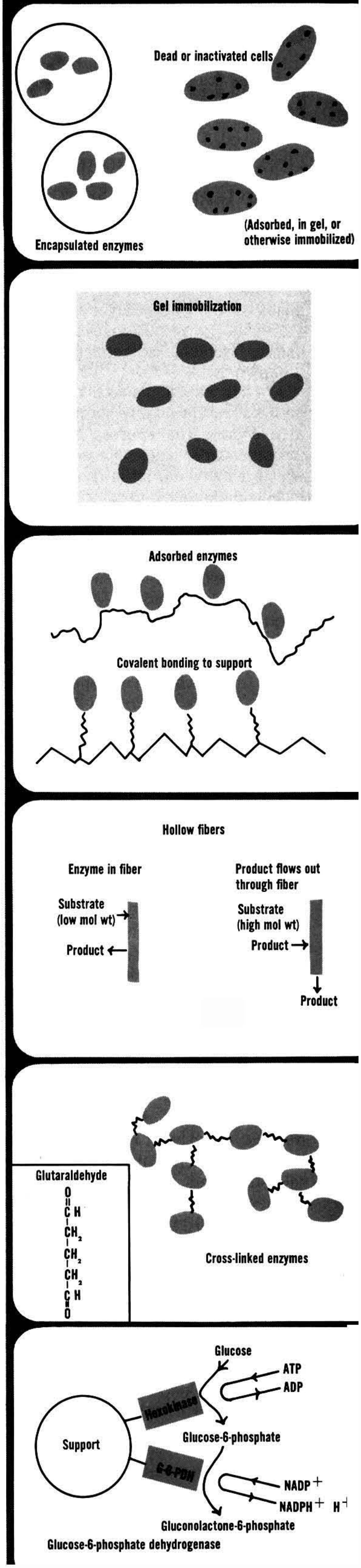
Who else is involved?

Scientists and companies are actively pursuing enzyme technology. The Japanese teams are quite active; so too are the British, at least up to very recently when they decided to cut certain fundings of their program. But within the U.S., the level of activity is substantial and will likely remain so, according to the program manager Bungay.

Only last October more than 80 investigators involved with the NSF/RANN program met in Philadelphia to discuss this rapidly growing and increasingly interesting area of technology. To get the word out to potential users—after, of course, the research is carried past "the proof of concept stage," there is a new publication, *Enzyme Technology Digest*, published by NEUS (New Extensions for Utilizing Scientists), a group of scientists in California working on a nonprofit basis in order to be eligible for federal research grants. (NEUS address is Box 1365, Santa Monica, Calif. 90406.) It's published three times a year; the first issue is dated July 1972; a second issue came out in November. Presently, the digest is being circulated free to about 1300 people.

In the not-too-distant future, various enzyme reactor configurations such as a continuous flow reactor or columnar reactors will be evolving. The age of immobilized enzyme reactor technology is dawning. But what is really important is that the RANN program is getting the message to industrial people in this area of advanced industrial processing on research that may well have a payoff in the short-term future. SSM

How to immobilize enzymes



BPI tackles polluters and politicos with business funds

Chicago-based urban problems/environmental action group teams research, legal action to right environmental wrongs

A coat of arms, hanging on the well-worn office walls of Chicago-based BPI, formerly Businessmen for the Public Interest, conveys, in mock heroic fashion, something of the group's story.

A white knight, flanked by a dragon on one side and by some presumably endangered species of bird on the other side, displays a shield upon which a mere mortal is running, perhaps significantly, uphill along a diagonal bend toward the dragon.

Above the knight are the latin words Age Aliquid—Do Something! And beneath the shield is emblazoned the motto "Agito, ergo sum"—I agitate, therefore I am.

Operating income

BPI is a nonprofit organization—a unique combination of watchdog, research center, law firm, and ombudsman. Its operating budget is approximately $250,000. It gets its money from private business contributions. Its chief benefactors are the GBS Foundation, the Weibold Foundation, The Woods Charitable Fund, and the Bell and Howell Foundation. Two other foundations, the Field Foundation and the CNA Foundation, have made specific grants for the Lake Michigan Study program.

BPI also receives numerous smaller contributions from other businessmen. BPI's latest annual report acknowledges some 40 contributions in the $1000–5000 range and says that support from the business community is broadening. Although BPI's scope is not limited to environmental matters, more than half of its annual budget is spent on environmentally related matters.

The staff of BPI is a full-time, paid group of five lawyers and engineers plus appropriate support personnel. BPI uses some volunteer labor, primarily graduate students in law, medicine, toxicology, and the like to aid in preparing studies. Under an arrangement with Northwestern University law school, 15 law students are now working full-time for BPI, paying tuition to the University, and receiving full academic credit for their work with the organization. But the fact that staff members are salaried employees enhances its effectiveness, according to Alexander Polikoff, BPI's executive director.

"Since the perpetrators of evil in our society are skilled, experienced professionals, who ply their nefarious trades full-time, they should be engaged not by callow youths, fresh and unlearned from college, not by part-time volunteers, torn between the demands of their coffers and their consciences, but by equally skilled, equally experienced professionals, serving full-time in the public interest," Polikoff asserts, although one suspects at least part of his tongue is tucked in his cheek.

BPI is not a national organization, in the sense that the Sierra Club and the Environmental Defense Fund are national organizations, but it does cooperate with national organizations on important issues. Nor is it a local organization.

Although BPI calls Chicago home, it is a Chicago organization only in the sense that it tackles issues in its environs which have a potential for broader relevance. BPI uses Chicago and Lake Michigan as a "test pad," according to the organization's Director of Environmental Research, David Dinsmore Comey. The waves BPI makes along the shores of Lake Michigan may also be felt along the banks of the Potomac.

Tactics and strategy

In going about its business of urban affairs and environmental protection, BPI uses a variety of tactics. Unlike most public-interest law firms, the group is not particularly fond of going to court to accomplish its objectives. It prefers the threat of litigation to actual courtroom fireworks and prefers to work things out with offending polluters in conference rather than threatening to sue.

BPI's Comey
Agito, ergo sum

BPI continues to be thought of as a litigator in the public behalf, despite the fact that a major portion of its work is the preparation of reports, studies, and background materials. But unlike the Nader organization's reports, which are often specifically designed simply to put information on the public record, BPI aims at following up its reports with positive action wherever possible, according to Comey. "Nader essentially produces a report and hopes someone will run with it," Comey says. "When we do it, we follow it up with intense pressure."

The pressure may take the form of a suit or threat of a suit—"intervention" as Comey puts it, or flashier techniques—newspaper ads and the like—designed to appeal directly to the public.

BPI has run head-on into Chicago Mayor Richard Daley's political organization with results which have been frequently embarrassing for His Honor. In October 1969, just a few months after BPI was organized, the fledgling organization scored a direct hit against the Mayor's Office.

The occasion was the 32nd anniversary of Chicago's Cleaner Air Week. BPI ran a full page newspaper advertisement in Chicago papers under the headline "Happy Cleaner Air Week to Mayor Daley and his Friends," blasting His Honor for allegedly passing out spots on Chicago's now defunct Air Pollution Control Appeal Board as rewards for political services rendered.

The advertisement pointed out alleged conflicts of interest and charged that few of the Board members had any qualifications for their posts other than personal friendships with the Mayor. The result, says Comey, was an acutely embarrassed Mayor Daley and a reshuffling of the Board to include more qualified members. Not only did the Board change faces but it also cracked down on air pollution, notably U.S. Steel Corp.'s South Works.

BPI also locked horns with the Mayor over the proposed airport in Lake Michigan, a project personally backed by Mayor Daley and vehemently opposed by area environmental groups. Once again, BPI's weapon of choice was the press. BPI launched a media campaign under the banner "Don't do it in the Lake," complete with buttons, bumper stickers, and other paraphernalia, charging, among other things, that the city was quietly spending large sums of money on feasibility studies despite the fact that leading environmental experts warned of serious ecological damage to Lake Michigan if the airport were to be built.

Although the Mayor announced last summer that the airport would not be built, BPI thinks the issue is not yet dead, vows to watch further developments and oppose any plans to put the airport in the Lake.

The ultimate tool available to BPI, of course, is the lawsuit. And BPI is not averse to legal action where the situation calls for it.

Changing the social order

But when BPI sues, it is with the objective of making major changes in the social order rather than righting any particular injustice. "We try to use the judicial process to bring about structural or institutionalized change, not just to win paper victories," Polikoff says.

Negotiation comes first. "We don't like to pick fights and go to court," Comey insists, "but our negotiations are credible simply because polluters know we will drag them into court."

Most polluters don't want to go to court either. The delays and legal proceedings are costly, but more than that, the polluters realize that they stand a good chance of losing. For in dealing with BPI's lawyers, corporate legal staffs know they are dealing with pros and trying to beat them at their own game. BPI has some of the best lawyers in Chicago.

In court or out of court, the byword is leverage. BPI's small staff can't possibly do, with its limited resources, what infinitely larger government and industry should do. But, there are ways of forcing the big boys to do what they don't like. And BPI looks hard for the ways to apply the necessary leverage.

The issue was nuclear power plant operation, public safety, and damage to the environment. BPI, in cooperation with several other environmental groups, intervened against Commonwealth Edison and Consumers Power Co. in startup of the Dresden and Palisades nuclear plants. Before nuclear power plants can begin operating, Comey points out, they must obtain licenses from the Atomic Energy Commission.

Taking on AEC

The first scuffle was about heated water discharge. After protracted hearings and negotiations, Consumers agreed to install cooling towers at its Palisades plant—a step which cost the company an estimated $15 million—rather than put hot water in the lake. The agreement broke the united resistance put forth by power companies along Lake Michigan and led to an eventual EPA pronouncement that all nuclear power plants on the Lake would have to install cooling facilities.

In related action, BPI intervened to force tighter standards of nuclear emissions in the Dresden case. It was here that the principle of leverage was most clearly demonstrated. AEC's standards for acceptable gaseous nuclear emissions were a hundred times greater than standards of safety proposed by Gofman and Tamplin.

The AEC wanted to write standards into the operating license that would have required the plant to use "best practicable" technology for controlling gaseous emissions but BPI, using the Gofman-Tamplin recommendations, wanted specific numbers—about 1% of the limits previously set by AEC. AEC balked and BPI filed suit, but a negotiated agreement with the power company allowed BPI to write its standards into the provisions of the operating license and BPI dropped the suit.

In the process, however, BPI had forced AEC to adopt standards for gaseous emissions which were a hundred times more stringent than previous AEC standards, and because the standards were incorporated in the operating license, AEC was made responsible for enforcing the standards as a condition of operation. The agreement established a valuable precedent and eventually a new standard for all boiling water reactors in the nation. A similar clause in the Palisades Agreement with Consumers Power Co. created the same type of legal precedent for liquid radiation wastes from all pressurized water reactors.

BPI plans to use its leverage policy to aid in preparing a toxic substances report which will examine "safe" levels of foreign substances in water. Such an effort would normally take vast sums of money and time, but the way BPI will go about it will, once again, force the government to foot the bill.

"We are going to do a complete review—everything that is known about each toxic substance," says Comey. "And the reason that we're doing it is that nobody else has done it; it's absolutely appalling."

Comey finds that the federal EPA and the National Institutes of Health have examined only three toxic substances in detail—lead, mercury, and vanadium. BPI will examine the others by an exhaustive literature search. "We'll take all available data and will come up with a dose-response curve," he says. "Then, if they want to disprove our curves, they will have to do the research necessary to disprove them. But by getting there first with the numbers, everybody else is going to have to work away from our figures."

The fact that EPA has authority and responsibility under the new water amendments to investigate toxic substances, doesn't particularly impress BPI. "Even though EPA is compelled to gather this information under the new water law, I'm afraid they're going to come up with numbers that are acceptable to industry, and that's just not good enough," Comey says. HMM

Polluter inventory is typical of BPI's work

One example of BPI's activity in generating reports is the Lake Michigan Major Industrial Polluter Inventory, prepared for the Lake Michigan Enforcement Conference late last September.

BPI took pollution figures from discharge permit applications filed pursuant to provisions of the 1899 Refuse Act, broke them out by industrial categories and listed discharge numbers for each of 117 major polluters of Lake Michigan.

The results, boiled down, were presented to the Enforcement Conference along with some pointed questions. Why, for example, were 62 of the 117 major polluters not even on the Status of Compliance list of the Lake Michigan Enforcement Conference?

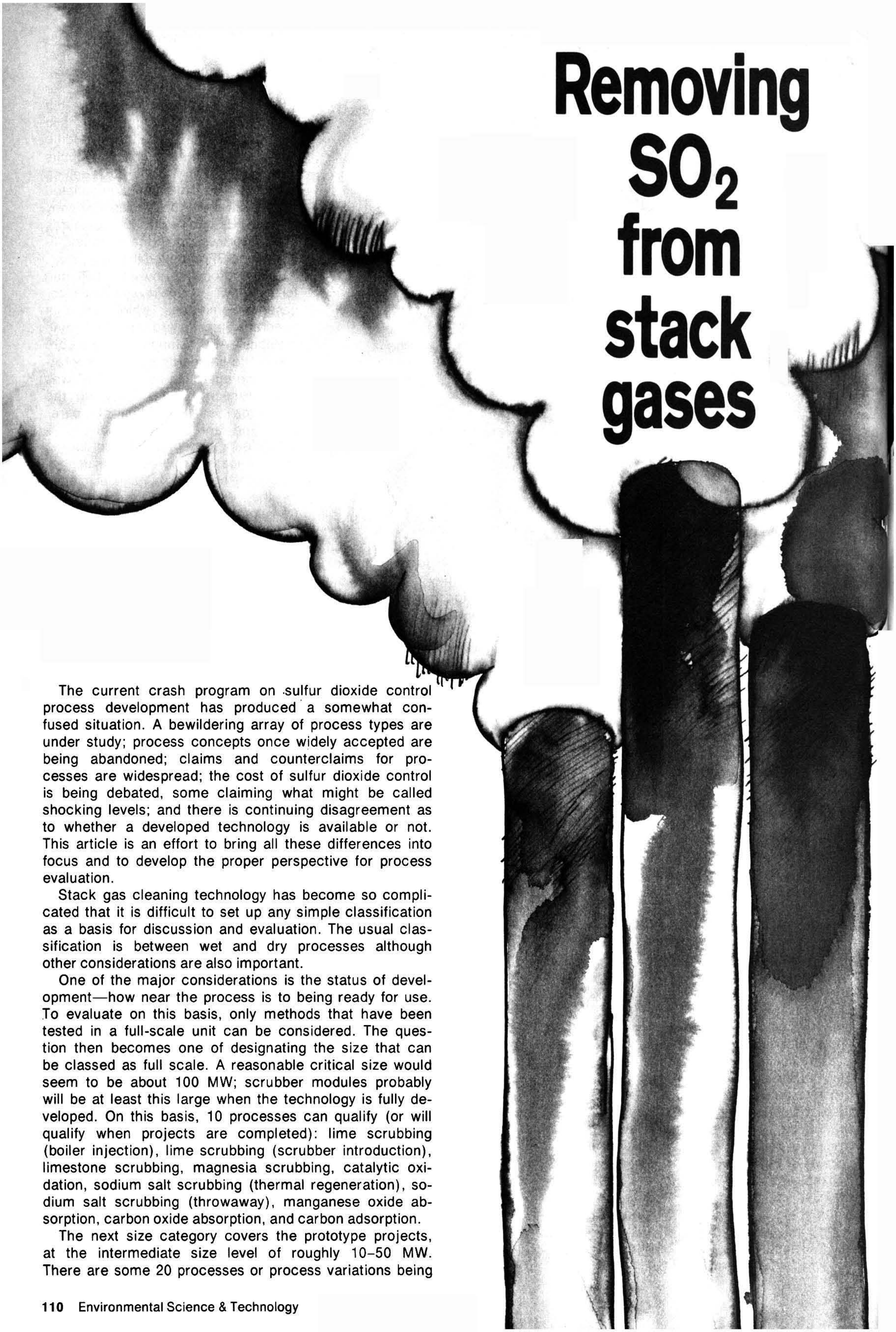
The inventory is part of a larger Lake Michigan Research project, an intense look at polluters along the Lake in a grandiose effort to find out anything and everything about pollution in Lake Michigan.

Such reports, while often helpful to government agencies, are extremely useful to citizen activist groups who may lack the training or resources to pull together generally available information in useful form.

In the inventory, BPI has included information on where to find original permit applications for further scrutiny, complete with names and phone numbers. It has ranked polluters in terms of the seriousness of their pollution and even provided a summary, in pounds per day, of the major pollutants entering the Lake Michigan Basin, based on the industries BPI says represent about 90% of the industrial pollution in the lake.

This type of research, according to BPI, is as valuable in checking pollution as lawsuits. By using industry's own numbers, supplied under penalty of fine or imprisonment for wilfull falsification, BPI is often able to shift the burden of proof back to the polluter.

Removing SO_2 from stack gases

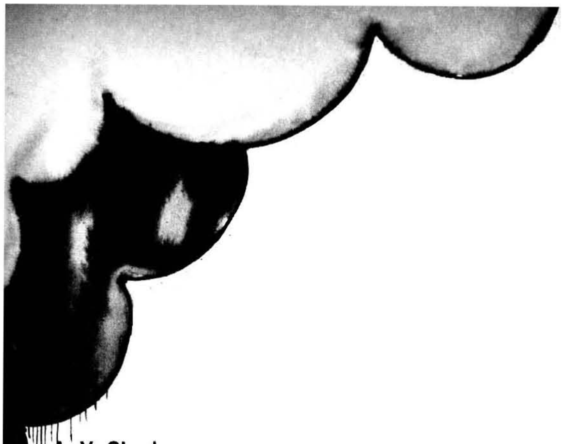


The current crash program on sulfur dioxide control process development has produced a somewhat confused situation. A bewildering array of process types are under study; process concepts once widely accepted are being abandoned; claims and counterclaims for processes are widespread; the cost of sulfur dioxide control is being debated, some claiming what might be called shocking levels; and there is continuing disagreement as to whether a developed technology is available or not. This article is an effort to bring all these differences into focus and to develop the proper perspective for process evaluation.

Stack gas cleaning technology has become so complicated that it is difficult to set up any simple classification as a basis for discussion and evaluation. The usual classification is between wet and dry processes although other considerations are also important.

One of the major considerations is the status of development—how near the process is to being ready for use. To evaluate on this basis, only methods that have been tested in a full-scale unit can be considered. The question then becomes one of designating the size that can be classed as full scale. A reasonable critical size would seem to be about 100 MW; scrubber modules probably will be at least this large when the technology is fully developed. On this basis, 10 processes can qualify (or will qualify when projects are completed): lime scrubbing (boiler injection), lime scrubbing (scrubber introduction), limestone scrubbing, magnesia scrubbing, catalytic oxidation, sodium salt scrubbing (thermal regeneration), sodium salt scrubbing (throwaway), manganese oxide absorption, carbon oxide absorption, and carbon adsorption.

The next size category covers the prototype projects, at the intermediate size level of roughly 10–50 MW. There are some 20 processes or process variations being



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tested in projects of this category around the world, for example, molten salt (Atomics International, Consolidated Edison), ammonia scrubbing-lime regeneration (Kuhlmann, Electricite de France), lime-limestone scrubbing (EPA-TVA-Bechtel), lime scrubbing (special scrubber—Bischoff; STEAG—Germany), and copper oxide absorption (Shell, Showa Yokkaichi Sekiyu—Japan). Some of the 20 or so test units are on slip streams, and others are on boilers small enough to fall in the prototype range. There are also several test units (or commercial in some cases) in industries such as smelting, paper pulp, and sulfuric acid; although there are important differences, the technology should be generally applicable to electric power production.

The next category is the pilot plant size, of which there are a large number. Many of these are concerned with the same process, for example, limestone scrubbing, but departures inevitably develop so that each can be said to cover a separate "process" or at least a process variation. Classification is also difficult because some are too small to be called pilot plants, and others are such short-term projects that including them is questionable. With a liberal classification, some 75 current or fairly recent pilot plant projects can be identified.

The category of processes on which only bench-scale work, or no work at all, has been done include many patented processes, those that surface only in discussions between research people, and many that have not been disclosed at all. No reasonable estimate can be made in this category.

A third major classification is between recovery and throwaway processes. In the U.S., the major emphasis, especially by utilities planning full-scale installations to meet environmental regulations, has been on the throwaway approach. Some 30 full-boiler installations (some involving full plants with several boilers) are known to be in various stages of planning, construction, or operation; of these, only four involve recovery. The uncertainties regarding market potential have made most utilities shy away from recovery until the regulation situation develops further.

Most throwaway processes involve use of lime or limestone since these are relatively inexpensive materials. One company in Nevada uses sodium carbonate. Lime is also used, in Japan, for sulfur dioxide recovery—the product is a marketable grade of gypsum.

Processes can also be classified on the basis of difficulty in applying to retrofit installation, a very important consideration if regulations require fitting existing plants with stack gas cleaning. Although all processes can be adapted to retrofit, some require the complication of gas reheating if major alteration of the boiler is to be avoided. These include molten salt (Atomics International), catalytic oxidation (Monsanto), and some of the in situ methods for sulfur dioxide reduction in the gas stream.

Dry processes—metal oxides, lime-limestone

The dry processes have the major advantage that the gas is not cooled. However, most of them involve absorption in a solid followed by regeneration of the loaded absorbent to give either a final product or a stream highly concentrated in either sulfur dioxide or an intermediate compound such as hydrogen sulfide. The drawback to this is that moving the absorbent from the absorber to the regenerator and back again causes attrition and breakage. The absorbent can be left in place and a "swing type" operation used in which the gas stream is shifted from one vessel to another in a cycle with flow of regeneration gas. This reduces mechanical stress on the absorbent but requires a very expensive dampering system to prevent hazardous leaks from one gas stream to the other.

Solid absorbents also should be quite porous to get as much reaction per cycle as possible. Researchers have found it quite difficult to develop such porosity and activity without seriously weakening the granule structure. Moreover, activity is difficult to maintain because of the sintering effect of many regeneration cycles and because solid impurities in the gas stream tend to plug the pores.

A further drawback is that full oxidation usually occurs on solid sorbents whereas oxidation can be held to less than 10% in wet scrubbing. Thus, even to make sulfuric acid, some solid absorbent processes require a reducing agent to reduce the sulfate to sulfur dioxide. If sulfur is the product, the overall reducing agent requirement is higher than if sulfite were formed during absorption.

There are five leading dry processes involving use of metal oxides. The copper oxide processes—Shell (full-scale unit planned for a 30-MW oil-fired boiler in Japan), Esso-B&W (150-MW unit planned in the U.S. on a coal-fired boiler), and U.S. Bureau of Mines (small scale)—give a rich stream of sulfur dioxide that can either be reduced to sulfur or used as feed to a sulfuric acid plant. All have the problems mentioned earlier for granular sorbents; in addition, since copper oxide sorption must be carried out at 600–750°F, either stack gas heating (to reaction temperature) or major alterations would be required for a retrofit. All this indicates that wet processes may be superior even with the plume reheat requirement.

The alkalized alumina process ($NA_2O \cdot Al_2O_3$) was once considered a leading contender. Although developed originally by the U.S. Bureau of Mines, the Central Electricity Generating Board (CEGB) in England worked independently and planned a full-scale installation. Difficulty in maintaining granule strength, however, was found to be a serious problem. CEGB dropped the project, and today there appears to be little activity on the process.

The Mitsubishi Heavy Industries (Japan) manganese oxide process, which is being tested in a full-scale, oil-fired 110-MW unit, makes ammonium sulfate, which is not a good product in the U.S. except for limited production. The finely divided absorbent used in an entrainment reactor avoids the problems of granular absorbents but introduces some problems in removal from the gas stream. The process is somewhat complicated and requires relatively complex equipment.

The major emphasis in attempts to develop a dry sulfur dioxide removal process has been on use of lime or limestone, in most cases injected directly into the boiler. The main efforts have been in Czechoslovakia, Germany, Japan, and the U.S.; the most extensive work has been done in the federal EPA-sponsored project at the Tennessee Valley Authority (TVA) Shawnee Steam Plant, completed last year.

Results have varied widely. In some of the earlier tests in relatively small units, 50% or higher removal of sulfur dioxide was reported. In the EPA-TVA test work (limestone injection) on a 175-MW boiler, however, only 10–15% removal per stoichiometric amount of limestone could be obtained. Moreover, boiler fouling occurred, and the limestone reduced electrostatic precipitator efficiency. The method does not appear usable where high sulfur dioxide removal is required, but may be applicable in special cases, especially when partial removal is acceptable.

Another major project is the test of the Foster Wheeler-Corson lime injection process under way on an 80-MW coal-fired boiler of the Dairyland Power Cooperative in Wisconsin. The lime is hydrated before injection. Results are said to be encouraging, but no data have been released.

Dry processes—carbon, molten salt

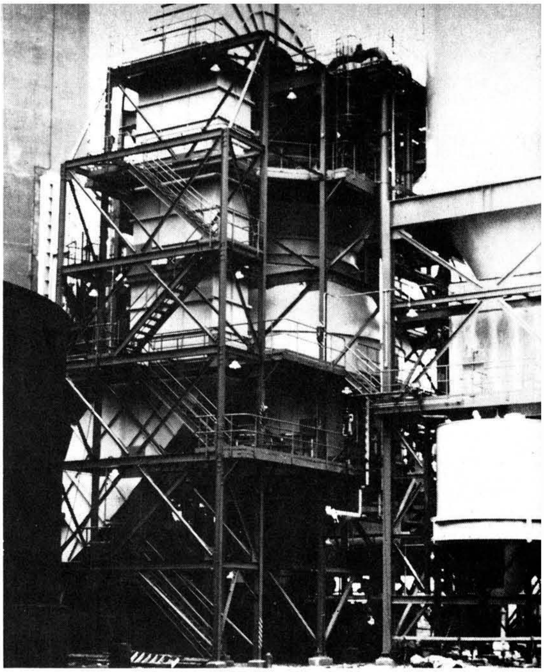
Adsorption on activated carbon has several potential advantages, including low-temperature operation and a simple method for direct oxidation to give sulfuric acid. Although the carbon processes have some important intrinsic advantages, there are also some troublesome problems. For example, the Reinluft prototypes (with a concentrated H_2SO_4 product) were subject to uncontrollable carbon combustion; Chemiebau, the present owner of the process, has reported improvement in this respect, but there have been no large-scale tests. A basic disadvantage for all carbon methods is the low gas velocity allowable and consequently the high carbon volume required; the velocity in most installations has been in the range of 0.5–1.5 ft/sec, as compared with as much as 10 ft/sec in wet-scrubbing processes.

An improved version of the Lurgi process will be tested in a small pilot unit on a coal-fired plant in Czechoslovakia. Although several commercial Lurgi units are in operation in nonpower industries, application to coal-fired power plants brings in some difficulties. The process also has the basic disadvantage that the water-wash method of getting the product acid out of the carbon pores yields weak sulfuric acid (10–20%).

Tests of the Bergbau-Forschung method (producing concentrated H_2SO_4) are planned at the STEAG Lunen plant in Germany next year. Like the Reinluft, the loaded carbon is heated to reduce sulfuric acid to sulfur dioxide by reaction with the carbon. Enlargement of the pores by the consumption of carbon eventually reduces activity and strength. Foster Wheeler has licensed the process in the U.S.

The Westvaco method is unique in that it utilizes fluidized beds and employs hydrogen sulfide developed in the regeneration train to reduce sulfuric acid to sulfur. The process cannot be adequately evaluated until experimental work is done on a larger scale.

The Hitachi (water wash) and Sumitomo (reduction to SO_2) methods are in full-scale operation in Japan. The weak Hitachi acid is neutralized with limestone to give a salable grade of gypsum. In the Sumitomo process, also similar to the Reinluft, hot combustion gas causes reduction of sulfuric acid and desorption of sulfur dioxide, which is then converted to a commercial grade of sulfuric acid. The carbon is recycled between the absorber and the desorber; attrition has been excessive in this process.



Magnesia slurry. *This demonstration SO_2 absorption system, partially funded by EPA, is at a Boston Edison plant*

The carbon processes afford a means for oxidizing sulfur dioxide to sulfur trioxide in the gas stream at low temperature. Getting the resulting sulfuric acid out of the carbon pores, however, complicates the process so—and the absorbent volume required is so large—that the economics are not encouraging.

The molten salt process developed by Atomics International (North American Rockwell) involves scrubbing with a eutectic melt of Na_2CO_3, K_2CO_3, and Li_2CO_3 at about 800°F. For coal-fired boilers, the ash must be first removed in a hot precipitator. The loaded melt is reduced with petroleum coke to give hydrogen sulfide, which is then converted to sulfur.

The method is being tested on a 10-MW slipstream at the Arthur Kill plant of Consolidated Edison. It is a unique process, with considerable promise; solutions to the peculiar problems involved will be sought in the prototype tests.

Atomics International has also carried out pilot plant work (at the Mohave station of Southern California Edison) with sodium carbonate in a spray-dryer type of operation that might be classed as a dry system in that it cools the gas only partially. Throwaway operation is contemplated.

Wet processes

Wet scrubbing methods are of both the clear solution and slurry types. Although solid material in the scrubber liquor introduces problems, it is necessary in some processes because of low sorbent or product solubility. In others, operation with a slurry of highly soluble crystals in a saturated solution may be desirable as a means of reducing recirculation requirement through the regeneration section.

In contrast to dry sorption, metal oxides have received little attention in wet scrubbing. Lack of advantage over the more reactive alkali absorbents is the main reason. Zinc oxide has been considered for special situations in the smelter industry, but the several small-scale projects on applying zinc oxide scrubbing to power plant gases have not progressed very far. One approach, studied at TVA, is to oxidize $ZnSO_3$ to $ZnSO_4$ and decompose the sulfate thermally to SO_3 and ZnO, thereby eliminating need for a sulfuric acid plant.

The main absorbents are the alkalis (sodium and ammonium) and the alkaline earths (calcium and magnesium). In addition, weak sulfuric acid is used in one process and an unidentified organic material in another. Most of the absorbents are used both in throwaway and recovery process types.

TABLE I

Sodium-based methods for stack gas cleaning

Developer	Status	Type and size of test unit	Location	Product
Wellman-Power Gas	Commercial operation, oil-fired, 60 MW	125 MW, coal-fired planned	Japan and U.S.	H_2SO_4 or S
Stone & Webster-Ionics	Piloted	70 MW planned	U.S.	H_2SO_4
UOP	Prototype in operation	. . .	U.S.	S
U.S. Bureau of Mines	Small scale	Piloting on coal-fired steam boiler planned	U.S.	S
Kureha Chemical	Commercial	Oil-fired; 75 MW	Japan	Crystal Na_2SO_3
Showa Denko	Commercial	Oil-fired; 45 MW	Japan	Na_2SO_3 solution
Oji Paper	Commercial	Oil-fired, several, up to 55 MW	Japan	Na_2SO_3 solution

The dust content of the gas is a very important consideration in wet scrubbing processes. For a new boiler, it is desirable to remove both dust and sulfur dioxide in the scrubber system to avoid the cost of an electrostatic precipitator. The question then is whether to use only one scrubber or two—one designed for dust and the other for sulfur dioxide. If the dust has relatively small particle size, the two-scrubber arrangement may be unavoidable. If not, it may still be desirable to avoid getting the dust mixed in with the sulfur dioxide recovery product. There is a major advantage, however, in use of only one scrubber and filtering the scrubber effluent liquor to separate the dust; the hot gas evaporates water from the scrubber solution and thus reduces heat requirement in the regeneration section. This applies only to recovery processes, but there is an advantage in throwaway operation also—more makeup water can be used in the scrubber (for example, for washing the mist eliminator) without incurring "open loop" operation. Single-scrubber operation in recovery processes of the slurry-scrubbing type probably would not be feasible, since it would be difficult to separate the collected dust from the solid absorbent.

For existing plants, the same considerations hold generally, except that most boilers will be already equipped with precipitators when the sulfur dioxide unit is installed. Some existing precipitators, however, will not meet regulatory standards for dust removal, and the scrubbers thus will have to remove the residual dust.

Another consideration is whether the boiler is fired with coal or oil, which affects not only the dust content of the gas but also the presence and nature of minor impurities. The content of soluble impurities will differ, which affects the purge situation in the scrubber system, and oxidation inhibitors and promoters will be present in varying amounts. Data obtained on one gas type are not necessarily applicable to the other.

The main competition in the alkali absorbent area is between sodium and ammonia. Both are excellent absorbents with a high affinity for sulfur dioxide and, with both, the sulfite-bisulfite equilibrium can be used to optimize the absorption-regeneration cycle. Moreover, the regeneration can be carried out in a liquid system at relatively low temperature, whereas the alkaline earths require high temperature for sulfite decomposition and absorbent regeneration. Another advantage is that the clear solutions used avoid the problems in alkaline earth slurry scrubbing systems.

Sodium has the advantage over ammonia that the cation is not volatile and therefore a simpler scrubbing system can be used. Also, no fume problem occurs as in ammonia scrubbing. Ammonia, on the other hand, solves the sulfate problem. Since some oxidation inevitably takes place in the scrubber with any absorbent, the resulting sulfate must be either regenerated, sold, or purged as a waste material. Purging is generally considered unacceptable because of potential water pollution; for regeneration or sale, particularly the latter, ammonium sulfate is much more desirable than sodium sulfate.

There are seven leading sodium-based methods for stack gas cleaning (Table I). The Wellman-Power Gas method (in commercial operation on an oil-fired, 60-MW power plant in Japan) involves thermal regeneration and is the most advanced. It is used on Claus and sulfuric acid plants as well as in the power industry; the product is sulfuric acid or sulfur. Most of the process problems appear to have been worked out with the exception of sulfate disposal; in Japan, for example, the sulfate solution is discarded to the ocean. Some progress has been made toward reducing oxidation, particularly in Japan where Sumitomo Chemical has developed an inhibitor that reportedly cuts oxidation in half. Nevertheless, even with inhibition a large power plant is likely to produce

TABLE II

Processes using ammonia to absorb sulfur dioxide

Developer	Status	Type and size of test unit	Product	Location
NIIOGAZ	Commercial; abandoned	Coal-fired; 75 MW	Liquid SO_2, $(NH_4)_2SO_4$	USSR
Cominco	Commercial; operation since 1930's	Smelter	H_2SO_4, $(NH_4)_2SO_4$	Canada
Cominco	Commercial	H_2SO_4 plants	H_2SO_4, $(NH_4)_2SO_4$	U.S.
JECCO	Commercial; abandoned	H_2SO_4 plants	$(NH_4)_2SO_4$	Japan
IFP	Prototype planned	...	S	France
EPA-TVA	Pilot in operation	Coal-fired; 1 MW	S	U.S.
RIIC	Pilot operated	Coal-fired; 4 MW	H_2SO_4, $(NH_4)_2SO_4$	Czechoslovakia
RIIC	Commercial	H_2SO_4 plant	H_2SO_4, ammonium nitrate	Czechoslovakia
IPRAN	Commercial	H_2SO_4 plants	H_2SO_4, ammonium phosphate	Romania
Monsanto	Under development	...	H_2SO_4 or S	U.S.

several tons of sodium sulfate per day. Various regeneration methods are available, but all appear quite expensive. An important phase in development of the process is a project cosponsored by EPA at Northern Indiana Public Service for a 125-MW, coal-fired test.

The Stone and Webster-Ionics method involves use of electrolytic cells to convert Na_2SO_4 to $NaHSO_4$, which is then added to the scrubber effluent solution to decompose sulfite and bisulfite—evolving sulfur dioxide and giving sodium sulfate (Na_2SO_4) for recycling. Sulfite oxidized to sulfate in the scrubber is converted in other cells to weak sulfuric acid which can be used in the sulfuric acid plant if acid is the main product. Otherwise, the waste acid probably would have to be neutralized with limestone.

The method will be piloted at a Wisconsin Electric Power plant in a joint project with EPA. If successful, a full-scale unit may be built. The main problem, other than possible high cost for power, appears to be sulfate disposal if the sulfur dioxide is reduced to sulfur.

The UOP process has not been disclosed in any detail; a prototype unit is in the startup phases. Sulfate disposal may be a problem here also.

The Bureau of Mines method is unique in that sodium citrate is the absorbent rather than the usual NaOH or sodium sulfite (Na_2SO_3). Use of the citrate allows regeneration of the scrubber effluent liquor by treatment with hydrogen sulfide, giving sulfur as the product without need for first evolving sulfur dioxide from the solution. Larger pilot plants, one at a smelter and another on a coal-fired steam boiler, are planned.

Sale of Na_2SO_3 as such to paper pulp companies, as in Japan, eliminates the cost of regeneration. The market for sulfite in the U.S., however, appears to be limited. Three companies in Japan operate commercial units that yield Na_2SO_3 in solution or crystal form.

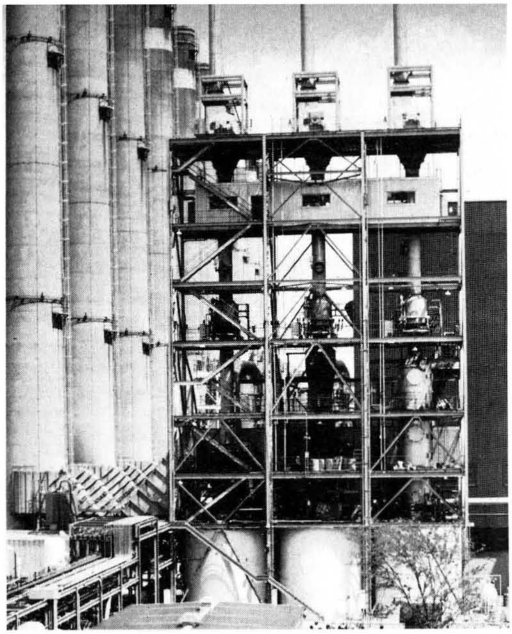
Use of ammonia to absorb sulfur dioxide is a very old process, used in the fertilizer industry long before the modern emphasis on sulfur dioxide emission control developed. Much of the use of ammonia, as shown in the following project tabulation, has been in fields other than power production (Table II).

For power plant application, the NIIOGAZ project in Russia seems to have been fairly successful, but the unit was abandoned when the power plant with which it was associated was converted to natural gas several years ago. So far, Russian government authorities have not seen fit to build another. The same situation holds in Czechoslovakia; the test unit is no longer operated, and there is no prospect for building a larger one. The emphasis on sulfur dioxide control does not appear so intense as in the U.S.

The IFP (Institut Francais du Petrole) method involves thermal decomposition of scrubber effluent liquor to give a gaseous mixture of ammonia, sulfur dioxide, and water, which is passed through a "wet Claus" reactor at elevated temperature to reduce the sulfur dioxide to sulfur by reaction with hydrogen sulfide. The ammonia is recycled. Sulfate produced in the scrubber can also be reduced. The method seems promising, although two thirds of the sulfur must be reduced to hydrogen sulfide and recycled. A full development program is planned.

The EPA-TVA pilot plant project involves treatment of scrubber solution with ammonium bisulfate (NH_4HSO_4) to evolve sulfur dioxide and give $(NH_4)_2SO_4$, which is crystallized and thermally decomposed to NH_4HSO_4 for recycling. The process has several attractive features, including low energy requirement and relatively simple separation and disposal of sulfate (by diverting part of the sulfate crystals to fertilizer use). Fume development in the scrubber, however, is a problem in all ammonia-scrubbing methods.

The only potassium-based recovery method known to be under development is the "formate" process of Consolidation Coal. The sulfur dioxide is absorbed in potassium formate solution, and the scrubber effluent is regenerated by a somewhat complicated procedure to give sulfur as the product. A pilot plant is in operation at the Phoenixville, Pa., station of Philadelphia Electric; data for evaluation are not yet available.



Lime-limestone. *Three 30,000 acfm scrubbers operate at test facility at TVA's Shawnee (Ky.) coal-fired plant*

The Monsanto NOSOX process is based on an undisclosed organic absorbent rather than an alkali. The scrubber solution is decomposed thermally to give sulfur dioxide; a separate, undisclosed step removes sulfates. Only bench-scale studies have been made.

Alkali absorbents (throwaway)

The major throwaway method, lime-limestone slurry scrubbing, is beset by many problems. Because of this, a considerable amount of development work has been done on what are generally called "double alkali" processes. A clear solution of sodium or ammonium salts is used to absorb the sulfur dioxide, and the resulting solution is treated with lime or limestone to precipitate calcium sulfite-sulfate for discard. Scrubber operation is improved considerably although an extra processing step is added.

Activity has been so intense in this area that it is difficult to present an accurate assessment of the status. In Table III, some of the processes listed are not strictly double alkali because the absorbent is something other than sodium or ammonium salts; all, however, have the calcium sulfite-sulfate precipitation step.

The pros and cons of sodium vs. ammonia in the double alkali field are about the same as in recovery. For sodium salt scrubbing, the sulfate can be regenerated if lime is used as the regenerant, but only a dilute solution of NaOH can be produced for recycling. Moreover, calcium dissolved in the regeneration step can cause scaling in the scrubber, a problem that can be avoided by treating the return solution with Na_2CO_3 to precipitate calcium as $CaCO_3$—but at the expense of a purge requirement to rid the system of the added sodium.

The General Motors (GM) work on the sodium system, with imput from A. D. Little, is the most significant in the U.S. GM used lime as the regenerant, as do several others whose work has not been disclosed sufficiently for inclusion in Table III, but limestone has also been used. In this case, only the $NaHSO_3$ is regenerated; the Na_2SO_3 is recycled to the scrubber, and the Na_2SO_4 builds up in the circuit. The Japanese companies have a special system for regenerating the sulfate, involving treatment of a side stream with $CaSO_3$ crystals and H_2SO_4; $CaSO_4$ precipitates, and $NaHSO_3$ is produced for recycling.

The sulfate problem can be handled much more easily if ammonia is the absorbent. In the EDF-Kuhlmann process, for example, the lime reacts well with $(NH_4)_2SO_4$ to volatilize ammonia and precipitate calcium sulfate. The evolution and removal of ammonia drives the reaction to completion. The EDF test unit is being moved from Paris to Champagneoise for further testing. The cost of the process can be reduced by using limestone as the regenerant. Again, only the bisulfite reacts but the ammonium sulfate can be separated and sold as fertilizer. TVA has done small-scale work to evaluate this approach and plans to carry out pilot plant studies as soon as possible.

Chiyoda uses dilute sulfuric acid rather than alkali as the absorbent. A catalyst in the liquor promotes oxidation of sulfurous acid to sulfuric, part of the sulfuric is reacted with limestone to precipitate calcium sulfate, and the residual acid is recycled. The main drawback is the very

TABLE III

Alkali absorbents (throwaway)

Developer	Status	Type and size of test unit	Absorbent/ regenerant	Location
General Motors	Piloted	Coal-fired, 40 MW planned	NaOH/CaO	U.S.
Chemico	Piloted	Various	$Na_2SO_3/CaCO_3$	U.S.
TVA	Small-scale	Pilot planned; coal-fired, 1 MW	$(NH_4)_2SO_3/CaCO_3$	U.S.
EDF-Kuhlmann	Prototype	Oil-fired, 30 MW	NH_4OH/CaO	France
Showa Denko	Pilot in operation	Oil-fired, 3 MW 175 MW planned	$Na_2SO_3/CaCO_3$	Japan
Kureha Chemical	Pilot in operation	Oil-fired, 1.5 MW	$Na_2SO_3/CaCO_3$	Japan
Chiyoda	Piloted	Commercial planned; oil-fired, 25 MW	Water/$CaCO_3$	Japan
Monsanto	Small pilot	Pilot planned; coal fired, 1 MW	Organic/CaO	U.S.
Eimco	Piloted	Coal-fired	NaOH/CaO	U.S.

TABLE IV

Lime–limestone SO_x scrubbing large-scale projects

Company	Developer	Status	Unit type and size	Absorbent
FULL SCALE				
Arizona Public Service	Research-Cottrell	Under construction	Coal-fired, 115 MW	$CaCO_3$
Commonwealth Edison	B & W	Operating	Coal-fired, 175 MW	$CaCO_3$
Detroit Edison	. . .	Planned	Coal-fired, 160 MW	$CaCO_3$
Duquesne Light	Chemico	Under construction	Coal-fired, 150 MW	CaO
Kansas City Power and Light	Combustion Engineering	Operating	Coal-fired, 2 × 120 MW	CaO
Kansas City Power and Light	B & W	Operating	Coal-fired, 117 MW	$CaCO_3$
Kansas City Power and Light	Combustion Engineering	Operating	Coal-fired, 125, 430 MW	CaO
Key West	Zurn	Operating	Oil-fired, 37 MW	$CaCO_3$
Louisville Gas and Electric	Combustion Engineering	Under construction	Coal-fired, 70 MW	$Ca(OH)_2$
Northern States	Combustion Engineering	Under construction	Coal-fired, 2 × 700 MW	$CaCO_3$
Ohio Edison	. . .	Planned	Coal-fired, 2 × 880 MW	CaO
TVA	TVA	Under construction	Coal-fired, 550 MW	$CaCO_3$
Union Electric	Combustion Engineering	Abandoned	Coal-fired, 120 MW	CaO
USSR (state-operated)	NIIOGAZ	Operating	Smelter, 900 MW equiv	$CaCO_3$
Nippon Kokan KK (Japan)	Mitsubishi	Operating	H_2SO_4 plant, about 20 MW equiv	CaO
Kansai Electric (Japan)	Mitsubishi	Operating	Oil-fired, 30 MW	CaO
Tomakomai Chemical (Japan)	Mitsubishi	Planned	Smelter, 15 MW equiv	CaO
Mitsui Aluminum (Japan)	Chemico	Operating	Coal-fired, 165 MW	CaO
Sodersjukhuset (Sweden)	Bahco	Operating	Oil-fired, 3 × 6 MW	CaO
Egypt (state-operated)	Chemiebau	Abandoned	H_2SO_4 plant, small	CaO
Public Service of Indiana	Combustion Engineering	Planned	Coal-fired, 650 MW	$CaCO_3$
Southern California Electric	SCE	Planned	Coal-fired, 2x150 MW	$CaO/CaCO_3$
PROTOTYPE				
EPA–TVA	Bechtel, EPA, TVA	Operating	Coal-fired, 3 × 10 MW	$CaCO_3$, CaO
STEAG (Germany)	Bischoff	Operating	Coal-fired, 35 MW	CaO
Ontario Hydro (Canada)	Ontario Hydro	Planned	Coal-fired, 30 MW	$CaCO_3$

large volume of liquor that must be recirculated through the scrubber. Moreover, the process has not been tested on gas from a coal-fired boiler; such gas is known to contain oxidation catalyst poisons.

The Monsanto absorbent is an undisclosed organic compound. The resulting sulfate is said to react easily with lime. A 2000-scfm pilot plant is being installed at an Indianapolis Power and Light plant.

Alkali scrubbing has also been used in installations where the alkali sulfite–sulfate is discarded. This is the process being installed at the Reid Gardner plant (125 MW) of Nevada Power. The plant is located in a very dry area where a soluble salt can be discarded with less question about water pollution than in other areas. Discard of sodium sulfate (to the ocean) is also planned by Kawasaki Heavy Industries in Japan. Investment is relatively low in such an approach, but raw material cost is high. The spray-dryer process tested by Atomics International can also be operated as a wet scrubbing system.

Magnesia (recovery)

Magnesia has received special emphasis as an absorbent for sulfur dioxide recovery. Lime and limestone have also been considered but have some disadvantages as compared with magnesia; the main use of lime in recovery is in Japan where calcium sulfite is oxidized to the sulfate and sold to the cement and wallboard industries.

All MgO processes involve scrubbing with $Mg(OH)_2$ slurry, separation of the resulting $MgSO_3$, and calcination of the sulfite to evolve a stream of sulfur dioxide and regenerate MgO. The calciner gases dilute the sulfur dioxide to a range that is acceptable for sulfuric acid production but which would increase cost if the sulfur dioxide were reduced to sulfur.

Venturi scrubbers are used in the Chemico-Basic process which is a full-scale operation. Demonstration projects, partially funded by EPA, are under way at Boston Edison (Mass.)—oil-fired—and Potomac Electric (Md.)—coal-fired. The separated and dried $MgSO_3$ is shipped from these plants to a sulfuric acid producer where the material is calcined and acid produced; the MgO is returned to the power plant. This is the central processing concept under which several power boilers supply loaded absorbent to a central regeneration plant large enough to be economical. The feasibility depends on whether a very large central plant, for instance, 2000–3000 tons of acid per day, could sell all the acid at reasonable net profit.

TABLE V

Lime–limestone pilot studies

Company	Absorbent	Station (or location)
Babcock and Wilcox	$CaCO_3$	Ohio
Combustion Engineering	CaO, $CaCO_3$	Connecticut; also others
Chemico	CaO, $CaCO_3$	Various
Ontario Hydro	$CaCO_3$	Toronto
American Metals Climax	$CaCO_3$	Pennsylvania
Smelter Control Research Association	CaO, $CaCO_3$	Nevada
American Air Filter	CaO, $CaCO_3$	Kentucky
Bechtel	CaO, $CaCO_3$	Nevada
UOP	CaO	Connecticut
Southern California Edison	CaO, $CaCO_3$	Nevada
Pennsylvania Power and Light	$CaCO_3$	Pennsylvania
Detroit Edison	$CaCO_3$	Michigan
Krebs Engineering	CaO	Minnesota
Marblehead Lime	CaO	Illinois
National Lime Association	CaO	Nevada
Research-Cottrell	$CaCO_3$	Ohio
Joy Manufacturing	$CaCO_3$	California, Pa.
EPA	$CaCO_3$	North Carolina
Du Pont	CaO, $CaCO_3$	Tennessee
TVA	$CaCO_3$	Colbert Station, Ala.
Environeering	$CaCO_3$	Illinois
Zurn	$CaCO_3$	Key West
Bahco	CaO, $CaCO_3$	Sweden
Mitsubishi	CaO	Japan
CHEPOS	$CaCO_3$	Czechoslovakia
NIIOGAZ	$CaCO_3$	USSR

The Grillo process employs manganese as well as magnesium in the absorbent, purportedly to get faster absorption and promote reduction of sulfate. A spray-type absorber is used. The method has been tested on a fairly small scale (about 7 MW) on an oil-fired boiler in Germany. In Japan, Mitsui Shipbuilding has taken a license and operates a small pilot plant; a 60-MW commercial unit (oil-fired) is planned.

The United Engineers process has not been publicized. A 120-MW unit will be constructed at Philadelphia Electric's Eddystone (Pa.) station.

The magnesia processes have some advantages over the alkali type, including absence of a sulfate problem; addition of coke or other reducing agent in the calcining step reduces any sulfate present. On the negative side, heat requirement is high, and the gas dilution would make sulfur production expensive.

Lime-limestone (throwaway)

The bulk of the research and development effort is being applied to throwaway processes using lime or limestone as the absorbent. There are so many projects, of various magnitudes and in various stages of progress, that it is difficult to summarize them. Tables IV and V list the more significant projects under way; no claim is made for completeness or for a high degree of accuracy.

The main problem by far in scrubbing with either lime or limestone is deposition of solids on surfaces in the scrubber and associated equipment from crystallization of calcium sulfate or sulfite (scaling) and from mechanical sticking of slurry solids to surfaces. The latter is especially troublesome at the two wet-dry interfaces—as the gas contacts the slurry and as it leaves the scrubber.

Scaling is a much more severe problem when lime is used rather than limestone. Because scaling is such a complex phenomenon, the reasons are not yet fully understood. Presumably they are associated with the generally higher pH in the system when lime is used and with the tendency of freshly hydrated lime to stick to surfaces.

For either lime or limestone, there are certain operating parameters that have an important effect on scaling. These effects were worked out by Imperial Chemical Industries (ICI) in England some 40 years ago, and none of the recent work controverts the ICI findings. The following factors help to reduce scaling:

- high liquor rate. If enough liquor is circulated (per unit of sulfur dioxide absorbed) to avoid exceeding a certain level of supersaturation wth sulfite and sulfate, and if this supersaturation is dissipated before the liquor returns to the scrubber, then no scaling can occur
- adequate delay time before the liquor is returned to allow dissipation of the supersaturation
- high content of sultite and sulfate crystals in the circulating slurry to provide surfaces on which dissolved sulfite and sulfate can crystallize
- high slurry velocity to scour off any deposits that tend to form
- dilution with fresh water to reduce the degree of supersaturation
- use of open-type scrubbers with no obstructing surfaces that might cause liquor stagnation or silting of solids
- use of scrubbers or scrubber stages in series, with separate slurry circulation to each, thereby reducing the

amount of sulfur dioxide absorbed per volume of liquor per pass.

Because of the higher reactivity of lime, there has been a major effort to juggle these factors in such a way to avoid scaling and still get the advantages resulting from the superior reactivity, including smaller scrubbers, lower liquor recirculation rate, and better absorbent utilization. The results have been mixed. In most cases, severe scaling has occurred. In a few cases, notably in the plants in Japan, scale-free operation has been obtained. Pilot plant tests with a spray scrubber on gas from low-sulfur western coal have also been successful. It appears, however, that no tests cover completely the situation faced by many utilities in the eastern part of the United States:

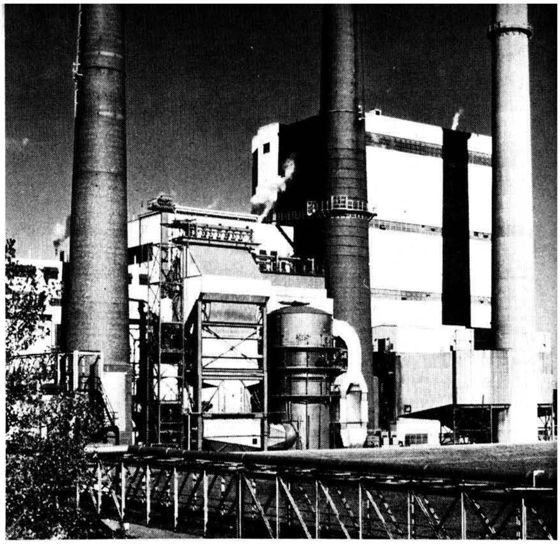
- high sulfur content (3.5–4.5%). The higher the sulfur content, the higher must be the circulation rate to avoid excessive supersaturation as the liquor passes through the scrubber. Thus lime scrubbing is much more applicable to low-sulfur western coals.
- closed liquor loop operation (except for liquor discarded with waste solids). Some of the successful tests have been with partial open-loop operation (discard of scrubber liquor and replacement with water), which probably cannot be tolerated in future practice because of the resulting water pollution
- lime kiln operation at the power plant. Freshly hydrated lime may stick to scrubber surfaces more than the "aged" hydrated lime used in most of the tests.

One problem is that two of the advantages expected from lime—low pumping rate and low solids content in the slurry (which reduces entrainment problems)—cannot be fully realized because of the high liquor rate and high solids content required for controlling scaling. However, smaller scrubber size (for a given degree of sulfur dioxide removal) and better utilization, which are important considerations, can be attained.

If lime is to be used, it appears that a self-scouring type of scrubber such as a venturi or spray-type (with high liquor velocity) is preferable and that stage operation would be helpful. Most of the more successful lime tests have been with equipment of this type. Producing the lime in a separate kiln also seems preferable to injection into the boiler, since in some of the tests the latter has caused boiler fouling.

Because of the question regarding scaling propensity of lime, there has been a trend toward use of finely ground limestone. Although this reduces the scaling problem, it is still there—and the general effect of variables is the same as for lime. The more successful projects have involved high liquor rate (on the order of 50 gal/mcf), high solids content (7–15%), 5–10 min delay time, and open scrubbers of the spray type or equipped with a very open type of packing (or mobile packing).

The "mud" deposition problem can be controlled by soot blowing or by washing with water or slurry. (Use of recycled waste pond water has generally resulted in severe scaling.) This problem is especially serious in the mist eliminator, where entrained solids can cause rapid plugging. The safest procedure, although expensive, is to place the mist eliminator in a horizontal duct section at the top of the scrubber and wash it with a separate flow of water. This opens the loop slightly but perhaps not to an unacceptable degree. Another approach is to place a valve tray or sieve tray in the top of the scrubber and irrigate it with water, which is thus kept separate from the scrubber liquor. The tray prevents solids from reaching the mist eliminator above.



Cat-Ox. *Monsanto's catalytic oxidation system is under test in an EPA-sponsored project at Illinois Power Co.*

By holding gas velocity and slurry solids content at relatively low levels, the mist eliminator (in the standard position) has been kept clean in some tests by washing with only that amount of makeup water available in closed-loop operation. Whether or not this is feasible in large-scale, long-term operation remains to be seen.

A major unresolved problem for both lime and limestone is sludge disposal. The solids do not compact well, and large tonnages are produced. This is probably the main drawback to the throwaway type of operation.

At the moment the industry is faced with the choice between relatively safe procedures on the one hand (use of limestone, special mist eliminator arrangements, high slurry solids content) and on the other, procedures that may save money but which increase the chances of unreliable performance. Reliability can also be improved by open-loop operation but at the expense of water pollution.

Technology is far from fully developed; however, the EPA-sponsored project at TVA's Shawnee station should provide many of the answers needed. The problems of both lime and limestone scrubbing are to be thoroughly explored.

Catalytic oxidation

Catalytic oxidation does not fit well into either of the preceding categories. The method is an old one but the only significant work is that done in the past few years by Monsanto. The gas is thoroughly cleaned of dust in a hot precipitator and passed through sulfur dioxide-oxidation catalyst at high temperature. The resulting sulfur trioxide condenses with moisture to form about 80% H_2SO_4 when the gas becomes cooled to the dew point by the normal cooling in the boiler. Acid mist is removed in a Brink mist eliminator.

The process is being tested in an EPA-sponsored project (100 MW) at the Wood River station of Illinois Power. There are several advantages, including simple operation, low labor requirement, and no cooling of the gas. The main drawback appears to be the grade of the acid produced—the concentration is lower and less pure than the usual commercial acid.

Costs

Although numerous cost estimates have been made for cleaning stack gases, the cost situation has become so complex that most of the published information is not definitive. The stage of development, for example, is a factor, because the projected cost of any process rises steadily as more is learned about it.

Throwaway investment has been generally assumed to be lower than for recovery because no regeneration facilities are needed. As more has been learned about the problems of scaling, mist eliminator plugging, and sludge disposal in lime/limestone scrubbing, however, this assumption has become less firm. It may be that the simpler recovery methods will actually be less expensive to install, but the product disposal problem still remains. If the utility and smelter industries should install recovery systems widely, the market structure would be upset no matter what the product. An extended period of market adjustment will be necessary, during which time throwaway installations will be essential on part of the capacity converted to stack gas cleaning.

As between lime and limestone for throwaway operation, the main factor is the scaling problem. For those situations in which lime is acceptable, the choice will be an economic one. If the delivered raw limestone cost is high, then calcining to reduce scrubber cost and improve utilization may reduce overall cost; if limestone cost is low, however, as it is in much of the eastern U.S., use without calcining would be indicated.

It is difficult to evaluate the recovery processes since so much depends on problems still to be identified during development. This situation should change soon, however, since there are now 10 processes (including both recovery and throwaway) on which design and operating data for units of 100 MW or more either are available now or will be when planned projects are completed. This should provide an adequate basis for a meaningful comparison both between throwaway and recovery and between the various processes in each group. It seems likely, however, that the situation will be more important than the process; in other words, although a particular process may be superior under one set of conditions, it will not be under some other. Moreover, even if the best process is chosen for the particular combination of conditions, the cost will vary widely depending on factors such as plant size and location, load factor, cost of raw material, difficulty of product disposal, and whether the installation is new or retrofit. The range cannot be projected with any assurance of accuracy until more definitive cost estimates are available. However, the present indication is that for power plants investment can easily be as high as \$75/kW and operating cost as high as 2.5 mills/kWh (about \$6.50/ton of coal or 27¢/10 million Btu). Cost both lower and higher than this can be expected, depending on the situation.

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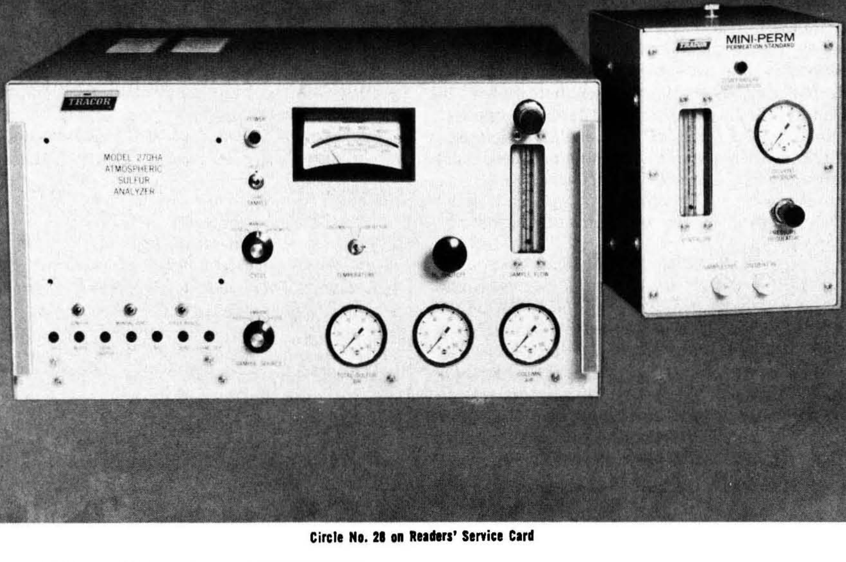
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CURRENT RESEARCH

Oil Spill Identification with Microencapsulated Compounds Suitable for Electron Capture

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■ A technique involving the microencapsulation of high-vapor-pressure compounds suitable for electron capture detection is proposed for the rapid, unambiguous identification of oil slicks. Experimental diffusion studies indicate that the tracer will remain within the microcapsules during the lifetime of an oil slick. Small-scale field studies were conducted with 30-μ diam microcapsules containing Freon 113. Initial tagging densities of around 100 particles/cm^3 were adequate to permit identification for periods up to at least a month after the spill. This identification technique allows the possibility of providing over a million distinguishable mixtures from 20 primary compounds. The analytical procedure associated with this technique is also reported.

As long as petroleum is transported on water, either as fuel or as cargo, coastal waters and beaches will be threatened with oil pollution. The growth of petroleum production and movement has been reviewed by Jagger (1971). According to the U.S. Coast Guard (Brown, 1972), in 1970 there were 3711 reported spills in U.S. waters which totaled over 15 million gallons of oil. Worldwide, the total annual influx of oil to the ocean has been estimated to be between 5 and 10 million tons (Ehrhardt and Blumer, 1972). With the anticipated rates of increase in oil production and transportation, spillage rates are expected to increase rapidly. It should be noted that the San Francisco Bay spill which resulted from the collision of the *M/T Arizona Standard* and the *M/T Oregon Standard* amounted to only 840,000 gallons.

The legal aspects associated with the role of the federal government in controlling pollution up to 1969 were reviewed by Edwards (1969). The Water Quality Improvement Act of 1970 currently forbids "all discharge of oil into or upon the navigable waters of the United States, adjoining shore lines or into or upon the waters of the contiguous zone." Retainment legal action will be successful only if there are techniques which can unambiguously identify oils and oil products of different origins in the sea and on the shores. In certain regions, the problem is further complicated due to natural submarine oil seeps (Allen et al., 1970). Rapid and accurate identification of an oil slick not only aids in forensic matters, but could be of great value in protecting those companies which have made significant improvement in oil-handling procedures.

Several proposed techniques for the identification of oil spills have been reviewed by Horowitz et al. (1969). These techniques have been divided into the categories of passive and active tagging. Passive tagging involves the identification of something naturally present within the oil, whereas active tagging involves adding known and identifiable substances to the oil.

In contrast to active tagging, passive tagging does not permit assignment of different "license plates" to different companies transporting the same kind of oil. Also, a passive tag "fingerprint" can be "smeared" as a result of evaporation of the light fractions, photochemical oxidation in the marine environment, and decomposition due to microbial attack (Zobell, 1969; Kinney et al., 1969). In spite of the many inherent problems associated with passive tagging, a great deal of progress has been made. For example, Brunnock et al. (1968) presented extensive analyses of hydrocarbons associated with weathering crude oils. Ramsdale and Wilkinson (1968) developed a gas-liquid chromatographic procedure for the examination of various oil pollution samples found on beaches. More recently Ehrhardt and Blumer (1972) presented characteristic compositioned parameters for eight different crude oils; distinguishing compositional features were still recognizable after more than eight months of weathering. Zafiriou et al. (1972) were able to correlate correctly about 80% of the spill samples with one source sample during their work with artificially aged oils and potential spill sources found in the greater New York Harbor and Portland, Me.

Much progress has been made in developing weather-resistant correlations used in passive tagging. However, we believe that if tagging of oil is seriously desired for forensic purposes, then the simplest and most unambiguous technique will be one of active tagging. Opponents of active tagging often point out that to be completely effective, active tagging requires international cooperation along with the governmental apparatus associated with the registry of tags. We recognize these difficulties but wish to reiterate that many environmental problems will *only* be solved through some level of international cooperation.

Techniques proposed for active tagging to date include the use of halogenated aromatics and particulate microspheroids (Horowitz et al., 1969). The first method involves adding low-vapor-pressure, halogenated aromatic compounds to the oil. These compounds would be detected by means of electron-capture gas chromatography (Lovelock, 1961). First, the tracer itself must be insoluble in water, and chemically inert in the marine environment. Second, since the tracer cannot be separated from the oil prior to introduction into the chromatograph column, there is always the possibility that other compounds within the oil will interfere with the tag's peak; since the tag would be present in very small amounts relative to the oil, interference of the tag's peak would probably occur from any peak associated with the oil which appears earlier or at the same time as that of the tag. Finally, since the tag itself is exposed to the marine environment, high-vapor-

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pressure tags could not be used. Furthermore, mixtures of compounds could not be used since one or more digits in the "license plate" might be lost, owing to unequal loss rates of different components of the mixture.

The second method involves adding microspheroidal particles to the oil. In this case, identification would be based on size, shape, color, phosphorescence, density, hardness, trace analysis, light absorption, fluorometry, and reflectance. One advantage of this method appears to be "the ease with which such particles may be produced by one basic technique: grinding, and spheroidizing of solids produced from an appropriate liquid melt" (Horowitz et al., 1969). Unfortunately, this method requires that the particulate tag be separated from other particulate matter (such as spores, pollens, fragments of tissue, hairs, microalgae, bits of feather, and dust), which is normally present in both crude and motor oils.

To avoid having to separate the particulate tag from the rest of the particulate matter, and to avoid the problems associated with the first method, a new technique is proposed.

Proposed Technique

General Technique. The proposed technique involves the microencapsulation of liquid compounds whose vapors are suitable for identification by electron-capture gas chromatography. This technique permits the use of mixtures, having preassigned relative amounts of primary compounds, such that each mixture may be unambiguously distinguished from all others.

Identification of the tag is based on detection of each primary compound. If detection were made on a present-absent basis, then $2^N - 1$ different tags could be derived from N primary compounds; over a million different tags could be built from as few as 20 primary compounds. Many more than $2^N - 1$ tags can be constructed if detection is based on measures of relative amounts of primary compounds present rather than on the "yes-or-no" binary system.

Processing Samples. The principal steps in testing a sample are: separating all of the particulate matter, including the microencapsulated tracer, from the oil; opening the microcapsules at the desired time to release the primary compounds into the airspace overhead; and injecting a portion of the overhead gas into the gas chromatograph column. It should be noted that this technique requires neither the separation of the microcapsules from the rest of the particulate matter normally present in crude and in motor oils, nor counting, handling, or examining the microcapsules themselves.

It is important to point out that there are two essential differences between the use of microspheres and the use of microcapsules. First, the solid microspheres must be separated from the oil *and* the solid debris, whereas the microcapsules are only separated from the oil and *not* from the solid debris. In the microsphere technique, detection is not made by electron-capture gas chromatography, whereas in the microcapsule technique, the tag is released into the overhead airspace which is then analyzed by electron-capture gas chromatography. The tag is released into the overhead airspace by heating up the microcapsules until the vapor pressure of the tagged compounds bursts the membrane of the microcapsules.

Sensitivity of Technique. The amount of tracer contained within a single microcapsule could be enough to permit unambiguous identification of the tag. For example, consider a tag comprised of 20 different primary compounds, with each of the primary compounds present in equal amounts by weight. If the density of the liquid tag were approximately 1 g/cm^3, then each microcapsule of 10 μ in diam would contain approximately 5×10^{-10} grams of tracer. If each of the primary compounds had a molecular weight of around 100, then each microcapsule would contain approximately 2.5×10^{-13} moles of each primary compound. At standard conditions, about 5×10^{-9} cm^3 of pure vapor would be produced from each primary compound. If the volume of air in the overhead space were 5 cm^3, the concentration of each primary compound in the overhead air would be about 1 ppb. Although variations in sensitivity exist between various compounds, concentrations of 1 ppb are at least two orders of magnitude greater than that required for minimum detection of many substances. Compounds such as Freon 112, Freon 113, Freon 114B2, the Freon E_n series, perfluorotoluene, hexafluorobenzene, perfluoromethylcyclohexane, perfluorodimethylcyclobutene, and many other fluorinated hydrocarbons would appear to be desirable as primary compounds.

The tracer used in the current studies was Freon 113. Both the tracer and the microcapsules were obtained commercially; the total cost for 1 lb of microencapsulated tracer was less than $100. The microcapsules had a nominal diam of 30 μ, as shown in Figure 1. This particular tag had a thin membrane casing made out of a urea-formaldehyde copolymer, which could be opened by simply crushing the particles as indicated in Figure 2. In the field studies described later, all of the collected particulate matter was heated until the tracer's own vapor pressure was sufficient to burst the microcapsules.

Diffusional Studies

Prior to the field studies, the microcapsule leak rate was determined for several temperatures including some higher than those encountered in the marine environment.

Relative leak rates were determined by flushing 7.5 mg (about 3.4×10^5 capsules) with high-purity nitrogen and periodically monitoring the effluent stream. The microcapsules were distributed in a wad of cotton enclosed within a glass tube through which the nitrogen flowed. The glass tube and 3 ft of tubing upstream were immersed in a constant-temperature bath. The gas chromatograph system consisted of a 6-ft, ⅛ in. o.d. column of Durapak

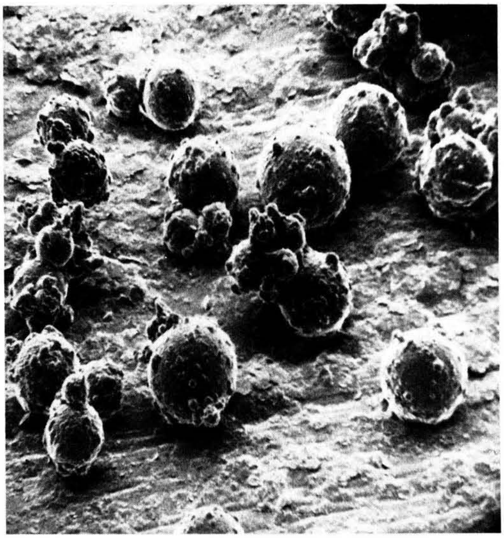


Figure 1. Freon 113 microcapsules, enlarged ~2000 times

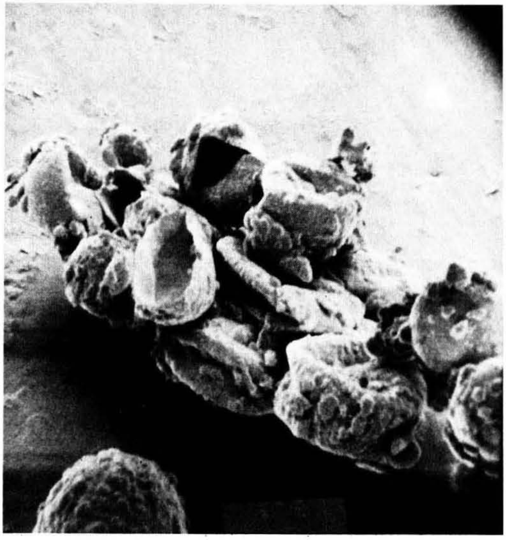


Figure 2. Crushed Freon 113 microcapsules, enlarged ~2000 times

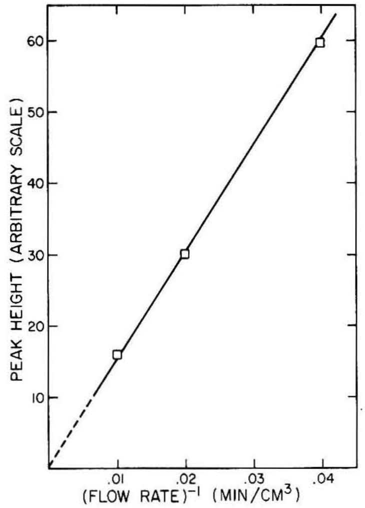


Figure 3. Diffusion study peak height vs. inverse flow rate at 40°C

Carbowax 400 (Waters Assoc., Waltham, Mass.) operated at room temperature; an electron-capture detector containing a tritium source; a General Radio 1217-B Pulse Generator; a Cary Model 31 Vibrating Reed Electrometer; and a Leeds and Northrup 10-mV Recorder. The total cost of this system is under $3000. The first study, conducted at constant temperature, indicated that the tracer peak was inversely proportional to the flow rate of nitrogen (Figure 3). Thus, diffusional transport across the capsule casing appears to be the rate-determining step, as was expected. The second study, conducted at constant nitrogen flow rate, indicated that the tracer peak height increases with increasing temperature; and the relation between peak height and temperature follows a trend which parallels the vapor pressure curve of the tracer (Figure 4). The data obtained in the diffusion experiments indicated that the half-life of this particular tag was between 0.5 and 5 years. The diffusion indicated that the tracer would probably remain with the microcapsule during the lifetime of an oil spill, and then disappear from the water surface.

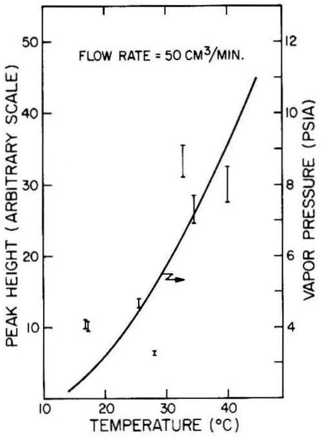
However, the possibility still remained that in continuous contact with oil in the marine environment, the microcapsule casing might be significantly weakened or even ruptured. Field studies were also needed to determine if the microcapsules would remain with an oil slick throughout its lifetime.

Small-Scale Field Studies

Although final verification of this technique should be obtained through a full-scale experiment, small-scale field tests were conducted to provide estimates of the probable microcapsules' performance in an oil slick. Small tanks, about 2 × 2 ft, were partially filled with water over which tagged oils were spread to a thickness of 3 mm. These spills were placed on a rooftop and periodically monitored.

The microcapsules collected at the oil–water interface. Field test data were obtained by analyzing 10-cm^3 samples collected in a beaker. The filtering apparatus consisted of a 20-cm^3 Millipore filter syringe used with a 5-μ mesh Selas Flowtronics silver filter (Selas Corp., Dresher, Pa.). The 10-cm^3 sample and an equal amount of toluene were poured into the filter syringe. After the plunger was inserted, the mixture was shaken vigorously and pushed through the filter. Full syringes of methanol and toluene were subsequently flushed through the filter to remove residual oil and water. The filter, containing the microcapsules along with the rest of the particulate matter, was then removed from the apparatus and allowed to dry. The dry filter was placed in a 1-cm^3 glass vial fitted with a septum. Heating the vial for about 30 sec on an asbestos pad over a Bunsen burner flame liberated the tracer from the microcapsule. A 1-cm^3 sample of the overhead air was withdrawn by a gas syringe and quickly injected into the chromatograph column. After each test the filtering apparatus was cleaned in order not to contaminate subsequent samples. Cleaning involved shaking the apparatus in a bottle of toluene, and then drying the apparatus for 5 min over an open flame. The entire analytical procedure, from the sample collection to the observation of the tracer peak, was accomplished in less than 10 min. A typical chromatogram is shown in Figure 5. In this preliminary study a column packed with Duropak/Carbowax 400

Figure 4. Diffusion study peak height and Freon 113 vapor pressure vs. temperature



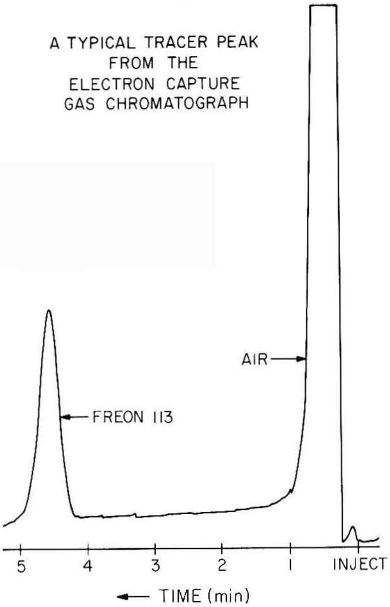


Figure 5. A typical Freon 113 peak from the electron-capture gas chromatograph

(Waters Assoc.) was used. A different column would probably be used to resolve a 20-component tracer mixture.

The first field study involved SAE-30 motor oil spread over fresh water. In this study, the tagging density was 70 microcapsules/cm^3 of oil. The second field study involved Alaskan crude oil spread over salt water, with a tagging density of 10 microcapsules per cm^3 of oil. The third field study involved SAE-40 motor oil, with a tagging density of 70 microcapsules/cm^3 of oil. The first spill was monitored for three weeks, the second for a week, and the third for a month. All three spills were exposed to wind, half an inch of rain, and sunlight. All three spills became so dirty, from the fallout of dust and other debris, that the microcapsules could not be observed by microscopic examination of the filter paper. Although the peak height varied from sample to sample, the tracer could easily be detected throughout each field test. These experiments indicate that it is now worthwhile to test this technique in large-scale studies, wherein the oil is allowed to continually spread. Of particular interest would be tests associated with the specific types of oil slicks which are found in major oil ports (Dudley, 1971) and tests associated with the different stages of a spreading slick (Fay, 1969).

The proposed tracer technique may be useful in studying the transport and dispersion associated with many problems involving fluid flow, and in other problems such as tracing the flow of illicit drugs.

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Nondestructive Instrumental Monitoring of Fuel Oil for Vanadium, Sodium, and Sulfur

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■ An analytical method for monitoring commercial grade heating fuel is described. Neutron activation analysis with a Cockroft-Walton accelerator was used for determining sodium and vanadium. X-ray fluorescence was employed for the assays of sulfur and vanadium. The methods are direct and nondestructive, with little sample preparation time required. Fuel oil samples can normally be monitored in approximately one-half hour. Results for sodium and vanadium are compared to those obtained by atomic absorption. Sulfur values found are in agreement with those reported using the Paar bomb method of analysis.

Much interest has recently been exhibited by various sources in contaminants contained in No. 6 (bunker) fuel oil for heating purposes. Since sulfur dioxide emission levels are regulated by state and city agencies, it is incumbent upon industry to maintain sulfur dioxide emissions within specific limits. Contaminants such as vanadium and sodium, in addition to being air pollutants, also have been found to have a detrimental effect on the fuel burner itself. After a period of operating time the boilers acquire a deposit on the impellers which must be removed for efficient burner operation. The resulting shutdown time is costly since it reduces the life of the impellers and increases maintenance.

Emission spectrographic analysis and X-ray diffraction indicate the major portion of the deposit is a compound composed mainly of sodium, vanadium, and sulfur. An additive is available which will prevent the accumulation of impeller deposit. However, the correct amount to be added requires that the Na, V, and S levels be known. A rapid analytical method was necessary to monitor the concentration of these elements in fuel oil. The two analytical methods investigated and found to be satisfactory are neutron activation analysis and X-ray fluorescence. Neutron activation analysis was used for determining Na and V, while X-ray fluorescence analysis was employed for the assay of S as well as V.

Neutron Activation Analysis of Na and V

Neutron activation analysis has been employed by Shah et al. (1970) for the determination of V and Na in petroleum. The method is reliable and rapid, though it requires access to a nuclear reactor. The present work involves the use of a laboratory accelerator to produce neutrons. Vanadium and sodium possess nuclear properties that are favorable for both thermal and fast neutron activation. The half-life of ^{24}Na which is formed by thermal neutron activation of sodium is relatively long. Since accelerator irradiation times necessary to achieve the sensitivity required would be prohibitive, fast neutron activation analysis with the formation of short-lived isotopes was investigated for sodium. The $^{23}\text{Na}(n,p)^{23}\text{Ne}$ nuclear reaction for determining sodium was considered initially, but was not used because of interferences encountered during the measurement of the 0.44 MeV γ-ray photopeak. A more favorable nuclear reaction was sought that would reduce interferences and yet still possess the required analytical sensitivity. The (n,α) nuclear reaction with the formation of ^{20}F was selected and found satisfactory. The resulting emission of the 1.63 MeV γ with an 11-sec half-life was used to determine sodium. Vanadium analysis was also studied using 14-MeV neutrons to expedite analysis times by avoiding the use of a moderator tank.

Experimental

A description of the neutron generator, transfer system, and detection system has previously been reported by Persiani and Cosgrove (1968). γ-Ray measurements are performed using a scintillation counter composed of two 3 × 3-in. NaI (Tl) crystals mounted on photomultiplier tubes. The combined output pulses are fed to a 1024-channel pulse height analyzer.

Total photopeak areas are obtained by totaling electronically the counts in each channel of the selected band. Net peak areas are computed by the TPA method of background subtraction described by Yule (1968). The polyethylene sample capsules used in this work are especially suited for liquids. A pressed fit with a ring seal at one end prevents leakage. The experimental conditions employed and nuclear data are given in Table I.

Sample Analysis and Standards

The samples were obtained from the fuel oil storage tanks at the Bayside Laboratories. The fuel oil sample is placed in half of the plastic container with an eyedropper. The other half is placed over the end of the loaded capsule and forced into place forming a liquid-tight seal ready for transfer and irradiation.

Commercially purchased organometallic resinate compounds previously analyzed by classical methods were used for both the vanadium and the sodium standards.

Results and Discussion

A series of No. 6 grade fuel oil samples weighing 2 grams were analyzed for vanadium and sodium by fast neutron activation. A comparative analytical study was conducted for vanadium using X-ray and atomic absorption spectroscopy. The results shown in Table II indicate satisfactory agreement, although the values obtained by activation analysis appear to be slightly higher than those found by the two other methods which require sample ashing.

Sodium determinations were carried out for the same samples that were used for vanadium assay. Sample recycling was employed in some cases where improved counting statistics were desired. Analyses were also performed by atomic absorption on the same samples. The results found by both methods as reported in Table II indicate good agreement.

No serious interferences were encountered during the course of the work. However, a primary minor interference due to a $^{54}\text{Cr}(n,\alpha)^{51}\text{Ti}$ nuclear reaction is possible for vanadium. Since ^{54}Cr is only 2.4% abundant, chromium would have to be present at much higher concentrations

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Table I. Nuclear Data and Experimental Conditions

Target	Nuclear reaction, 14-MeV neutrons	Half-life	γ-Ray, MeV	Irradn time	Delay time, sec	Counting time	Estimated sensitivity, mg
V	$^{51}V(n,p)^{51}Ti$	5.8 min	0.32	3–5 min	60	5–10 min	0.04
Na	$^{23}Na(n,\alpha)^{20}F$	11.6 sec	1.63	30 sec	5	30 sec	0.03
	$^{23}Na(n,p)^{23}Ne$	40.0 sec	0.44				

before its contribution would become significant. Emission spectrographic analysis indicated only trace quantities of chromium in the oil.

The levels of vanadium and sulfur found in the fuel oils analyzed appear to be in the concentration range that normally occurs in most heating fuels. However, the relatively high amounts of sodium indicate that some fuel oil contamination might have occurred (Gorski et al., 1969). A possible explanation of these higher-than-expected values for sodium may be the method of oil storage delivery. Apparently, tanker ships, after delivering their cargo of fuel, replace the oil in the storage tanks on return with seawater for weight compensation purposes. Residual seawater in the tanks before oil reloading could account for the sodium contamination.

The estimated relative errors for vanadium and sodium are 20 to 10%, respectively. These errors are based essentially on counting statistics which are dependent to a large extent on the neutron output of the generator at the time of analysis.

X-Ray Fluorescence Analysis of S and V

Until the present time, sulfur concentration in this type of oil was monitored destructively using the Paar bomb technique (ASTM, 1957). Though this method was efficient and fairly accurate, it was time-consuming. There was a glaring need for rapid and accurate control techniques which would enable the analyst to monitor the fuel oil for sulfur and vanadium as well as sodium within an hour or less. Ideally, monitoring should be done before the oil is pumped. X-ray spectroscopy was used to analyze the material for sulfur and was also used as a backup comparison technique for vanadium. The feasibility of using X-ray spectrographic techniques has been shown previously in the work of Shibuya et al. (1967) in the concentration range of 2.10–4.15%.

Table II. Comparative Results of Elements Determined in No. 6 Fuel Oil

	Vanadium, ppm			Sodium, ppm		Sulfur, %	
Sample	naa	X-ray	aa	naa	aa	X-ray	Classical
B-1	95	80	—	410	430	0.81	0.88
B-2	80	70	53	425	470	0.71	—
B-3	69	54	55	310	297	0.79	0.90
B-4	33	25	30	110	96	0.84	0.82
B-5	70	68	62	350	280	1.14	1.01

Table III. X-Ray Operating Conditions: Sulfur and Vanadium in No. 6 Fuel Oil

Vanadium	Sulfur
X-ray tube: W target, FA-60, Philips	W Target, FA-60 Philips
Tube voltage: 50 kV	50 kV
Current: 40 mA	40 mA
Detector: Flow proportional, 1600 V dc	Flow proportional, 1655 V dc
PHA: Integral	Differential
Crystal: LiF	PET
X-ray path: Vacuum	Helium
Collimator: 5 mil	20 mil
Wavelength: 76:87° 2-θ	75.85° 2-θ

Experimental

Apparatus. A Norelco Universal Vacuum X-Ray Spectrograph with inverted X-ray optics was used in conjunction with a Philips FA-60 tungsten target X-ray tube and standard polystyrene disposable sample cells with 0.25-mil Mylar windows secured from Spex Industries, Metuchen, N.J.

Procedure. For the determination of sulfur, a sample of the oil was analyzed using the method of successive additions. This method involved the spiking of 1.000-gram portions of fuel oil with increasing known amounts (by weight) of sulfur added as amyl ziram (50% solution of zinc diamyldithiocarbamate in oil, 12.11% sulfur by weight), and then back-calculating to the original concentration of sulfur present. The amyl ziram solution was secured from Pennsalt Chemicals Corp. (Philadelphia, Pa.). The calculation is usually expressed graphically as X-ray intensity in counts per second (cps) above background of S K_α vs. concentrations added in each case. After results for sulfur were noted for these samples and confirmed by classical chemical techniques, they were then used as standards for succeeding samples. Sample and standard comparisons took the form of linear plots of S K_α X-ray intensities in cps above background vs. percent sulfur. X-ray operating conditions are listed in Table III.

For vanadium, X-ray spectrographic analysis was used as a comparison and check for results determined by neutron activation analysis. The X-ray method is essentially destructive in that 2.5 grams of oil sample were carefully ignited to the ash and the subsequent residue redissolved in nitric acid and dried on 1.0 gram of high-purity graphite powder. The weight of ash was about 0.10% of the sample weight. The powder mixture was triturated in a Spex Mix-A-Mill for one-half hour and compared against powder standards composed of V_2O_5 and graphite. The standard and sample comparison took the form of linear plots of V K_α X-ray intensities in cps above blank vs. concentration expressed in parts per million.

Results and Discussion

Table II compares analytical results between classical and X-ray spectrographic methods for sulfur. The agreement appears to be within satisfactory limits. For X-ray spectrographic analysis a detection limit of 10 and 500 ppm for vanadium and sulfur, respectively, was determined. A relative precision of ±5.0 and ±1.0% for vanadium and sulfur, respectively, was calculated for replicate determinations on a single specimen. One problem associated with the sulfur determination was the excessively high background at the location of the S K_α peak. This was removed effectively using pulse height discrimination procedures. The peak-to-noise ratio was increased almost by a factor of 10 by use of pulse height discrimination.

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Ammonia Intermediacy as a Basis for Catalyst Selection for Nitric Oxide Reduction

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■ This laboratory study of the effect of catalyst composition on the products formed in the reduction of nitric oxide is part of a continuing effort to understand the catalytic chemistry of automotive emission control. The ratio of ammonia to nitrogen in the products of the NO reduction is shown to be primarily a function of the catalyst's ability to promote the decomposition of ammonia. The effects of catalyst composition on product formation can be rationalized on the basis of a mechanism involving the formation and subsequent decomposition of ammonia. Dual functionality and synergistic effects are noted for catalysts containing nickel in combination with copper, platinum, or palladium. In these catalysts the ammonia decomposition function resides primarily in the nickel while the reduction activity is derived from the other metal. Ruthenium is an unusual material that is able to perform both functions efficiently. The effects of water and oxygen on the product distribution are discussed.

The control of nitrogen oxide emissions from automotive exhaust requires their conversion to harmless forms of nitrogen. The catalytic reduction of exhaust nitrogen oxides can result in the formation of ammonia as well as nitrogen (N_2) (Bernstein et al., 1971; Lunt et al., 1972; Hunter, 1971). Recent work in this laboratory and elsewhere has uncovered some of the chemical features of this system (Klimisch and Barnes, 1972; Shelef and Gandhi, 1972). In this work several reactions were identified including the water gas shift reaction (1), the reaction of hydrogen with nitric oxide (2), and the decomposition of ammonia (3).

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (1)$$

$$5\,H_2 + 2\,NO \rightarrow 2\,NH_3 + 2\,H_2O \quad (2)$$

$$2\,NH_3 \rightarrow N_2 + 3\,H_2 \quad (3)$$

Much of this past work was carried out with catalysts which converted most of the nitric oxide to ammonia. In dual catalyst emission control systems, these catalysts would be considered unsatisfactory because ammonia formed in the first (reduction) bed tends to be oxidized back to NO in the second (oxidation) catalyst bed.

Several improved catalyst compositions have been developed to overcome this problem. The present laboratory work examines these improved catalysts to try to gain a better understanding of the catalytic process itself and of the effect of catalyst composition on the products formed in the nitric oxide reduction reaction.

Experimental

The single- and two-component catalysts prepared are listed in Table I along with their chemical compositions and surface areas. The various active components were applied by soaking a preformed alumina support (Kaiser KC/SAF gel-derived alumina, surface area = 250 m^2/g, $^1/_8$-in. spheres) in a concentrated aqueous solution of the appropriate metal salt. Hydrated nitrates were used for the base metal components (copper, chromium, and nickel) while the precious metal components used were chloroplatinic acid, palladium chloride, and ruthenium chloride. For the two-component catalysts, a two-stage impregnation procedure was utilized. After each impregnation, the material was air-dried and then calcinated at 620°C for 4 hr in an airstream (ghsv = 500). The catalyst compositions listed were verified by elemental analysis.

The catalytic reactor and techniques for gas handling and continuous analysis have been described by Klimisch and Barnes (1972). A catalyst charge of 15 cc resulted in a bed depth of 5 cm. The gas hourly space velocity (ghsv) was 38,000 unless otherwise specified. The feed stream used for the NO reduction experiments resembled automotive exhaust gas and consisted of 1% CO, 0.3% H_2, 0.1% NO, 10% H_2O, and 10% CO_2 in a nitrogen atmosphere. The catalysts were reduced in these gases in the catalytic reactor at 650°C before use. The data points all represent steady-state conversion taken at descending temperatures and were periodically checked for repeatability. The feed stream for the ammonia decomposition experiments consisted of 0.10% NH_3, 10% H_2O in a nitrogen atmosphere.

Results and Discussion

Copper Catalysts. The product distribution as a function of catalyst temperature in the nitric oxide reduction reaction is shown in Figure 1 for a Cu-Ni-Al_2O_3 catalyst. This metal combination was suggested by the interesting results with a copper-nickel metallic alloy catalyst system obtained by Bernstein et al. (1971). The Cu-Ni-Al_2O_3 catalyst was especially selective in forming nitrogen at

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Table I. Composition and Surface Area of Catalysts

Catalyst	Composition, %	BET surface, m^2/g
Al_2O_3	. . .	182
$Cu-Cr-Al_2O_3$	6.3 Cu, 4.4 Cr	109
$Cu-Ni-Al_2O_3$	8.1 Cu, 9.2 Ni	147
$Cu-Al_2O_3$	8.2 Cu	179
$Ni-Al_2O_3$	9.2 Ni	177
$Pt-Ni-Al_2O_3$	0.2 Pt, 9.2 Ni	166
$Pd-Ni-Al_2O_3$	0.3 Pd, 9.2 Ni	165
$Pt-Al_2O_3$	0.2 Pt	178
$Pd-Al_2O_3$	0.3 Pd	170
$Ru-Al_2O_3$	0.1 Ru	153

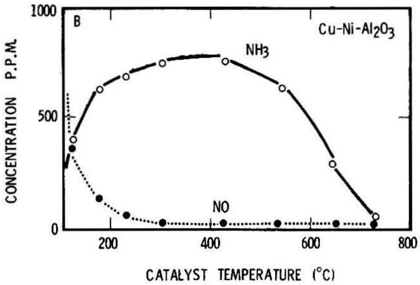

Figure 1. NO removal and NH_3 formation over $Cu-Cr-Al_2O_3$ and $Cu-Ni-Al_2O_3$ catalysts

Feed: 1.0% CO, 0.10% NO, 0.30% H_2, 10% H_2O, 10% CO_2, and balance N_2; ghsv = 38,000.

high temperature—i.e., above 700°C. A $Cu-Cr-Al_2O_3$ catalyst on the other hand (Klimisch and Barnes, 1972) converted most of the nitric oxide to ammonia even at temperatures as high as 750°C.

The decomposition of ammonia on the catalyst surface has been suggested as an explanation for the decrease in ammonia formation at high temperature (Klimisch and Barnes, 1972). To investigate this possibility further and to understand the contribution of the various components to the overall catalytic activity, the reactivities of the individual metals supported on alumina were examined. Figures 2 and 3 show the ammonia formation and decomposition tendencies for copper-on-alumina and nickel-on-alumina catalysts. The $Cu-Al_2O_3$ catalyst is effective for the reduction of nitric oxide, but converts most of the NO to ammonia (Figure 3). The data in Figure 2 confirms that the $Cu-Al_2O_3$ catalyst is ineffective for ammonia decomposition in this temperature range.

The behavior of the $Ni-Al_2O_3$ catalyst is a study in contrast. This catalyst is ineffective for nitric oxide reduction (Figure 3) but shows good activity for the decomposition of ammonia (Figure 2). The two-component catalyst system, $Cu-Ni-Al_2O_3$ (Figure 1), appears to represent a classical case of dual functionality (Weisz, 1962). The NO reduction activity of the $Cu-Ni-Al_2O_3$ catalyst derives from the copper while the ammonia decomposition function resides primarily in the nickel component. The results in Figure 2 also indicate that a synergism exists whereby copper is able to improve the ammonia decomposition activity of nickel even though its own activity for promoting this process is poor.

The dual functional catalyst provides a major path to elemental nitrogen (Reaction 4).

$$NO \rightarrow HN_3 \rightarrow N_{2(4)} \qquad (4)$$

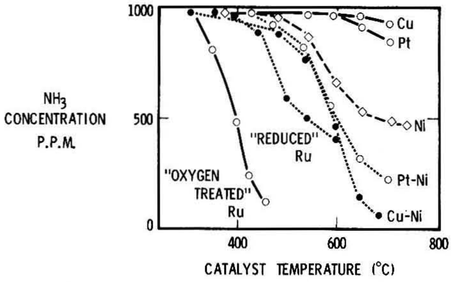

Figure 2. Ammonia decomposition over $Cu-Al_2O_3$, $Ni-Al_2O_3$, $Pt-Al_2O_3$, $Pt-Ni-Al_2O_3$, $Cu-Ni-Al_2O_3$, and $Ru-Al_2O_3$

Feed: 0.10% NH_3, 10% H_2O, and balance N_2; ghsv = 38,000

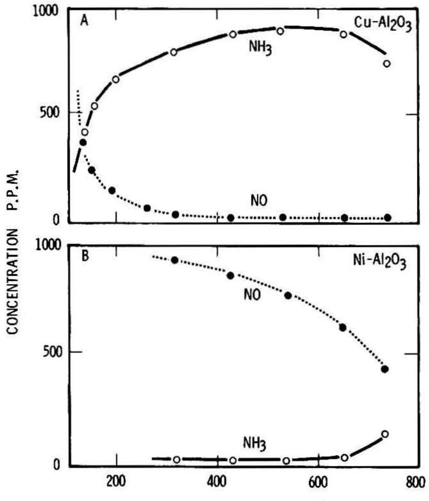

Figure 3. NO reduction and NH_3 formation over $Cu-Al_2O_3$ and $Ni-Al_2O_3$ catalysts

Feed: 1.0% CO, 0.10% NO, 0.30% H_2, 10% H_2O, 10% CO_2, and balance N_2; ghsv = 38,000

If this is true, an appropriate automotive emission control catalyst might be one that is able to promote both the formation and the decomposition of ammonia, albeit at different temperatures. In any event, it provides a useful hypothesis for rationalizing the effects of catalyst composition on products formed from NO reduction.

Platinum and Palladium Catalysts. The above results suggest that for reduction activity the copper might be replaced by platinum, which is known to catalyze the reduction of nitric oxide to ammonia (Sabatier, 1922). The NO reduction and NH_3 formation tendencies for platinum supported on alumina are shown in Figure 4*A*. The platinum catalyst was moderately effective in removing nitric oxide, but considerable ammonia was noted which corresponded to a rather poor ability of this catalyst to decompose ammonia (Figure 2). When the platinum was combined with nickel, however, the same kind of dual functionality occurred as was observed for the copper-nickel catalyst system. The data in Figure 4*B* show that the $Pt-Ni-Al_2O_3$ catalyst was especially selective for N_2 formation at high temperature—i.e., above 650°C. In addition, the ammonia decomposition activity (Figure 2) indi-

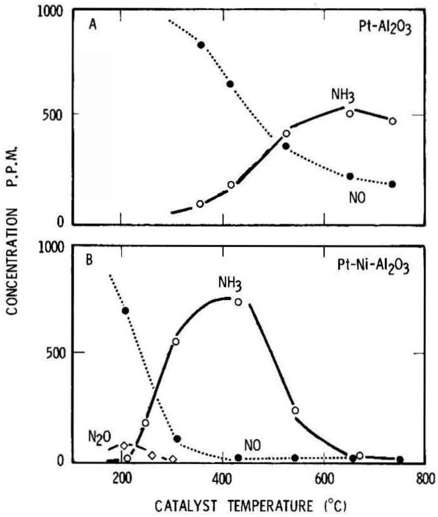

Figure 4. NO reduction and NH_3 formation over $Pt–Al_2O_3$ and $Pt–Ni–Al_2O_3$ catalysts

Feed: 1.0% CO, 0.10% NO, 0.30% H_2, 10% H_2O, 10% CO_2, and balance N_2; ghsv = 38,000

cates a synergism between the precious metals and nickel which parallels the synergism between copper and nickel. The nitric oxide reduction and ammonia decomposition figures for $Pd–Al_2O_3$ and $Pd–Ni–Al_2O_3$ are not shown since they were similar to the corresponding figures for the platinum catalysts. The N_2O results in Figure 4*B* will be discussed in a later section.

An interpretation of the synergism of the $Pt–Ni–Al_2O_3$ catalyst in nitric oxide removal (Figure 5) might be that the precious metals are promoting the activity of the nickel. A number of reports (Nowak and Koros, 1967; Charcosset et al., 1971; Verhoeven and Delmon, 1966) have shown that small quantities of platinum or palladium can effectively promote the hydrogen reduction of alumina-supported nickel oxide which is otherwise very difficult to reduce (Hill and Selwood, 1948). Figure 3*A* showed that $Cu–Al_2O_3$ which is readily reducible (Voge and Atkins, 1962) removes NO at low temperature. This suggests that nickel, when it is rendered reducible by platinum or palladium, resembles copper in the catalytic reduction of nitric oxide.

The promoting effect of various metals for nickel oxide reduction may be due to the ability of these metals to activate and chemisorb hydrogen (Nowak and Koros, 1967). For the nitric oxide reduction reaction, the presence of chemisorbed hydrogen on the surface may be more important than the reduction of the nickel oxide per se. Thus, one might expect hydrogen atoms on the surface to react with NO to produce primarily ammonia, which is what is observed at low temperature over the $Pt–Ni–Al_2O_3$ catalyst (Figure 4*B*).

Ruthenium Catalysts. Figure 6*A* shows NO removal and NH_3 formation for a catalyst containing 0.1% ruthenium supported on alumina. The low-temperature ammonia formation observed in Figures 1 and 4 did not occur for this catalyst. Instead, ammonia formation was fairly small and relatively constant over the whole temperature range studied (150–750°C). The data in Figure 6*A* could not be repeated after the ruthenium catalyst had been exposed to excess oxygen for 10 min at 538°C. This oxygen-treated catalyst gave the steady-state data in Figure 6*B* for conversions measured at ascending temperatures. Ammonia formation was not detectable between 500° and 650°C. This low ammonia-producing condition of the catalyst was lost at 700°C where the ammonia production slowly increased and leveled out at 20% (based on conversion of NO in the inlet). After the 700°C reducing treatment, the catalyst had reactivity characteristics identical to those shown in Figure 6*A* and had apparently returned to its original state which will be referred to as reduced-$Ru–Al_2O_3$. The catalyst was converted between the two states several times and the same steady-state reactivity effects were found. The source of the reversible conversion has not been established.

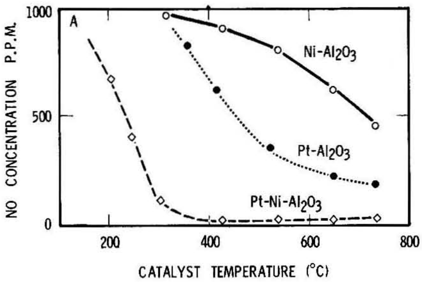

Figure 5. Comparison of NO removal activities for precious metal nickel catalysts

Feed: 1.0% CO, 0.10% NO, 0.30% H_2, 10% H_2O,10% CO_2, and balance N_2

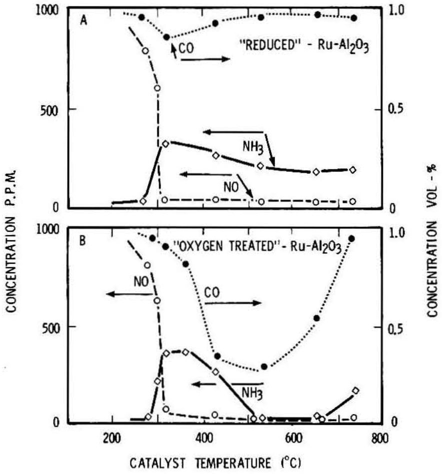

Figure 6. NO reduction and NH_3 formation over $Ru–Al_2O_3$ catalysts

Feed: 1.0% CO, 0.10% NO, 0.30% H_2, 10% H_2O, 10% CO_2, and balance N_2; ghsv = 38,000

The unusual behavior of this catalyst suggested that a different mechanism might be operating in this case. However, ammonia decomposition experiments for steady-state conversion (Figure 2) did not confirm these suspicions or contradict the hypothesis mentioned previously. The reduced catalyst was quite effective for ammonia decomposition, comparing favorably with the platinum-nickel catalyst (Figure 2) for this reaction. Furthermore, the oxygen-treated ruthenium catalyst (Figure 2) exhibited even greater activity for ammonia decomposition provided the catalyst temperature did not exceed

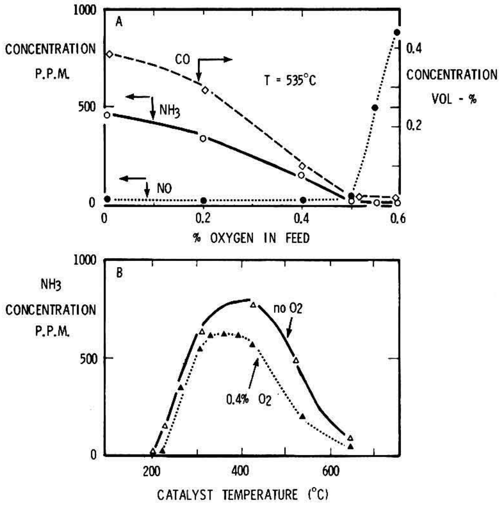

Figure 7. Effect of oxygen on NO removal and NH_3 formation over $Pt-Ni-Al_2O_3$

Feed: 1.0% CO, 0.10% NO, 0.30% H_2, 10% H_2O, 10% CO_2, and balance N_2; ghsv = 38,000

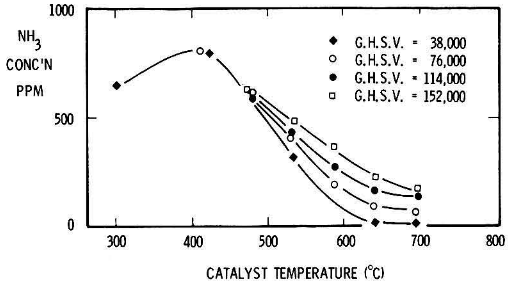

Figure 8. Effect of space velocity on ammonia formation for an alumina-supported platinum–nickel catalyst

Feed: 1.0% CO, 0.30% H_2, 0.10% NO, 10% H_2O, 10% CO_2, and balance N_2; ghsv = 38,000

Table II. Effect of Water on Ammonia Decomposition Over Various Alumina-Supported Catalysts

Feed stream: 0.10% NH_3, 0 or 10.0% H_2O, and balance N_2 ghsv = 38,000

Catalyst	Temp, °C, required for 50% conversion	
	0% H_2O	10% H_2O
$Cu-Cr-Al_2O_3$	580	>775
$Cu-Al_2O_3$	555	>775
$Pt-Al_2O_3$	565	>775
$Pd-Al_2O_3$	560	>775
$Ni-Al_2O_3$	555	660
$Cu-Ni-Al_2O_3$	482	590
$Pt-Ni-Al_2O_3$	560	605
$Pd-Ni-Al_2O_3$	580	590
$Ru-Al_2O_3$	504	546
$Ru-Al_2O_3$[a]	343	382

[a] Activity of $Ru-Al_2O_3$ catalyst after treatment with excess oxygen at 538°C.

500°C. Thus, the change in ammonia decomposition activity for the two states of the ruthenium catalyst can account for the difference in the ammonia observed for these same two states. Low-temperature activity (350–400°C) for ammonia decomposition over a reduced ruthenium-on-alumina catalyst has been reported by Amano and Taylor (1954).

Steady-state data for carbon monoxide removal is also presented in Figures 6*A* and *B* since a significant change in the activity of the catalyst for the water gas shift after oxygen treatment was found. The data were taken at steady-state so carbon monoxide removal cannot represent simple catalyst reduction. For the oxygen-treated ruthenium catalyst, the water gas shift reaction is near equilibrium at 523°C. The reduced state of the catalyst (formed at 700°C) does not promote the shift reaction. These effects are not well understood and deserve further study.

Other Nitrogen Oxides. As mentioned in the experimental section, the reaction streams were continuously monitored for nitrogen dioxide (NO_2) and for nitrous oxide (N_2O). Nitrogen dioxide never appeared in the reduction product stream. The occurrence of nitrous oxide, however, was noted at low temperature over several of the catalysts. Figure 4*B*, for example, shows the data obtained over the $Pt-Ni-Al_2O_3$ catalyst. The N_2O concentration at 200°C accounted for 16% of the inlet NO. The yield over the $Pd-Ni-Al_2O_3$ catalyst was 24% of the inlet NO at 160°C. Nitrous oxide formation was very low (<5%) for all the other catalysts studied and is not included in the figures.

Effect of Oxygen. Automotive exhaust gas contains oxygen even at rich air-fuel ratios owing to flame quench phenomena (Daniel, 1970). All the catalysts examined in this study showed decreased ammonia formation as oxygen was added to the feed stream. Figure 7*A* shows some typical results for the $Pt-Ni-Al_2O_3$ catalyst at 535°C. As oxygen was added, the ammonia content in the exit gases decreased and the level of NO did not increase as long as the system was maintained net reducing. Carbon monoxide was also removed with oxygen addition to the feed stream. The effect of oxygen on ammonia formation as a function of temperature is shown in Figure 7*B*.

Two reasons for this oxygen effect may be proposed. Ammonia decomposition could be enhanced by the reaction of oxygen with ammonia decomposition fragments similar to the effect of oxygen on the catalytic reduction of NO by NH_3 (Markvart and Pour, 1967). A second possibility is that ammonia formation may be affected by oxygen. Unlike NH_3 formation, nitrogen formation requires that a reaction take place between two nitrogen-containing species. Through competition with NO for surface sites, CO may lower the probability for adjacent nitrogen species (Shelef and Gandhi, 1972). Oxygen may reverse this effect by lowering the surface CO concentration. Klimisch and Barnes (1972) have shown that the role of CO in these reactions is more complex than just providing H_2 via the shift reaction since NH_3 formation was not increased when H_2 was included in the NO-CO-H_2O feed gases for a $Cu-Cr-Al_2O_3$ catalyst. Furthermore, Shelef and Gandhi (1972) have observed that with a NO-H_2 feed where H_2 is the principal reducing agent, adding CO increased NH_3 formation over several catalysts.

Effect of Water. The 9–13% water (by volume) in automotive exhaust at normal air-fuel ratios has some rather significant effects on the catalytic chemistry of exhaust gas. For example, water strongly inhibits ammonia decomposition over alumina-supported catalysts (Klimisch and Barnes, 1972). The magnitude of this inhibition for the catalysts employed in this study is shown in Table II. For catalysts not containing nickel or ruthenium, water displaced the conversion-temperature curve by over 200°C. This large inhibiting effect of water is undoubtedly a result of the similarity in the chemisorption behavior of ammonia and water on the alumina support (Peri, 1965) coupled with the hundredfold concentration advantage of water in the feed stream—i.e., 10.0 vs. 0.1%. With nickel or ruthenium present in the catalyst the temperature difference between the wet and the dry experiments was less than 100°C.

Intermediacy of Ammonia. The correspondence between the effect of temperature on ammonia formation from NO on the one hand and ammonia decomposition on the other suggested that a major part of the conversion of NO to N_2 follows the rather circuitous pathway (Reaction 4) involving the intermediacy of ammonia. Over the platinum-nickel catalyst, ammonia formation reaches a peak and begins to decrease rather rapidly above 425°C (Figure 4*B*), which is the temperature range where the ammonia decomposition begins to be significant (Figure 2). This correspondence in temperature profile was also found for the other catalyst systems studied.

The above results confirm that ammonia is not stable at high temperature, which is known from thermodynamics (Bernstein et al., 1971), but do not establish whether ammonia is an intermediate in the reduction of NO to N_2. However, it was also found (Figure 8) that ammonia formation over the $Pt-Ni-Al_2O_3$ catalyst is significantly affected by space velocity. Thus, at higher space velocity (lower residence time), more ammonia is formed under conditions where NO removal was complete for all the space velocities studied. These space velocity effects would seem to provide substantiating evidence that ammonia is actually formed and then undergoes elemental decomposition. Thus, the path represented by Reaction 4 is an important route for the conversion of nitric oxide to elemental nitrogen.

There is probably another path from NO to N_2 that does not go through ammonia. This other path may involve the oxidation reduction sequence:

$$NO + M \rightarrow \tfrac{1}{2} N_2 + MO \qquad (8)$$

$$CO + MO \rightarrow CO_2 + M \qquad (9)$$

where M and MO are respectively the reduced and oxidized forms of the catalyst. The present results only identify the path from NO to N_2 through ammonia as an important mechanism in the reduction of NO. The identification of other paths and the estimation of their relative importance remains for future work.

Acknowledgment

Many of the techniques for catalyst preparation and testing were developed by R. M. Sinkevitch during the course of this work. His inventiveness and diligence in obtaining the results presented herein cannot be over-emphasized. The assistance of C. M. Nannini in obtaining the surface area measurements is also gratefully acknowledged.

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Contamination of Soil and Vegetation Near a Zinc Smelter by Zinc, Cadmium, Copper, and Lead

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■ Metal oxide fumes escaping from two zinc smelters in Palmerton, Pa., have highly contaminated soil and vegetation with zinc, cadmium, copper, and lead. Within 1 km of the smelters, 135,000 parts per million (ppm) zinc, 1750 ppm cadmium, 2000 ppm copper, and 2000 ppm lead have been measured in the O_2 horizon. Approximately 90% of metals deposited on the soil surface have been retained in the top 15 cm of the soil profile. Depauperate trees within 2 km of the smelters contained up to 4500 ppm zinc and 70 ppm cadmium by weight in washed, oven-dried foliage. Metal aerosols may enter the leaves directly, presumably through open stomates.

Contamination of soil and vegetation owing primarily to airborne heavy metals occurs in urban areas (Purves and Mackenzie, 1969), along highways (Motto et al., 1970; Daines et al., 1970; Lagerwerff and Specht, 1970; Hutchinson, 1971), and near smelters and foundries (Toumey, 1921; Lundegardh, 1927; Greszta and Godzik, 1969; Costescu and Hutchinson, 1971). Soil contamination by zinc, lead, and copper aerosols has been recognized for decades, but cadmium was overlooked until recently. The first published study reporting soil contamination due to airborne cadmium is probably that of Greszta and Godzik (1969), who found high concentrations of cadmium, zinc, and lead in soil near a zinc smelter in Poland. Subsequently Lagerwerff and Specht (1970) and Hutchinson (1971) found cadmium contamination in roadside soil. Elevated cadmium levels near a battery smelter in British Columbia have also been reported (John et al., 1972).

Study Area

Palmerton is situated on the Lehigh River, just north of the Lehigh Water Gap, in Carbon County, Pa. The town is in a narrow valley, bounded on the south by Blue Mountain and on the north by Stony Ridge. The soils are Dekalb and Laidig series stony loams derived from shale, sandstone, and conglomerate (Fisher et al., 1962). These soils are normally very acid, ranging from pH 4.0 to 5.0. The slopes of Blue Mountain at Lehigh Gap are sparsely vegetated or completely barren over an area of about 485 ha. *Sassafras albidum, Nyssa sylvatica,* and *Arenaria patula* are common species in the severely denuded areas.

Smelter History

The New Jersey Zinc Co. currently operates two zinc smelters in Palmerton, referred to as the east and west plants, respectively. There are no mines in the area; all ores are brought in by railroad. The primary ores smelted today are concentrated zinc sulfide ores containing approximately 55% zinc, 31% sulfur, 0.15% cadmium, 0.30% lead, and 0.40% copper. The metal oxide fumes driven off during roasting and processing are recovered by baghouses and electrostatic precipitators of up to 99% efficiency. Approximately 96% of the sulfur dioxide in the roaster off-gases is recovered as sulfuric acid. Based on a tentative emissions inventory, daily metal emissions since 1960 have probably ranged from 6000 to 9000 kg of zinc and 70–90 kg of cadmium. Emissions of both copper and lead are probably less than 90 kg/day. The east plant is the source of approximately 60% of the zinc oxide and at least 70% of the cadmium oxide fumes which escape into the atmosphere.

Methods

Samples of the lower portion of the O_2 (decomposed leaf litter) horizon were collected at various distances from the smelters along Blue Mountain ridge. Near the smelters where the O_2 horizon had been removed by erosion, upper A_1 horizon soil was collected instead. In addition, a soil pit 1 × 1 meter square and approximately 1 meter deep was excavated at each of five sites on Blue Mountain. The sites ranged from 1 to 40 km east of Lehigh Gap. Soil samples were collected at various depths in each pit. All samples were allowed to air dry and then were forced through a 2-mm stainless steel screen. Approximately 10-gram subsamples of mineral soils were ground to less than 200 mesh in a tungsten carbide–lined ball mill.

Foliage samples were collected from tree, shrub, and herb species. Leaves intermediate in position on the twigs were picked. For trees, usually only the lower branches could be reached. The entire plant of the herb *Aralia nudicaulis* was collected at each site. The leaves were washed by hand, using a sponge, in an ivory soap solution and rinsed four times with distilled water. The samples were dried in a forced air oven at 70°C and ground in a stainless steel–lined Wiley Mill.

Plant tissue and organic horizon samples were digested with a 4:1 mixture of concentrated nitric and perchloric acids. Mineral soil samples were boiled for 2 hr in perchloric acid. The resulting solutions were diluted to volume with distilled water, and the heavy metal contents determined by atomic absorption spectrophotometry. A Perkin-Elmer Model 303 atomic absorption spectrophotometer, a one-slot burner, and an acetylene–air gas mixture were used.

Transplant experiments were initiated in March 1969. Organic matter and soil were removed from the O_2 and A_3 horizons, respectively, on top of Blue Mountain at sites 2 km and 40 km from the east plant smelter. Soil collected at 2 km will be referred to as "near" and soil collected at 40 km as "distant." Blue Mountain ridge topsoils are in the Dekalb series, and do not vary appreciably in physical and chemical properties.

Five sites on Blue Mountain at various distances from the smelter were selected. At each site two holes about 20 cm deep and 25 cm in diam were dug, lined with vinyl sheeting, and filled first with 15 cm of A_3 soil, then 5 cm of O_2 horizon organic matter. One hole was filled with "near" and one with "distant" soil. At each site, four *Quercus rubra* L. (red oak) seedlings were planted in both soil types. In September 1970, after two growing seasons, surviving seedlings were harvested, washed and analyzed for heavy metal content. Additional seedlings were similarly planted in "near" and "distant" soil in clay pots kept outdoors in the courtyard of the Rutgers University greenhouse, in New Brunswick, N.J.

All statistical analyses were performed using prepared programs run on an IBM 360 computer.

Results and Discussion

Soil. The data have been transformed to the logarithmic scale, which linearizes the relationship between metal content and distance from the smelter. This transformation also normalizes the data, for in the original scale the standard deviations were directly proportional to sample means. The sample means were analyzed by broken line regression. This technique fits a straight line to that portion of the data exhibiting a significant linear relationship between metal content and distance, and determines the break point (intersection of the sloping and horizontal lines) beyond which this relationship ceases (Figure 1). The break points represent the theoretical limits of soil contamination due to smelter emissions. Beyond these points, observed metal contents represent normal, or background levels, as listed in Table I. The distance in kilometers at which background levels are reached are given below:

	Zn	Cd	Cu	Pb
East	25	21	19	39
West	16	16	12	16

The east plant smelter was used as the zero point in regression analysis, since it is the major emissions source. The west plant is located 4 km west of the east plant. In all cases, background levels are reached nearer the smelters to the west (upwind) than to the east (downwind). Zinc oxide particles in smelter fumes range from 0.01 to 0.3 μ in diam (Corn, 1968). Particles this small are removed from the atmosphere very slowly, and may be carried many kilometers before settling out.

The data represented in Figure 1 include analyses of only ridge top Dekalb soils. The highest metal levels occur in Laidig stony loams, at the base of the north slope of Blue Mountain, within 1 km of the east plant. In this area the upper A_1 horizon contains 50,000–80,000 ppm zinc, 900–1500 ppm cadmium, 600–1200 ppm copper, and 200–1100 ppm lead. The metal content is variable due at least in part to severe erosion of the exposed A_1 soil. The very highest levels were found in isolated patches of O_2 horizon material, composed of partly broken down *S. albidum* and *A. patula* litter. One sample contained 135,000 ppm zinc, 1750 ppm cadmium, 2000 ppm copper, and 200 ppm lead. These values are comparable to concentrations in zinc ores mined commercially. Such highly contaminated material may have received some direct deposition of

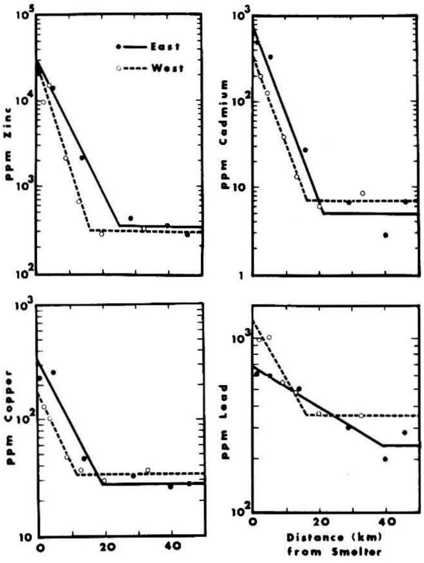

Figure 1. Zinc, cadmium, copper, and lead content of the O_2 horizon as a function of distance from the east plant zinc smelter

All samples were collected along the top of Blue Mountain ridge, from Dekalb stony loam soils. A total of 26 samples were collected to the east and 25 samples to the west of the smelter. Each data point represents a mean of between two and eight samples. Equations for the lines for data to the east are: $\log Zn = 4.45 - 0.076 D$, $\log Cd = 2.89 - 0.104 D$, $\log Cu = 2.54 - 0.058 D$, $\log Pb = 2.83 - 0.011 D$. Those to the west are: $\log Zn = 4.42 - 0.121 D$, $\log Cd = 2.50 - 0.104 D$, $\log Cu = 2.24 - 0.060 D$, $\log Pb = 3.10 - 0.034 D$, where D = distance in kilometers

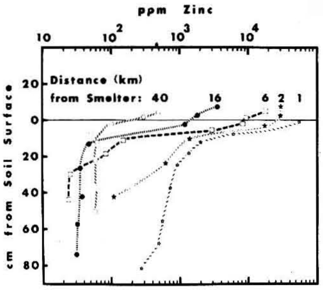

Figure 2. Soil zinc content as a function of depth and distance from the east plant zinc smelter

The site 1 km distant was at the base of the north slope of Blue Mountain; all other sites were on the ridge top. The top four data points on each curve (with the exception noted below), from the uppermost point downward, represent samples from the O_1 (fresh leaf litter), O_2 (partially decomposed leaf litter), A_1 (humus), and A_3 (mineral soil) horizons, respectively. Remaining data points represent samples from the B horizon (mineral soil). The O_1 and O_2 horizons are missing at the 1-km site, due to removal by erosion. The 0-cm line marks the boundary between the O_2 and A_1 horizons

Table I. Background Level Zinc, Cadmium, Copper, and Lead Content of the O_2 Horizon

		Zn	Cd	Cu	Pb
$\bar{x}$, ppm	East	346	5.05	27.5	240
	West	311	7.00	32.8	355
95% C.I.[a]		±104	±1.41	±4.50	±49.6
d.f.		8	7	9	3
N		13	11	14	6

[a] The confidence intervals are based on arithmetically pooled variances for all background level samples, both east and west of the smelter. Variances of background level samples were homogenous.

windborne dust from exposed piles of ore concentrates. Metal oxide fumes from smelting are still a major source of contamination, however. Most metal emissions occur within 30 meters of the ground surface (Ord, 1972), and Blue Mountain is immediately adjacent to the east plant in the prevailing downwind direction. Thus any metal emissions "shadow area" is probably minimal.

Zinc deposition rates in Palmerton in 1969, based on dustfall data gathered by the Pennsylvania Department of Health, varied between 1.75 and 5.25 g/m^2/month, or 187-561 lb/acre/year. Assuming the relationship between deposition rate and emission rate for cadmium to be the same as that for zinc, cadmium deposition should have been about 3.0 lb/acre/year. Even assuming lower deposition rates in the past, these rates of metal deposition would be sufficient to account for the estimated 12,000 lb/acre of zinc and 160 lb/acre of cadmium present today in the solum near the east plant smelter.

The concentration of all metals decreases sharply with depth in the soil. Data for zinc are plotted in Figure 2. About 85-95% of the estimated total zinc, and 95% of the estimated total cadmium in the soil profile are in the top 15 cm in the highly contaminated areas. Brown et al. (1963) have also reported very little downward movement of zinc oxide applied to a soil surface. They postulate that this immobility is due to the insolubility of zinc oxide in water, and to the high fixation of zinc added to soil.

In the vicinity of smelters emitting large amounts of sulfur compounds, soil acidity is commonly increased. This is not the case at Lehigh Gap. The pH of the A soil horizons at Lehigh Gap varies from about 4.5 to 6.0, which tends to be higher than the normal range for Dekalb soils of 3.8-5.0. If this pH increase at Lehigh Gap is real, it might be due to the deposition of zinc oxide, an amphoteric compound (Lott, 1938; Buchauer, 1971).

The ratio of zinc to cadmium in the soil has been affected near the smelters. In Laidig stony loams along the base of the north slope of Blue Mountain 10 km or more from Lehigh Gap, the mean Zn/Cd concentration ratio in the O_2 horizon varies from about 60 to 90. Near the east plant smelter, the ratio has been depressed to a mean of 40-50. Near the west plant smelter the ratio has been elevated to a mean of 115-142. The probability that these differences are due to chance alone is less than 2.5%, as revealed by analysis of variance. These differences in the Zn/Cd concentration ratio are to be expected, since the east plant is the primary source of emitted cadium.

Vegetation. Transformation to a log-log scale best linearized and normalized the data. In the original scale the standard deviations were directly proportional to sample means. Linear regression analysis of the transformed data reveals for every species a significant ($P < 0.05$) negative linear correlation between the logarithm of foliar zinc content and the logarithm of distance from the east plant smelter. This decline in metal content with increasing distance is readily apparent in Figure 3. A statistically significant linear correlation between cadmium or lead content and distance exists only for the six tree species (Figure 3, graphs A and B) and also for *A. nudicaulis* for cadmium only. A significant correlation between copper content and distance exists only for *Q. rubra, N. sylvatica, S. albidum,* and *K. latifolia.*

Table II. Metal Content of *Q. rubra* Seedlings Planted in Distant Soil as a Function of Distance from the East Plant Zinc Smelter[a]

Distance, km	No. of seedlings	Zn, ppm	Cd, ppm	Cu, ppm	Pb, ppm
		Foliage			
1[b]	4	2120	38	33	100
1	4	500	10	8.0	62
5	4	195	3.0	N.D.[c]	11
14	2	165	1.5	N.D.	11
40	3	155	N.D.	16	11
		Stems			
1[b]	4	1560	25	42	35
1	4	575	10	7.5	25
5	4	120	2.0	5.0	N.D.
14	2	437	2.0	5.0	N.D.
40	3	262	5.0	5.0	N.D.
		Taproot[d]			
1[b]	4	90.0	N.D.	5.0	N.D.
1	4	40.0	N.D.	18	N.D.
5	4	12.5	N.D.	5.0	N.D.
14	2	27.5	N.D.	28	N.D.
40	3	37.5	N.D.	28	N.D.

[a] Values are one analysis of one composite sample.

[b] At the base of the lower north slope of Blue Mountain; all other sites were on top of the mountain.

[c] Not detectable; for copper less than 5 ppm, for cadmium less than 1 ppm, and for lead less than 10 ppm.

[d] Vascular cylinder; bark removed prior to analysis.

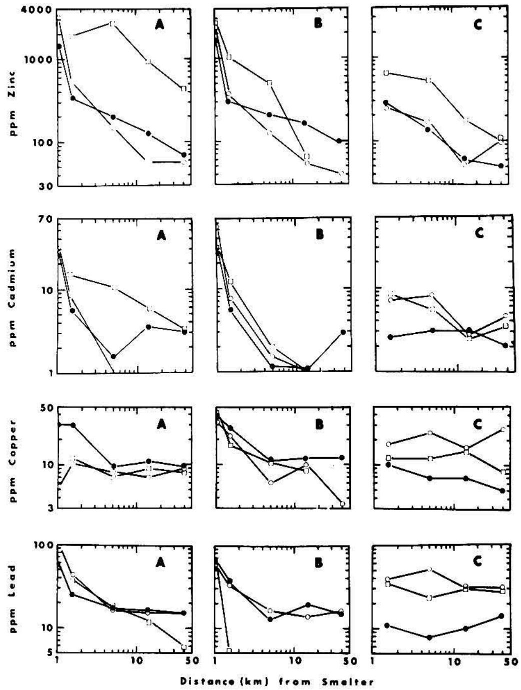

Figure 3. Mean zinc, cadmium, copper, and lead content of foliage as a function of distance from the east plant zinc smelter

Each point represents a mean of two plants per site, collected September 1, 1970. The site 1 km distant was at the base of the north slope of Blue Mountain; all other sites were on the ridge top. The detectable limit for cadmium is 1 ppm and for lead is 5 ppm. Key to species: Graphs A: ○ *Quercus prinus;* ● *Quercus rubra;* □ *Betula lenta* (trees). Graphs B: ○ *Nyssa sylvatica;* ● *Acer rubrum;* □ *Sassafras albidum* (trees). Graphs C: ○ *Vaccinium vacillans;* ● *Kalmia latifolia* (shrubs); □ *Aralia nudicaulis* (herb).

The foliar zinc content of most species appears to be near background levels in samples collected 14 km from the east plant smelter. For those species in which elevated levels of cadmium, copper, and lead were detected, foliar background levels appear to be reached between 1 and 5 km.

The vegetation of the Lehigh Gap area is scrubby and generally depauperate in appearance. The foliage develops an interveinal chlorosis by mid June, and by July the red and yellow foliage is suggestive of autumnal coloration. Marginal necrosis is also common, which may be due to acute sulfur dioxide injury. Occasional periods of higher than 0.4 ppm ambient sulfur dioxide have been recorded in Palmerton (McGrogan, 1971). Since significantly elevated foliar sulfur levels can be detected only within 1 or 2 km of the east plant, and only by the end of the growing season, it is highly unlikely that chronic sulfur dioxide injury accounts for the foliar chlorosis. In contrast, levels of zinc and cadmium in the foliage are far higher than the minimal levels of 200 ppm and 20 ppm, respectively, associated with toxicity and chlorosis in native tree species (Buchauer, 1971).

As much as 4500 ppm zinc and 70 ppm cadmium have been found in the foliage of trees near the east plant smelter. It seems unlikely that so much zinc and cadmium are in biologically available forms in the cytoplasm of the cells. Surface contamination cannot be ruled out. However, since the leaves were thoroughly washed prior to analysis, and unwashed leaves contained two to six times more metals than washed leaves, most of the metals in washed leaves presumably are physically inside the leaves. It is possible that metal particles may enter directly through the stomatal apertures, and be deposited within the leaves. Just such a mode of entry has been postulated by Motto et al. (1970) for ambient lead particles. Since most zinc, and presumably cadmium, oxide particles in smelter fumes are less than 1 μ in diam, and stomatal apertures commonly range from 5 to 30 μ, entry through the stomates seems likely.

Transplant experiment data are presented in Table II. All seedlings grown in "near" soil died after one growing season. Soil metal contents are listed below:

	Zinc, ppm		Cadmium, ppm	
Horizon	"near"	"distant"	"near"	"distant"
O_2	20,000	300	500	3
A_3	2,000	100	10	2

There is a steady increase in the metal content of oak seedling leaves and stems, but not roots, with decreasing distance from the east plant zinc smelter (Table II). The additional metals in seedlings near the smelter apparently entered the plant tops directly, from the air, rather than via root uptake. Surface contamination may account for a large proportion of the increased stem metal content near the smelter, since it was difficult to thoroughly wash the bark. The seedlings grown in "distant" soil exhibited no signs of toxicity, even at 2120 ppm foliar zinc and 38 ppm foliar cadmium. In contrast, foliage of severely stunted seedlings grown in pots of "near" soil at the greenhouse contained only 400–500 ppm zinc and 4–7 ppm cadmium. Apparently, ambient metal oxide particles entering foliage directly, perhaps through the stomates, largely remain biologically inert, whereas metals entering via root uptake can produce immediate and significant toxic effects. Thus, in situations where ambient foliar intake of metal oxide particles could occur, measurement of total foliar metal content may be inadequate to gauge the severity of plant toxicity.

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Heavy Metal Levels of Ottawa and Rideau River Sediments

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■ Sediment samples were collected at two-mile intervals along the Ottawa and Rideau Rivers near Ottawa, Canada, in July, 1971. The sediments were analyzed for lead, mercury, zinc, copper, nickel, cobalt, iron, manganese, and chromium using atomic absorption spectrophotometry. The surface areas of the samples were measured and taken into consideration when deciding whether or not metal levels were unusually high. Some anomalously high heavy metal concentrations found in the sediments in certain locations appeared to be related to pollution of the rivers by municipal and industrial waste water discharges and waste disposal practices.

In the aquatic environment, heavy metals are a serious pollution problem since they are toxic to fish (Doudoroff and Katz, 1953; Aronson, 1971), may be transported and concentrated in the food chain (Gavis and Ferguson, 1972; Tornabene and Edwards, 1972), and, when present at elevated levels in water supplies, can be a hazard to public health. Industrial and urban waste water discharges into rivers may increase the heavy metal concentration of the water and also lead to an accumulation of heavy metals in the sediments. The present article reports Hg, Pb, Zn, Cu, Ni, Co, Fe, Mn, and Cr levels in river sediments with a view to identifying sources of heavy metal discharge into the Ottawa and Rideau Rivers.

Experimental

The study area is shown in Figure 1. Surface sediment samples were collected with a Lane sediment sampler at two-mile intervals along the Ottawa River from Ottawa to Thurso and along the Rideau River from Smith Falls to Ottawa from July 19-24, 1971. Three samples were taken at each sampling station about 10 yards from each bank and in the center of the river.

A portion of the sediment sample was spread out on a petri dish and air-dried for four days. A representative part of each sample, obtained by coning and quartering, was finely ground. One gram was accurately weighed and digested in 60 ml of acid solution—4.0*M* HNO_3, 0.7*M* HCl—for 2 hr at 70-90°C. The efficiency of this partial extraction technique is quite variable depending on the nature of the sample. But the difference between the amount of metal obtained using a $HF-HNO_3-HClO_4$ total extraction and the above procedure was roughly constant for 20 representative samples collected throughout the study area. This indicates that the dilute HNO_3-HCl technique has little effect on the metals bound in the sediment minerals but removes only surface adsorbed or precipitated metals from the sample.

The acid extracts were analyzed for lead, mercury, zinc, copper, nickel, cobalt, iron, manganese, and chromium using a Perkin-Elmer Model 403 atomic absorption spectrophotometer. Conventional atomic absorption techniques are not sensitive enough to measure the concentration of mercury in the extract, so a flameless method was used for this metal (Hatch and Ott, 1968). The precision of the analyses is shown in Table I. A compilation of the complete analyses, sample classification, the locations of sampling sites, and more detailed experimental procedures, have been reported by Oliver and Kinrade (1972).

The porous nature of sediments leads to great discrepancies between measured surface areas and those calculated geometrically (Weiler and Mills, 1965). Therefore, the surface areas of the samples were measured by the

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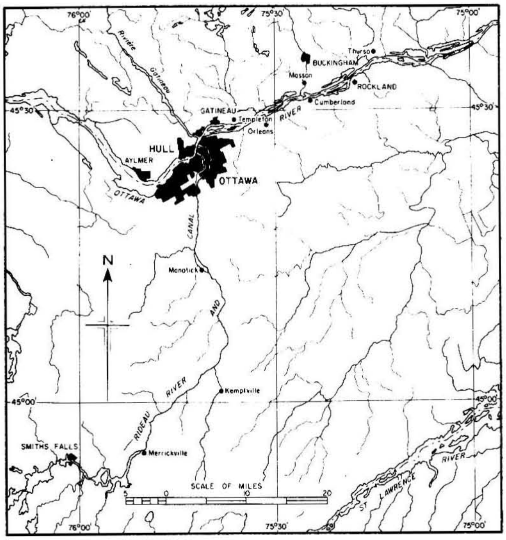

Figure 1. Study area

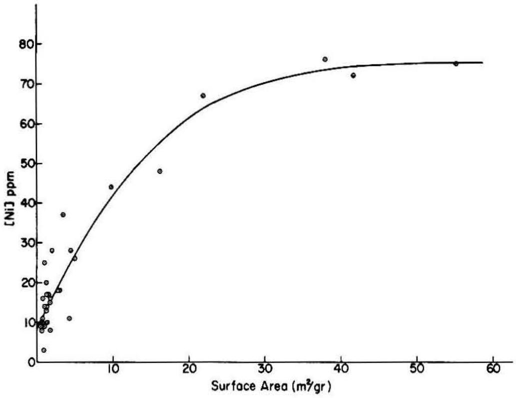

Figure 2. Plot of nickel concentration in ppm vs. surface area in m^2/g

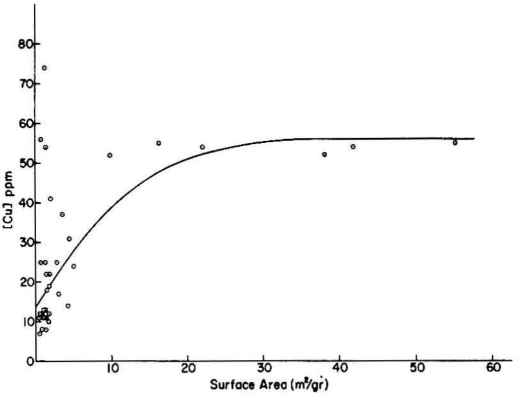

Figure 3. Plot of copper concentration vs. surface area in m^2/g

Table I. Mean Background Concentration of Adsorbed and Precipitated Heavy Metals in Ottawa River and Rideau River Sediments

Heavy metal	Mean background concn in sediments, ppm		Precision at mean concn, %
	Ottawa River	Rideau River	
Pb	26	42	20
Hg	0.28	0.20	3
Zn	84	86	1
Cu	28	24	4
Ni	22	23	5
Co	11	13	10
Fe	9200	12,700	2
Mn	118	241	1
Cr	22	21	5

one-point BET method using a Perkin-Elmer Shell Model 212 D Sorptometer (Nelsen and Eggertsen, 1958). The sediment sample was degassed at 150°C for 24 hr. Then the volume of nitrogen adsorbed by the sample at −195°C was measured and, with the dimensions of the nitrogen molecule in the monomolecular film known, the surface area was calculated. The precision of the method is about ±5%.

Results and Discussion

The use of river sediment heavy metal levels in geochemical exploration for mineral deposits is now widespread (Hawkes and Webb, 1962; Rose et al., 1970). In the study area, the mineralogy is approximately constant and there are no known mineral deposits of any consequence (Wilson, 1964). Therefore, it should be possible to detect heavy metal discharges into the rivers in the Ottawa area by measuring the loosely bound heavy metal concentration of the sediments. Also, since sediments constitute a more permanent record of dumping into the river, sediment analysis may be preferrable to periodic water analysis which may miss peak discharges. To detect discharges it is necessary to be able to distinguish between an unusually high or anomalous reading and the background noise. The usual geochemical criteria is to take the mean plus 2 std dev to establish a threshold value. Any reading above this threshold value is termed anomalous. The mean background concentrations of the heavy metals in the river sediments are shown in Table I. The markedly high erratic values more than five times the mean are excluded from the calculation of the average. A statistical analysis of the data is probably not justified in this case because of the relatively small number of samples (48 and 68 for the Ottawa and Rideau Rivers, respectively). Therefore, as a first approximation the anomalous samples were qualitatively differentiated by plotting metal concentration vs. sample location and simply picking out the samples which were unusually high. This method did not prove to be entirely satisfactory because of the widely varying texture of the samples.

Initially the sediment samples were classified into particle size groups as follows: clay <0.004 mm; silt 0.004–0.062 mm; fine 0.062–0.5 mm; medium 0.5–2.0 mm; coarse >2.0 mm. The finer sediment samples generally contained more heavy metal than the coarser samples. For example, the average metal concentration in ppm of the silt samples was: Pb, 33; Hg, 0.22; Zn, 88; Cu, 25; Ni, 29; Co, 15; Fe, 17,440; Mn, 189; Cr, 27, whereas the average metal concentration in ppm of the medium-sized samples was: Pb, 5; Hg, 0.15; Zn, 24; Cu, 9; Ni, 10; Co, 6; Fe, 4300; Mn, 63; Cr, 9. The difference is so pronounced that it seems imperative to take the particle size of the sample

Table II. Statistical Correlation Between Surface Area and Metal Concentration

Metal	r^a for Ottawa River sediments	r^a for Rideau River sediments
Pb	0.41	0.40
Hg	0.00	0.00
Zn	0.59	0.66
Cu	0.70	0.37
Ni	0.91	0.68
Co	0.89	0.70
Fe	0.84	0.77
Mn	0.93	0.64
Cr	0.90	0.72

[a] Correlation coefficient = $r = \dfrac{\Sigma XY - \dfrac{\Sigma X \Sigma Y}{N}}{\left\{\left[\Sigma X^2 - \dfrac{(\Sigma X)^2}{N}\right]\left[\Sigma Y^2 - \dfrac{(\Sigma Y)^2}{N}\right]\right\}^{1/2}}$

into consideration when determining whether or not a sample is anomalous.

One way to approach the problem is to separate the sediment into specific size fractions. A background level for each fraction of the sediment could be established and the unusual samples could be distinguished. Since the main reason for the higher metal content in the finer samples is their larger surface area and, therefore, their higher adsorption capacity, perhaps, if some correction could be made for the changing surface area it wouldn't be necessary to fractionate the samples.

The surface areas of the sediment samples were measured by the BET method and found to vary from 0.33 to 55.2 m^2/g in the Ottawa River and from 0.40 to 19.7 m^2/g in the Rideau River. The metal concentration of the sediments is definitely related to surface area as illustrated by the correlation coefficients presented in Table II. There is a statistically significant correlation between surface area and metal content for all the elements except mercury. Cranston and Buckley (1972) observed that mercury levels were higher in the finer river sediment fractions, so it is somewhat surprising that no correlation between surface area and mercury concentration was found in this study. But it should be pointed out that the actual magnitude of the concentration increase observed by Cranston and Buckley (1972) is much smaller than the concentration change observed for the other heavy metals in this study.

Plots of nickel and copper concentration vs. surface area are shown in Figures 2 and 3, respectively. The overall shape of these typical curves is roughly the same for all the metals except mercury, but the actual contour of the curves varies from metal to metal. It is now possible to make allowances for varying surface areas of the samples. Readings which are considerably above the concentration vs. surface area curve are termed anomalous. In effect there is no longer a single mean or threshold value but one which continuously varies with surface area. Samples 4-3, 8-3, 12-1, and 14-3, which are well above the normal range in nickel concentration, are clays with high surface areas (55.2, 22.0, 41.8, and 38.0 m^2/g, respectively). These samples are close to the nickel concentration–surface area curve (Figure 2), and thus it appears that these high nickel levels are a result of surface adsorption. No unusually large discharge of nickel into the river in these locations is indicated.

Now that a method has been established for distinguishing unusually high metal concentrations in the sediments, the reason for these readings can be investigated. The sediments collected near three paper mills on the Ottawa River at Hull, Gatineau, and Masson had mercury concentrations of 1.89, 1.99, and 2.64 ppm, respectively, well in excess of the background level 0.28 ppm. Samples collected about a mile downstream from the paper mills contained somewhat less mercury 0.74, 0.85, and 0.72, respectively. Methoxyethylmercuric acetate formerly was used in significant quantities by the pulp and paper industry as a slimicide to inhibit the growth of fungus during the manufacture of pulp and paper (Bangay, 1971), but the use of mercury by the industry was discontinued in the spring of 1971. The persistence of mercury in the sediments at such high concentrations indicates that its half-life must be fairly long. Continued sampling of sediments in the vicinity of the pulp and paper plants would be useful in assessing the long-term effects of mercury on the environment.

A sediment sample, taken close to a sewage plant contained several heavy metals in the following concentrations in ppm: Pb, 390; Hg, 232; Zn, 846; Cu, 236; Ni, 71; Co, 128. The source of these metals may well be industrial, with industries using the municipal sewage system to dispose of their waste water. However, another source could be commercial household products such as chlorine bleaches which contain up to 0.2 ppm mercury (Jonasson, 1970).

At a sampling site on the Rideau River in Ottawa the lead concentrations were 336 and 1344 ppm and just downstream the lead concentration was 180 ppm. The city of Ottawa formerly used this location as a river snow dump. Therefore, it would seem that the high concentration of lead in the sediments is a direct result of dumping snow, containing lead from automobile exhausts, into the river. High lead values at locations in Smith Falls are also probably due to river snow dumping. Also Zn and Fe levels are unusually high in these sampling locations probably for the same reason. This practice was discontinued in the province of Ontario in late 1971 when the Ontario Water Resources Commission requested a 100-ft buffer zone between snow dumps and water courses.

The reason for other high anomalous readings is not as clear and, therefore, further study is warranted in the locations where they were collected.

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Treatment of Effluent from Manufacture of Chlorinated Pesticides with a Synthetic, Polymeric Adsorbent, Amberlite XAD-4

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■ A new process is described for treating chlorinated pesticide waste effluents. Pesticides are adsorbed on Amberlite XAD-4, a newly developed synthetic, polymeric adsorbent possessing high porosity (50 vol %), high surface area (850 m^2/g) and an inert, hydrophobic surface. The adsorbent is regenerated with an organic solvent, and the adsorbed pesticides are recovered in a concentrated form. Laboratory studies are reported in which XAD-4 and a commercial, granular activated carbon were compared for treating the effluent from a pesticide manufacturing operation. The leakage of unadsorbed pesticides from the XAD-4 column was significantly lower than that from the activated carbon column. The adsorbed pesticides were efficiently desorbed from XAD-4 by eluting with isopropanol. The activated carbon could not be regenerated effectively with isopropanol. An estimate of capital and operating expenses for a full-scale facility is presented. This projection indicates that pesticides waste treatment via XAD-4 and chemical regeneration will be more economical than granular activated carbon employing external thermal regeneration.

Amberlite (trademark of Rohm and Haas Co.) XAD-4 is a synthetic, polymeric adsorbent. It is characterized by an inert—i.e., not activated—hydrophobic surface and by high porosity and surface area. As a consequence, XAD-4 is capable of efficiently adsorbing large quantities of hydrophobic, organic species from water. Furthermore, the adsorption process is reversible so that XAD-4, unlike most other adsorbents, can be easily regenerated chemically. This report considers the specific application of the treatment of industrial waste streams which contain chlorinated pesticides. Presented are the results of laboratory experiments which were performed with pesticides waste effluents from a pesticide manufacturing facility. Based on these studies a waste treatment process utilizing XAD-4 adsorbent has been developed and is now being used to treat the effluent at this pesticide manufacturer's facility.

Background

Some pertinent physical properties of Amberlite XAD-4 are: composition, crosslinked polystyrene copolymer; form, 20–50 mesh beads; bead porosity, 51 vol %; surface area, 750 m^2/g; average pore diam, 50 Å. These characteristics provide XAD-4 with adsorption properties which offer certain advantages over conventional adsorbent such as activated carbon. In the form of hard, resilient, polymeric beads, XAD-4 is highly attrition resistant. The chemically inert surface permits a reversible adsorption mechanism which allows efficient chemical regeneration. The high porosity, high surface area, and uniform pore distribution favor rapid adsorption kinetics and hence high operating capacity and low leakage.

A large amount of laboratory data has been generated using model compounds of the type often encountered in industrial waste treatment problems. Typical is the work performed with phenol and chlorophenols (Paleos, 1969). As seen in Table I, under practical operating conditions, large quantities of these materials can be adsorbed on a column of XAD-4 adsorbent with no detectable leakage. Note that the capacity of Amberlite XAD-4 is greatest for the most hydrophobic species as indicated by decreasing solute solubility in water. Pesticides, in general, are extremely hydrophobic. This suggests that XAD-4 should be effective for removing these materials from aqueous systems. The data available in the literature support this hypothesis. The adsorption of two pesticides—Parathion and Sevin—on Amberlite XAD-2 adsorbent has been reported

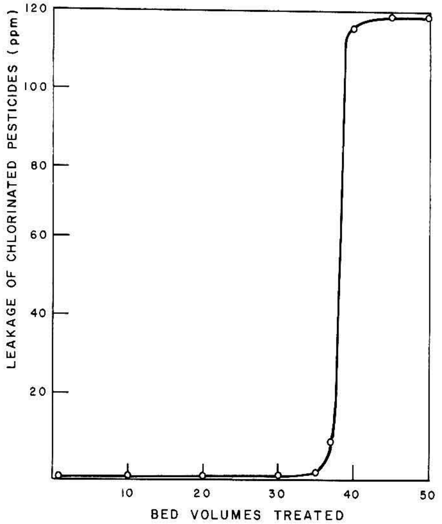

Figure 1. Treatment of a waste effluent from the manufacture of chlorinated pesticides with Amberlite XAD-4

Table I. Column Operating Capacity of Amberlite XAD-4 for Some Model Compounds

Flow rate: 0.5 gpm/ft^3
Leakage level: <0.1 ppm
Temp: 25°C

Compound	Max. solubility in water, ppm	Influent concn, ppm	Capacity of XAD-4, lb/ft^3
Phenol	82,000	250	0.78
2-Chlorophenol	26,000	350	2.40
2,4-Dichlorophenol	4,500	430	5.09
2,4,6-Trichlorophenol	900	510	12.0

(Leenheer, 1970). XAD-2 is chemically nearly identical to XAD-4, differing mainly in its lower surface area and, hence, lower capacity for adsorption of organic solutes. These pesticides are both strongly adsorbed, even from very dilute solution. The data indicate that a high degree of loading of these pesticides could be attained in a waste treatment application. The adsorption of traces of pesticides from seawater onto Amberlite XAD-2 has also been studied (Harvey, 1972). It was found that aldrin, dieldrin, DDT, DDE, and DDD were all very strongly adsorbed on the resin and tend to displace even the most strongly sorbed natural constituents of seawater. In the present study, we report on the use of XAD-4 adsorbent to remove chlorinated pesticides from actual manufacturing waste effluents.

Experimental Methods

Amberlite XAD-4 was evaluated in comparison with a granular activated carbon widely used in waste treatment applications. The surface areas of Amberlite XAD-4 and the carbon, as determined from their nitrogen adsorption isotherms, are 750 and 921 m^2/g, respectively. The porosities of the adsorbents, as determined by helium densitometry, are 51 vol % for XAD-4 and 67 vol % for the carbon which yield calculated average pore diameters of 50 and 40 Å, respectively.

The effluents treated were obtained from a manufacturer of chlorinated pesticides and contained a variety of chlorinated pesticides and precursors. Samples were analyzed, except as noted, by a technique involving a liquid-liquid extraction concentration step followed by gas-liquid chromatography employing an electron-capture detector. The chromatograph monitored 10 separate compounds in the effluent at levels down to 0.05 ppm. Effluent pesticide content was characterized by total chlorinated pesticide, which is the sum of the concentrations of the 10 individual compounds expressed as ppm of 4,4′-dichlorobenzophenone.

Laboratory adsorption experiments were performed in 1.77-cm i.d. glass columns. A coarse glass frit in the bottom of the column was used to retain the adsorbent bed. Forty milliliters of adsorbent (ca. 32-cm bed depth) was used in each experiment. Solutions were pumped through the column with a Hach variable flow piston pump. Column effluent samples were collected periodically and analyzed for total chlorinated pesticides.

Flow rates are expressed throughout as gpm/ft^3 (gal./min/ft^3 of adsorbent bed. A flow rate of 1.0 gpm/ft^3 is equivalent to 8.0 bed volumes/hr.

Results and Discussion

The first laboratory experiments were performed with an acidic, filtered plant waste effluent from the manufacture of a chlorinated pesticide. A column of Amberlite XAD-4 adsorbent was used at a flow rate of 0.5 gpm/ft^3 to treat 50 bed volumes of waste effluent which contained 118 ppm of chlorinated pesticides. The leakage of pesticide from the column was monitored using a total carbon analyzer. The results of this experiment are presented in Figure 1. Less than 1 ppm of pesticide leakage occurs until just before saturation capacity is reached. This is indicative of very efficient adsorbent utilization.

The next effluent to be examined was one arising from the manufacture of another chlorinated pesticide. This highly acidic, filtered waste was also treated very effectively with XAD-4 adsorbent. In Figure 2 are presented leakage curves comparing XAD-4 and the granular, activated carbon run under identical conditions using the same influent. It is apparent that XAD-4 is superior to the activated carbon both in terms of pesticide leakage and in overall operating capacity. At no time does the leakage of pesticides from the XAD-4 column exceed 0.25 ppm. In a number of cases, the leakage was below the employed analytical detection limit of 0.05 ppm.

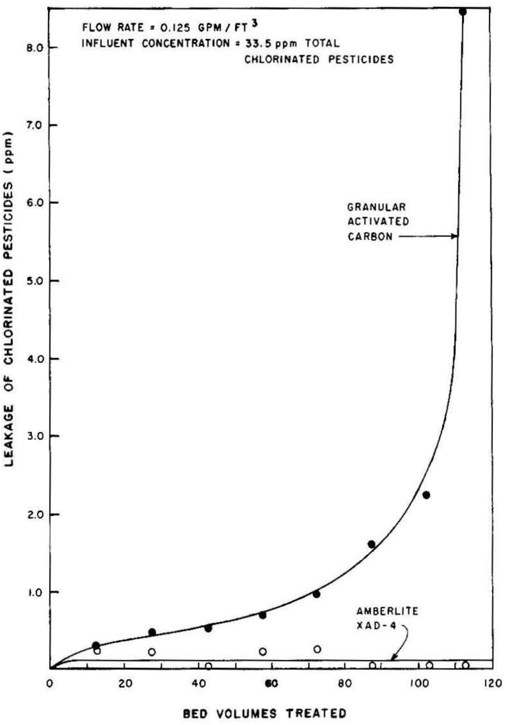

Figure 2. Adsorption of chlorinated pesticides with Amberlite XAD-4 and a granular activated carbon

Table II. Regeneration of an Amberlite XAD-4 Column Loaded With Chlorinated Pesticides

Column loading: 150 Bed volumes of waste containing 33.7 ppm total chlorinated pesticides
Regeneration flow rate: 0.250 gpm/ft^3

Regenerant	Concn of total chlorinated pesticides in column regenerant, ppm	% Regenerated
3 Bed volumes isopropanol	131.4	15
3 Bed volumes acetone	730.8	85
Total % Regeneration	. . .	101

Another XAD-4 column was loaded with 150 bed volumes of effluent (far short of saturation) to determine the efficiency of chemical regeneration. Two organic solvents, acetone and isopropanol, were examined, sequentially, as regenerants. The results of this experiment are presented in Table II. Overall regeneration of XAD-4 adsorbent is essentially quantitative. Of the two solvents, acetone is the more effective regenerant. However, the high flammability of acetone precludes its use in the manufacturer's plant without equipment modification. Therefore, isopropanol and methanol were selected for further laboratory evaluation, recognizing that in practice a somewhat larger volume of regenerant would be required.

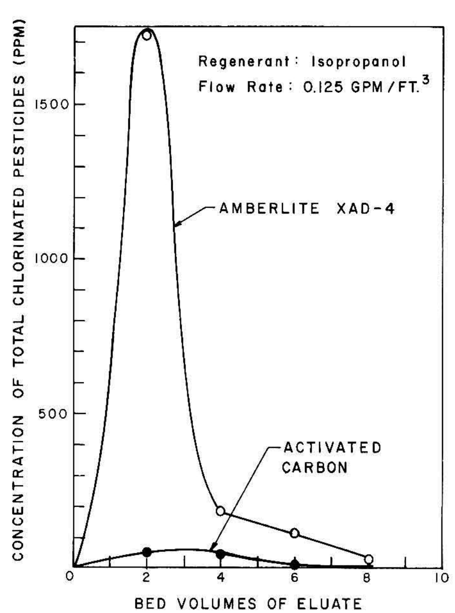

Figure 3. Regeneration of Amberlite XAD-4 and a granular activated carbon with isopropanol

Table III. Comparative Regeneration of Chlorinated Pesticides From Amberlite XAD-4 and Activated Carbon With Isopropanol and Methanol

Loading: 100 Bed volumes of neutralized, filtered effluent, pH 9.0, 3.20 ppm total chlorinated pesticides, 0.125 gpm/ft^3

Regeneration: 10 Bed volumes of solvent at 0.125 gpm/ft^3

	Adsorbent	
	XAD-4	Activated carbon
% Regeneration with menthanol		
After 5 bed volumes	18	6
After 10 bed volumes	51	13
% Regeneration with isopropanol		
After 5 bed volumes	79	50
After 10 bed volumes	93	67

Table IV. Comparative Loading of Chlorinated Pesticides Onto Amberlite XAD-4 and Activated Carbon

Influent: 35.3 ppm total chlorinated pesticides
Flow rate: 0.25 gpm/ft^3
pH: 1.0

	Leakage of chlorinated pesticides, ppm	
Bed volumes treated	XAD-4	Activated carbon
12	0.20	1.95
24	0.25	3.10
36	1.25	12.0[a]
48	1.00	3.15
60	1.15	5.15
72	2.30	. . .
84	2.50	. . .
Total loading	58.0 mg	38.0 mg

[a] This value suspected of being an artifact. (A comparative regeneration of these columns is presented in Figure 3.)

Additional regeneration experiments were carried out to compare the regeneration efficiencies of XAD-4 adsorbent and the activated carbon. In the first experiment the relative regeneration efficiencies of methanol and isopropanol were also determined. The influent used was similar to that of the previous experiment except that it had been neutralized with sodium carbonate prior to filtering. This was done to simulate existing plant capabilities where the lack of an acid-resistant filter press temporarily necessitated the use of a neutralized influent. The results are presented in Table III.

Two observations can be drawn from the data in Table III. First, isopropanol is a more effective regenerant than methanol. A fairly high degree of regeneration efficiency can be attained for XAD-4 with only 5 bed volumes of this regenerant. Second, XAD-4 is confirmed to be superior to granular activated carbon in regeneration efficiency. However, owing to the low influent concentration used (and, hence, the low degree of loading) it was felt the results obtained were conservative. Therefore, a loading/regeneration experiment was performed using a much more highly concentrated influent.

In the next experiment, an acidic waste effluent was used to load columns of XAD-4 adsorbent and the activated carbon. Each column was regenerated with isopropanol. The results are seen in Table IV and Figure 3. The leakage of pesticide from the XAD-4 column during loading (Table IV) is again much lower than that of activated carbon, but not as spectacularly low as in the experiment shown in Figure 1. The regeneration of XAD-4 with isopropanol (Figure 3) is seen to be highly efficient. The great majority of adsorbed pesticide is removed with only 2 bed volumes of regenerant. By comparison, the activated carbon is very poorly regenerated even with 8 bed volumes of isopropanol.

Economic Considerations

There are indications that the cost of pesticide waste treatment will be less for an Amberlite XAD-4 adsorbent system than for a granular activated carbon system. This arises, despite the higher unit cost of XAD-4, from two principal sources:

Rapid Adsorption Kinetics. In every case so far examined in our laboratories, XAD-4 has demonstrated superior adsorption kinetics to granular activated carbons. In the present study this is manifested in the lower leakage rates of XAD-4 at constant flow rate (Figure 1 and Table IV). Conversely, for an equivalent leakage level, it is possible to operate XAD-4 at a considerably higher flow rate. A higher flow rate (treating the same volume of effluent) means that a correspondingly lower volume of adsorbent is required. In addition to reducing installed adsorbent costs, a further capital savings is realized in the correspondingly smaller adsorption equipment required.

Efficient Chemical Regeneration. The efficient chemical regeneration characteristics of XAD-4 adsorbent demonstrated in the present study are characteristic of this material. This regeneration efficiency represents a considerable advantage over granular activated carbon in small installations since disposal of waste regenerant from XAD-4 should be less costly than rebedding with fresh carbon. In larger installations, where thermal regeneration of activated carbon becomes practical, chemical regeneration should still retain its advantages. Thermal regeneration involves a considerable capital expense for the furnace and associated equipment. Furthermore, as much as 10% of the activated carbon is lost during regeneration which results in a significant operating expense. In such a

Table V. Treatment of a Waste Stream Arising From the Manufacture of a Chlorinated Pesticide

Influent: 200 ppm total chlorinated pesticides, pH 1.0, 150,000 gpd, run to 1 ppm leakage

Summary of Expenses:

	Granular activated carbon	Amberlite XAD-4
Capital investment (uninstalled)	$175,800	$99,500
Operating expenses	$73,000/year	$45,150/year
Total operating costs	$1.33/1000 gal.	$0.83/1000 gal.

Breakdown of Capital and Operating Expenses

Activated carbon

Capital expense
$35,400 Regeneration furnace
$41,700 Furnace afterburner and HCl scrubber
$23,700 Adsorption vessels and carbon storage
$26,500 Piping and associated expenses
$18,500 Activated carbon (54,000 lb; 50% excess at 0.125 gpm/ft^3)
$30,000 Miscellaneous

$175,800 Total

Operating expense
$15,000/year Carbon replacement (10% loss per regeneration)
$ 8,000/year Furnace operator's salary
$50,000/year Furnace operation, depreciation, etc.
$73,000/year Total

Equivalent to $1.33/1000 gal. treated

Amberlite XAD-4

Capital expense estimate
$45,000 Acid-resistant equipment, piping, etc.
$54,500 XAD-4 (400 ft^3, 100% excess at 0.50 gpm/ft^3)
$99,500 Total

Operating expense
$10,500/year XAD-4 replacement (5-year life)
$ 4,650/year Equipment depreciation (10-year life)
$30,000/year Regeneration chemical make-up
$45,150/year Total

Equivalent to $0.83/1000 gal. treated

large-scale facility, chemical regeneration becomes even more advantageous since it is now feasible to practice regenerant recovery and reuse. Recovery and recycle of adsorbed pesticides can be used as a credit toward operating expenses.

Presented in Table V are comparative cost data which illustrate the above points. The activated carbon data are those of an actual operating plant (Henshaw and Bawden, 1970). The XAD-4 cost data were generated from laboratory results using a synthetic waste effluent similar to that produced by the operating plant. These data are based on accepted ion exchange technology and costs. As a result of the factors discussed above, both the capital and the operating cost of Amberlite XAD-4 adsorbent are projected to be less than those of the granular activated carbon.

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Measurements of Laser Light Backscattering vs. Humidity for Salt Aerosols

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■ He-Ne laser light was used to illuminate aerosol particles generated from aqueous solutions by a Collison atomizer. The backscattering of the light by the particles was measured as a function of relative humidity in a chamber having an effective scattering angle of 173.5°. NaCl, KCl, and NaBr particles having mass mean diameters of 0.2-0.4 μ all scattered more than twice as much light when humidified as they did when dry. The change of phase from solid to liquid occurred at lower humidities than those appropriate for the bulk salts. The changes in phase from liquid to solid occurred at lower humidities than did the changes from solid to liquid. Humidity is a very significant variable in the backscattering of hygroscopic aerosols and can be expected to affect LIDAR measurements.

Airborne particles, both liquid and solid, contribute to air pollution and contamination control problems. Often the concentrations of these aerosols are measured by devices which illuminate the particles and measure the light scattered by them. One promising method of obtaining information on the spatial and temporal distribution of aerosol particles in the atmosphere is LIDAR, which is analogous to RADAR, using light pulses (from lasers) rather than lower frequency radio pulses. Early work on LIDAR was done by Ligda (1965), and Johnson (1969) has reviewed its air pollution applications.

The light scattered by an aerosol particle is a complicated function of the ratio of particle size to light wavelength, and it also depends on the index of refraction of the particle, the angle between incidence and scattering directions, the polarization of the light, and the shape of the particle. There are tabulated solutions of the Mie scattering equations for spheres (Davies, 1966) but few for nonspherical particles of dimensions on the order of the light wavelength, the situation often encountered in practice. The degree to which nonspherical particles scatter light in comparison to spheres of equivalent dimensions is still an open question, but Huffman and Thursby (1969) found significant deviations from the spherical patterns for irregular ice particles.

Hygroscopic particles are present in the atmosphere; a number of atmospheric hygroscopic salt nuclei have been studied by Twomey (1954) and others. Acid mists occur in industrial situations, and humidity plays a role in the formation of some photochemical aerosols (Renzetti and Doyle, 1960). Maritime air masses contain sodium chloride particles from the sea spray. Light scattering is affected by changes in humidity, as can be inferred from the degradation of visibility on humid days; this effect has been measured for continental aerosols (Lundgren and Cooper, 1969) as well as for sea salt sprays (Pueschel et al., 1969) but these two investigations lacked the combination of monochromatic illumination and backscattering detection characteristic of LIDAR. Although many LIDAR probings of the atmosphere have been done, few light scattering experiments have been done with backscattering from aerosols whose size, general shape, and refractive index are known, and we are familiar with none which before this measured the change in backscattering which occurs as a hygroscopic aerosol is humidified, undergoing changes in phase (thus shape), and refractive index. (This combination of changes is not amenable to calculation, primarily owing to problems of shape).

The goal of this investigation was to measure the effect on laser light backscattering that changes in humidity produced for aerosols which were hygroscopic and similar in size and index of refraction to those aerosols found in the atmosphere.

Equipment

The experimental set-up had to provide for generation and transport of the aerosol, control and measurement of the aerosol humidity, illumination of the aerosol, measurement of the scattering of light by the aerosol, and measurement of the aerosol size distribution.

A schematic of the aerosol generation system is given in Figure 1. Compressed air was piped through filters and a drying column (silica gel) so that when it reached the pressure regulator it was clean and dry. The pressure regulator was set at 30 lb/in.^{2} (2 atm) above atmospheric. The air was then divided between a Collison atomizer and a tube containing a critical orifice which maintained a dilution flow into the mixing chamber.

The flow path of the aerosol after it left the mixing chamber is diagrammed in Figure 2. After leaving the mixing chamber, the aerosol was sampled through 10 cm of 0.15-cm diam glass capillary tubing into a plastic container (volume 8.5×10^3 cm^3), used to reduce concentration fluctuations. From there it flowed into a mixing tee where it was mixed with filtered air of a controlled humidity. The diluted aerosol then went to the relative humidity (r.h.) chamber, where its humidity was measured during its 78-sec residence time (flow rate 13×10^3 cm^3/min). The diluted, humidity-controlled aerosol flowed next through a tee containing a thermometer and then into the cylindrical scattering chamber; turbulence resulted in mixing. After the aerosol left the scattering chamber, it was caught on a filter, except when its size distribution was being determined as described below.

The aerosols (with the exception of the polystyrene aerosols) left the mixing chamber with humidities under 20% r.h. After they were mixed with filtered (Gelman glass fiber filter, Type E), humidity-controlled air (11×10^3 cm^3/min) there resulted aerosol humidities ranging from 10 to 85% r.h. Humidities above 85% r.h. were obtained by passing the aerosol over the surface of the water in a one-pint (0.5×10^3 cm^3) jar one-quarter filled with water, the prehumidifier.

The humidity of the diluted aerosol was measured in

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the r.h. chamber, a metal canister about 30 cm in diam and 30 cm high. The humidity sensors were glass coils impregnated with various hygroscopic salts; the conductivities of the coils are functions of relative humidity (the system was a Model 15-3001 Hygrometer Indicator and Model 4-4824 Hygrosensors from Hygrodynamics, Inc., Silver Spring, Md.). The sensors are rated to respond to 65% of an instantaneous change in humidity within 3 sec and are accurate to within ±1.5% r.h. according to the manufacturer. Sensors were intercompared at the limits of their ranges and no discrepancy with the claimed accuracy was found. The use of two thermometers, one in the r.h. chamber and one in the inlet to the scattering chamber, allowed for a correction for temperature differences, usually a few tenths of a degree centigrade.

The illumination of the aerosol and the measurement of its scattering of the incident light was done with the scattering chamber, a long cylinder lined throughout with black velvety material to absorb light. It is light-tight and air-tight. The laser beam enters through a window made from a microscope slide cover glass, and the beam ends in a light horn made of bent glass tubing painted outside with optical black paint. Optical stops determine how much of the beam can be viewed by the light pipe, which transmits light to the photomultiplier tube (RCA 7265, with 2000 V applied). The details of the optical geometry are given in Figure 3.

The light was provided by a He-Ne laser (Quantum Physics Model LS-32), having a nominal output of 3 mW in multimode operation at a wavelength of 0.6328 μ, with the electric vector of the light polarized vertically, perpendicular to the scattering plane. The constancy of the laser output was monitored with a GE X-6 photoconductive cell.

Light scattering from particles varies with the angle between the directions of incidence and scattering, so it is useful to know the response of the scattering chamber to light scattered from various positions (various angles) along the laser beam. This response was measured by moving a diffuse reflector (0.45-μ pore, white Millipore membrane filter) along the path of the laser beam, with its face perpendicular to the beam, and recording the current from the photomultiplier tube.

Calculation of the effective scattering angle gave the result that the amount of light received by the light pipe from particles which scattered diffusely (Lambert's law) would be equal to that received if all the particles had been placed 15.0 cm (perpendicular distance) from the light pipe face. This corresponds to an effective scattering angle of 173.5°. Similarly, half the light scattered by diffusely scattering particles would have come from positions corresponding to angles greater than the median scattering angle of 170°.

General Procedure

Aqueous solutions of the materials were prepared, either 8 or 1% by volume (v/v) for the salt aerosols and 1% v/v for the dyes, and the solutions were poured into the atomizer. After atomization had begun, and after the electronic instruments had warmed up, the humidity was varied by changing the ratio of wet air to dry air. Initial readings were taken for dry (<20% r.h.) conditions, then the humidity was raised and allowed to stabilize (about 10 min) and the backscattering at that humidity was recorded. After one to three such measurements at elevated humidities, another dry scattering reading was taken to establish a baseline. The values used for the scattering ratios were net scattering, the difference between the scattering from the aerosol and from filtered air; such filtered air scattering measurements were made regularly and showed a negligible humidity dependence.

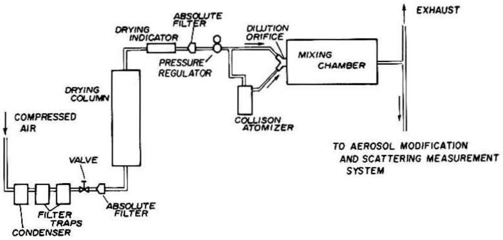

Figure 1. Aerosol generation system

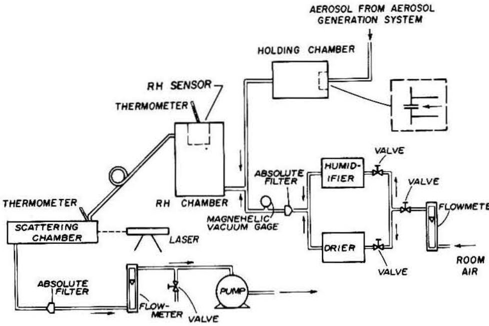

Figure 2. Aerosol modification and scattering measurement system

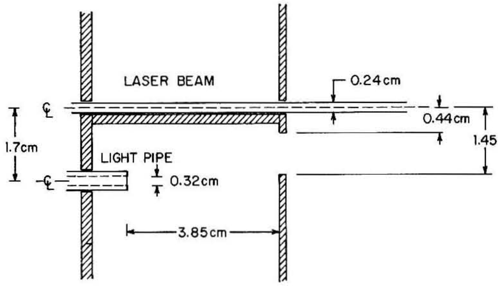

Figure 3. Scattering geometry

Results

Size Distributions. The properties of aerosol particles are strongly size-dependent. To ascertain the size distribution of the aerosol, samples were collected at the outlet of the scattering chamber on aluminum foil, using a Bendix electrostatic sampler. Electron microscope pictures of the samples on the foil were taken at 10,000× magnification, and sizing was done by comparing the area of the particles to the areas of circles. Size information is given in Table I and Figure 4. Figure 4 shows mass distributions, since light scattering is more closely related to particle volume (hence, mass) than to particle diameter to the first, second, or fourth powers when particle diameter

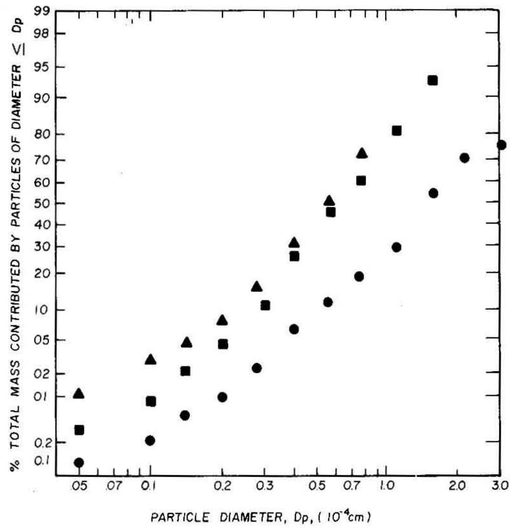

Figure 4. Cumulative size distributions for aerosols generated from 1% v/v NaCl (▲), 1% v/v KCl (■), and 8% v/v NaCl (●) solutions

is on the order of incident light wavelength (Charlson et al., 1967; Cooper and Byers, 1970; Noll et al., 1968). The smallest particles were least accurately sized. Those particles counted as having diameters around 0.05 μ were actually all those that small or smaller; more particles were not seen when the magnification was doubled.

Backscattering vs. Relative Humidity. The results of the measurements of backscattering as a function of relative humidity are shown in graphs in Figures 5–8. Backscattering ratio is the ratio of net backscattering at indicated humidity to that at low humidity (<20% r.h.). The ratio allows comparisons between aerosols scattering different amounts of light.

The behavior of the hygroscopic salt aerosols NaCl, KCl, and NaBr is illustrated in the graphs of Figures 5–8. The theory of the growth of hygroscopic particles was presented quite clearly in the work of Orr et al. (1958). That description is paraphrased in the following paragraph.

At low humidities, hygroscopic particles adsorb a thin layer of water a few molecules, or less, thick. Increasing the humidity brings the particles to a point where they become droplets of a concentration which is in equilibrium with the water vapor (relative humidity) present; these droplets continue to grow as the relative humidity is increased. They contract if the humidity is decreased. If the humidity continues to decrease, the droplets become solid again; this change of phase takes place at a lower humidity than that

Table I. Size Parameters of Particles Formed by Nebulizing Salt Solutions with a Collison Atomizer

Soln nebulized	No. mean diam, μ	Mass mean diam, μ	Mass median diam, μ	Geometric std dev
8% v/v NaCl	0.14	0.43	1.5	2.3
1% v/v NaCl	0.08	0.18	0.55	2.2
1% v/v KCl	0.13	0.28	0.62	2.1

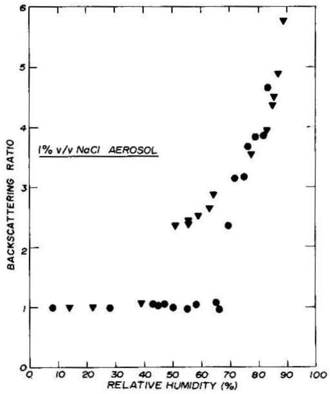

Figure 5. Backscattering vs. relative humidity for 1% v/v NaCl aerosol
Prehumidified (▼) and not prehumidified (●)

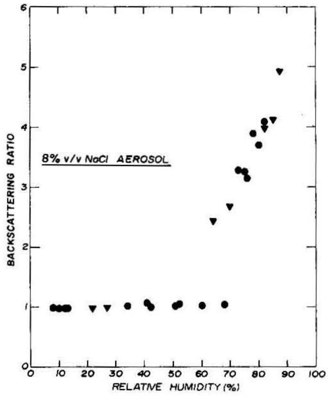

Figure 6. Backscattering vs. relative humidity for 8% v/v NaCl aerosol
Prehumidified (▼) and not prehumidified (●)

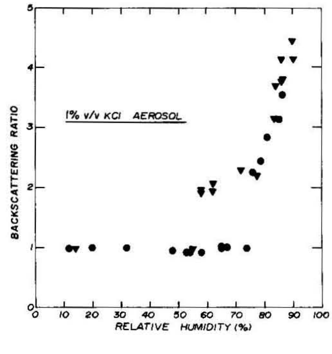

Figure 7. Backscattering vs. relative humidity for 1% v/v KCl aerosol
Prehumidified (▼) and not prehumidified (●)

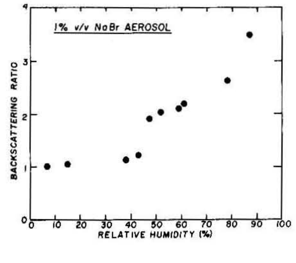

Figure 8. Backscattering vs. relative humidity for 1% v/v NaBr
Not prehumidified

at which droplets changed phase when the humidity was increasing. Additionally, the change-of-phase humidity for increasing humidity conditions depends on particle size, smaller particles changing phase at lower relative humidities.

Although the thin film of water on a particle exists even at low humidities, no significant changes were measured in the scattering from the KCl and NaCl aerosols from 10 to 60% r.h. when they were not prehumidified. The theory for scattering from concentric spheres of different refractive indices has been worked out (Aden and Kerker, 1951) and some computations have been made (Kerker et al., 1962). The exact scattering computations are rather difficult, but a very small size change is involved in the formation of this water film, and this is believed to be the explanation for our observation of no appreciable change in scattering for different low humidities. Orr et al. (1958) gave an equation for the thickness of an adsorbed molecular film at a given vapor pressure of the film's constituent. It predicts a water shell 1.4 molecules thick (5×10^{-8} cm) for NaCl at 30% r.h., an increase in size of only one part in 300 for a particle with a diameter of 0.3 μ.

Our measurements are in general agreement with the theory of Orr et al. (1958). Each salt exhibited increased backscattering for increasing humidities above a characteristic critical humidity, associated with the transition from solid to liquid for some or all of the aerosol particles. In parentheses are listed the critical humidities for each salt (the lowest humidity for each salt for which the backscattering ratio was 1.2 or greater), along with the next lowest humidity measured: 1% v/v NaCl (69, 66% r.h.), 8% v/v NaCl (73, 68% r.h.), 1% v/v KCl (76, 74% r.h.), 1% v/v NaBr (43, 38% r.h.). These critical humidities are lower than the transition (change-of-phase) humidities for the bulk salt material (Twomey, 1954). Although the sizes were different, the backscattering ratios for 1% v/v NaCl and 8% v/v NaCl were indistinguishable above the critical humidity for 8% v/v NaCl.

Some fraction of the KCl and NaCl aerosols which passed through the prehumidifier became droplets; then they displayed the hysteresis noted in Orr et al. (1958); that is, they remained droplets even below the critical humidity.

NaCl droplets changed back to solid particles below 40% r.h., and KCl droplets changed back to solid particles below 55% r.h.

Additionally, measurements made with aerosols from 1% v/v aqueous solutions of uranine dye indicated a slight decrease in backscattering with increasing humidity (15% decrease at 85% r.h.). Methylene blue dye aerosols (from 1% v/v solutions) increased in backscattering to a ratio of 1.2–1.3 at 70–80% r.h. and started to decrease for higher humidities. The changes in scattering for these dyes are less than those found by Lundgren and Cooper (1969), who illuminated similar aerosols with white light and measured forward scattering.

Subsidiary Tests. Humidity changes resulted in changing the scattering from the filtered air by amounts which were less than a few percent of the net scattering for the aerosols.

The backscattering ratio for a polystyrene latex aerosol (0.71-μ diam) was between 1.0 and 1.1 from 20 to 84% r.h.

The mass concentrations of the aerosols used were approximately 500 $\mu g/m^3$ for those nebulized from 1% v/v solutions and 3500 $\mu g/m^3$ for the 8% v/v NaCl. The average backscattering per unit dry particle volume was 0.44, 0.61, 0.67, 0.57 (10^{-3} A/cm^3) for the 1% v/v KCl, 1% v/v NaCl, 1% v/v methylene blue, 8% v/v NaCl aerosols, respectively. (Error in average scattering measurements was estimated to be ± 10–20%.)

We measured the forward scattering by the dry aerosols with a Sinclair-Phoenix Aerosol Photometer. The ratios of forward scattering of white light to backscattering of red light were in the following (descending) order: NaCl, methylene blue, uranine dye. Such comparisons might give useful information about atmospheric aerosols.

Losses were calculated for NaCl particles with dry diameters from 0.1 to 4.0 μ, both in the dry condition and at 80% r.h., for settling of particles in the scattering chamber and in the r.h. chamber. The sedimentation calculations (Byers et al., 1971) show 10% or less difference (wet vs. dry) for diameters of 2 μ or less. The size distribution data indicates that 5% or less by mass of the 1% v/v aerosols was greater than 2.0 μ in size, but 30% by mass of the 8% v/v NaCl aerosol was greater than 2.0 μ. The loss calculations indicate appreciably greater losses for this latter aerosol at 80% r.h. than when dry; thus, the scattering ratio of 8% v/v NaCl as given in Figure 6 is probably artificially low.

Possible increases in aerosol losses due to the prehumidifier were tested. The 1% v/v NaCl aerosol was passed through the prehumidifier, then its scattering was measured at <30% r.h. Differences of 0, 1, 3, and 2% in scattering were found by alternately passing through and bypassing the prehumidifier. The same tests for 8% v/v NaCl aerosol, however, gave scattering losses of 15 and 16%, so that the experimental values for the scattering for 8% v/v NaCl aerosol were increased by 16% before being plotted as prehumidified data points in Figure 6.

Discussion

The large changes in backscattering which varying humidity produced in the hygroscopic aerosols would be expected to occur in situations involving LIDAR probes of the atmosphere; the better the match between these test aerosols and atmospheric aerosols with respect to size, shape, index of refraction and hygroscopicity, the more nearly identical the magnitude of the changes. The extent of this matching is discussed first.

Particles which contribute most significantly to natural light scattering in the atmosphere are those of about ½ μ in diam (Pueschel and Noll, 1967), and for aerosols of approximately this size the scattering is nearly proportional to the particle volume (Charlson et al., 1967; Cooper and Byers, 1970). The volume mean diameters of the aerosols used in this work were approximately 0.2–0.4 μ and the volume median diameters were 0.6–1.5 μ. Measurements made by Whitby et al. (1972) in Pasadena, Calif., gave a bimodal size distribution for the atmospheric aerosol, which in the light-scattering size region approximated a log-normal distribution of 0.3-μ median diam and 2.25 geometric std dev, quite similar to the aerosols used here. We know very little about the shape of atmospheric aerosols and can make no comparison with these cubic salts.

Refractive index is another characteristic it was desired to match between atmospheric and test aerosols. Eiden's (1966) measurements at Mainz gave indices of 1.5 for dry conditions and 1.44 for moist. Hanel's (1968) measurements indicated for the atmospheric aerosol a refractive index of 1.57 at 40% r.h., with the values of refractive index ranging from 1.7 to 1.33 as the relative humidity went from 0 to 100%. NaCl has a refractive index of 1.54. (KCl and NaBr have indices of 1.49 and 1.64, respectively). Water has a refractive index of 1.33. As relative humidity increases, the refractive index of the salt droplets will approach that of water. NaCl would seem well suited with regard to index of refraction to model some atmospheric aerosols.

One must be careful not to overstate the applicability of the NaCl data in the case of continental aerosols. The work of Meszaros (1968) showed that the water-soluble fraction of these aerosols has a much greater mass fraction of sulfate and ammonium particles than chloride particles, and that the mass fraction of water-soluble materials in the particulates over Budapest in the summer was only 20% for particles with radii smaller than 0.14×10^{-4} cm and 8% for particles with radii larger. Thus water-soluble particulates are a fraction of the atmospheric aerosol, and chlorides a fraction of the water-solubles.

On the other hand, Twomey (1954) did find that the primary hygroscopic aerosol particles in both continental and maritime Australian air masses were sea salt. Lundgren and Cooper (1969) dried and humidified ambient air (State College, Pa.) while measuring its forward light scattering with a Sinclair-Phoenix aerosol photometer; they found no differences in scattering below 50–55% r.h., but increased scattering at humidities above this level, which is a behavior similar to that of hygroscopic salts.

How do these measurements relate to earlier experimental work? There are few available data on the effect of humidity on light scattering. Aerosols generated by Pueschel et al. (1969) from an aqueous solution of 3% w/w NaCl (1.4% v/v) by vigorous bubbling gave 3.1 times the scattering at 75% r.h. as they did when dry (40% r.h.) measured by the integrating nephelometer which sums the scattering over an angular range of 8–170° from the forward direction. Lundgren and Cooper (1969), using NaCl aerosols similar to the 1% v/v NaCl used here, found an increase in forward scattering of about a factor of seven at 75% r.h. for white light. The backscattering ratio for the 1% v/v NaCl aerosol used here was 3.5 at 75% r.h. These tests suggest that LIDAR or the integrating nephelometer may be less sensitive to humidity as an interference than is the forward-scattering photometer.

This experimental investigation has been partially duplicated by Roberts and Byers (1972), using equipment modeled after the equipment used here. For somewhat larger NaCl aerosols (mass mean diameter 1.0 μ) the increase in scattering was a factor of 2.5–2.8 at 80% r.h. and these researchers found no change produced by adding SO_2 (0.3–10,000 ppm) to the humidified aerosols for contact times greater than 80 sec. As particle size increases from <0.05 μ to greater than 50 μ or so, the scattering changes from Rayleigh scattering to Mie scattering to geometrical optics scattering, the dependence on size going from sixth power to second power, diminishing the importance of the size change at the phase transition for larger particles, as borne out by the results of Roberts and Byers.

Although few experiments have been done relating humidity and light scattering, the behavior of hygroscopic aerosols has been studied by mobility measurements. On the basis of theory and experiment, Orr et al. (1958) concluded that smaller hygroscopic particles would change phase at lower humidities than large ones of the same material; for example, bulk NaCl changes phase at 75–76% r.h. but such particles 0.1 and 0.06 μ in size change phase at 73 and 68%; the corresponding figures for KCl are 86, 83, and 82%, from the graphs of Orr et al. (1958). Cinkotai (1971) predicted growth of NaCl particles under conditions found in the human lungs, at a temperature of 36°C, and concluded that smaller particles would change phase at higher, not lower, humidities than does the bulk material. Under our conditions (23°C) the aerosols behaved as Orr et al. predicted; significant increases in scattering for the 1% v/v NaCl and KCl aerosols occurred (under increasing humidities) at 66–68% and 74–76%, respectively, humidities lower than those at which the bulk materials change phase.

At the change of phase, the volume of hygroscopic particle increases to approximately $1/(1 - \text{r.h.})$ times its original volume (Neiburger and Wurtele, 1949; limiting case for Orr et al., 1958), which means the NaCl and KCl aerosols increased in volume three to four times upon changing phase, giving rise to increased light scattering. MacKinnon (1969) calculated the effect on laser light backscattering from a Junge (1963) size distribution of sodium chloride particles, assumed spherical, and predicted an increase in backscattering of less than a factor of two upon change of phase in going from 73 to 80% r.h. Our measurements for the test aerosols from 1% v/v and 8% v/v NaCl indicated a greater increase in backscattering, a factor of 3.5 to 4.

Conclusions

The aerosols studied were similar in size and refractive index to those which dominate atmospheric light scattering. These salt aerosols all scattered several times more light as droplets than they did as solid particles. These increases in scattering are due to changes in size, shape, and refractive index. Those who make LIDAR measurements should take into account that, as shown here, humidity will significantly alter backscattering from hygroscopic aerosols, and such effects may take place at humidities well below the transition humidity of the bulk material (which for NaCl is 75% r.h.), especially for the aerosol particles which have diameters less than a micron or which have previously been subjected to humidities above their transition humidities and have not changed back to solids (viz, the prehumidified aerosol data in Figures 5–7). The dependence of backscattering on relative humidity for hygroscopic aerosols may be viewed as an interference or it may be used with other information to obtain humidity (or composition) profiles of the atmosphere.

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Generation of Monodisperse Aerosol Standards

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■ A vibrating orifice monodisperse aerosol generator capable of generating primary aerosol standards from a variety of solid and liquid materials is described. The generator produces monodisperse aerosols of a known size from approximately 0.50 to 50 μ diam with an average geometrical standard deviation of 1.014. The particle diameter is calculable from the generator operating conditions to an accuracy of better than 2% in routine operations, and ultimately to 0.1% or better accuracy. The generator is very stable in operation with concentration fluctuations showing a relative standard deviation of less than 3%. The generator can be used to generate primary standard aerosols for instrument calibration, aerosol research, and performance testing of particulate control devices.

Basic aerosol standards, consisting of monodisperse aerosols of a high degree of monodispersity and accurately known particle sizes, are needed for a variety of purposes ranging from fundamental aerosol research to the calibration of aerosol sampling and measuring instruments. They are also useful for testing particulate control devices such as cyclones, filters, and scrubbers and for studying the effects of particulate air pollutants. Conventional monodisperse aerosol generators, such as the spinning-disk generator, condensation generator, and atomizer generator are not suitable for producing basic aerosol standards either because the aerosol is not sufficiently monodisperse or because it is difficult to measure the particle size sufficiently accurately for use as a basic standard.

To a limited extent, polystyrene latex (PSL) aerosols produced by atomizing a dilute suspension of monodisperse PSL particles (available from Dow Chemical Co., Midland, Mich.) have been used as an aerosol standard, particularly as a calibration standard for optical particle counters. However, the usefulness of the PSL aerosol as a general-purpose test aerosol is limited because the physical and chemical properties of PSL are not always the ones needed for the particular application, and the aerosol can be generated only at the few selected sizes that are available. Further, the atomization process also produces numerous water droplets which do not contain PSL particles. These empty droplets, upon evaporation, give rise to residue particles of the dissolved impurity in water, and the aerosol is therefore not truly monodisperse (Whitby and Liu, 1968). A new approach is therefore needed in the generation of aerosol standards for instrument calibration and standardization work.

The vibrating orifice monodisperse aerosol generator described in this paper is based on the instability and break-up of a cylindrical liquid jet. A cylindrical liquid jet is unstable for mechanical disturbances and breaks up into droplets. When these mechanical disturbances are generated at a constant frequency (within a limited frequency range) and with sufficient amplitude on a liquid jet of constant velocity, the jet will break up into equal-sized droplets. To form a monodisperse aerosol, these uniform droplets must then be dispersed and diluted before significant coagulation occurs.

The generator described in this paper (now available from RNB Associates, P.O. Box 18005, Minneapolis, Minn. 55418) is capable of producing particles from a variety of solid and liquid materials. The generator is unique in that it can produce particles of a known size, the particle size being calculable from the generator operating conditions routinely to an accuracy of 2% or better. With some care in measuring the operating parameters, an accuracy of 0.1% or better in particle size can be achieved. Since the particle size does not have to be measured by an independent method, the generator produces aerosols which can be used as a true primary standard. In addition, the generator has the following features: The droplets are exceedingly uniform in size—the std dev is approximately 1% of the mean droplet diameter which is comparable to or better than the best monodisperse particles available, namely monodisperse polystyrene latex spheres. The output particle concentration of the generator is very steady with concentration fluctuations showing a rel std dev of <3% over a 1-hr period. The ultimate size range of the generator is approximately 0.25–50 μ and the useful size range is approximately 0.5–50 μ based on present design.

Theoretical Background and Previous Work

The phenomenon of uniform liquid jet break-up was first observed experimentally by Savart (1833) and studied theoretically by Plateau (1873) and Rayleigh (1878, 1879). From the consideration of surface energy, Plateau derived the minimum wavelength (distance between disturbances) for a disturbance to be unstable on an infinitely long liquid cylinder as:

$$\lambda_{\min} = \pi D_j \qquad (1)$$

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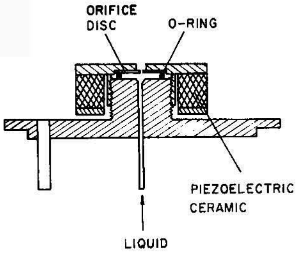

Figure 1. Schematic diagram of droplet generator

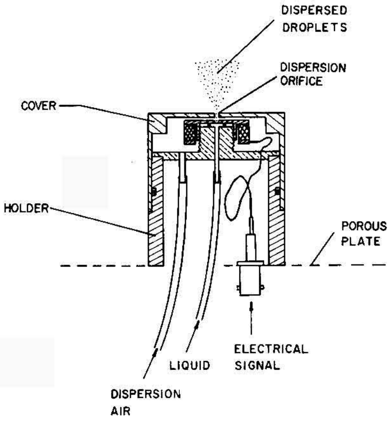

Figure 2. Schematic diagram of dispersion system

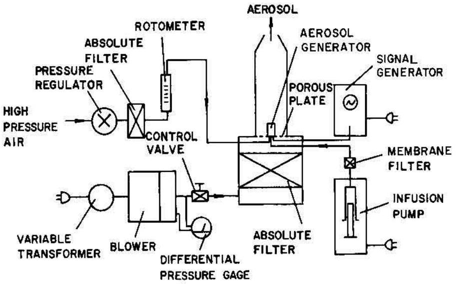

Figure 3. Schematic diagram of vibrating orifice monodisperse aerosol generator

where D_j is the liquid cylinder (jet) diameter. For an inviscid, incompressible, cylindrical liquid jet sprayed into a vacuum, Rayleigh derived the optimum wavelength for a disturbance to be most unstable as

$$\lambda_{\text{opt}} = 4.508\ D_j \tag{2}$$

Schneider and Hendricks (1964) experimentally determined that uniform droplets could be produced by varying λ within the following limits

$$3.5\ D_j < \lambda < 7\ D_j \tag{3}$$

Considering the conservation of energy, Lindblad and Schneider (1965) derived that a minimum liquid velocity is needed to form a liquid jet from a capillary tube,

$$V_{j,\min} = \left(\frac{8\ \sigma}{\rho D_j}\right)^{1/2} \tag{4}$$

where σ is the surface tension and ρ is the density of the liquid.

The uniform break-up of a liquid jet has been used experimentally by various investigators to produce uniform droplet streams and particles. A detailed survey of these investigations including the means for producing the mechanical disturbances needed to break up the jet uniformly has been given by Berglund (1972).

Vibrating Orifice Monodisperse Aerosol Generator

The vibrating orifice monodisperse aerosol generator described in this work consists of four major parts: the liquid feed system, the droplet generator, the droplet dispersion system, and the aerosol flow system.

The liquid feed system consists of a syringe pump which forces the liquid through a membrane filter into the droplet generator at a constant rate. A 0.50-μ membrane filter is used with a 25-μ-diam liquid orifice, and a 0.50-μ membrane filter is used as a prefilter and a 0.25-μ membrane filter is used as a final filter with 8-μ and 3-μ diam liquid orifices.

The droplet generator pictured in Figure 1 consists of a stainless steel cup with a 1.15-in. diam flange and a hole in the bottom. A 0.375-in. o.d. orifice disc is placed in a groove inside the bottom of the cup; a Teflon O-ring is placed on top of the orifice disc; and a stainless steel cap is tightened onto the O-ring holding the orifice disc in place. A ring-shaped piezoelectric ceramic with two silvered faces is epoxied to the flange on the cup with conductive epoxy. The liquid from the liquid feed system is fed through the cap into the cup and is then sprayed through the orifice. An ac voltage is applied to the piezoelectric ceramic which vibrates the cup and disturbs the liquid jet at a constant frequency. Because the syringe pump delivers the liquid at a constant rate, the liquid jet then breaks up into uniform droplets at the frequency of the ac voltage. The uniform droplet stream then enters the dispersion system.

The droplet dispersion system pictured in Figures 2 and 3 consists of a stainless steel holder and cover for the droplet generator, a pressure regulator, a flow meter, and an absolute filter. The cover has a dispersion orifice through which both the droplet stream and a turbulent air jet pass. When the droplet stream reaches the turbulence of this air jet, it is dispersed into a conical shape. The dispersed droplets (aerosol) then enter the aerosol flow system.

The aerosol flow system consists of a blower and flow meter for the main dilution air, an absolute filter, a perforated plate which supports the droplet generator assembly, and a vertical plastic tube (5-in. diam and 24 in. long) for diluting and drying the volatile liquid droplets. Air from the blower passes through the absolute filter, through the perforated plate, and then mixes with the dispersed droplets. This clean air dilutes and transports the aerosol, and, in the case of a nonvolatile solute in a volatile solvent, the clean air also evaporates the volatile solvent. The monodisperse aerosol then leaves at the top of the plastic tube. Figure 3 is a schematic diagram of the entire flow system of the vibrating orifice monodisperse aerosol generator.

Operation Envelope

When the liquid jet is illuminated with a strobe light which is triggered from the signal generator, the nature of the liquid jet break-up can be observed through an optical microscope. The nature of the liquid jet break-up can be classified into three modes: uniform break-up of the liquid jet resulting from mechanical disturbances by the piezoelectric ceramic; nonuniform break-up of the liquid jet (such as satellite droplets) resulting from mechanical disturbances by the piezoelectric ceramic; and polydisperse break-up of the liquid jet showing no effect of mechanical disturbances by the piezoelectric ceramic.

The conditions of the ac voltage signal controlling the three different modes of break-up of the liquid jet can be seen in Figure 4 which is a plot of the RMS ceramic voltage vs. the disturbance wavelength divided by the liquid jet diameter (λ/D_j) for an 8.25-μ-diam orifice with a liquid flow rate of 0.0623 cc/min. The liquid jet diameter was chosen so that the minimum value of λ/D_j for uniform break-up of the liquid jet would equal π as predicted by Plateau (1873). When the ac voltage is kept at a maximum and the value of λ/D_j is increased from zero to infinity (frequency decrease), the major modes of breakup of the liquid jet go from polydisperse, to uniform, to nonuniform, to polydisperse with two small islands of satellites within the uniform break-up region. Figure 4 shows that very low voltages (<1.0 V RMS) are needed to cause uniform break-up of the liquid jet.

Operating Range of the Generator

Orifice diameters of 2.96–22.1 μ have been used with the generator to generate monodisperse aerosols. Table I shows the range of droplet diameters (by varying the frequency of the ac voltage applied to the piezoelectric ceramic) which each orifice can produce. Using the technique of solvent evaporation, the aerosol diameter can be made considerably smaller than the droplet diameter, the smallest aerosol diameter being determined by the concentration of the nonvolatile impurities in the solvent. The ultimate aerosol size range indicated in Table I for each orifice corresponds to an impurity concentration of 20 ppm by volume. However, to avoid having to size the aerosol particles by an independent method, the nonvolatile aerosol material added to the solvent must be at a higher concentration than the impurity concentration of the solvent. Further, when a viscous material such as DOP is used as the aerosol material, it is necessary to add a certain amount of solvent to make the liquid less viscous in order to spray it properly through the orifice. Thus, the useful size range of the aerosol for each orifice is somewhat narrower than its ultimate size range. This useful size range is also given in Table I. The upper limit corresponds to that for DOP. For a less viscous liquid that can be sprayed through the orifice, the upper size limit will be larger. For a material with a finite solubility in the given solvent, the upper limit may be smaller.

The basic droplet generator is capable of generating considerably larger droplets than those shown in Table I. The same droplet generator has been used to produce droplets as large as 500 μ, using an orifice of an appropriate size. However, larger droplets than those shown in Table I would require a different airflow and aerosol transport system to avoid excessive losses of particles during transport.

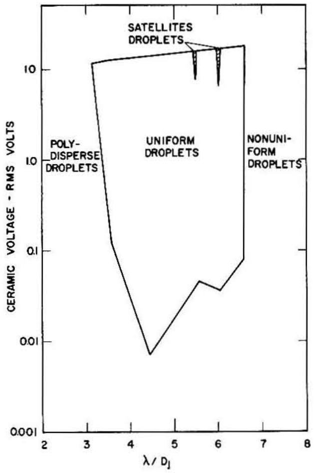

Figure 4. Plot of RMS ceramic voltage vs. λ/D_j

The output aerosol concentration of the generator is equal to the ratio of the frequency of the applied ac voltage on the piezoelectric ceramic and the total airflow through the generator, reduced by any loss of particles in the airflow system. With the Kr-85 charge neutralizer in place, it was found that the output aerosol concentration was about 80% of the theoretical concentration based on frequency and airflow measurements. However, without the charge neutralizer, the output concentration was considerably lower, due to electrostatic charge effects. The nominal aerosol concentration given in Table I is based on an airflow of 3 cfm and with the piezoelectric ceramic operated at the optimum frequency corresponding to the particular orifice size.

Accuracy of Calculated Particle Size

One advantage of the vibrating orifice monodisperse aerosol generator over other aerosol generators (such as the spinning-disk aerosol generator) is that the diameter of the aerosol particles does not have to be measured. The diameter of the liquid droplet particles from the vibrating orifice generator can be calculated from the liquid flow rate and the disturbance frequency by the following formula:

$$D_d = \left(\frac{6Q}{\pi f}\right)^{1/3} \qquad (5)$$

When the liquid droplet is nonvolatile, the aerosol particle diameter is equal to the droplet diameter; however, when a nonvolatile solute is dissolved in a volatile solvent, the aerosol particle diameter is given by

$$D_p = C^{1/3} D_d \qquad (6)$$

Table I. Operating Range of the Vibrating-Orifice Monodisperse Aerosol Generator

Orifice diam, μ	Liquid flow, cc/min	Frequency range, kHz	Operation frequency, kHz	Droplet diam range, μ	Ultimate aerosol diam limit, μ	Useful[a] aerosol diam range, μ	Nominal[b] aerosol concn, particles/ft^3
22.1	0.214	55–80	70	49.8–44.0	1.19	2.30–36.5	1.12×10^6
8.25	0.0623	295–625	450	18.9–14.7	0.399	0.82–13.0	7.20×10^6
2.96	0.0220	555–895	725	10.8–9.21	0.250	0.49–7.8	1.16×10^7

[a] See text.
[b] Based on nominal airflow and operating frequency.

Table II. Comparison of Calculated and Measured Particle Diameters of a DOP Aerosol Using an Optical Microscope

Orifice diam = 24.3 μ
Liquid flow rate = 0.214 cc/min

Run	Frequency, kHz	DOP:alcohol soln	$D_{p,\text{calcd}}$,[a] μ	$D_{p,\text{meas}}$, μ	$D_{p,\text{meas}}$[a] / $D_{p,\text{calcd}}$	Corr $D_{p,\text{calcd}}$,[b] μ	$D_{p,\text{meas}}$[b] / Corr $D_{p,\text{calcd}}$
1	63.363	1:50,000	1.291	1.641 ± 0.32	1.271	1.641	1.000
2	63.355	1:10,000	2.207	2.625 ± 0.32	1.189	2.352	1.116
3	63.319	1:2000	3.775	3.828 ± 0.32	1.014	3.827	1.000
4	63.359	1:500	5.991	6.124 ± 0.32	1.022	6.012	1.019
5	63.368	4:500	9.510	9.515 ± 0.32	1.001	9.518	1.000

[a] Not corrected for concentration of nonvolatile in the solvent impurity.
[b] Corrected for impurity concentration.

Table III. Comparison of the Calculated and Measured Particle Diameters of a DOP Aerosol Using an Electrical Mobility-Size Analyzer

Orifice diam, μ	Liquid flow, cc/min	Frequency, kHz	DOP:alcohol soln	$D_{p,\text{calcd}}$, μ	Corr $D_{p,\text{calcd}}$, μ	$D_{p,\text{meas}}$, μ	% Error	Geometric std dev
8.25	0.0615	405.55	Pure alcohol	. . .	. . .	0.47	. . .	1.010
8.25	0.0615	405.59	1:8000	0.8445	0.8904	0.888	+0.27	1.000
8.25	0.0615	405.29	1:4000	1.064	1.094	1.115	−1.9	1.016
8.25	0.0615	405.32	1:1000	1.689	1.701	1.695	+0.35	1.029

where C is the volumetric concentration of a nonvolatile solute in a volatile solvent.

Any nonvolatile impurities in the volatile solvent will cause an error in the calculated aerosol particle diameter. When the amount of nonvolatile impurities in the volatile solvent is known, the error in the calculated aerosol particle diameter may be eliminated by

$$D_{p,\text{corr}} = \left(1 + \frac{I}{C}\right)^{1/3} D_p \qquad (7)$$

where I is the volumetric fraction of nonvolatile impurities in the solution. The final accuracy in the calculated particle diameter, however, is determined by the accuracy with which the quantities Q, f, I, and C are measured. This accuracy is normally ±2% in routine operations. Based on an estimate of the measurement accuracy that can be obtained, a final accuracy of 0.1% or better in the calculated particle diameter is believed to be attainable.

DOP Aerosol

Table II compares the calculated and measured particle diameters of five DOP aerosols generated with the vibrating orifice monodisperse aerosol generator using five different solutions of DOP and ethyl alcohol with about 0.002% nonvolatile impurities. The DOP aerosol particles were collected with an impactor on glass slides treated in a 0.004 wt % solution of a 3M Co. Fluorocarbon (L-1083) and demineralized water for about 10 min. The diameter of the DOP particles on the treated glass slides was measured using an optical microscope and a Cooke image-splitting eyepiece. Because the liquid DOP drops become flattened and are not spherical on the treated glass slides, the diameter of the DOP aerosol particles suspended in air must be calculated using a spread factor. A correction factor of 1.45 (ratio of apparent drop diameter on slide to the true diameter of the spherical drop) was used as determined by Whitby and Vomela (1965). Figure 5 is a photograph taken with an optical microscope of a typical sample of a DOP aerosol on a 3M Co. Fluorocarbon treated glass slide.

The larger calculated and measured particle diameters in Table II compare within experimental measurement error; however, the fact that the measured particle diameter becomes larger than the calculated particle diameter for the smaller particles is illustrative of the error caused by nonvolatile impurities in the volatile solvent. When Equation 7 is used to correct the calculated aerosol particle diameters, the corrected calculated aerosol particle diameters then agree with the measured aerosol particle diameters within the experimental error of the optical microscope measurements. The impurity concentration of the alcohol was chosen so that the corrected calculated and measured particle diameters of the 1.291-μ diam aerosol are equal. The data can also be used as an alternative verification of the spread factor determined by Whitby

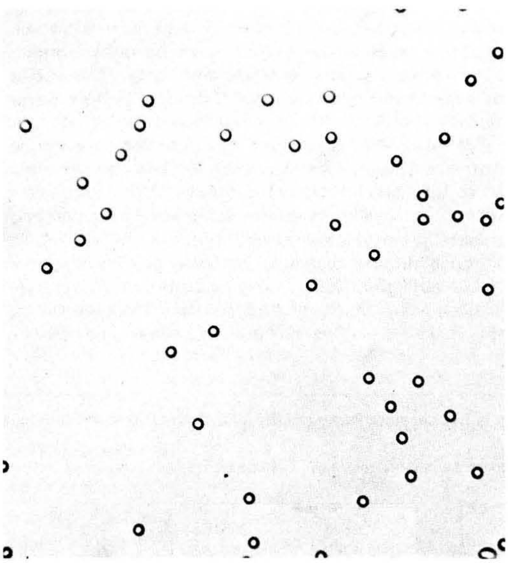

Figure 5. Photograph taken with an optical microscope of a typical DOP aerosol (9.5-μ diam) sampled on an oilphobic slide

Table IV. Comparison of Calculated and Measured Particle Diameters of a Methylene Blue Aerosol Using an Optical Microscope and a Scanning Electron Microscope

Orifice diam = 22.1 μ
Liquid flow = 0.214 cc/min

Frequency, kHz	Methylene blue:liquid soln (50:50 alcohol: water)	$D_{p,\text{calcd}}$,[a] μ	Op. micro $D_{p,\text{meas}}$, μ	El. micro $D_{p,\text{meas}}$, μ
66.152	1:2000	3.718	. . .	3.7 ± 0.37
67.550	1:2000	3.692	3.98 ± 0.37	. . .

[a] Assuming the density of the methylene blue particles is the same as the density of the methylene blue powder measured by an air pycnometer.

and Vomela (1965) for DOP particles on 3M Co. Fluorocarbon (L-1083) treated glass slides.

An electrical mobility-size analyzer described by Bademosi (1971) and Knutson (1971) was used as an alternative method for sizing DOP aerosol particles, and these results are listed in Table III. It can be seen from Table III that the calculated DOP particle diameters, corrected for the alcohol impurities, agree within 2% error with the diameters measured using the electrical mobility-size analyzer. The impurity concentration of the alcohol in this case was determined by spraying the alcohol and measuring the impurity particle diameter with the electrical mobility analyzer upon complete evaporation of the alcohol. These results show that when a liquid aerosol is being formed, Equations 5 and 7 can be used to calculate the aerosol particle diameter to within the experimental accuracy of the direct sizing methods.

Methylene Blue Aerosol

A solid aerosol was generated by spraying a solution of methylene blue, ethyl alcohol, and water. The alcohol and water then evaporated leaving solid spherical particles of methylene blue. A 50:50 liquid mixture of ethyl alcohol and water gave the most spherical dried particles of methylene blue. Figure 6 is a photograph taken with a scanning electron microscope of typical methylene blue particles.

Table IV compares the calculated methylene blue particle diameter (assuming the density of the methylene blue particles is equal to the true density of methylene blue measured by an air pycnometer) with the particle diameter measured using an optical microscope and a Cooke image-splitting eyepiece and the particle diameter measured from a scanning electron microphotograph. Table IV shows that the calculated methylene blue particle diameter agrees within experimental error with the measured particle diameters. This result indicates that the assumption that the density of the methylene blue particles is the same as the parent material from which the particles are made is valid under the experimental conditions.

Sodium Chloride Aerosol

A sodium chloride aerosol was generated using the method described for generating a methylene blue aerosol. Figure 7 is a scanning electron microphotograph of typical sodium chloride particles. Although particle shapes differ, all the particles have equal volume.

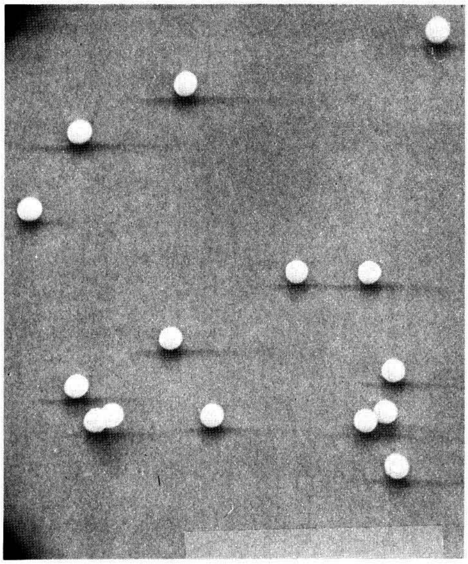

Figure 6. Photograph of methylene blue particles (3.7-μ diam) taken with a scanning electron microscope

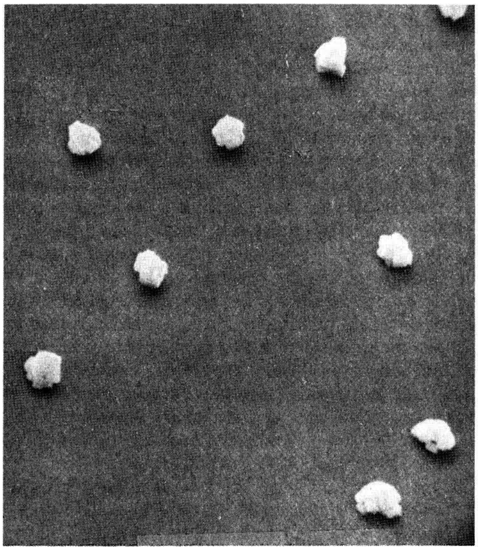

Figure 7. Photograph of NaCl particles of 27.4-μ^3 volume taken with a scanning electron microscope

Uniformity of Generated Particles

The uniformity (monodispersity) of the particles is very good for an aerosol made with a vibrating orifice generator. Figure 8 is a photograph of DOP particles on a 3M Co. Fluorocarbon treated glass slide taken through a Cooke image-splitting eyepiece. It can be seen from Figure 8 that the particles are so uniform that no size difference can be detected between them using an optical microscope. Therefore, the geometric standard deviation of the aerosol from a vibrating orifice monodisperse aerosol generator is very close to unity.

The electrical mobility method gave an average geometric standard deviation of 1.014 for the measured DOP particles.

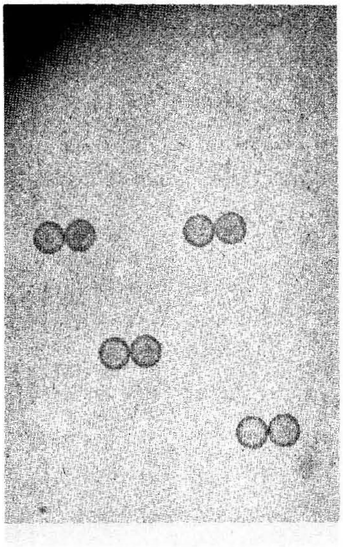

Figure 8. Photograph of typical DOP particles taken through an image-splitting eyepiece and an optical microscope

Dispersion of Droplet Stream

The method of dispersing the liquid droplet stream by spraying it through an orifice into a turbulent air jet has proved to be very satisfactory.

The quality of the dispersion of the aerosol was determined using a Bausch and Lomb 40-1 optical particle counter modified to give the particle voltage pulses at a BNC connector output and a Hewlett-Packard multichannel analyzer. The optical counter was able to resolve between singlets and doublets. Therefore, the number of pulses greater than the single particle pulse size was taken to be the number of multiplets present.

Because there is a possibility of two or more particles going through the optical counter viewing volume at the same time and generating a larger voltage pulse which may be mistaken for a multiplet, a correction for coincidence loss must be made for aerosols of high concentration. Mattern et al. (1957) showed that the theoretical ratio of instrument count to actual number of aerosol particles passing through the viewing volume is

$$\frac{N_{t,i}}{N_{t,a}} = \frac{1 - P_o}{1 + \sum_{n=0}^{\infty}(n - 1)P_n} \tag{8}$$

where $N_{t,i}$ = total instrument counts; $N_{t,a}$ = actual total particles; $P_n = (m^n e^{-m}/n!)$; m = average number of particles per unit of viewing volume. This transcendental Equation 8 may be solved by a graphical method for $N_{t,a}$ when $N_{t,i}$ is known. Therefore, assuming that two or more particles in the optical counter viewing volume at the same time would cause a voltage pulse large enough to be mistaken for a multiplet pulse, the fraction of multiplets measured by the optical counter may be corrected as follows:

$$\frac{N_{m,a}}{N_{t,a}} = \frac{N_{m,i} - N_{t,a} + N_{t,i}}{N_{t,a}} \tag{9}$$

where $N_{m,i}$ = multiplet instrument counts, and $N_{m,a}$ = actual multiplet particles.

The dispersion of the uniform droplet stream was measured as a function of the dispersion airflow for dilution airflows of 150 and 300 lpm. Figures 9*a*, *b*, and *c* are plots of the percent of multiplets vs. dispersion airflow with dilution airflow as a parameter for 22.1-, 8.25-, and 3.60-μ-diam orifices. It can be seen from Figures 9*a*, *b*, and *c* that for good dispersion conditions, the percent of multiplets is about 5%. This quality of dispersion is very good for most applications.

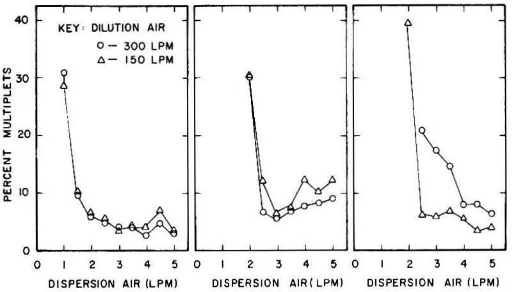

Figure 9. Percent multiplets vs. dispersion air for (a) a 22.1-μ-diam orifice, (b) an 8.25-μ-diam orifice, and (c) a 3.60-μ-diam orifice

Table V. Electrostatic Charge on Aerosol

Orifice diam = 24.3 μ
Liquid flow = 0.214 cc/min
Frequency = 65 kHz
1 DOP: 2000 Alcohol soln
D_p = 3.75 μ

Run	Neutralizer	Neutralizer flow, cfm	Av charge, charge/part
1	. . .	. . .	7300
2	Kr-85 (2 Mc)	10.5	2430
3	Kr-85 (2 Mc)	0.1	4
4	Po-210 (25 Mc)	31.2	60
5	Po-210 (25 Mc)	10.5	40

Stability of Aerosol Concentration

To determine the stability of the aerosol concentration, 10 consecutive 1-min counts and 10 consecutive 5-min counts were made for the 22.1-, 8.25-, and 3.60-μ-diam orifices using a Bausch & Lomb 40-1 optical particle counter and a Hewlett-Packard multichannel analyzer. It was determined that the aerosol concentration is very stable with a rel std dev <3.0%.

Electrostatic Charge on Aerosol

The average electrostatic charge on a 3.75-μ-diam DOP aerosol (generated using a 24.3-μ-diam orifice and a DOP–ethyl alcohol solution in the vibrating orifice monodisperse aerosol generator) was measured using a parallel plate precipitator as described by Thomas and Rimberg (1967). The results of these electrostatic charge measurements are listed in Table V. It can be seen from Table V that the aerosol is highly charged (7300 charges/particle) when it comes from the generator but can be neutralized very effectively (4 charges/particle) using a Kr-85 or a Po-210 radioactive source.

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Response Characterization of the Melpar Flame Photometric Detector for Hydrogen Sulfide and Sulfur Dioxide

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■ The response of the Melpar flame photometric detector to hydrogen sulfide and sulfur dioxide is predictably nonlinear due to the loss of emitted energy to self absorption. A single general equation, $R = k_1 k K S^2 (10^{-\alpha K S^2})$, describes the detector response, R, in terms of sulfur mass, S, in the sample. The constants k_1, k, K, and αK are experimentally determined. The fraction of emitted energy lost to self absorption, F, is a function of the sulfur mass in the sample and is described by the equation $F = 1 - 10^{-\alpha K S^2}$. A plot of F vs. sulfur mass provides a basis for the selection of a sample size to achieve optimum detector performance.

As preparations were being made to use the Melpar flame photometric detector (Brody and Chaney, 1966) for stack and ambient air monitoring in and around a kraft pulp mill, it was found that specificity and sensitivity of the detector had been well established for sulfur (Stevens and O'Keeffe, 1970; Grice et al., 1970; Mizany, 1970; Mulik et al., 1971; Stevens et al., 1971). However, for routine use, the relationship between the detector response and sulfur mass and the working range of the detector were not well defined (Brody and Chaney, 1966; Bowman and Beroza, 1968; Stevens et al., 1969; Grice et al., 1970; Mizany, 1970). This study was undertaken to define more fully the mass-response characteristics for sulfur over a wide range of sulfur masses and establish a procedure for accurate calibration of the detector.

Apparatus

The analyses were performed using a Tracor Model MT150 gas chromatograph (Tracor, Inc., Austin, Tex.) equipped with a Melpar flame photometric detector, 8-port and 10-port air-actuated rotary Teflon valves, and a 34-ft by ⅛-in. Teflon column packed with 5% polyphenyl ether and 0.05% phosphoric acid on 30/60 mesh Teflon.

The primary analytical standards of hydrogen sulfide and sulfur dioxide in air were generated using a Tracor Permeation Standard. Ten-centimeter Teflon permeation tubes (Metronics Associates, Palo Alto, Calif.) were used for the source of hydrogen sulfide and sulfur dioxide.

Procedure

Since stack gas monitoring does not usually require the maximum sensitivity obtainable from the photometric detector, operating parameters were selected to provide a quiet stable flame and signal rather than maximum sensitivity. Total gas flow through the detector and the oxygen-to-hydrogen ratio of the gas stream entering the detector have been shown to affect both its signal-to-noise ratio and sensitivity (Mizany, 1970; Stevens et al., 1971). Therefore a total flow of 150 ml/min with an oxygen-to-hydrogen ratio of 0.25 was experimentally determined to provide the desired detector performance. The operating conditions, gases, and flow rates used in this study are: column oven temperature, 50°C; detector block temperature, 135°C; carrier gas and flow rate, nitrogen at 30 ml/min; detector gases and flow rates, air at 15 ml/min, oxygen at 18 ml/min, hydrogen at 90 ml/min; electrometer range setting, 10^4; electrometer attenuator setting, variable 1 to 256.

A 5-ml Teflon gas sample loop was purged with a minimum of 100 ml of sample before the sample loop was switched into the carrier gas stream. Two such loops were used alternately.

The instrument response was defined to be the mean peak height in millimeters multiplied by the electrometer attenuator setting. The mean peak height was determined from a minimum of 5 and a maximum of 17 analyses on a given stream sample. The number of such sets of analyses

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performed was 22 for hydrogen sulfide and 20 for sulfur dioxide, over a range of sulfur masses from 0 to 263.4 ng for hydrogen sulfide and 0 to 130 ng for sulfur dioxide. These data are presented in Table I.

The sample streams were generated in air using gravimetrically calibrated Teflon permeation tubes (O'Keeffe and Ortman, 1966) as the sulfur gas source. The permeation tube air bath temperature was maintained at 30° ± 0.1°C. The permeation rates were 4.419 $\mu g/min$ for hydrogen sulfide and 4.010 for sulfur dioxide. The 95% confidence level for the hydrogen sulfide permeation rate was ±5.5%, and ±4.4% for the sulfur dioxide permeation rate.

Results and Discussion

From spectroscopic evidence, Brody and Chaney (1966) attributed the emission at 394 $m\mu$ to the S_2 species. If this assignment is correct, the total emitted energy, I_o, may be defined as follows:

$$I_o = k[S_2] \tag{1}$$

For S_2 to be present in the flame there must be an equilibrium or steady-state condition in which S_2 is formed. Either condition leads to similar results. The following derivation is based on an equilibrium condition such that

$$S + S \overset{K}{\rightleftharpoons} S_2 \tag{2}$$

where

$$K = \frac{[S_2]}{[S]^2} \tag{3}$$

and

$$K[S]^2 = [S_2] \tag{4}$$

For a given set of gas flow rates through the detector, the system may be considered to be a constant volume. If it is further assumed that $[S_2]$ is small compared to $[S]$, then the following may be stated:

$$S_2 = KS^2 \tag{5}$$

where S_2 and S represent the masses of the respective materials present in the flame and S is considered to be the original sulfur mass in the sample. Substituting for $[S_2]$ in Equation 1,

$$I_o = kKS^2 \tag{6}$$

$$\log I_o = \log kK + \log S^2 \tag{7}$$

Equation 7 predicts a straight line having a slope of one from a log-log plot of detector response vs. the square of the sulfur mass. For sulfur masses less than 70 ng, such a plot for hydrogen sulfide (Figure 1) had a slope of 1.005 and a linear correlation coefficient of 0.987. For sulfur dioxide, the slope was 0.958 with a linear correlation coefficient of 0.951. These data correlate well with those previously reported for concentrations encountered in ambient air (Stevens et al., 1971), where slopes of 1.939 for hydrogen sulfide and 1.950 for sulfur dioxide were obtained from log-log plots of detector response vs. sulfur mass.

The apparent loss of detector sensitivity above sulfur masses of 70 ng could be due to fatigue of the photomultiplier tube or to self-absorption of the emitted energy. If photomultiplier tube fatigue were the cause, erratic responses or no response would be expected to subsequent samples. Since this was not observed, fatigue was ruled out as the possible cause.

Table I. Analytical Data

Hydrogen sulfide		Sulfur dioxide	
Sulfur mass in sample, (ng)	Instrument response, (mm)	Sulfur mass in sample, (ng)	Instrument response, (mm)
4.4	16.3	23.6	700.0
6.9	45.8	35.3	1866.9
16.0	518.4	38.0	1831.0
16.0	407.2	42.2	2741.8
19.7	763.2	45.6	2382.7
19.9	776.0	47.3	2481.3
33.2	1539.5	49.4	3354.9
40.0	1971.2	54.1	3344.0
50.2	3273.6	56.1	3892.5
65.3	4691.8	58.3	3832.3
67.2	4832.0	59.8	3951.4
68.9	5008.0	63.6	4208.6
74.1	5234.8	68.6	4377.0
76.6	5305.6	76.1	4828.8
90.0	6290.0	80.1	5153.3
93.6	6689.3	81.6	5305.6
108.0	7333.1	90.3	5305.0
119.6	7351.0	104.6	5680.0
138.1	7654.4	116.6	5822.7
148.6	7889.0	129.1	6021.1
171.5	8275.0		
263.4	8627.2		

If the negative deviation from the straight line is caused by self-absorption of energy, then I_o does not reach the PM tube. The surviving fraction of the energy, I, actually reaching the PM tube may be determined from the Beer-Lambert law:

$$I = I_o(10^{-\alpha[S_2]}) \tag{8}$$

where α is a proportionality constant. Substituting for I_o and S_2

$$I = kKS^2(10^{-\alpha KS^2}) \tag{9}$$

Since the detector response, R, is proportional to I, the following may be stated:

$$R = k_1kKS^2(10^{-\alpha KS^2}) \tag{10}$$

or

$$\log R = \log k_1kK + \log S^2 - \alpha KS^2 \tag{11}$$

For small sulfur masses (less than 70 ng) the αKS^2 term is negligible and the straight lines of Figure 1 result from a log-log plot of instrument response vs. the square of the sulfur mass. The intercept from such a plot provides a value for the log k_1kK term and makes it possible to evaluate αK:

$$\alpha K = \frac{\log k_1kK + \log S^2 - \log R}{S^2} \tag{12}$$

Nine data points were used to determine average values for αK for both gases. This represented all of the data generated for sulfur dioxide that were not used to establish the straight line, and all but the largest sulfur mass for the hydrogen sulfide. The values of αK were 2.54×10^{-5} ng^{-2} for hydrogen sulfide with a std dev of 0.17×10^{-5} ng^{-2}, and 4.05×10^{-5} ng^{-2} for sulfur dioxide with a std dev of 0.26×10^{-5}. These values were determined

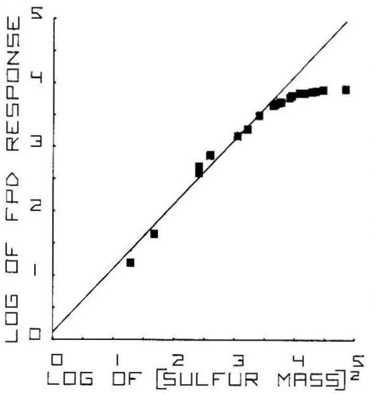

Figure 1. Log-log plot of flame photometric detector response vs. the square of the sulfur mass in hydrogen sulfide samples

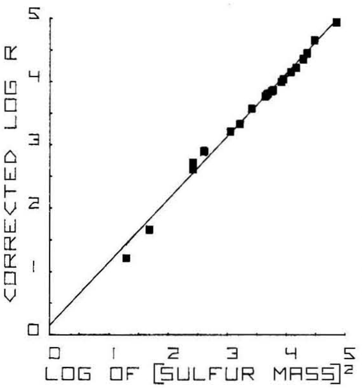

Figure 2. Log-log plot of the flame photometric detector response corrected for self-absorption (corrected log R) vs. the square of the sulfur mass in hydrogen sulfide samples

using a range of masses of 70–170 ng for hydrogen sulfide and 60–130 ng for sulfur dioxide.

From Equation 11, a plot of the quantity log $R + \alpha KS^2$ (corrected log R) vs. log S^2 would be expected to yield a straight line having a slope of one and an intercept of log k_1kK. Figure 2 is such a plot of the data for hydrogen sulfide, which has a slope of 1.001 and a linear correlation coefficient of 0.995. The corresponding values for sulfur dioxide are 1.108 and 0.980.

To determine a working range for the detector, an estimate of the energy lost to self-absorption was needed. Using previously defined terms, the energy lost, $I_o - I$, is defined as follows:

$$I_o - I = I_o - I_o(10^{-\alpha KS^2}) = I_o(1 - 10^{-\alpha KS^2}) \qquad (13)$$

Expressing the energy lost as a fraction, F, of the emitted energy, I_o, the following relationship results:

$$F = \frac{I_o - I}{I_o} = 1 - 10^{-\alpha KS^2} \qquad (14)$$

A plot of F as a function of sulfur mass, S, such as Figure 3, provides a basis for the selection of a sample size to optimize detector performance. If maximum sensitivity were needed, the sample mass should be less than 60 ng where 90% of the emitted energy is reaching the PM tube. Good sensitivity for routine use could be expected for sample masses up to 100 ng where 50% of the energy is available for the analysis. Above 100 ng the detector would be expected to be less sensitive to increases in the sample mass, which is shown to be true in Figure 1.

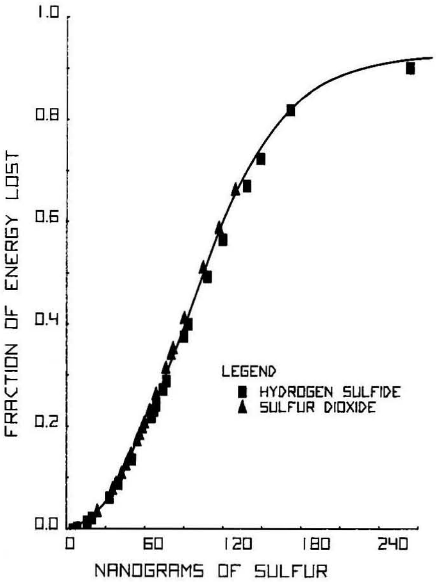

Figure 3. Plot showing fraction of total emitted energy lost to self-absorption, $(I_o - I)/I_o$, as a function of sulfur mass in samples of hydrogen sulfide and sulfur dioxide

Conclusions

The relative loss of detector sensitivity at higher sulfur masses is due to self-absorption rather than photomultiplier tube fatigue.

The flame photometric detector response to hydrogen sulfide and sulfur dioxide can be defined by the general equation $R = k_1kKS^2\ 10^{-\alpha KS^2}$, where the constants may be determined experimentally.

For routine detector use, the most simple theoretically sound calibration curve may be prepared as a log-log plot of detector response vs. sulfur mass. A straight line with a slope of 2 will result up to the point at which self-absorption becomes significant. At that point a negative deviation from the line will be observed.

A plot such as Figure 3 together with a log-log calibration curve allow for the sample size to be selected to optimize detector performance. For the operating conditions used in this study, a good working range would be between 0 and 100 ng of sulfur. Maximum detector sensitivity could be expected between 0 and 60 ng where approximately 90% of the emitted energy is available to the photomultiplier tube.

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INDUSTRY TRENDS

Peabody Engineering will design and furnish a second wet scrubbing system for Potomac Electric Power Co. in Washington, D.C. The first system was announced in July. Total cost of the fly ash removal units is over $4.2 million.

Process Equipment Pacific, Inc. (Honolulu, Hawaii) will handle the entire line of Rex Chainbelt–manufactured water and waste water screening and treatment equipment for Hawaii. Jack Leong is president of Process Equipment Pacific, a newly organized firm.

Research-Cottrell will supply electrostatic precipitators for Units 1 and 2 of Georgia Power Co.'s Wansley, Ga., plant.

Drew Chemical Corp. will market Bio-Pure Inc.'s Bio-Pure sewage treatment package worldwide in marine applications. Drew will market the units on a nonexclusive basis within the United States and on an exclusive basis outside the United States.

North American Rockwell has signed a contract with the Office of Saline Water for a one-year continuation of development work on a proprietary direct-contact, multistage flash distillation process for desalting brackish water.

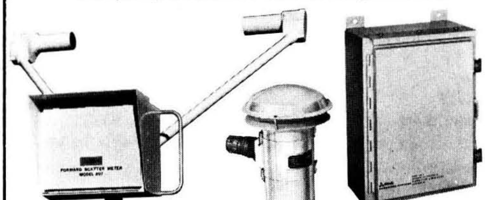
Peabody Galion Corp. has reached agreements in principle to acquire two consulting firms specializing in design of large pollution control installations. The two are Hayden, Harding & Buchanan, Inc. (Boston, Mass.) and Leonard S. Wegman Co., Inc., (New York City). The two firms had 1971 revenues of about $3.7 million. Combined backlogs of fees for projects currently under contract total over $6.5 million.

Ralph M. Parsons Co. (Los Angeles, Calif.) has received a $736,000 contract from the Office of Coal Research to assist in development of commercial processes for the economic production of clean synthetic fuels from coal.

Babcock & Wilcox says construction is under way on a $2 million sulfite liquor incineration unit which will help Scott Paper Co. reduce water pollution at its Everett, Wash., mill.

Babcock & Wilcox has received a $27 million contract to fabricate and erect the Unit #3 steam generator at the Homer City (Pa.) station of Pennsylvania Electric Co. and the New York State Electric and Gas Corp. Initial construction will begin this year and startup is scheduled for 1976.

Hercules has chosen Union Carbide Corp.'s PuraSiv N control system to check nitric acid plant emissions from the company's 55-tpd acid plant in Bessemer, Ala.



Research-Cottrell has received a contract for three electrostatic precipitators to collect hematitic iron ore dust from the Cleveland-Cliffs Iron Co.'s Tilden Mine pelletizing grate kiln system.

The Institute of Gas Technology (Chicago, Ill.) has received a $16.5 million contract for continued research in connection with the Institute's coal gasification program.

The Phillips-Croftshaw Division of Phillips Manufacturing Co. (Chicago, Ill.) has been awarded a turn-key contract for an undisclosed amount to design and construct a solvent recovery system and auxiliary systems for Phoenix Closure, Inc., also of Chicago. The unit will recover heptane vapors.

International Combustion Australia, a licensee and associated company of Combustion Engineering, Inc., has been awarded a contract valued at $30 million (U.S. currency) for steam generating facilities at Newport Power Station on the Yarra River west of Melbourne.

GCA Technology (Bedford, Mass.) has received a $201,000 contract from the Environmental Protection Agency to study the effects of automotive traffic on air pollution in seven of the country's major urban areas.

Zurn Industries' Board of Directors has approved acquisition of three companies: Vinylplex, Inc., and an affiliated company, Hydroline, Inc., both of Pittsburg, Kan., and Cipra, Inc. of Denver, Colo. Vinylplex compounds and extrudes PVC pipe. Hydroline is engaged in industrial water supply, utility and irrigation systems, and pollution control. Cipra is involved with designing and engineering complete air handling and contamination control systems.

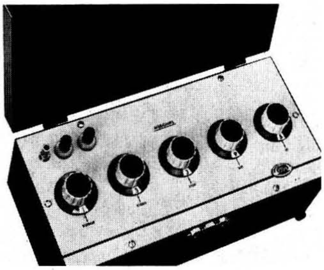
Eriez Magnetics (Erie, Pa.) has acquired the assets of the Syncro-Matic division of State Steel Products Co. of Industry, Calif. Syncro-Matic makes vibratory circular screen separators and oscillating conveyors for a variety of sizing, separation, and material movement applications.

Aerovent, Inc., is the new name selected by the Board of Directors of the Aerovent Fan Co. (Piqua, Ohio). The old name no longer accurately reflects the broad air-handling capabilities of the company, the Board said.

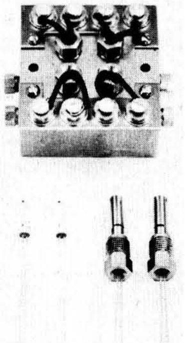
Browning-Ferris Industries, Inc. has entered into an agreement with Ecological Recycling Co (Newark, N.J.) to acquire Ecological Recycling for $2.5 million in Browning-Ferris stock.

NEW PRODUCTS

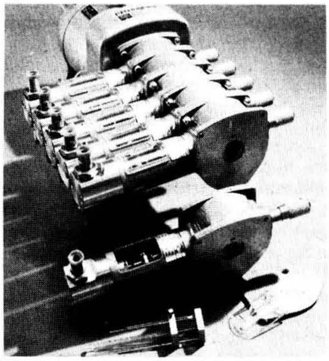
Recorders
New generation of strip chart recorders, series 2500, boasts many innovative features and improvements based on experience of thousands of users. Line includes five single-pen and four double-pen models with linear and log/lin modes, with and without integrators. Brinkmann Instruments, Inc. **61**



Decade box
Precision, high-range decade resistance box is first ready-made instrument ever offered incorporating resistance values above 10 megohms in convenient box form. Instruments are available in two accuracy classes, 0.1% and 1.0%. James G. Biddle Co. **62**



Thermal conductivity detector
High-performance off-the-shelf thermal conductivity detector features choice of either standard of microvolume geometry. Designs cover temperatures from subambient to 500°C. Hot-wire elements are tungsten, tungsten-rhenium alloy, platinum, or other metal, depending on service requirements. Condyne Instruments, Inc. **63**



Pump
MPL series II Micro-Pumps are small, accurate sampling pumps for laboratory or small-scale process requirements. Six variable-stroke controls can be mounted independently on the pump to regulate pump output. Ace Industrial Division **64**

Composter
A $3\frac{1}{2}$-hp portable leaf-mill and 5-hp composter, tractor-mounted composter, and trailer sweeper are among new products being introduced by company to dispose of leaves and twigs in an ecologically sound manner. Allis-Chalmers Corp. **65**

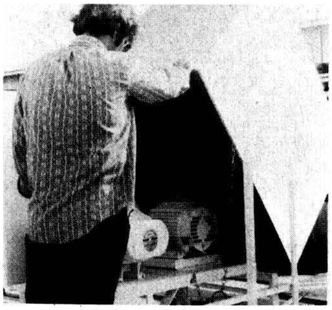
TDI monitor
Newly developed British instrument continuously monitors concentrations of toluene diisocyanate in the atmosphere at toxic levels. Detection is by chemiluminescence. REM, Inc. **66**

Smoke monitor
Solid state smoke density indicators have fully adjustable sensing heads, designed for easy lens cleaning, which provide Ringlemann readouts. Relay output continuously setable from 0.5–4.5 Ringlemann units. De-Tec-Tronic Corp. **67**

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

NO$_x$ measurement
Glassware apparatus for determination of nitrogen oxides emissions from stationary sources by Method 7 as published in the *Federal Register* consists of collection flask, T-bore stopcock, sampling probe, pump valve, and U-tube manometer. Ace Glass, Inc. 68

Packaging resin
New nitrile-based plastic resin has been developed specifically for soft drink and beer containers. Bottles made from the material have sufficient strength to withstand carbonation pressures while retaining their shape at elevated temperatures. Provide barriers necessary to protect product quality and flavor. Du Pont 69

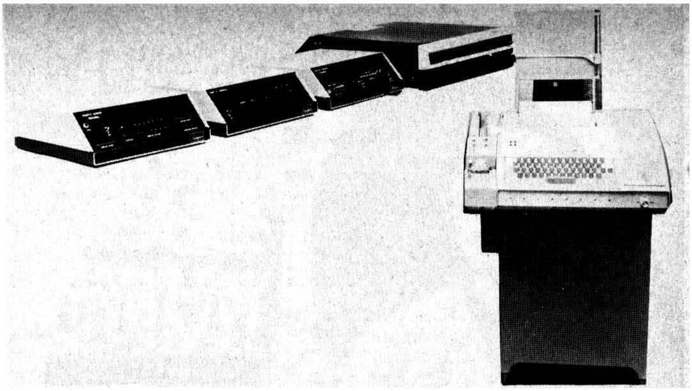


Shelter
Weatherproof protection of any type equipment is provided by rugged metal stand and Fiberglas hood. Hood is noncorrosive and is double hinged to the stand for easy access to equipment. Stand is either plain-welded steel or hot dip galvanized. Engineered Products 70

Probe
Research quality conical probes designed for high-velocity use measure total and static pressures as well as pitch and yaw angles of supersonic streams. Standard models are $^1/_8$ or $^1/_4$ in. diam and other models are available. United Sensor and Control Corp. 71

Weir kit
Kit contains a V-notch weir with clamping wedge for pipe from 8 through 12 in. and appropriate equipment for larger pipe sizes up through 42 in. to test for tightness in sewer lines. NB products, Inc. 72

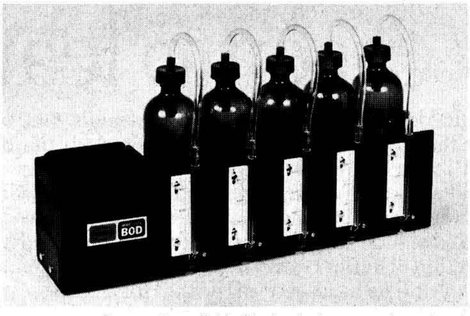
Sulfur determinator
Sulfur titrator automatically determines and digitally displays sulfur content in all oils normally analyzed by bomb, quartz tube, or induction furnace method. Also analyzes oil additives, coal and coke, and can determine sulfur levels in iron, steel, nonferrous metals, and inorganic materials. LECO Corp. 73



Air quality system
Low-cost telemetry system uses signal stream multiplexing techniques to keep track of air quality. System uses multidrop party-line telephone circuits for two-way communication between a single central station and 16 or more remote stations. Can be adapted for use with dial-up telephone circuits, radio nets or direct-wired in-plant circuits. Receptors 74

Water monitor
Model 920 monitor is a direct-reading, multirange water monitor which uses a unique circuit employing two thermistors in thermal contact with the water to provide correct temperature compensation throughout the 0–20, 0–2, and 0–0.2 megohm-cm ranges. Monitor can compute and display correct specific resistivity referred to 25°C, with accuracy within 2% of full scale. Balsbaugh Laboratories 74

Hydrogen generator
Unit generates laboratory quantities of hydrogen purified by palladium, for use in environmental gas chromatographs and sulfur detectors. Trienco, Inc. 76



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We're making brainpower grow in Indianapolis. One fertile field will be the proposed Indianapolis Center for Advanced Research. It's to be located in the heart of the new Indiana University/Purdue University city at Indianapolis and will specialize in advanced bio-engineering research.

Private education is also moving ahead in Indianapolis with the construction of Butler University's new 10-million dollar science complex. The heart of it will be the Holcomb Research Institute which will explore new frontiers in environmental biology.

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Fate of Organic Pesticides in the Aquatic Environment

ADVANCES IN CHEMISTRY SERIES No. 111

A symposium sponsored by the Division of Pesticide Chemistry of the American Chemical Society with Samuel D. Faust, Chairman.

Chemical contamination of the Great Lakes and evidence of DDT in Lake Michigan illustrate the serious problems presented by organic pesticide pollution in aquatic environments today.

This up-to-date collection of thirteen papers gathers together scientific evidence on the distribution and stability of organic pesticides in aqueous systems. These studies report the latest and most challenging research on: occurrence; recovery by liquid-liquid extraction; confirmation by mass spectrometry and NMR techniques; interaction with particulate matter and with natural organic polyelectrolytes; sorption by organic clays; herbicidal residues; photodecomposition of picloram and other pesticides; chemical hydrolysis and oxidation of parathion and paraxon; persistence of carbomate insecticides; and degradation of diazinon chlorinated hydrocarbons.

If you are a pesticide chemist, industrial engineer, or ecology expert, you will find this book invaluable.

280 pages with index. Cloth (1972) $10.50 Postpaid in U.S. and Canada, plus 40 cents elsewhere.

Order from:
Special Issues Sales
American Chemical Society
1155 Sixteenth St., N.W.
Washington, D.C. 20036

NEW LITERATURE

Water clarification. New booklet takes mystery out of water clarification by clearing up some commonly misunderstood aspects of coagulation, flocculation and other aspects of water clarification. Bulletin has sections on coagulation theory, chemicals, equipment, process mixing and feeding, precipitation softening, and sludge handling. Nalco Chemical Co. **105**

Computer planning. Brochure entitled "Urban and Environmental Technologies" is comprised of three sections: City Planning, Environment, and Energy Systems. Computer Sciences Corp. **106**

Tertiary treatment. Booklet discusses centrifugal waste water concentrators which remove most suspended solids from many effluents including those from paper, textile, tobacco, meat packing, potato, and poultry industries. SWECO, Inc. **107**

Pelletizer. Literature describes an attendant-free, completely automatic system that changes dust to easily disposable pellets. Can be used with existing or planned dust collection system. Hartley Controls Corp. **108**

Instrumentation selection. Technical bulletin discusses variables involved in selecting appropriate instrumentation for waste water systems. Photos of typical installations and process flow diagrams illustrate text. Graver Water Conditioning Co. **109**

Freon. Technical bulletin tells of the use of Freon fluorocarbon as an extraction solvent for determining the presence of oils and greases in waste water analysis. The product is highly volatile and low in residue on evaporation. It is nonflammable and low in toxicity. Du Pont **110**

Power plants. Reprint of technical paper reviews the status of technology for controlling pollutants from fossil fuel-fired power plants. Paper reviews state of the art of particulate collection and control of SO_2 and NO_x emissions. Research-Cottrell **111**

Panel design. 12-page booklet highlight's Hach panel design and fabrication capabilities for engineered water analysis systems. Hach Chemical Co. **112**

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

Phosphate removal. Study entitled "Phosphate removal in secondary systems," describes method for practical phosphate removal from secondary effluents. Can-Tex Industries **113**

Film. Free-loan film entitled "Slimming your Waste" describes current advances in solid waste processing and recycling through the eyes of a homemaker. American Iron and Steel Institute, 201 East 42nd Street, New York, N.Y., 10017 (Write direct.)

Gel filtration chart. Wall chart measuring 18 by 25 in. shows upper exclusion limits, linear operating ranges, and lower exclusion limits of gel filtration materials. Bio-Rad Laboratories, 32nd & Griffin Avenues, Richmond, Calif. 94804 (Write direct.)

BOOKS

Proceedings: Workshop on Sediment Control. James M. Stewart, Joseph A. Phillips. v + 116 pages. Water Resources Research Institute, North Carolina State University, 124 Riddick Bldg., Raleigh, N.C. 27607. 1972, $2.50, paper.

Workshop provided various organizations and governmental agencies within North Carolina an opportunity to discuss the problems of sediment control. Objective was to increase understanding of the problem and to develop guidelines for a sediment control program on the state level.

Environmental Quality and Safety. Vol. 1: Global Aspects of Chemistry, Toxicology and Technology as Applied to the Environment. Frederick Coulston, Friedhelm Korte, Eds. x + 267 pages. Academic Press Inc., 111 Fifth Ave., New York, N.Y. 10003. 1972. $18, hard cover.

Serial publication comprising original publications, monographs, and review articles dealing with global environmental aspects of chemistry, toxicology, ecology, engineering, physics, etc.

Physicochemical Processes for Water Quality Control. Walter J. Weber, Jr. xxxvi + 640 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, N.Y. 10016. 1972. $19.95, hard cover.

Treatise on the principles and applications of chemical and physical-chemical methods of water and waste water treatment. Textbook and reference for students and practicing engineers in sanitary, environmental, civil, chemical, and mechanical engineering. Also recommended for those working in public health, environmental sciences, natural resources, and the chemistry of water.

Emissions from Continuous Combustion Systems. Walter Cornelius, William G. Agnew, Eds. x + 479 pages. Plenum Publishing Corp., 227 W. 17th St., New York, N.Y. 10011. 1972. $25, hard cover.

Describes current basic and applied research directed toward solving the problem of emissions from continuous combustion systems. Proceedings of a symposium sponsored by General Motors Research Laboratories.

Metals As Pollutants in Air and Water. Ocean Engineering Information Series, Vol. 6. Evelyn Sinha. vii + 85 pages. Ocean Engineering Information Service, P.O. Box 989, La Jolla, Calif. 92037. 1972. $15, paper.

Bibliography contains 583 abstracts of worldwide literature providing scientific and technological information on detection, analysis, and measurement of metals as pollutants in air and water; domestic, industrial, urban, and other sources; biogeochemical and meteorological processes involved in pollutant distribution; effects on human health and that of various other life forms; and standards and controls.

Analytical Chemistry: Key to Progress on National Problems. NBS Special Publication 351. W. Wayne Meinke, John K. Taylor, Eds. x + 470 pages. Supt. of Documents, Govt. Printing Office, Washington, D.C. 20402. 1972. $3.50, hard cover.

Proceeding of 24th Annual Summer Symposium on Analytical Chemistry sponsored by the National Bureau of Standards. Includes analytical chemistry applied to air and water pollution.

Environmental Pollution & Control Weekly Government Abstracts. National Technical Information Service, Dept. of Commerce, Springfield, Va. 22151. Weekly. $22.50 per year, paper.

Contains environmental impact statements and covers federal publications on air, noise, solid wastes, and water pollution and control. Briefly describes listed publications.

Chlorine: An Annotated Bibliography. Ralph G. Smith. 165 pages. The Chlorine Institute, Inc., 342 Madison Ave., New York, N.Y. 10017. 1972. $6.00, paper.

Selection of 488 abstracted references of the world's literature on the medical, toxicological, industrial hygiene, and environmental aspects of exposure to chlorine. References from 1824 through 1971. Supplements will be published from time to time.

The Environmental and Ecological Forum 1970–1971. A. Burt Kline, Jr., Ed. viii + 186 pages. National Technical Information Service, U.S. Dept. of Commerce, Springfield, Va. 22151. 1972. $3.00, paper.

Papers presented in the 1970–71 Environmental and Ecological Forum which covered the significant social, environmental, and economic aspects of electric power generation and, more specifically, the pros and cons of nuclear power generation.

Environmental Engineering Unit Operations and Unit Processes Laboratory Manual. John T. O'Conner, Ed. 270 pages. Association of Environmental Engineering Professors, 305 Engineering Labs Bldg., Univ. of Texas, Austin, Tex. 78712. 1972. $10, paper.

Compilation of 35 laboratory experiments pertaining to 18 different biological and physiochemical processes employed for water and waste water treatment. Can be used for undergraduate and graduate engineering courses. Also suitable for technical education centers.

Regionalized Waste Management. 216 pages. Technical Guidance Center for Environmental Quality, Rm 210, Flint Lab, University of Massachusetts, Amherst, Mass. 01002. 1972. $3.00, paper.

Compilation of papers presented at a conference held in June 1972. Comprised of four sections: barriers and advantages to regional disposal through evaluations of technological alternatives and their known environmental consequences; legislative, political, sociological, and financial implications; solid waste management proposal for a statewide regional master plan; and the planning process.

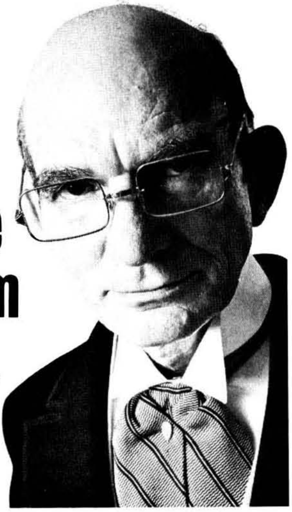
Arts of the Environment. Gyorgy Kepes, Ed. 244 pages. George Braziller, Inc., One Park Ave., New York, N.Y. 10016. 1972. $12.50, hard cover.

Emphasizes the role of the artist, in collaboration with the scientist and engineer, in stimulating man to a new awareness of and involvement with his surroundings. Wide use of photographs to emphasize what is said in the text.

Watersheds Within River Basins. 168 pages. National Watershed Congress, 1025 Vermont Ave., N.W., Washington, D.C. 20005. 1972. $5.00, paper.

Proceedings of the 19th Annual Congress held in 1972. The subject was river basin planning. Includes papers presented, floor discussion, and delegates' names.

There Is A Way To Generate Palladium Pure H_2...



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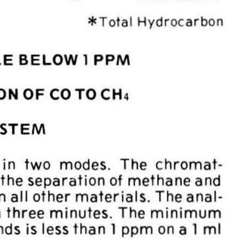

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In the total hydrocarbon mode the 1 ml air sample from the gas sampling valve goes directly to the FID detector where a single peak is obtained. This peak is proportional to the total organic carbon in the sample.

In less than five minutes the Model 514 provides low level determination of carbon monoxide, non reactive hydrocarbon (methane) and reactive hydrocarbons (total hydrocarbon less methane) in a fully portable mode.

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Olympus has added a trinocular system to its SZ-III. Result: our SZ-III-Tr, the first stereo zoom instrument with photomicrographic capabilities at a down-to-earth price.

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Olympus Corporation of America, Two Nevada Drive, New Hyde Park, New York 11040.

In Canada: W. Carsen Co. Ltd., 31 Scarsdale Road, Don Mills, Ontario.

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MEETING GUIDE

Feb. 21–22 Pittsburgh, Pa.

1973 Industrial Wastes Management Symposium. American Marketing Association

Will cover the sociological, economic, legal, and technical aspects of industrial waste management. *Contact:* Shirley Long, American Marketing Assoc., Benedum-Trees Bldg., Pittsburgh, Pa. 15222

Feb. 26–27 San Diego, Calif.

Regional Environmental Management Conference. County of San Diego, Ford Foundation, EPA, and CEQ

Will cover technical and management issues relevant to regional environmental management. *Write:* Patricia Bonner, Public Information Officer, IREM, County of San Diego, 1600 Pacific Hwy., San Diego, Calif. 92101

March 4–9 Pacific Grove, Calif.

Environmental Engineering in the Food Industry Conference. Engineering Foundation

Fee: $175. *Contact:* Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

March 5–6 Louisville, Ky.

Third Annual Environmental Engineering and Science Conference. University of Louisville and others

Will analyze the status of our present environmental problems and present pragmatic solutions. *Write:* Joseph L. Pavoni, Dept. of Civil Engineering, Speed Scientific School, University of Louisville, Louisville, Ky. 40208

March 5–7 Chicago, Ill.

Technical Association of the Pulp & Paper Industry. 58th Annual Meeting

Technical sessions include environmental developments, recycling, energy, etc. *Contact:* W. B. Manning, TAPPI, One Dunwoody Park, Atlanta, Ga. 30341

March 6–9 Washington, D.C.

Coordinating Research Council, Inc. Meeting

Theme: Results of air pollution research pertaining to the automotive and petroleum industries. *Write:* Alan E. Zengel, Coordinating Research Council, Inc., 30 Rockefeller Plaza, New York, N.Y. 10020

March 8–9 Santa Clara, Calif.

5th Annual Solid Waste Symposium. City of Santa Clara, Calif.

Write: Sam M. Cristofano, Director of Public Works, City Hall, 1500 Warburton Ave., Santa Clara, Calif. 95050

March 11–15 New Orleans, La.

American Institute of Chemical Engineers. 74th National Meeting

Includes session on desalting for water reuse. *Contact:* AIChE, 345 E. 47th St., New York, N.Y. 10017

March 12–15 Chicago, Ill.

24th National Plant Engineering & Maintenance Conference and Exhibition. Clapp & Poliak, Inc.

Includes sessions on pollution control, OSHA special sessions, and others. *Write:* Clapp & Poliak, Inc., 245 Park Ave., New York, N.Y. 10017

March 13–15 Washington, D.C.

1973 Conference on Prevention and Control of Oil Spills, American Petroleum Institute, EPA, and the U.S. Coast Guard

Covers subjects dealing with administrative, technical, and legal problems concerning oil spills. *Contact:* J. R. Gould, Secretary, 1973 Conf. on Prevention and Control of Oil Spills, Suite 700, 1629 K St., N.W., Washington, D.C. 20006

March 14–15 New York, N.Y.

ASME Incinerator Division Seminar. American Society of Mechanical Engineers

Will cover design criteria for incinerators. *Contact:* James A. Fife, Metcalf & Eddy, Statler Bldg., Boston, Mass. 02116

March 14–16 Chicago, Ill.

Industrial Water and Pollution Conference and Exposition. Water and Wastewater Equipment Manufacturers Association

Will focus on the industrial market of water supply, air, water, and noise pollution, and solid waste disposal. *Contact:* WWEMA, 744 Broad St., Newark, N.J. 07102

March 15–21 New York, N.Y.

National Association of Secondary Material Industries, Inc. 60th Annual Convention

Write: NASMI, 330 Madison Ave., New York, N.Y. 10017

March 18–21 Washington, D.C.

North American Wildlife & Natural Resources Conference. Wildlife Management Institute

Theme: "National resources and national priorities." *Write:* Laurence R. Jahn, Wildlife Management Institute, 1000 Vermont Ave., N.W., Washington, D.C. 20005

March 18–22 New York, N.Y.

Society of Toxicology. Annual Scientific Meeting

For more information: Robert A. Scala, Secretary, Society of Toxicology, Esso Research and Engineering Co., P.O. Box 45, Linden, N.J. 07036

March 19–23 Columbus, Ohio

Mid-West Workshop in Environmental Science. Ohio State University

Contact: John Lindamood, Dept. of Food Science and Nutrition, Ohio State University, 2121 Fyffe Rd., Columbus, Ohio 43210

March 20–22 Lake Kiamesha, N.Y.

Flexible Vinyls and Human Safety: An Objective Analysis. Society of Plastics Engineers

Will cover effects of phthalic acid ester plasticizers on human health as well as the environmental aspects of the use of lead, cadmium, mercury, and antimony in plastics colorants and stabilizers. *Write:* Roger P. Fox, Society of Plastics Engineers, 656 W. Putnam Ave., Greenwich, Conn. 06830

March 21–24 Logan, Utah

Symposium on Environmental Biogeochemistry. Utah State University and others

Will emphasize the cooperation of soil scientists, organic geochemists, and biologists in contributing to solving contemporary environmental problems. *Contact:* J. Skujins, Ecology Center, Utah State University, Logan, Utah 84322

March 23–25 Chicago, Ill.

National Symposium on the Future Status of Earth Resources in Society. National Assoc. of Geology Teachers

Contact: Musa Qutub, Symposium Chairman, Dept. of Earth Sciences, Northeastern Illinois University, Bryn Mawr at St. Louis Ave., Chicago, Ill. 60625

March 26–28 Syracuse, N.Y.

Food Processing Waste Management Conference. EPA, Cornell University, and National Canners Association

Focus will be on results of research and practical applications dealing with waste water management in the food processing industry. *Contact:* Agricultural Waste Management Program, 1973 Conference Committee, 207 Riley Robb, Cornell University, Ithaca, N.Y. 14850

March 28–30 Des Moines, Iowa

Soil Conservation Society of America. National Conservation Tillage Conference

Contact: H. Wayne Pritchard, Director, Soil Conservation Society of America, 7515 N.E. Ankeny Rd., Ankeny, Iowa 50021

March 29–30 St. Louis, Mo.

Greater St. Louis Section of APCA. Specialty Conference

Titled "Design, Operation, and Maintenance of High Efficiency Particulate Control Equipment." *Write:* James G. Richeson, District Manager, Carborundum Co.-The Pangborn Corp., 10406 Manchester, Kirkwood, Mo. 63122

March 29–30 Knoxville, Tenn.
Third Annual Industrial Air Pollution Control Conference. University of Tennessee and APCA

Contact: Joseph R. Duncan, Program Chairman, University of Tennessee, Dept. of Civil Engineering, Knoxville, Tenn. 37916

April 1–3 San Antonio, Tex.
National Petroleum Refiners Association. 71st Annual Meeting

Sessions on environmental requirements and associated costs. *Contact:* National Petroleum Refiners Assoc., Suite 802, 1725 Desales St., N.W., Washington, D.C. 20036

April 1–5 Anaheim, Calif.
Institute of Environmental Sciences. 19th Annual Technical/Tutorial Meeting and Equiment Exposition

Will provide a forum for exchange between educational, industrial, and governmental activities to impart U.S. environmental programs with realism. *Write:* Institute of Environmental Sciences, 940 E. Northwest Hwy., Mt. Prospect, Ill. 60056

April 1–6 Pacific Grove, Calif.
Environmental Needs as Part of the Quality System in Construction. Engineering Foundation

Fee: $175. *Contact:* Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

April 4–5 Edgewood Arsenal, Md.
Fourth Annual Symposium on Environmental Pollution. American Ordnance Assoc.

Theme will be "Reclamation and Disposal of Hazardous Materials." *Contact:* Commander Arthur Sullivan, USN (Ret.), American Ordnance Assoc., Union Trust Bldg., 740 15th St., N.W., Washington, D.C. 20005

April 5–9 Washington, D.C.
CIMAC 73—10th International Congress on Combustion Engineering. ASME and others

Covers field of internal combustion engines, environmental problems, alternative fuels, etc. *Contact:* ASME, 345 E. 47th St., New York, N.Y. 10017

April 8–11 Washington, D.C.
Second National Symposium on State Environmental Legislation. Council of State Governments

Contact: Council of State Governments, Iron Works Pike, Lexington, Ky. 40505

April 8–13 Dallas, Tex.
American Chemical Society. 165th ACS National Meeting

Write: A. T. Winstead, ACS, 1155 Sixteenth St., N.W., Washington, D.C. 20036

April 10–12 Charlotte, N.C.
1973 Textile Engineering Conference. American Society of Mechanical Engineers

Includes papers on environmental control in the textile industry. *Write:* ASME, 345 E. 47th St., New York, N.Y. 10017

April 16–18 Hiron, Ohio
Sixteenth Conference on Great Lakes Research. International Association for Great Lakes Research.

Covers physical, chemical, biological, engineering, and socio-economic problems of the Great Lakes. *Contact:* Charles E. Herdendorf, Center for Lake Erie Area Research, 484 W. 12th Ave., Columbus, Ohio 43210

April 23–27 Washington, D.C.
National Meeting on Complete Water Reuse. American Institute of Chemical Engineers and EPA

Sessions will cover the broad topics of engineering, administration, economics, and public. *Contact:* Larry Cecil, Chairman, Water Section, Environmental Division, AIChE, 345 E. 47th St., New York, N.Y. 10017

April 25–27 Palm Beach Shores, Fla.
American Nuclear Society and Marine Technology Society. National Topical Meeting

Theme "The Ocean, Nuclear Energy & Man." *Contact:* M. Jack Ohanian, Chairman, Dept. of Nuclear Engineering, University of Florida, Gainesville, Fla. 32601.

April 26–27 Durham, N.C.
National Symposium on Ultimate Disposal of Wastewaters and Their Residuals. Research Triangle Universities and others

Sessions on land disposal, marine disposal, sludge handling, design practice, recovery, and recycling. *Contact:* F. E. McJunkin, Associate Director, Water Resources Research Institute, North Carolina State Univ., 124 Riddick Bldg., Raleigh, N.C. 27607

April 28 Chicago, Ill.
Second Annual National Symposium on Societal Problems of Water Resources. Illinois Earth Science Assoc. and American Water Resources Assoc.

Contact: Musa Qutub, Symposium Chairman, Northeastern Illinois Univ., Bryn Mawr at St. Louis Ave., Chicago, Ill. 60625

April 29–May 2 St. Louis, Mo.
National Association for Environmental Education. 1973 Annual Meeting

Write: National Association for Environmental Education, P.O. Box 1295, Miami, Fla. 33143

April 29–May 2 Houston, Tex.
Fifth Annual Offshore Technology Conference. American Institute of Chemical Engineers and others

Session topics include: environmental conservation, control of oil spills, remote sensing and navigation, and other subjects. *Contact:* Offshore Technology Conference, 6200 N. Central Expressway, Dallas, Tex. 75206

May 1–3 Lafayette, Ind.
28th Annual Purdue Industrial Waste Conference. Purdue University

Will cover numerous phases of industrial waste treatment through research, design, operations, and/or case history aspects. *Write:* David W. Hawkins, Civil Engineering Dept., Purdue Univ., West Lafayette, Ind. 47907

May 9 Chagrin Falls, Ohio
4th Annual Engineering Your Environment Conference. Cleveland Engineering Society

Contact: Cleveland Engineering Society, 3100 Chester Ave., Cleveland, Ohio 44114

May 14–16 San Francisco, Calif.
Technical Association of the Pulp and Paper Industry. 1973 Environmental Conference.

Theme will be "Pollution Solutions." *Write:* B. G. Beeland, TAPPI, One Dunwoody Park, Atlanta, Ga. 30341

May 22–24 New York, N.Y.
1973 Pollution Engineering & Equipment Exposition & Conference. Technical Industry Expositions, Inc.

Contact: Technical Industry Expositions, Inc., 34 W. Putnam Ave., Greenwich, Conn. 06830

Courses

Feb. 19–20 Madison, Wis.
Institute of Solid Wastes As a Source of Energy. University of Wisconsin–Extension

Will deal with the environmental impact, economic feasibility, financing methods, and design of plants which burn municipal waste and produce heating and cooling. Fee: $100. *Write:* William C. Dries, Program Director, Univ. of Wis.–Extension, 432 N. Lake St., Madison, Wis. 53706

March 6–7 Madison, Wis.
Sanitary Engineering. University of Wisconsin–Extension

Fee: $70. *Contact:* University of Wisconsin–Extension, Dept. of Engineering, 432 N. Lake St., Madison, Wis. 53706

March 12–16 Madison, Wis.
Design of Air Pollution Control Facilities. University of Wisconsin-Extension

Fee: $275. *Write:* University of Wisconsin–Extension, Dept. of Engineering, 432 N. Lake St., Madison, Wis. 53706

March 19–23 Austin, Tex.
Advanced Water Pollution Control: Biological Waste Treatment. University of Texas at Austin

Write: Engineering Institutes, P.O. Box K, University of Texas at Austin, Austin, Tex. 78712

March 29–30 Milwaukee, Wis.
Water Pollution—Law & Regulation. University of Wisconsin-Extension

Fee: $95. *Contact:* University of Wisconsin-Extension, Dept. of Engineering, 600 W. Kilbourn Ave., Milwaukee, Wis. 53203

April 16–20 Nashville, Tenn.
Development of Design Criteria for Wastewater Treatment Processes. Vanderbilt University

Seminar will cover two categories: biological waste treatment and physical-chemical waste treatment. Fee: $275. *Write:* W. Wesley Eckenfelder, Box 6222, Station B, Vanderbilt University, Nashville, Tenn. 37235

April 16–20 Austin, Tex.
Advanced Water Pollution Control: Physical and Chemical Waste Treatment. University of Texas at Austin

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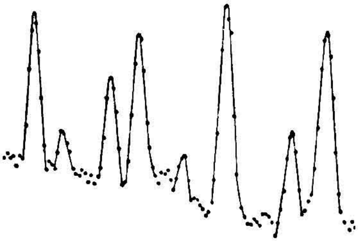

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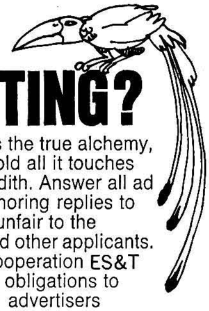

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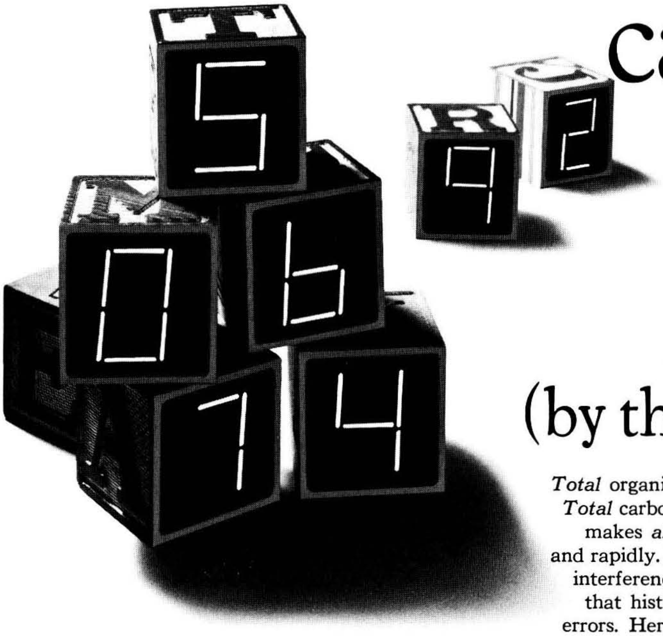
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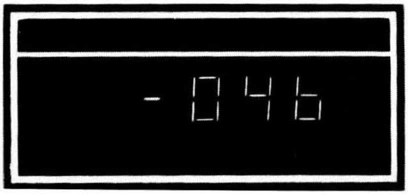
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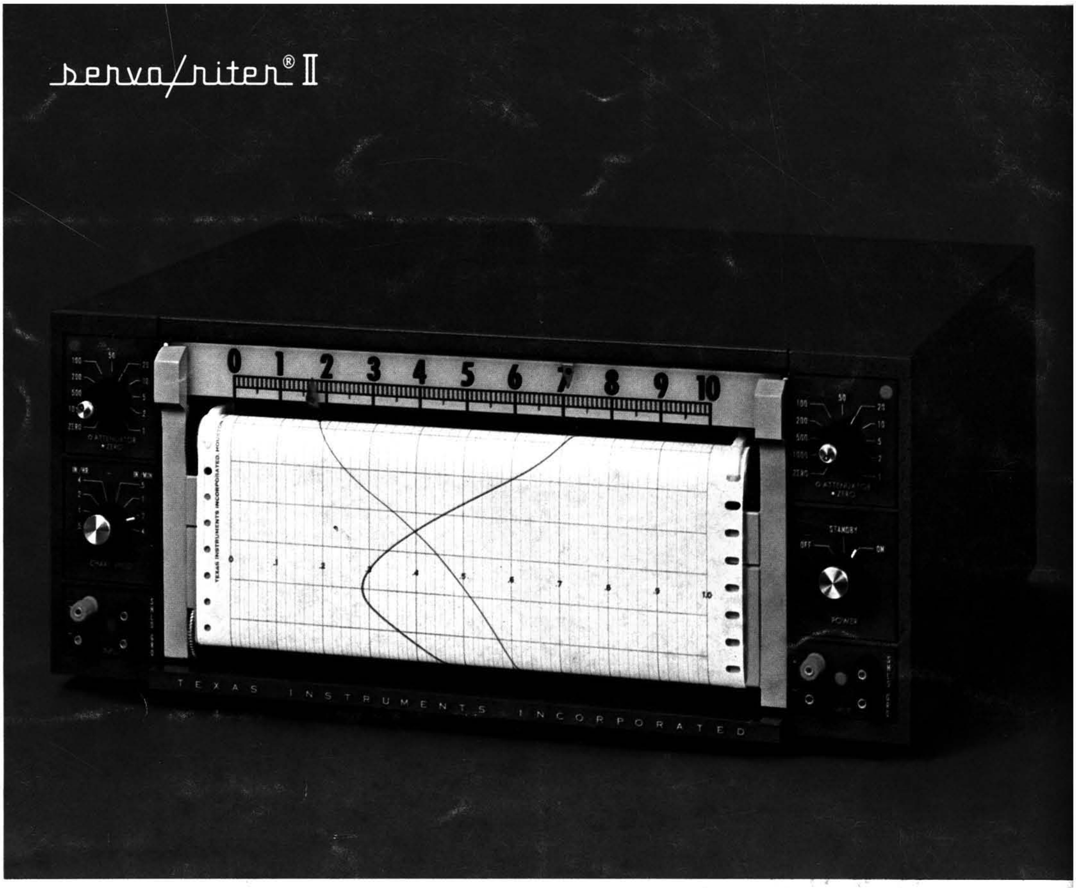
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STANDBY
OFF
ON
POWER

TI MO. 25