ENVIRONMENTAL Science & Technology

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FEBRUARY 1970



Oil spills: time for action 97

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ESTHAG

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Factors affecting the use of monomolecular surface films to control oil pollution on water

W. D. Garrett and W. R. Barger

One chemical approach to the problem of oil spills is the use of monolayer film forming materials. The film acts as a confining pressure to compress and reduce the surface area occupied by the spilled oil. These materials may prove useful in driving oil out of inaccessible locations between ships and under docks. Seven materials were evaluated, and films of dodecanol-1 and sorbitan monooleate were found effective for oil slicks whose thickness did not exceed 0.5-1.0 cm.

Removal of submicron particles in packed beds

J. T. Cookson

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Filtration efficiency depends on physical and chemical parameters which can be described by two steps—a particle transport and an attachment step. In this study, the chemical characteristics are maintained at optimum condition for virus attachment, but the physical characteristics are varied. Virus removal was monitored through nine carbon beds, each bed being subject to different flow rates. The virus removal closely followed mass transfer theory.

Capture of small particles by London Forces from low speed liquid flows

L. A. Spielman and S. L. Goren

The recent study has modified the existing filtration theory of such an event. The earlier theory of particle capture by interception from low speed flows predicts that the filter coefficients vary as the square of the particle size, the inverse cube of the collector size, and are independent of flow rate. But now, this study shows that the filter coefficients vary as the first power of the particle size, the inverse 2.5 power dependence on fiber size, and the inverse 0.25 power dependence on flow rate.

Accumulations of lead in soils for regions of high and low motor vehicle traffic density

A. L. Page and T. J. Ganje

Although regions of high motor vehicle traffic density (more than 580 vehicles per square mile) accumulate lead in the soil whereas regions of low motor vehicle traffic density (less than 80 vehicles per square mile) do not, the amounts of lead accumulated in the surface of soils (2.5 cm.) ranged from 15-36 p.p.m., based on the analysis of soil samples from 10 different locations (southern California) over the last 40 years. These amounts are considerably below levels which may cause toxicities to economic plants, or which may cause abnormally excessive accumulations of lead in the plants.

Hydrocarbon and carbon monoxide analysis by the selective combustion method

W. B. Innes and A. J. Andreatch

Automotive exhaust gases, a major factor in air pollution, can be analyzed by a new instrument which holds promise as a tool for economically detecting and correcting improper engine operation. The instrument can be tailored either to correlate roughly with the current flame ionization or infrared methods or to give good correspondence with probable future standards based on photochemical reactivity. The instrument also can be used to analyze other exhaust streams containing hydrocarbons and for air monitoring.

Direct gas chromatographic analysis of low molecular weight substituted organic compounds in emissions 150

T. A. Bellar and J. E. Sigsby

Photochemical oxidants such as oxygenated hydrocarbons in automotive exhaust gases and other combustion effluents can be analyzed directly using an automated gas chromatographic technique. In this way, C_2 through C_5 oxygenates from both vehicular and stationary emission sources and the ambient atmosphere are measured.

Communication

Possible source of atmospheric pollution of selenium 157

Y. Hashimoto, J. Y. Hwang, and S. Yanagisawa

Fuel oils such as raw and heavy petroleum can be an important source of selenium in the atmosphere. Determination of the selenium to sulfur ratio in these materials is used as the method of tracing this pollutant source. Analytical data show that the Se:S ratio in fuel oils is the same order of magnitude as that found in atmospheric precipitation and particulates.

editorial

Air pollution and health

The right to breathe clean air may have to be established before air pollution control can really begin in earnest

It is an unfortunate—but nevertheless accurate—characteristic of such industrialized societies as ours that the richest areas usually are the dirtiest. The old Yorkshire saying "Where there's muck, there's brass" puts it quite succinctly, if smugly. Even today, industrial managers in America sometimes smilingly refer to the acrid stench from their profitable plants as "the smell of money." As a society, we somehow have become convinced that dirty air is an unavoidable adjunct to a booming industrial economy.

In the most industrialized and prosperous parts of the world, there can be little argument that the local air is dangerous to breathe. In the U.S., we have the laughable situation in which local health officials in reseveral urban regions seriously doubt whether the air quality standards adopted for those regions can be met. In all cases, these standards were adopted on the basis of health criteria published by the federal government. In other words, responsible officials are saying quite soberly that public health is likely to suffer because industry cannot or will not reduce its emissions to the required extent.

One might usefully challenge the assumption that less than good health is the price that must be paid for the benefit of living in a prosperous society. Are we really faced with a choice between being poor but healthy or being rich but unhealthy? Many experts do not think so. More important, it is becoming increasingly evident that people are no longer willing to tolerate, as they have for so long, an assault on their lungs, even though mounted in the name of prosperity. The public has shown much increased interest in air pollution, especially air pollution regulations. In one state, air quality standards had to be revised and made more stringent because of public pressure. This close interest is likely to continue and even intensify, and industrialists would do well to take it seriously, because, one day soon, they will be forced to take action.

One hundred years ago, workers were resigned to the most dreadful working conditions they had no choice but to be so. In this century, however, legislation has established the right of the worker to a reasonably safe and healthful working environment. In retrospect, providing workers with a safe place to work does not seem to have put industry out of business, any more than paid vacations have, although there were, doubtless, many forebodings of doom when concessions first were made to employees.

What may be looming ahead very soon is the establishment of the right of workers (and thus of all the people) to inhabit a safe and healthful *living* environment away from work. Perhaps, only when this right is established will air pollution control begin in earnest. Certainly, control will cost lots of money—ES&T has repeatedly emphasized that fact. But the benefits of good health for all the people in urban as well as in rural areas—are important enough to make the effort worthwhile.

D. H. Michael Loven

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viewpoint

John T. Middleton Commissioner National Air Pollution Control Administration

Sulfur oxides must be controlled

Just a couple of years ago, we were estimating that about 26 million tons of sulfur oxides were being emitted annually into the atmosphere over the U.S.-an assessment which proved to be conservative. As we gathered better data and as demand for energy continued to expand, our estimate moved up to 31 million tons. The estimate for 1970 is 37 million tons. By 1990, our potential to emit sulfur oxides could hit 95 million tons-and again our calculations may well prove on the conservative side. Power plants-the major source of sulfur oxides pollution-are being built more rapidly than indicated by earlier projections, as nuclear power plants are coming in more slowly than was projected. The result probably will be a large increase in plants burning coal or oil (particularly coal) and, along with it, increase in the potential for sulfur oxides pollution.

This growing potential represents a serious problem. Sulfur oxides irritate the respiratory system, particularly in the young, the old, and those already crippled with respiratory afflictions. They attack a wide variety of materials. Metals corrode, paints disintegrate, fibers weaken and fade, building materials discolor and deteriorate. Agricultural production drops as plant growth and yield are suppressed. Sulfur oxides contribute to the reduction in visibility that often accompanies air pollution. Health, economics, aesthetics—all suffer when our air is polluted with sulfur oxides.

Learning how to control this pollution represents a major effort of the National Air Pollution Control Administration. Although scattered projects were underway earlier, fiscal year 1968 marks the beginning of a comprehensive sulfur oxides research program. We spent \$9.8 million on the program that year; in fiscal 1970, we will spend an estimated \$12.5 million.

The burning of fossil fuel—by public utilities, industry, and commercial and residential buildings—accounts for about 75% of the total national emissions of sulfur oxides. Industrial processes, principally smelting of nonferrous metals and refining of petroleum, account for most of the remainder. To halt the alarming rise of pollution by sulfur oxides requires new or improved methods for control of all these sources. Varying as they do in size, design, age, and location, they call for a diversity of highly flexible processes.

We are putting major emphasis on developing control technology for public utilities. Since they account for more than half the national emissions, progress there could mean a big payoff. The technology developed for utilities also may be applicable with suitable modification to large industrial combustion operations. For the most part, however, in industry, as in commercial and residential combustion, use of low-sulfur fuel appears to be the most practical solution at present.

Defining the technical problems and finding practical solutions to the control of sulfur oxides pollution is a tremendous task—one the federal government can't do by itself. Private industry knows the problems first hand, and it has the skills to carry a control idea through all the developmental stages. Even more importantly, industry alone can integrate new processes or devices into existing technology. The federal government is beginning to tap the technical resources of the private sector. In fiscal 1969, we had about 200 contracts totaling \$20 million with the private sector; a little less than half the funds went to sulfur oxides projects.

But the nation needs more than industry's technical skills. It also needs its financial resources. Fortunately, industry is beginning to respond. For example, the petroleum industry spent \$23 million during 1966, 1967, and 1968 on research and development on sulfur oxides, according to estimates of the American Petroleum Institute. The chemical industry is beginning to put its own money into the effort. But we need more help, and especially from the electric power industry. There are, of course, some economic risks in such efforts. Thus far, the industry has not assumed its rightful share of these risks. It *must* do so. In particular, we need industry help in large-scale demonstrations of techniques that have cleared testing in laboratories and pilot plants.

Practical solutions, economic solutions can be found to control sulfur oxides research—but only with participation of all segments of the American economy.



John T. Middleton has been NAPCA commissioner since January 1967. Formerly, he was professor at the University of California, Riverside, and chairman of the California Motor Vehicle Pollution Control Board

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WASHINGTON President Nixon aims for environmental quality

Departing from the standard form for a State of the Union message, President Nixon looked ahead into all the years of the 70's decade with a vision for clean air and clean water. By 1976—the 200th anniversary of this nation—the administration hopes to have waste treatment plants in all needy municipalities and plans soon to send Congress its \$10 billion, five year program along with a balanced 1971 budget.

Water pollution control agency realigns

"The Federal Water Pollution Control Administration (FWPCA) will be the cutting edge in dealing with one of our most pressing environmental problems," says David D. Dominick, FWPCA commissioner. Last month, Dominick announced four top management posts in his office and other changes in headquarters and regional staffs. New assignees and incumbents include associate commissioner Bryan F. LaPlante; executive assistant to the commissioner Frank M. Covington; and scientific and technical advisor to the commissioner John T. Barnhill. In addition, an office of assistant commissioner for environmental and program planning will be headed by Allan Hirsch. Other headquarters changes include: • Designation of an office of enforcement and standards compliance—formerly the office of enforcement. • Creation of an office of oil and hazardous materials headed by Kenneth E. Biglane. • Appointment of a new assistant commissioner for operations—Eugene T. Jensen, FWPCA's Middle Atlantic regional director will be nominated for the position.

FPC reports on its environmental activities

The Federal Power Commission's (FPC) actions to protect the environment while providing for orderly growth of the electric power and natural gas industries, which it regulates, include: • Collecting data useful in pollution control activities. • Assisting federal pollution control agencies. • Adopting appropriate additional regulations covering the licensing of hydroelectric projects. FPC will issue its updated National Power Survey later this year, according to its report, "Federal Power Commission Interests in Environmental Concerns Affecting the Electric Power and Natural Gas Industries." Recently, FPC announced a new office of advisor on environmental quality to be headed by Frederick H. Warren.

Watchdog agency is needed for environmental protection

Sen. Edmund S. Muskie (D.-Me.), a leader in the nation's antipollution fight, called for the creation of a new independent agency to exercise the regulatory functions associated with environmental protection, at the recent AAAS meeting (Boston, Mass.). Critical of the Nixon administration for showing more form than substance on environmental protection policies, and of the proliferation of activities and overlapping of responsibilities in the federal bureaucracy, Sen. Muskie noted that the agency would have the following responsibilities:
Developing and implementing federal environmental quality standards.
Supporting basic research on problem of environmental quality.
Stimulating and supporting research on control techniques.
Providing technical assistance to state, interstate, and local agencies.

FWPCA's new regional directors

Southeast H. W. Poston

Middle Atlantic John R. Thoman

South Central Richard A. Vanderhoof

Ohio William C. Galegar

STATES North Carolina has first air pollution consortium

Triangle Universities Consortium on Air Pollution will pool the training resources of three universities—Duke, North Carolina State, and the University of North Carolina (UNC). One of the main functions of the consortium is to furnish technical advice to state and local air pollution control agencies. The manpower in these agencies nationwide must increase threefold if the 1967 federal act is to be fully implemented. A course in meteorology, offered during the 1970 spring term, is the first educational venture of the consortium. Last November, UNC (Chapel Hill) hosted an international symposium on urban diffusion modeling; other air pollution training consortia are planned for the southern California, Gulf, and New York areas.

Airlines pressured to install pollution controls

Aircraft emissions may be under control sooner than most air pollution control experts had expected. In a New Jersey court action, the airlines operating from Newark airport (ES&T, October 1969, page 897) have been given until the ninth of this month to come forth with a plan to correct air pollution from aircraft. In a similar type action, Illinois has filed suit against airlines operating from two Chicago airports. However, one airline, Overseas National Airways (ONA), based in New York City, leads tre industry's attempt to control jet aircraft smoke. ONA has written the National Air Pollution Control Administration (NAPCA) that it will install smokeless combustors on all its JT₈D engines during the first scheduled major overhaul after the new combustors become available.

Progress made on water facilities

Created in 1967 as a special task force to assist municipalities, the New York State Pure Waters Authority now has contracts valued at more than \$46 million for pollution control construction with 21 municipalities, according to its chairman, George A. Dudley. By the end of last year, the authority also had: • Arranged 26 loan agreements for a total of \$27 million to help finance construction. • Signed contracts to supply advisory services to 12 other communities. • Conducted precontract negotation for other projects valued at \$72 million. In 1967, Pennsylvania voters approved a \$500 million conservation bond issue, of which \$100 million was earmarked for municipal waste treatment facilities. By the end of 1969, 166 water projects were in various stages of completion, according to Wesley E. Gilbertson, deputy secretary for environmental protection in the state department of health.

New England installs environmental warning system

Covering five major river basins and capable of providing early environmental warning data for air pollution, meteorology, hurricanes, flood conditions, forest fires, and other phenomenon, the Automatic Hydrologic Radio Reporting Network was made operational last month. The network includes 41 remote reporting stations from northern Vermont to Long Island Sound. A prime purpose of the network is to determine the early and efficient operations in flood control dams, hurricane barriers, and local flood control projects which were constructed at a cost of \$300 million.



Tidal station at Old Saybrook, Conn.

INDUSTRY Control equipment markets look bright

Pollution control equipment markets may be one bright spot in an otherwise sluggish 1970 economy. James B. Cook, Jr., president of the Water and Waste Equipment Manufacturers Association, notes that the \$800 million federal appropriation for water treatment facilities is within \$200 million of authorized funding, and projects the effect of this record appropriation on the total equipment market. In 1968, when Congress appropriated only \$203 million, local governments took up the slack and actually spent \$1.35 billion; if this ratio of federal to local spending holds for 1970, a total expenditure of \$5 billion could be projected. Even half this amount of spending by municipalities would still be nearly double that of 1968, Cook argues. Carborundum president William H. Wendel is equally optimistic: "The market for pollution abatement equipment and supplies will grow significantly in 1970, regardless of what may happen in other sectors of the capital goods field." Carborundum, Wendel noted, is expanding its activities in air and water pollution control systems and is entering the solid waste disposal field.

Wisconsin code curbs pulp industry expansion

A Wisconsin pulp and paper industry executive has stated that new state pollution abatement orders effectively prohibit any significant increase in production of mills along the Fox River. W. R. Nelson, director of research and development for Green Bay Packaging, told a meeting of the Great Lakes Basin Commission that our expanding economy will demand more pulp, but "it will have to be manufactured elsewhere. This will create another waste load for some other river basin." Referring to recent state orders that mills must control 95% of dissolved solids and 99% of suspended solids, Nelson predicted the industry somehow will meet these standards. He added, "We who live here must protect our region from disruptive changes that would impair our ability to work and earn a living in today's competitive world. Yet, we must achieve results that produce the maximum benefits in the shortest time with best use of people, materials, and money." That is a tall order, but one that we have to meet."

Firms announce new pollution control plans

• Chemagro Corp. is planning a \$2.5 million control facility for its Kansas City (Mo.) agricultural chemicals complex. The first stage, a phosphate removal process, is due on stream in July, and a second stage, an activated sludge unit, will be finished in 1973. • Firestone's defense products division has installed a unit to treat chromic acid waste from a 90 millimeter gun plating line (Akron, Ohio). The system uses sodium bisulfite reduction of the chromates, neutralization with caustic, and sedimentation. • Witco Chemicals has announced construction of a waste water treatment facility at its specialty organic chemicals plant (Petrolia, Pa.). The 400,000 g.p.d. unit is being built by Monsanto's Biodize division. • National Lead will lay out \$9 million in the next three years for air pollution control equipment at its titanium dioxide plant (Sayreville, N.J.) to comply with state air quality standards; the expenditure is in addition to \$5.5 million already spent at the Sayreville facility.



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TECHNOLOGY A second look at dry limestone injection

Evaluation of dry limestone injection for sulfur oxides removal is moving into a second phase: A new 18 month, \$3.3 million NAPCA study at TVA's Shawnee station (Paducah, Ky.) to tune up the process. NAPCA admits that earlier tests achieved only 20-30% removal, and that the goal of the new program is 50% or better. Research-Cottrell, Inc., (Bound Brook, N.J.) has a NAPCA contract, apparently part of the new program, to study one minor shortcoming of the limestone process—its effect on the electrostatic precipitators used for particulate control. The company says the NAPCA contract recognizes that removal of sulfur oxides can affect collection efficiency of precipitators not designed for low sulfur applications. A previous NAPCA report blamed the reduced efficiency on increased resistivity of SO₃-free flue gas, and hinted that this might be overcome by precipitator redesign and operation at higher temperatures.

Interest peaks in low emission vehicles

Federal and industry interest in low emission motor vehicles continues to gain momentum: • A recent Institute of Gas Technology seminar in Chicago, which attracted more than 200 representatives of the auto and utility industries, featured a display of four conventional passenger cars that had been converted by gas companies to operate on natural gas. Robert M. O'Mahoney of the General Services Administration (GSA) told the seminar that GSA, which is testing 12 such vehicles, expects 1000 to be in use by year's end, and that, by 1973, the number may grow to 3000. • Low emission mass transit vehicles are also in the offing. General Motor's truck and coach division has made available to the Department of Transportation for testing five prototype modification packages for diesel powered transit buses. Transportation Secretary John A. Volpe says the units may cut hydrocarbon losses by 90% and CO emissions by 30%. • In California, four firms have been selected to design and supply steam powered buses for evaluation by two California transit lines. The companies are: William P. Brobeck and Associates (Berkeley, Calif.), General Steam Corp. (Newport Beach, Calif.), Lear Motors (Reno, Nev.), and Steam Power Systems (San Diego, Calif.).

Hickel asks review of deep well practices

A U.S. Geological Survey report on underground waste disposal has prompted Interior Secretary Walter J. Hickel to ask for a review of present practices and regulations. Hickel said underground waste injection is increasing dramatically, and the report "serves as a sober warning." Written by Arthur Piper, the report attacks several common assumptions behind deep well injection—for example, that the total pore space of an aquifer is available for receiving liquid waste, and that down-fold rock formations form natural waste traps. More often, the report points out, pore spaces already are filled with brine, and abnormal pressure may lead to waste leakage, since movements of fluids are determined by hydraulic gradients rather than by geological configurations. Hickel has directed the Geological Survey "to take the lead in a research program to evaluate the effects of underground waste disposal." Up to this time, much of Interior's work on deep well disposal was centered in FWPCA.



Natural gas fueled vehicles on view

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Oil spills: An environmental threat

What will the year 1970 hold in the way of a major oil spill incident? Hopefully, nothing (and, hopefully, not Alaska). But previous years have produced significant incidents—the *Torrey Canyon* grounding (1967), the *Ocean Eagle* spill in San Juan Harbor (1968), and the Santa Barbara Channel blowout (1969).

It is true that the nation is alerted to the dangers of widespread pollution by such disasters. But the U.S. still does not have adequate oil spill technology, and has not yet provided the means for bringing an adequate technology into being. Such are the conclusions of the recent report by the President's special panel on oil spills, comprised of 12 distinguished scientists and engineers and chaired by the President's science adviser, Lee A. Du-Bridge.

Had it not been for the Santa Barbara blowout (January 28, 1969), perhaps the petroleum industry would not have seen fit to hold this recent conference. Sponsored by the American Petroleum Institute (API) and the Federal Water Pollution Control Administration (FWPCA), the Joint Conference on Prevention and Control of Oil Spills (New York City) drew more than 1100 attendees to hear 30 papers on the subject and to see the wares of more than 40 exhibitors; not surprisingly, 10% of the attendees came from foreign countries.

But a massive spill such as those that receive headlines is not the only concern of the U.S. and oil companies around the world. "Recently, the U.S. Coast Guard estimated that the nation may be experiencing a spillage of polluting materials to U.S. waters approaching 10,000 incidents annually, with oil leading all other categories by a ratio of about three to one," says Kenneth E. Biglane, director of FWPCA's Office of Oil and Hazardous Materials.

The U.S. arsenal of oil combatants includes the National Contingency Plan, industry cooperatives, physical corralling and removal devices, chemicals, industry and government sponsored research and development contracts, and industry and government



Slick. Oil can spread on water to 1/100th of an inch over a 25 square mile area in eight hours making removal operations extremely troublesome

members who stand ready to assume their responsibility in cleanup.

The problem boils down to one of how the U.S. proceeds with this arsenal, and this concern causes differences of opinion. "Some would have the public and others believe that a single technique or system, applied to either the control or cleanup of the oil spill, is the ultimate goal in the problem. Those of us in the FWPCA do not happen to share this view and are recommending that we continue to concentrate our research and operational efforts along the lines of multiple systems response as opposed to single systems panaceas," Biglane elaborates.

Prevention plans

The National Contingency Plan completed in September 1968 and approved in November of the same year —is the first item in the U.S. arsenal. What the plan does nationwide is to provide a mobilization scheme in the event of a major oil spill incident (Es&T, July 1968, page 512). Other nations have similar lines of defense. Last March, Britain and eight other countries joined in signing the North Sea Pact. "The Board of Trade has



outlook

Aerial view. Santa Barbara leak spreads oil over a wide area of channel water

been charged with the responsibility of dealing with oil on the seas in excess of one mile from United Kingdom coasts," says H. Jagger, pollution control coordinator, Esso Petroleum Co., Ltd. (London).

On the industry scene, oil companies now are assisting one another on oil spills. Referred to as cooperatives, an agreement is made in advance by an oil company to help a neighbor who has an oil spill. "Today, the petroleum industry has 23 cooperatives fully operational and another 27 in the development stages," says Gulf Oil Corp.'s Ernest Cotton.

Removal

Once the oil is on the water it becomes a difficult and expensive operation to remove it. The next line of defense is corralling and containment of the oil. If this is successful, the physical removal of the oil from the water by vacuum line transfer, skimming devices, or separators should be tried next. And if the oil gets on the beach, use straw to absorb it. Other than these rather elementary rules of operation, there are no remedies.

Oil spreads quite rapidly from a catastrophic release. Comdr. W. E. Lehr (U.S. Coast Guard) estimates that oil has been known to spread 1/100 of an inch over a 25 square mile area in eight hours, for example. Consequently, for the oil removal equipment to be effective, it must be modularized and capable of aerial transport and delivery within an extremely short period of time. Furthermore, the equipment must constitute a total system with all parts being compatible. Earlier operational experience



Removal. Vacuum lines are used after floating booms corral the spilled oil

revealed that, in some instances, booms from different manufacturers could not be joined together. "Additionally, the booms should be able to perform efficiently in 40 m.p.h. winds, currents of two knots, and 10 foot waves," says Lehr. "A readily transportable system will be ready in early 1970."

Chemicals also are in the oil combatants arsenal; more than 400 are on the market today for dealing with spilled oil. U.K. spokesman J. Wardley Smith, of the Ministry of Technology, notes that, despite the large quantities of the toxic solvent emulsifier mixtures which were used around the Cornish coast at the time of the *Torrey Canyon* incident, no reduction in the total weight of fish caught was observed, nor was there a reduction in the weight of crabs, shellfish, and the like landed in the two subsequent years.

However, these chemicals are not recommended for use in rivers, lakes, and estuaries. Nevertheless, a dispersant toxicity test procedure has been developed which should help in the further evaluation of these materials, according to Clarence M. Tarzwell, director of National Marine Water Quality Laboratory (Narragansett, R.I.). Hopefully, it will be issued as a standard test early this year.

Another procedure which has been proposed for evaluation was developed at FWPCA's Water Quality Laboratory (Edison, N.J.). Thomas A. Murphy notes that results from the procedure, referred to as the Simulated Environmental Tank (SET) test, correspond well with results from field tests. In Murphy's presentation, data are given for five families of dispersants (each chemically distinct) with four test oils.

Research and development

Both the federal government and the petroleum industry sponsor a number of projects which aim at increased knowledge of how to deal with oil spills. Similarly, the British government and the U.K. oil industry support an ongoing R&D program.

Last year, API spent more than \$600,000 on seven industrial R&D projects; reports are due early this year. A Battelle Memorial Institute report contains a compendium listing all available agents for oil spill cleanup, giving information on the manufacturers' recommendations, availability, cost, physical properties, etc. An Arthur D. Little, Inc., report determines where various types of agents can be used best. According to Little's findings, the only operationally feasible method of oil pollution cleanup appears to be physical absorption by the use of straw.

"The federal R&D program in oil and hazardous substances spills is emerging from the planning stage and beginning to make progress," says Allen Cywin, director of FWPCA's division of applied science and technology.

Today, 55 federal contracts are active at a funding level of about \$10 million. These studies can be divided into the following categories:

- Prevention of oil (17).
- Surveillance (11).
- Control of spills (14).
- Effects of spills (8).
- Beach and shore restoration (3).
- Miscellaneous (2).

Western Co. (Richardson, Tex.) is investigating techniques for gelling tanker cargoes to prevent oil loss in the event of an accident. American Oil Co. (Chicago, Ill.) has been awarded the largest federal oil contract, nearly \$1.75 million, for demonstration of a 30 m.g.d. plant for treating refinery effluent by a combination of biological conditioning, chemical coagulation, and air flotation. Another large contract, about \$1.5 million, has been awarded to National Oil Recovery Corp. (Bayonne, N.J.) for demonstration of a process for the complete conversion of crankcase waste oil into useful products without producing pollutant materials.

Other federal contracts have been awarded for the development of oil sensors, beach cleanup, and better mechanical recovery and separation devices. For beach cleanup, a sand cleaning process is being developed by Aerojet General Corp. (El Monte, Calif.). A full-scale 30 ton per hour unit will be demonstrated this summer, Cywin asserts.

Industry steps

"Until recently, oil pollution was looked upon mostly as a problem associated with tanker operations," says L. P. Haxby, chairman of the API subcommittee on oil spills cleanup. "The API Board of Directors has, thus far, appropriated \$1.2 million to fund the work of the subcommittee through 1970. Most of the money will go for R&D on new methods of cleanup."

The load-on-top method of retaining oily residues on board for disposal in proper facilities ashore is proving beneficial for eliminating pollution from tanker discharges.

In addition, the industry voluntary plan for tanker liability is well underway, according to the API spokesman. "More than half of the free world's tanker owners are now enrolled in the plan," Haxby notes. "Referred to as Tanker Owners Voluntary Agreement concerning Liability for Oil Pollution (TOVALOP), the plan provides liability at \$100 per gross registered ton or \$10 million, whichever is smaller. Under the plan, participating tanker owners accept responsibility to reimburse any national government for the costs it incurs in cleaning up oil spills they negligently cause."

Cleanup costs

At the recent conference, Thomas H. Gaines (Union Oil Co. of Calif.) noted that Santa Barbara cleanup costs ran to about \$4.5 million. In addition, pending legal actions against Union Oil approximate \$2.5 billion.

Although the governments of France and the U.K. brought suits against the owners of the *Torrey Canyon* for \$22 million, the settlement was made out of court last November for \$7.2 million.

On the average, cleanup costs for massive spills are approximately \$1 per gallon, according to FWPCA's Biglane. But the costs may be a bit higher for inland waters. The Battelle Northwest report notes that the cost for removing oils from harbors ranges from \$1.35-3.00 per gallon. Other data are presented in the Little, Inc., report which notes that the direct costs for oil cleanup range from \$1700-4100 for small (1000 gallons) harbor spills, from \$64,000-115,000 for a medium (100,000 gallons) offshore spill, and from \$4.5-8.5 million for a large (10 million gallons or 30,000 tons) offshore spill.

IMCO

Two international conventions on oil spills and cleanup are the most important recent achievements of the Intergovernmental Maritime Consultative Organization (IMCO), the specialized agency of the United Nations that provides cooperation in all shipping matters, and involves 68 member governments (Es&T, July 1968, page 510). At its International Legal Conference on Marine Pollution Damage, held in Brussels last November, IMCO adopted two conventions which include authority for:

• Right of coastal states to intervene in oil spill casualties if their shoreline is threatened by the incident.



Absorption. Straw proves its usefulness as Number 1 material for cleanup

• Civil liability to both coastal states and owners of shoreline property for oil cleanup.

"The purpose of this conference was to finalize the conventions which were in the draft stage by IMCO's legal committee for the last two years," says Louis P. Georgantas, a member of the U.S. delegation from the State Department. These conventions are significant because they hold ship owners and operators to strict liability and are broader than pending U.S. legislation which does not cover third party liability, and is limited only to the ability of the U.S. government for oil cleanup.

The first convention applies only to the high seas, outside the territorial limit, so that this international convention does not interfere with the rights of a coastal state. It is a fact that this convention effectively would have taken care of the situation presented by the Torrey Canyon, for example, when it grounded off the English coast. Under this convention, the U.K. government would have had authority to take immediate cleanup action and prevent further damage from the oil being spilled. Precious time was lost in the Torrey Canyon incident over the question of legal authority to take action against the grounded tanker.

The second convention imposes strict liability on owners and operators with certain exceptions including acts of God, war, and negligence of the coastal state. Limits of liability are set at \$134 per gross registered ton or \$14 million, whichever is the lesser. The surprising event at the Brussels conference was the fact that the London P&I Clubs, the insurance underwriters for tanker liability, were able to secure financial backers for underwriting such policies. Peter N. Miller, the spokesman for the insurance underwriters, was able to ensure that these limits of liability specified in the second convention were insurable.

In practice, under the second convention, compulsory financial responsibility is required, and certificates to this effect would be issued by the state of registry verifying that the vessel had financial liability to cover spills of any oil by that vessel. Also, a state could exclude a ship from its port if the ship did not have this certificate of financial liability. A state also could exclude ships from noncontracting states (not parties to the convention) unless they otherwise had obtained a certificate of insurance.

By way of an example of strict liability, Georgantas cites the case of a moored tanker containing oil that is rammed by a second cargo ship carrying dry goods, resulting in the spill of oil from the tanker. The moored vessel is held liable for the damage caused by the oil, but the tanker's owner then can take legal action against the owner of the dry goods vessel to recoup his losses. In any case, the victims are compensated.

Ratification by each IMCO member government is the next step for these conventions. "Although 49 governments participated in the Brussels conference, only 20 had authority to sign the conventions for their governments, and 16 did so, including the U.S. and leading European industrial countries —Germany, France, Italy, and the U.K. Although the Scandanavian countries—leaders in tanker tonnage—did not sign these conventions, their representatives voted for them.

In the U.S., ratification will proceed in the following manner: The State Department will submit a request to the U.S. Senate asking advice and consent for the U.S. government to become a party to the convention. Then, after hearings, the Senate will vote on the proposal. A two thirds vote by the Senate and signature by the President will make the conventions binding on the part of the U.S.

When ratified, these conventions become binding internationally. "The coastal states intervention convention becomes binding when 15 member governments ratify the convention, and the civil liability convention becomes binding after eight IMCO member states ratify the convention, but five of the eight must have more than 1 million tanker tonnage each," Georgantas says.

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Detergent phosphates under fire

Ban on phosphate builders debated in Congress

The problem of the role of detergent phosphates in the eutrophication of the nation's lakes and waterways-a problem which has been waiting in the wings for some time-finally has come center stage. In mid-December, Rep. H. S. Reuss (D.-Wis.) held a two day round of hearings before the House Subcommittee on Conservation and Natural Resources devoted to the question of replacement of phosphate builders with less innocuous substances. At issue was Reuss' bill, H.R. 12435, which is before the House Committee on Public Works. The bill would effectively ban the manufacture or importing into the U.S. of phosphate-based detergents. The hearings took on added weight in light of the findings of the International Joint Commission advisory group on the pollution of the lower Great Lakes (ES&T, December 1969, page 1243). It was obvious that the recommendations to the commission on phosphate controls were behind much of the committee's probing.

The witnesses summoned to testify before Rep. Reuss' committee presented a broad spectrum of opinion on the advisability-and efficacy-of such stern measures as the Reuss bill. Charles G. Bueltman, vice president and technical director of the Soap and Detergents Association (SDA), contended that "there are no definitive data establishing the impact of detergent phosphates on algal growth," and that, despite substantial efforts within the detergent industry, no suitable phosphate substitute has been found. Bueltman called for further work on advanced technology for waste water treatment and on the question of whether control of other biological cycles, such as algal carbon dioxide requirements, might be the most effective way of controlling eutrophication.

In support of the SDA position, spokesmen for the three major detergent manufacturers (Colgate, Procter & Gamble, and Lever Brothers) pointed out that the research for more effective nonphosphate builders has had top priority among detergent makers and raw material suppliers for a number of years, if only for competitive reasons. Despite this effort, the detergent makers contended, the industry has not found a substitute material of demonstrated safety to aquatic environments that will meet performance standards which detergent consumers have come to expect.

Substitutes

Other witnesses took issue with the SDA position on the availability of suitable phosphate substitutes. John J. Singer, Jr., president of Hampshire Chemical division of W.R. Grace, presented a brief for what appears to be the front running candidate as a replacement for phosphate buildersnitrilotriacetic acid (NTA). "While Hampshire still feels that the best possible detergent is made with a combination of both NTA and polyphosphates, there are indications that NTA, either alone or with greatly reduced polyphosphate levels, can fill the role of the builder in a detergent," said Singer.

P. H. Jones, a microbiologist at the University of Toronto's civil engineering department, described work being



done at Toronto on the development of phosphate-free detergents. He said that this work on NTA, which has included manufacture of 50 pound lots by commercial methods of synthesis, for consumer evaluation, shows these detergents to be very suitable, and better than some commercial brands.

I. A. Eldib, president of Eldib Research and Engineering, maintained that polyelectrolyte builders such as carboxymethyl cellulose also are a readily available substitute for phosphates. "We have found that laundry household detergents built only with polyelectrolytes can indeed be successfully spray dried into a product suitable for the housewife," Eldib said. Furthermore, polyelectrolytes, which contain only carbon, hydrogen, and oxygen, are biodegradable, and preliminary testing shows adequate cleaning effectiveness, Eldib added.

Middle ground

Interior Department spokesmen, while agreeing with the theory that detergent phosphates eventually must be eliminated, testified against any such precipitate action as the Reuss bill. Undersecretary Carl Klein held that "reducing the amount of phosphates in detergent formulations, or even eliminating phosphorus altogether, should be put on as tight a time schedule as possible. Nevertheless, we do not believe that the introduction of substitutes for phosphates should be forced by legislative edict at this time."

The introduction of large amounts of a relatively unknown material, such as a substitute builder, is a major concern of Federal Water Pollution Control Administration (FWPCA) commissioner David P. Dominick. He pointed out that substitute materials can not now be evaluated adequately as to their eutrophication potential. Dominick added that only when the joint industry-government task force on eutrophication completes development of a provisional algal assay procedure (PAAP) will FWPCA be able to consider phosphate replacement as a viable method of pollution control.

Work on the PAAP test is scheduled for completion by 1972. In the interim, both Klein and Dominick spoke strongly for vigorous development of advanced waste treatment methods for phosphate removal. Such treatment facilities, they argue, will be needed even after the PAAP test paves the way for eventual detergent phosphate replacement, in order to cope with the 680 million pounds per year of phosphorus that enter waste streams from sources not associated with detergents-mainly human wastes and urban and farm runoff. "Our primary thrust in controlling the phosphorus problem has been the development of phosphorus removal technology at municipal waste treatment plants because it attacks all of the phosphorus in municipal wastes regardless of its origin," Klein said.

Role of builders

The current controversy over phosphate detergent builders invariably brings to mind the detergent foam problem that led the industry in 1965– 66 to convert from nondegradable, alkyl benzene sulfonate (ABS) surfactants to linear alkylate sulfonate (LAS) materials in detergent formulations. Indeed, there is at least one parallel: Although the industry had a 10 year, \$150 million conversion project underway prior to 1965, it was a Reuss bill in Congress that heightened interest in the problem.

What effect the threat of H.R. 12435 will have remains to be seen, especially since the phosphate builder problem is a distinctly different one than the ABS-LAS conversion. The ABS problem involved the detergent surfactant—the active material itself—and the conversion to LAS involved simply the commercial development and production of a material from the same general chemical class as ABS. Detergent builders, on the other hand, perform a more subtle, but, in some ways, a much more complex, role in detergent formulations.

Builders by themselves possess little or no detergent effectiveness, but, when used in combination with such surfactants as LAS, produce marked improvements in performance. Low cost builders also allow the use of lower concentrations of the relatively expensive surfactant materials. The builders perform this function by:

• Chelating, sequestering, or otherwise deactivating water hardness.



Rep. H. S. Reuss *Reduce or eliminate phosphates*

• Lowering the critical micelle concentration at which the surfactant is effective.

• Contributing some alkalinity or buffering capacity.

A number of inorganic compounds has been used as builders, among them carbonates, bicarbonates, borates, and silicates. But none has proven as effective as the phosphates, the most commonly used of which is sodium tripolyphosphate. Today, a typical detergent may contain as much as 50% phosphate, and detergent markets account for about 2 billion pounds per year of phosphates.

It's a moot point as to whether phosphate builders would have reached their present position had their role in eutrophication been adequately investigated prior to their introduction. In any case, it is clear that any new substitute builder must meet the twin criteria of being as effective as phosphates and, at the same time, not be detrimental to water quality. Hence, Undersecretary Klein's fears that "sub-



Undersecretary Klein No forced substitution yet

stitutes could be equally stimulating to algal growth; it is even possible that these materials or their degradation products could cause other more severe pollution than does phosphorus."

Biologically safe

Thus, advocates of NTA as a candidate replacement for phosphates are forced to build a case for the lack of harmful effects in waste water. University of Toronto's Jones points out that his work on NTA has shown it to be "completely acceptable to microorganisms in the biosphere." Ecological studies are not yet complete, but "with 90% of the vote in, the results look encouraging," he adds.

Chemical's Hampshire Singer pointed out that significant data exist today which speak for the safety, biodegradability, and harmlessness of NTA. "Although nitrogen is known to be a major plant nutrient," he said, "in most instances, nitrogen is not believed to be the controlling factor, and the small nitrogen content contributed by NTA would not be significant." Singer does add that more data would be desirable to cover the broadest range of conditions over which NTA might be used, and warns against any forced elimination of phosphates. NTA should be increased slowly over a period of time, he added.

And, indeed, in spite of such lessthan-complete assurances, NTA already is seeing some use in commercial detergent formulations, both in the U.S. and abroad. For example, in Sweden, NTA has become a major component in some commercial formulations. Hans O. Bouveng, of Sweden's Institute for Air and Water Pollution, told the Reuss committee that 15% of the Swedish market is covered by products with 20% NTA content in which phosphate levels have been reduced to 10%.

In the U.S., the use of NTA in detergents has not as yet been significant, but it is growing. Singer pointed out that, since 1966, when NTA became available in volume production, the total market for this material has grown to 150 million pounds per year. And at least some of this material is finding its way into detergents; J. A. Bruck, associate director of product development for Procter & Gamble, admits that small amounts of NTA are used in two Procter & Gamble household laundry products, although with no significant reduction in phosphate content as yet.

Congress focuses on environmental quality

Activities of the first session of the 91st Congress produced some significant gains on the environmental front

The first session of the 91st Congress can be remembered as the one to hand President Nixon his first setback—rejection of the Haynsworth nomination. It also was the Congress that cleared the tax reform bill, which was signed by the President after adjournment.

In the field of environmental quality, it certainly will be remembered most for its landmark legislation-the National Environmental Policy Act of 1969. And, as the logjam of appropriations bills broke loose in mid-December, federal departments and agencies were assured considerably more funds for ongoing environmental programs than in previous years. Coupled with the emphasis that President Nixon gave to the environment in his first State of the Union message last month. these are strong indicators of increased legislative and executive attention to environmental matters.

All in all, there were gains as well as holding actions. Increased appropriations for the federal environmental programs can be rated as gains. For example, the public works appropriations of \$800 million for the construction of waste water treatment facilities for fiscal year 1970 is nearly four times the amount appropriated for water pollution control efforts in any previous year under the basic water pollution legislation of 1965.

On holding actions, the failure of the water quality improvement act to emerge from this session is perhaps the biggest disappointment. After early passage by each house and numerous Senate-House conferences, members adjourned without coming to any agreement on the differences between the House version (H.R. 4148) and the Senate version (S. 7). Hopefully, the legislative proposal will emerge early in the second session so that adequate pollution protection from oil spills, vessel discharges, and thermal loadings can be added to the Water Pollution Control Act of 1965.

New laws

The National Environmental Policy Act undoubtedly is the most important and far reaching conservation-environmental measure ever cleared by any Congress. Sen. Henry M. Jackson's (D.-Wash.) proposal, S. 1075 and now P.L. 91-190, does the following:

• States a national environmental policy and declares national goals.

• Authorizes and directs all federal agencies to administer their existing laws, regulations, and policies in conformance with this act.

• Requires submission of an annual environmental quality report.

• Establishes a three member Council of Environmental Quality in the Executive Office of the President not to be confused with the President's Environmental Quality Council (Es&T, December 1969, page 1249), nor with the Office of Environmental Quality in the pending water quality improvement legislation.

One important function of the new council would be to consult with state and local governments and other interested groups and individuals, and to utilize the services, facilities, and information of these agencies. For the first time, the council would establish an effective liaison between the federal government and individual states, thereby creating a long-needed central clearinghouse of information.

In many respects, the only precedent and parallel to P.L. 91-190, which was signed by President Nixon on the first day of the new decade at the West Coast White House (San Clemente, Calif.), is in the Full Employment Act of 1946, which declared an historic national policy on manage-



Sen. Henry M. Jackson

ment of the economy and established the Council of Economic Advisers (Es&T, August 1969, page 701).

The tax reform legislation, P.L. 91-172, was the most time consuming and biggest piece of legislation to emerge from this session. Repeal of the 7% investment tax credit for pollution control equipment—which has been in effect since 1962—is a major environmental concern in the law. (Where a bill is referred to as Public Law—P.L. —it means that the bill has been passed by both Houses of Congress and has been sent to the White House and signed into law.) No longer will businesses be permitted to buy a piece of pollution control equipment for \$10,000, for example, and then subtract 7% of the cost, or \$700, from federal taxes otherwise due.

Included in the tax reform legislation is the five year amortization of air and water pollution control facilities completed or acquired in 1969 and subsequent years. Since P.L. 91-172 repeals the tax credit retroactive to April 18, 1969, the credit will be available only for machinery and equipment acquired by that date, or on which construction was started by that Machinery and equipment date. placed in service before 1976, if acquired under binding contract commitments entered into by April 18, 1969, also will be eligible for the credit.

Other than increased appropriations for water pollution control in the Department of the Interior, and the public works appropriations, few new laws for the improvement of environmental quality were enacted. The funding of air pollution and environmental control agencies awaits action by the second session.

But the appropriations actions for fiscal year 1970 in themselves serve as strong indicators of congressional attention to matters pertaining to environment.

On the fringe of environmental concern are three items:

• P.L. 91-15 continues the function of the National Council on Marine Resources and Engineering Development until the end of fiscal year 1970 (ES&T, October 1968, page 738).

· For water resource development, P.L. 91-81 authorizes the Secretary of the Interior to conduct feasibility studies of three water units of the Missouri River Basin Project.

• P.L. 91-137 extended for one year the National Air Pollution Control Administration's (NAPCA) authorization for research relating to fuels and vehicles to \$45 million for fiscal year 1970.

A number of regional compacts for water resources planning and development and for air conservation were referred to the Judiciary committees. Although Congress approved one water compact, it deferred action on air compacts to some later date. The Lake Tahoe regional planning compact (P.L. 91-148), will ensure the wise use and conservation of the water of Lake Tahoe (Calif. and Nev.) and the resources of the area around the lake. Also, the Secretary of the Interior is authorized to cooperate with the planning agency to adopt a regional plan of resource conservation.

Appropriations

Agriculture's appropriations (P.L. 91-127) of slightly less than \$7.5 billion include several items for environmental control. In the Agricultural Research Service allotment of \$131 million for research, there are included items for the control of aquatic weeds (\$324,900) and for pollution research concerned with animal waste management (\$661,800).

Labor and HEW's appropriations, of \$19.7 billion, include two items of top environmental priority-air pollution and solid waste management. Approved by the Senate after Congress reconvened, but prime target for presidential veto, this appropriations bill calls for \$108.8 million to NAPCA. an increase of \$13 million over the \$95.8 million budget request (ES&T, February 1969, page 113). The Bureau of Solid Waste Management would receive an appropriation of \$14.8 million, the requested amount (ES&T, August 1969, page 705).

Included in HEW's appropriation is \$18.3 million for the National Institute of Environmental Health Sciences (NIEHS), same as the budget request. Elevated to the status of a national institute of health more than a year ago, NIEHS (Research Triangle Park, N.C.), is charged with the responsibility of identifying the chemical, physical, and biological factors in the environment that can adversely affect man (ES&T, October 1968, page 758).

Housing and Urban Development's (HUD) appropriation of slightly less than \$2.76 billion (P.L. 91-126) contains three programs with definite environmental quality concerns. Perhaps, the most important is HUD's 701 comprehensive planning grants program, which received \$50 million for fiscal year 1970. The other two are its water and sewer grants program (\$135 million), and its open space program (\$75 million). In addition, other HUD programs with small but undefined environmental quality enhancement overtones are its programs for urban renewal (\$1 billion), model cities (\$575 million), and neighborhood facilities grants (\$40 million).

Interior's appropriations (P.L. 91-98) include funds for two agencies with water responsibilities. The Office of Saline Water received \$26 million, and the Office of Water Resources Research received \$11.2 million. And the Public Works appropriations (P.L. 91-144) specified \$886 million for the Federal Water Pollution Control Administration (FWPCA) (ES&T, January 1970, page 9).

Signed after Congress adjourned, Transportation's appropriation of slightly more than \$2.0 billion (P.L. 91-168) contains a number of programs for environmental improvement, including aircraft noise reduction, sonic



SEC. 2. The purposes of this Act are: To declare a national policy which will encourage productive and enjoyable harmony between man and his environment; to promote efforts which will prevent or elimi-nate damage to the environment and biosphere and stimulate the health and welfare of man; to enrich the understanding of the eco-logical systems and natural resources important to the Nation; and to establish a Council on Environmental Quality.

TITLE I

DECLARATION OF NATIONAL ENVIRONMENTAL POLICY

SEC. 101. (a) The Congress, recognizing the profound impact of Pelicies and man's activity on the interrelations of all components of the natural geals. environment, particularly the profound influences of population growth, high-density urbanization, industrial expansion, resource exploitation, and new and expanding technological advances and recognizing further the critical importance of restoring and maintain-ing environmental quality to the overall welfare and development of man, declares that it is the continuing policy of the Federal Govern-ment, in cooperation with State and local governments, and other con-cerned public and private organizations, to use all practicable means and measures, including financial and technical assistance, in a man-ner calculated to foster and promote the general welfare, to create and

boom investigations, and a national buoy data system. Usually, these programs are included in the research and development funds of Transportation agencies—the Federal Aviation Administration (FAA) and Coast Guard.

Since the various research and development programs are not broken down specifically, it is often uncertain whether particular programs received gains or not. For example, the Coast Guard received \$14.5 million for research, development, testing, and evaluation, whereas the amount requested was \$14.9 million; and FAA funds were reduced to \$41 million, from \$47.5 million requested. Transportation's aircraft noise reduction program is included in the FAA appropriation.

However, FAA received \$85 million for the development of the supersonic transport (SST), which caused one environmental leader in the House to voice his objection. Rep. Henry S. Reuss (D.-Wis.) commented, "In addition to the sheer waste of taxpayers' dollars involved in the SST, a substantial question is presented concerning the affront to the environment caused by the sonic boom and airport noise of the proposed plane."

Due to be implemented in 1975-76, the Coast Guard buoy network will be deployed along the Continental Shelf and deep oceans adjacent to the U.S. This network will be used to assess the reliability and effectiveness of the prototype development and to provide better scientific understanding of the marine environment. The National Science Foundation's appropriation includes an item of \$10 million for the National Sea Grants College and Program Act, calling for a program of education and research relating to the development of marine resources (ES&T, October 1968, page 756). The amount that was requested was \$15 million.

In addition, this session of Congress expressed the nation's continued support and interest in the International Biological Program (IBP) (ES&T, July 1968, page 411), and permission to participate in the forthcoming U.N. Conference on the Human Environment (ES&T, January 1969, page 9). In the IBP effort, which is aimed at understanding man's relationship to the environment, Congress urges federal departments and agencies, as well as persons and organizations, public and private, to support the program.

Hearings

Other environmental concerns received attention by being on the agenda of various Congressional committee and subcommittee hearings. These include the Joint Committee on Atomic Energy hearings on the environmental effects of producing electric power; hearings on environmental effects of nuclear detonations for excavations (S. 3042); solid wastes hearings before the Senate Subcommittee on Air and Water Pollution (ES&T, November 1969, page 1160); as well as hearings on pesticides and detergents (see this issue, page 101).



[To accompany S. Res. 179]

The Committee on Foreign Relations, to which was referred the resolution (S. Res. 179) expressing the sense of the Senate that the United States should actively participate in and offer to act as host to the 1972 United Nations Conference on Human Environment, having considered the same, reports favorably thereon with an amendment and recommends that the resolution as amended **d**o pass.

PURPOSE

The resolving clause of Senate Resolution 179 states the sense of the Senate that "the United States should actively support and

Next session

There is little doubt that the environmental issue has caught the imagination of Congressmen and the public alike. Last December, 82 Congressmen joined in the call of Rep. Henry S. Reuss for an environmental decade for the 70's. As the needs for the Vietnam war diminish, the needs of the environment will be met.

When Congress reconvened last month, a number of similar proposals dealing with environmental matters were awaiting Congressional attention. Hopefully, these proposals will be called up quickly for action by the various committees and subcommittees. One proposal is that of Sen. Frank E. Moss (D.-Utah) urging creation of a federal Department of Conservation and the Environment (S. 2312). "Perhaps, we can follow the 'Great Society' with a 'Clean Society,' " says Sen. Moss, who introduced the basic bill in 1965 and every year thereafter (ES&T, October 1967, page 774).

A short list of some of the more important proposals includes Sen. Gaylord Nelson's (D.-Wis.) proposal (S. 3151) for environmental education from the preschool to graduate level of training: Interior's new financing plan for the construction of waste treatment facilities-one plan (H.R. 13358) was introduced by Rep. William C. Cramer (R.-Fla.) last August but was not called up for action; Sen. William Proxmire's (D.-Wis.) proposal (S. 3181) for industries to pay for their water pollution; Sen. Edmund S. Muskie's (D.-Me.) proposal (S. Res. 78) for a select committee on technology and the human environment (ES&T, April 1969, page 305); the proposal (S. 3072) for the procurement of low emissions vehicles: extension of the Clean Air Act (S. 3229), calling for authorizations of \$150 million in fiscal year 1971, \$175 million in fiscal year 1972, and \$200 million in fiscal year 1973; and continuing efforts on the part of members to resolve the differences in the two versions of the water quality improvement act (H.R. 4148 and S. 7).

What actions these proposals receive from the second session of the 91st Congress surely will set the pace for attention to environment in the decade of the 70's. Certainly, some of the proposals will be the subject of hearings and, perhaps, a few will achieve the status of new laws. Environment will be a hot issue in the 70's, and partisan in-fighting promises to be much sharper this election year.

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Hurricane seedings appear encouraging

After waiting several years, Project Stormfury scientists score with five seedings on each of two days

Man may have made scientific history last August 18 and 20 when Hurricane Debbie's wind force was weakened by seeding operations with silver iodide. But, until the data are refined and the experiment is repeated, it is not absolutely certain that hurricanes can be modified or controlled by such operations.

Nevertheless, Secretary of Commerce Maurice H. Stans and Navy Secretary John H. Chaffee announced at a news conference (December 1969) that the wind speed of Hurricane Debbie was weakened, decreasing 31% (from 98 knots to 68 knots) several hours after seeding operations were completed on August 18, and 15% (from 99 knots to 4 knots) on August 20. (Hurricane wind speed is 75 knots.) On August 19, when there was no seeding, the storm reintensified.

R. Cecil Gentry, director of Project Stormfury-a joint Department of Commerce-Department of Defense experiment involving Commerce's Environmental Science Services Administration and Defense's Navy-explains that the seeding is done outside the radius of maximum wind speed. He goes on to note that the seeding involved the dropping of pyrotechnic canisters, each containing 120 grams of silver iodide, at two hour intervals five times each day. According to Gentry, each gram of silver iodide produces from 1012-1014 freezing nuclei. The pyrotechnic was designed and developed by Pierre St. Amand, project manager at the Naval Weapons Station (China Lake, Calif.).

The model

Theoretically, the liquid water should be converted to ice and the heat effect associated with the freezing should change the wind structure of the storm. If the release of heat is performed in the right area, the seeding can cause a redistribution of energy and reduction in peak wind velocities.

Seeding experiments are not performed over land areas. Under project guidelines, the only storms that are eligible for seeding are those whose centers have a 10% or less chance of coming within 50 miles of a popu-



Satellite view. Photographed by the Environmental Science Services Administration's ESSA9 cameras, Hurricane Debbie was 500 miles northeast of Puerto Rico

lated area during the ensuing 24 hours. Two good reasons exist for these restrictions:

• First, the effects of the experiments are expected to disappear in less than 24 hours after seeding so that a storm will revert to a natural state before striking land.

• Second, because hurricane structure changes markedly when a storm passes over land, the 24 hours will provide ample time to measure seeding effects before they are obscured.

Potential

Earlier storms were seeded in 1961 and 1963, but the 1967 and 1968 hurricane seasons provided no storm that met Stormfury's criteria. In neither of the earlier experiments was the seeding performed more than once on any day (ES&T, September 1969, page 791; October 1967, page 774).

Stormfury scientists estimate that if one storm such as last season's destructive Hurricane Camille can be weakened so that resulting damage can be reduced even 10%, the investment (estimated as \$250,750 annually by Gentry) will have been returned tenfold.

In any event, Stormfury's hurricane hunters will be on alert for 1970's forthcoming tropical storms. Perhaps then, the seedings will be repeated on one or more tropical storms as soon as practical to seek further confirmation of these hopeful findings.

Plant licks solvent emission problem

Control system completely eliminates smoke and odor from oven exhaust gases

Last October, a lady called GAF Corp.'s vinyl floor covering plant (Fullerton, Pa.) to ask when the plant had shut down. She wasn't calling to sympathize; she was-frankly-glad that one of the Lehigh Valley's air pollution problems seemed to have been licked, even if it apparently meant the loss of a local employer. The lady caller was astounded to be told that the plant, far from being closed, was, in fact, running at full production. The reason for astonishment was simple: For 10 years the GAF plant had emitted a white smoke that smelled, according to Lehigh Valley Air Pollution District director R. Emmet Doherty, like 3-inone oil, and which frequently blanketed the area with a haze that severely reduced visibility. Citizen complaints that the plant quite literally made them sick had not gone unheeded by GAF, but a solution to the problem was not found until 1969, when a new air pollution control system was installed. Fortunately for all concerned, this system has proven a complete success.

Air pollution source

The Whitehall plant of GAF Corp. at Fullerton produces vinyl coated flooring products for a rapidly expanding market that includes offices and mobile homes as well as private homes. The process involves preparing a continuous blank backing sheet with a coating of vinyl polymer, then printing the surface with an attractive pattern and, finally, coating the sheet with a thin, wear-resistant layer of vinyl polymer. The heart of the process, and the reason for the product's popularity is the vinyl layer over the patterned surface. This coating may only be ten thousandths of an inch in thickness (perhaps twenty thousandths in the most expensive products) and is completely transparent, but it is entirely responsible for the long-wearing qualities of the flooring material.

The coating is applied to the continuous sheet by a cylinder which rotates in a bath of fluid containing vinyl monomers dissolved in mineral oil solvent (its exact composition is a proprietary secret). The wet sheeting is transported through a long oven in which the solvent is driven off and the monomers polymerize to yield the clear, wear-resistant coating. The exhaust gases from the ovens were the source of air pollution from the plant.

Development of problems

The plant initially was owned by the Sandura Co. Sandura was bought by the Ruberoid Co. in 1965, and, in 1967, Ruberoid was merged with GAF Corp.

In 1948, Sandura Co. started up the Whitehall plant with one, nine foot wide coating line. Then, in 1957, a second, 12 foot wide line was added in a major expansion move. The added production capacity of the plant, and the need to work more than one shift, brought the pollution problem to the notice of the public and under the eye of the Lehigh Valley Air Pollution District.

Initially, there were no controls whatsoever on emissions from the ovens. In an attempt to control the problem, plant management installed a catalytic oxidation system which was intended to convert the gases to carbon dioxide and water. Unfortunately, the oxidation unit could not be operated so as to provide complete conversion. The result was that the air pollution nuisance became greater than ever: The smell coming from the plant now was reminiscent of *burnt* 3-in-one oil.

Effective system

After a search in which over a dozen firms were contacted, GAF eventually contracted with Clermont Engineering Co. (Philadelphia, Pa.) for supply of a control system that would eliminate the air pollution problem.

Clermont's approach was to engineer a system that would recover as much as possible of the mineral oil solvent, so that it could be reused as the carrier for the vinyl monomers at the coating stage in the plant. Consequently, combustion processes were not considered.

In the Clermont design at the Whitehall plant, exhaust gases from the ovens first are sent to a scrubber-condenser unit in which many of the less volatile components in the gases condense out on the surface of water coils. Some of the condensate recovered



Job complete. Construction firm and GAF plant officials pose in front of new unit



from the scrubber-condenser is recycled to spray heads; the spray is used to prevent condensate from coating the coils and thus causing reduced heat transfer rates. The rest of the condensate is piped to tanks where the oil and water fractions are separated.

The gases leaving the scrubber contain a fine oil droplet mist; most of the drops are less than one micron in size. Final removal of the mist is accomplished in a pair of towers containing Brink mist eliminator elements (Monsanto Enviro-Chem Systems, Inc., Chicago, Ill.). These fiber filters are widely used to trap particles less than three microns in size at high collection efficiencies.

The liquid draining from the mist eliminators, together with condensate from the scrubber, is pumped over to a pair of settling tanks where the heavier water fraction separates out from the lighter oil fraction. The water is drained away periodically, and the oil is available for reuse. In practice, GAF has sent this oil back to its supplier of coating liquid for reprocessing before it is reused.

Efficiencies

Clermont claims that 80% of the contaminants in the oven exhaust gases are removed in the scrubber-condenser. At the stack outlets above the mist eliminators, 90-95% of the volatilized organics have been removed (and recovered), according to Clermont. (The Brink mist eliminator elements are claimed to remove 99+% of the mists and other condensate reaching them. The residual low boiling organics escape as vapors.) GAF agrees with

these figures, but quotes no precise poundages, for competitive reasons. The 90-95% removal figures are not arrived at by measurement, but by subjective evaluation of the state of the exhaust plume rising from the stack. The plume is remarkably light, even on a cold, dry day when the presence of water in the gases always tends to produce a white plume.

GAF claims that maintenance of the control system is both easy and inexpensive; there are few moving parts to service. The fans which draw the gases through the scrubber and force them through the mist eliminators do, of course, require servicing. Their operation is the prime operating expense: Together, the two blowers move 33,-000 c.f.m. of gases while requiring 175 h.p.

Economics

The goal-at least ideally-of every pollution control system is to pay for itself. Systems in which a raw material or byproduct is recovered for reuse obviously have a much better chance of meeting this goal than those in which wastes are burned or otherwise converted to valueless products. In the case of the GAF vinyl sheeting plant, there seems to be some reason for optimism. Although Don Dorfman, president of Clermont Engineering, insists to J. Paul Lasley, manager of the Whitehall plant, that the system eventually will save more than it cost (\$363,000), Lasley understandably is reluctant to make unequivocal statements on the subject. After all, the plant manager says, the control system has been in operation only a few months (since October 1969), and it is too early yet to say anything with assurance. Nevertheless, Lasley is certainly delighted that a problem which has plagued him for years appears to have gone forever.

Even though effort was continually expended, it took 10 years to arrive at a satisfactory solution to the Whitehall plant air pollution problem. The fact that so much time was needed brings up an important point that seldom is appreciated fully: Eliminating air pollution is rarely just a simple matter of purchasing a piece of control equipment off the shelf and installing it on line.

Especially interesting in this connection is the Pennsylvania plant's poor experience with its catalytic oxidation system. Such systems have regularly been employed with success to solve difficult air pollution problems (see, for example, the description of catalytic oxidation of monomer emissions at a wax plant in ES&T, November 1969, page 1159). Yet, recurrent problems with incomplete conversion forced abandonment of catalytic oxidation at the Whitehall plant.

One is compelled to recognize that even pollution problems which are similar in nature may not be amenable to solution in the same ways. This is a sobering thought, for it means that experience in controlling one type of air pollution may be practically worthless in controlling another. Little wonder, then, that air pollution control can not be achieved overnight, even by firms such as GAF that have shown themselves to be in earnest in tackling their emissions problems.



phenol...dye...insecticide wastes... Filtrasorb® solves tough waste problems



SUBSIDIARY OF MERCK & CO., INC.

Problem: Waste from a chemical manufacturing plant containing up to 2,500 ppm phenol and other pollutants was being pumped into lagoons. Capacity was about to be exceeded. Overflow would have been disastrous.

Solution: A simple filter bed of Filtrasorb granular activated carbon, supplied by Calgon Corporation, averted an expensive problem. Lagoon wastes are filtered through the Filtrasorb which adsorbs (removes) phenol and other organic wastes including a deep red color. Chemical regeneration is being used to restore the adsorptive capacity of Filtrasorb for re-use, and at the same time it provides a bonus in recovered phenol.

Problem: An insecticide plant was ordered to shut down on a specified date by regulatory agencies because of heavy organic wastes in plant effluent.

Solution: Adsorption with Filtrasorb proved to be the best answer. Filtrasorb engineers designed a plant that could be constructed quickly to prevent shutdown. The plant will treat an effluent containing mixtures of organic acids, phenol, mixed alcohols and many other chemicals. Filtrasorb will handle this complex job

economically because it will be regenerated thermally for repeated re-use.

Problem: A new carpet mill expects to use 1,000,000 gallons of water a day eventually in its dyeing and rinsing operations. Projected costs for using municipal sources for this amount of water were well over \$100,000 a year.

Solution: Calgon Corporation water specialists showed how Filtrasorb granular activated carbon could reclaim waste water economically. As a result, Calgon was awarded a contract for the design and construction of a complete Filtrasorb water reclamation plant which will provide a very substantial overall reduction in costs for the carpet manufacturer.

For the *tough* waste water treatment problems, call on the total capabilities of Calgon Corporation. Calgon can supply all, or any part of, the products and design technology for any Filtrasorb waste water treatment facility. For details, write or phone Filtrasorb Department, Calgon Corporation, Calgon Center, Pittsburgh, Pa. 15230. Phone (412) 923-2345.

Circle No. 18 on Readers' Service Card

A guide to scrubber selection

Air pollutants, certainly a farranging industrial problem, are perhaps best classified by their physical characteristics and not necessarily by individual source. The following list of major types of air pollutants is useful for discussing control techniques.

• Noxious gases—substances like hydrogen chloride or sulphur dioxide, that normally are emitted in a vapor state.

• Liquid entrainment—liquid particles 10 microns and over in size created by sprays, dragout, agitation, or bubbling, and picked up in exhaust air streams.

• Mists—liquid particles formed by condensation of molecules from the vapor state; particle size is usually 10 microns or lower.

• Dusts—solid particles, usually five microns and larger, formed by grinding or disintegration of solids.

• Fumes—solid particles smaller than one micron, formed by condensation, sublimation, or oxidation of metallic vapors.

• Entrained particles—particles of mists, liquids, dust, or fumes, that are collected and conveyed by an air stream through an exhaust ventilation system.

Once the type of pollutant is thus broadly defined, the engineer responsible for environmental quality faces the question: "What system can best handle the problem?" Wet scrubbers are versatile, and are probably the closest to a universal answer; if the pollutant is corrosive or exists in a corrosive environment, glass fiber reinforced plastic (FRP) systems are most often called for. Yet, confusion does exist about wet scrubbers and about FRP. This confusion is understandable for two major reasons. Wet scrubbers abound in a wide variety of designs, sizes, efficiencies, and collection principles. At the same time, engineers are hard-pressed to keep abreast of advances in corrosion-resistant materials development, especially plastics. I propose to discuss typical wet scrubber designs and the advantages and limitations of reinforced plastics in designing for corrosive environments.

Wet scrubbers are suitable for a wide range of corrosive applications for which other types of collectors may require expensive modifications or unusual designs. The main advantage of wet collectors are constant exhaust volume, elimination of secondary dust problems during disposal, small size, and ability to clean hot or moisture-laden gases. Possible trouble spots for wet scrubbers are applications where costly water clarification may be necessary before disposal or reuse. Freezing of water lines is a potential hazard, and vapor plumes may be present during cold weather operation.

Principles

Scrubbers can remove either soluble gases, mists, or particulate matter in two basic ways: By gas absorption or by impingement or interception. Nucleation—a third collection method —is a patented process used for dust and fume particles in the submicron range.

Gas absorption involves the transfer of noxious gas from an exhaust stream into a liquid phase. Basic factors controlling the gas absorption process are the degree of solubility or chemical reactivity of the gas to be removed in the scrubbing liquid, and the means of obtaining intimate contact between the gas and liquid streams. Normally, plant water is used to remove such gases of high solubility as hydrogen fluoride or hydrogen chloride. In some cases, caustic or sait solutions may be used because they chemically react with less soluble gaseous contaminants. For example, sodium hydroxide scrubbing liquid is used to react with chlorine gases to produce sodium hypochlorite.

Impingement can be described as interception of the contaminant and its removal from the air stream. Particles impinge or impact upon targets—packing or other media—placed in their path. The contaminants then are washed away. The nucleation process employs a humidification and cooling cycle to cause water condensation on submicron particles. The particle size builds up to a level where particles can be removed by impingement on the packing.

Selection criteria

Basically, there are five major types of wet scrubbers: Cross-flow, countercurrent, wet cyclone, venturi, and vertical air washer. Packing is used in the first two types. These packed scrubbers—as well as spray towers and baffles—are described below, along with their most efficient pollution control use.

In cross-flow packed scrubbers, the air stream moves horizontally through a packed bed and is irrigated by the scrubbing liquid which flows vertically down through the packing. Cross-flow designs are characterized by low water consumption and fairly high air flow capacity at low pressure drop. They are commonly used for removing entrained particles from air streams, as well as for eliminating gaseous pollutants. Packed beds will effectively remove mist and spray particles three microns and larger by impingement.

Particulate matter in the air stream strikes the wet packing, adheres to the surface and is washed away by the scrubbing liquid. The packing—especially for removing particulates must be kept wet to prevent the particles from becoming reentrained in the gas stream.

A large amount of entrained liquid particles themselves may provide irrigation of the packed bed. In most industrial applications, however, the packing usually is irrigated because of the nature of particulates removed, the low fluctuating concentration of particles removed, or the possibility of reentrainment if not washed away. For removal of mists and entrained particles greater than three microns in diameter, either cross-flow or parallel-flow scrubbers give satisfactory collection efficiency and low operating costs.

The parallel-flow design is a modification of the cross-flow design in which a front washing spray is used to

feature





achieve a parallel flow of both the gas stream and scrubbing liquid. This system is particularly effective for removing entrained liquids where the stream is loaded with solid dust particles. (The front spray prevents solid buildup on the packing which causes excessive pressure drop.) Because the scrubbing liquid drops through the packed bed, no more than one foot of packing depth can be used. Often, the cross-flow and parallel-flow designs are combined when front-washing is required for packing depths of more than one foot. This combination is effective for control of air streams carrying solid and liquid particulates and trace amounts of noxious gases.

The cross-flow packed scrubber is also used to remove submicron dust and fume particles. In the patented nucleation process, cross-flow packed scrubbers can obtain high collection efficiencies at particle sizes in the submicron range. This involves pretreatment of the inlet air, before it enters the scrubber, to achieve the proper stream conditions. The stream passes through a packed bed and rapid condensation around the dust particles takes place. This process enlarges the particles to a size such that they can be removed effectively by the packed bed. With proper humidification and operating conditions available for nucleation, a one micron particle can be built up to five or six microns. With this increase in particle size, collection efficiencies of 90-99% can be achieved on a four to five foot bed in a cross-flow scrubber.

In the counter-current packed scrubber, the gas stream moves upward in direct opposition to the scrubbing liquid stream, moving downward through the packed bed. With the use of specific tower packings, liquid surface regeneration is obtained with no increase in energy consumption. Liquid surface regeneration is more critical to the efficiency of a packed column than the surface area of the packing used in the column.

The gas stream—rich in contaminants—comes into contact with spent liquor at the bottom of the packed bed. Fresh liquid coming in at the top of the scrubber is in contact with the least contaminated gas. This characteristic provides a fairly constant force throughout the packed bed for driving the gaseous contaminant into the scrubbing liquid. There also is less chance that the dissolved gases will be stripped out of the liquid.

A modification of the counter-current design is the concurrent packed scrubber. Here, the gas and liquid streams move in the same direction usually down—through the packed bed. These scrubbers can be operated at high gas rates, and, in the case of gas absorption, at high liquid rates. They easily remove gases of high water solubility and usually are efficient enough for removal of less soluble gases.

This design is useful in limited spaces, since it handles high gas velocities, and relatively low cross-sectional areas can be utilized. High gas velocities in these designs do not cause flooding, as they would in counter-current design, because the gas stream helps to push the liquid stream through the packing.

Cross-flow and counter-current scrubbers appear to perform the same function, but where highly soluble gases or mists are to be removed, the cross-flow packed scrubber has several advantages. The benefits are derived from the ease with which gas and water streams pass through the crossflow design, compared to the resistance of the opposing streams in counter-current flow. Using the same gas and liquid mass flow rates, a crossflow scrubber has lower total liquid rate and pressure drop. Besides reducing water consumption drastically, the cross-flow principle also reduces pump and fan motor sizes. Other advantages include less plugging from solids dropout at the packing support plate and the possible use of higher gas and liquid rates because of the extremely low pressure drop.

The economical break-even point between the two scrubber designs is based on the packing depth required. If packing requirements for crossflow exceed six feet, the counter-current flow design usually has a lower operational cost. As previously noted, cross-flow and counter-current scrubbers use packings. Traditionally, ceramic packings have been common; plastic packings, however, are coming into wider use. Plastic packings have the advantage of being virtually unbreakable, and their lighter weight also permits smaller wall scrubbers, providing equipment cost savings. One example of the newer polyethylene packings (trademarked Tellerette), has the shape of a helix that is formed into a doughnut (toroid) shape. In addition to a low pressure drop, it has

Comparison of scrubber operating costs

| Scrubber type | Liquid rate (g.p.m.) | Liquid pressure (p.s.i.g.) | Pump h.p. | Scrubber pressure drop (in. water) | Total pressure drop (in. water) | Fan h.p. | Total h.p. | Annual power cost |
|----------------------|----------------------------|----------------------------------|-----------|---|--|----------|------------|-------------------------|
| Cross flow | | | | | | | | |
| Tellerette packing | 50 | 5 | 0.3 | 0.5 | 1.5 | 4.3 | 4.6 | \$ 370 |
| Berl saddle packing | 60 | 5 | 0.4 | 1.2 | 2.2 | 6.3 | 6.7 | 540 |
| Raschig ring packing | 60 | 5 | 0.4 | 3.8 | 4.8 | 13.8 | 14.2 | 1140 |
| Counter-current | | | | | | | | |
| Tellerette packing | 120 | 5 | 0.7 | 0.75 | 1.75 | 5.0 | 5.7 | 460 |
| Berl saddle packing | 140 | 5 | 0.8 | 2.2 | 3.2 | 9.1 | 10.0 | 810 |
| Raschig ring packing | 140 | 5 | 0.8 | 6.7 | 7.7 | 22.0 | 22.8 | 1840 |
| Wet cyclone | 80 | 60 | 5.6 | 3.5 | 4.5 | 12.8 | 18.4 | 1490 |
| Spray tower | 100 | 80 | 9.6 | 2.0 | 3.0 | 8.6 | 18.2 | 1470 |
| Jet | 600 | 60 | 42.0 | | 1.0 | none | 42.0 | 3380 |
| Venturi | 80 | 20 | 1.9 | 15.0 | 16.0 | 46.0 | 47.9 | 3860 |

a superior ability to provide liquid surface regeneration.

Absorption is relatively rapid when gas first comes into contact with a liquid. After the surface of the liquid becomes saturated, however, the dissolved gas must diffuse from the surface—a slow process. Turbulence will bring fresh liquid to the surface and hasten the absorption, but this requires additional energy and higher operating costs.

Tellerette packing was designed with a large number of interstitial holdup points at which the liquid comes together and disperses again, exposing new surface for absorption without adding energy to the system. This means that the liquid surface is constantly changing and is renewed as the liquid progresses through the packed bed.

Wet cyclone scrubbers are efficient for removing entrained liquids and dusts from air streams. High gas throughputs are achieved by forcing the gas into a spiral flow pattern. Centrifugal force on the entrained particles because of this flow pattern reaches a force of several hundred times the force of gravity; larger entrained particles are forced to the wall of the scrubber, since their mass is much greater than that of the air stream.

High pressure spray nozzles generate minute liquid spray droplets which intercept smaller particles and further increase collection efficiency. The scrubbing liquid from the spray systems also is thrown to the wall by centrifugal force and, along with the larger particles, drains down the wall to the sump.

The wet cyclone design is effective when the air stream contains dust particles. These are removed along with the liquid particles by centrifugal force and interception. Limiting features of this design are its higher pressure drop, greater pumping costs for the spray nozzles, and inability of most wet cyclone designs to remove particles smaller than five microns. A patented liquid injection process, however, is available that reduces pressure drop to two to four inches of water compared to the six to eight inches common to standard cyclone scrubbers. This process, in turn, eliminates the high pressure drop and reduces pumping costs.

Venturi scrubbers are best suited for applications where solid or liquid particulates in the low and submicron ranges—.05-5 microns—must be removed from exhaust air streams. Such particulates are created by condensation of a liquid or metallic vapor or when a chemical reaction causes the formation of a mist or fume. Typicat examples are ammonium chloride fumes from steel galvanizing, phosphoric acid concentration, mists from dry ice plants, and zinc oxide fumes from reverberatory furnaces.

To effectively remove these particles, turbulent contact must occur between the gas stream containing the particulates and the scrubbing liquid. The venturi scrubber does this by passing the two streams concurrently through the extremely small throat section of the venturi. The velocity of both streams is accelerated in the venturi throat, causing the liquid to break up into extremely fine drops. These liquid drops collide with the particles carried by the gas stream to effect their removal. The drops then agglomerate to form larger particles again. The cleaned gas stream then is passed through a separator unit to eliminate relatively large entrained liquid particles.

A dominant operating feature of venturi scrubbers is their high pressure drops, which can range from five inches of water to as high as 100 inches. Venturi scrubber design dictates that the pressure drop must be increased as the particle size being removed becomes smaller.

Venturi scrubbers also are used for removing soluble gases from air streams. Usually, such applications are limited to those cases where small particulates also are present, because the high energy requirements for operating venturi scrubbers do not normally make them economically feasible for controlling gaseous pollutants.

The vertical air washer is a lowcost design used primarily for removing liquid particulates (entrainment, carryover, and mists) from exhaust air streams in metal finishing and plating operations. Using a concurrent upward irrigation system with shallow packed beds, the vertical air washer is used to remove liquid particulates from anodizing, pickling, etching, cleaning, rinsing, and some plating operations. This design is effective in removing particle sizes down to eight microns at high collection efficiencies.

Two important features of this design are its low irrigation rate (which can be as low as 2 g.p.m. per 1000 c.f.m.), and its low pressure drop (which usually is less than 1.0 inches of water). The low presure drop results in extremely low operating costs, because of the savings in required fan horsepower. However, this washer design should not be used where a relatively high concentration of gaseous contaminants is present in the air stream.

Spray chambers utilize the principles of interception—contact between the mist particle and spray droplet. They are an economical solution for removing large liquid particles from air streams where efficiencies below 90% are satisfactory.

Baffle spray towers require a high gas velocity, with a resultant high pressure drop to force particles against the baffles which are wetted continually with spray droplets. Well designed spray towers give collection efficiencies to 90% on entrained liquid particles greater than 10 microns. They are expensive to operate because of high pressure, high volume, and high fan operating requirements.

Several types of scrubbers are sometimes in series. A wet cyclone/concurrent packed scrubber combination, for example, removes highly soluble noxious gas and dust present in the same gas stream. This combination consists of two sections built essentially into one housing or shell. The top section is a wet cyclone design which removes the dust particles by centrifugal force. The dust is washed down the shell of the scrubber into a launder placed above the packed bed. After passing through the cyclone section, the gas stream enters a packed bed where the highly soluble gas is absorbed in the irrigating liquid. This particular design permits a high face velocity in both the cyclone section and concurrent packed section. This reduces the space requirements for the main scrubber shell, but a separate entrainment separator must be provided when this combination is used.

The wet cyclone does provide some initial gas absorption while removing a large percentage of the solid particulates. The concurrent section removes the majority of the remaining soluble gases and most of the remaining solid particulates down to five microns.

The disadvantages of this approach (wet cyclone/concurrent combination) are that the height requirements are excessive and may not be available. A top inlet/bottom outlet arrangement may not suit the total system require-

Industrial wet scrubber applications

| Steel | Gases—HCl Liquid entrainment—H₂SO₄ |
|-----------------|--|
| Metal finishing | Gases—HF, NO _x Liquid entrainment—NaOH, HNO₃, H₃PO₄, cyanides Mists—H₂CrO₄ |
| Aluminum | Dusts—AIF₃, Al₂O₃ Gases—HF Fumes—AICl₃ |
| Pulp & paper | Gases—Cl ₂ , ClO ₂ , CSO ₂ |
| Pharmaceuticals | Liquid entrainment—CH ₃ OH, (CH ₃) ₂ CHOH, amines DSMO monochlorobenzene |
| Food processing | Gases—H₂S, CS₂ Liquid entrainment—H₃PO₄, acetic and maleic acids |
| Textiles | Gases—H₂S, CS₂, HCl Liquid entrainment—H₂SO₄ |

ments. An entrainment separator must be supplied.

Another typical combination is a wet cyclone followed by a cross-flow packed scrubber. Similar to the concurrent combination, this combination will handle dusts above five microns at high loadings, and highly soluble gases.

The wet cyclone/cross-flow combination provides economical recovery of gases from an air stream loaded with solid particulates. Again, the wet cyclone acts as a pretreatment or initial scrubbing section while the cross-flow acts as the tail gas scrubber. The heaviest portion of the solids is knocked out in the wet cyclone. The gases and smaller particulates are removed in the tail gas packed scrubber. Elimination of the solid particulates before the gases enter the packed scrubber lessens the possibility of blinding the packing support plate or building up heavy solid depositions in the packed bed.

The advantages of a wet cyclone/ cross-flow combination over the wet cyclone/concurrent flow are:

• Greater flexibility in choice of scrubbing liquors for each section.

• Recovery in either stage without contamination from previous stage.

• More efficient gas absorption with greater overall efficiency.

• Separate housing permits separate installation, allowing for spreading of initial investment over a greater time period.

• A flexibility that permits addition of more packing at later date for increased gas absorption.

• The cross-flow scrubber acts as a built-in entrainment separator.

Other combinations, such as venturi's followed by cross-flow scrubbers, concurrent followed by counter-current, venturi followed by counter-current, etc., can be adapted to handle a specific requirement. The exact combination best suited for the problem would be based on performance requirements, nature of contaminants, and costs (initial and operating).

Reinforced plastic

Construction materials available for scrubbers used in corrosive service include glass fiber reinforced plastic, lined steel, stainless steel, and costly titanium and nickel alloys. Reinforced plastic, for a number of reasons, is probably better suited to more corrosive services than any other material. Three major criteria—resistance to temperature, corrosion, and abrasion—decide what FRP scrubbers can handle.

• Temperature limitation of FRP is usually in the range of 250° F.-300° F. Quench chambers located before FRP wet scrubbers, however, frequently can solve a high temperature problem.

• Corrosives generally are not a problem; polyester, epoxy, or furan resin systems handle most corrosive materials. The exceptions are a few concentrated oxidizing agents, such as sulfuric acid above 70% concentrations. Reinforced polyester offers the broadest range of corrosion protection; furans usually are used where solvents or organics are present in quantity; and epoxies have the best alkali resistance.

• Abrasion resistance usually does not present a problem with FRP wet scrubbers, because adding air and water in the control process reduces the abrasive action of the solids.

Generally, initial equipment costs of FRP units are as low as three quarters the cost of rubber-lined steel. one third the cost of ceramic, and one half the cost of acid brick-lined equipment, and much less than units of stainless steel and more exotic alloys. On large equipment, reinforced plastic may be competitive with such common materials as carbon steel because the cost of handling and field-welding large steel equipment is high. Installation cost generally is low, due to lighter weight, less supports, flexibility of location, reduced shipping cost, and less field fabrication (equipment frequently is shipped assembled).

Maintenance of FRP equipment is minimal, as FRP resists corrosion and weathering. Repairs, if necessary, can be made by nonspecialized personnel. Maintenance costs can be as low as one half to one fifth that of comparable lined steel equipment, since there is no external corrosion. The equipment can either be shipped in unitized or packaged form, or fabricated at the job site from subassemblies. The limitation in equipment size for reinforced plastic is the same as other construction materials—limitation of shipping size of the equipment.

Due to the much lighter weight of reinforced plastic, large equipment frequently can be shipped in several pieces for final field assembly with a total overall savings over a completely field assembled steel construction. For example, in a recent installation, the FRP scrubber assemblies were completely unitized, including a design for roof-mounting into a standardized steel grid system. This concept involved a wet scrubber/fan/pump assembly mounted on a plastic coated steel skid that tied directly into the roof grid structure. The systems are controlling air quality where acid etching and cleaning of integrated circuits produce a variety of corrosive mists and gases.

Total weight of the packed wet

scrubber/fan/pump on the skid was 10,000 pounds. Light weight of the reinforced plastic system permitted minimum steel reinforcing. An estimated 15-20% cost savings resulted by assembling the scrubber package on skids at the factory and shipping it to the customer as a unit.



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Conductivity measurements monitor waste streams

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-he seriousness of water pollution problems generally is recognized, and it is well established that the most economical and positive control method is to prevent losses from occurring and entering plant effluents. Such losses usually can be stopped if their source is known; however, some sources are difficult to locate in a complex plant. A successful pollution control program may utilize all of the several methods available for monitoring waste streams. We shall discuss only one such procedure-electrolytic conductivity measurements. Conductivity measurements have been used for decades for process control, especially in steam power plants, but only recently have they been applied to pollution abatement. Waste water from many types of plants contains large amounts of such materials as phosphates, nitrates, ammonia, and potash. Solutions of these materials conduct electricity, thus making their presence, as well as their relative quantities, easily detectable. With continuous measurements, this information is immediately available and can be used as the basis for prompt corrective action.

Conventional methods of sampling and analyzing waste streams have inherent time lags which prevent the information from being useful for control purposes. But conductivity measurements can show exactly when a loss occurs, for how long, and can give an indication of its magnitude. Conductivity recorders strategically placed help operators locate leaks and spills rapidly, and the recorder chart is a valuable aid to the supervisor responsible for pollution control.

Theory

The ability of a solution to transmit a current depends primarily upon the number of ions per cubic centimeter. Electrolytic conductivity—also called specific conductance—is defined as the reciprocal of the resistivity, in ohmcentimeters, of a 1 cm. cube of solution at a specified temperature. The units of measurement are reciprocal ohmcm. or mho/cm. In waste control work, the conductivities encountered are generally one millionth of this unit, or in the micromho/cm. range. For example, pure water has a conductivity of 0.055 micromho/cm., and a good quality raw water about 100-200 micromhos/cm. In contrast, seawater has a conductivity of about 50,000 micromhos/cm., and 30% sulfuric acid about 1,000,000 micromhos/cm.

An alternating current Wheatstone bridge is used widely in measuring electrolytic conductivity. The use of alternating current and electrodes coated with platinum black virtually eliminates polarization effects. In the bridge circuit, the input current is divided proportionally by the resistances of two halves of the bridge. Since all resistances are fixed except for the resistance of the conductivity cell, the cell's total resistance determines the current division. When the conductivity cell or probe is immersed in a conducting solution, there is a temporary change in its resistance which creates a potential difference across the bridge until the circuit is balanced. In the simplest conductivity meter, a variable resistance is manually repositioned to restore the balance, and this gives a measure of the change in conductivity of the solution being tested. In transmitting type meters, the change in voltage drop across the variable resistor will cause a change in voltage to a high impedance amplifier. The amplifier then sends a signal to the balancing motor proportional to the voltage change. The balancing motor mechanically repositions the sliding contact on the variable resistor, thereby causing the voltage to the amplifier to return to its original balanced condition. As the balancing motor moves, it also positions the sliding contact of a resistor in the transmitter circuit. This provides a voltage signal output from the transmitter directly proportional to the change in conductivity of the sample cell.

Commercial instruments

Most standard industrial conductivity instruments use a bridge voltage that ranges from a few thousandths of a volt to 50 volts. Theoretically, the Wheatstone bridge can be used with any voltage. High voltages increase the sensitivity and accuracy of the Wheatstone bridge; however, instrument manufacturers prefer to design their units for commonly used voltages to keep the cost low and to ensure the safety of operating and maintenance personnel. Most industrial users are satisfied with an accuracy of 1-2% of the full-scale range, and the voltage is chosen to provide this accuracy. Our work at Tennessee Valley Authority (TVA) used a 110 volt supply at 60 cycles per second for the instrument and 3-10 volts for the bridge.

The electrolytic conductivity of aqueous solutions usually increases with temperature at a rate of about 0.5-3% per degree Centigrade. If measurements are made at temperatures other than 25° C., the instrument circuits usually are compensated so the readings will indicate the conductivity at the reference temperature (25° C.). This is accomplished by incorporating into the Wheatstone bridge circuit a resistor which can be changed with temperature. This resistor can be either a calibrated rheostat for manual adjustment or a thermistor with the proper temperature coefficient combined with fixed resistors.

In a typical conductivity cell, the electrodes are annular bands surrounding the liquid flow opening and recessed in an insulating plastic housing. Electrode spacing is determined by the instrument design. When the cell is immersed, current flows through liquid between the electrodes and completes the Wheatstone bridge circuit.
feature

Each cell has a cell constant that depends on the exposed electrode area, the spacing, and the material and shape of its electrodes. If the total resistance is kept in the range of 50-100,000 ohms by the proper choice of cell constant, standard low-cost components can be used to make the Wheatstone bridge. If a cell with a constant of 0.01/cm. is used to measure the conductivity of distilled water, the total resistance is $1,000,000 \times 0.01$, or 10,000 ohms, a value within the range of 50-100,000 ohms of less expensive common components. Cells with constants ranging from 0.001/cm. to 100/ cm. are commercially available. Therefore, when a conductivity cell is being bought, it is important to know the micromho/cm. conductivity range of the liquid to be measured so that the cell obtained will give a total resistance within the range of 50-100,000

ohms. Conductivity indicators, transmitters, and recorders are available from most large instrument manufacturers, but only one or two U.S. companies manufacture conductivity cells in quantity.

Except for the cell, the components of conductivity instruments are common, simple parts used in many types of instruments. The components of a Wheatstone bridge are resistors, which seldom fail; other components are standard circuits which have been thoroughly engineered for long service life. Simple, portable conductivity instruments with manual temperature compensation cost about \$200, and semiportable recorders with automatic temperature compensation run to \$1000. Permanent installation using multipoint recorders are usually less expensive than those which use an equivalent number of semiportable recorders.

Solution conductivities

The conductivity of a stream will vary with the rate of material loss, the kind of material, and the stream flow. A five g.p.m. flow of contaminated water might have a conductivity in excess of 10,000 micromhos/cm. and actually be carrying less contamination than a large flow (2000 g.p.m.) which might show a barely perceptible increase in conductivity over that of uncontaminated water. Therefore, before any conductivity instruments are used. a laboratory study should be made to determine the normal conductivity of the raw water used and how its conductivity changes as different amounts of the various possible contaminants are added. To be of any use, the instrument must be sensitive enough to detect that conductivity level which represents the threshold of pollution, and, often, this value is relatively low.



The electrolytic conductivities of most solutions are given in the literature, but these values are usually for pure compounds dissolved in distilled water. In manufacturing plants, uncontaminated raw water has an appreciable background conductivity, and the materials which may contaminate it are not pure. For these reasons, each plant must prepare its own conductivity vs. concentration curves, using its raw or treated water to prepare the solutions to be measured.

Conductivity curves may be prepared by successively diluting a portion of a stock solution of known compositions with raw water and measuring the conductivity of the solution after each dilution.

Fertilizer materials made at TVA's National Fertilizer Development Center include phosphoric and nitric acids, anhydrous ammonia, diammonium phosphate, and several solid and fluid fertilizers containing ammonia, nitrate, and phosphate in varying proportions. In addition, there are several process or waste materials such as sulfuric acid and fluorine compounds. These materials can contaminate waste streams either singly or in combination. In several manufacturing operations, waste streams can be contaminated by only one material. In that case, the concentration of the contaminant can be estimated reliably from the proper conductivity vs. concentration curve.

Most of the conductivity curves for possible contaminants at TVA plants are straight lines or uninflected curves. An inflection in the ammonia curve occurs at a concentration of about 4%NH₄OH, but this is unimportant in detecting contamination of raw water because such contamination undoubtedly would have been detected before the concentration reached this value.

An inflection also occurs in the phosphoric acid curve between 0-75 p.p.m. of P_2O_5 . This can complicate leak detection. The literature reports the conductivity inflection for ammonia found in the TVA work and an inflection for phosphoric acid at a concentration between 50-70% H_3PO_4 , but no inflection has been reported for concentrations between 0-75 p.p.m. P_2O_5 . This inflection is possibly caused by a reaction of the phosphoric acid with some constituent in water used at TVA.

Types of meters

Portable conductivity instruments weigh about four pounds, are dry cell

powered, and utilize a center reading null meter or an electron ray eye tube as balance indicators. A 25 foot cell cable is a convenient length, although longer cables are available. If the cable length is changed significantly on any instrument, the bridge must be recalibrated. The instruments normally use manual temperature compensation, but automatic compensation can be obtained.

Semiportable instruments weigh about 25 pounds, are battery operated, splashproof, and have a circular chart recorder. They are designed to operate on two 6 volt lantern batteries and, thus, can be portable. Our experience has shown that the lantern batteries have a short service life and usually are replaced with a 12 volt storage battery in a protective case. This makes the unit semiportable, requiring a car or truck for movement. It is worthwhile to purchase an instrument model which has a watertight windowed door. In damp, corrosive atmospheres, a pullover shroud of pliable transparent plastic will protect the aluminum case and door hinges and still permit the chart to be inspected without exposing the case or the electronic components to the atmosphere. If exposed, the instrument should be supported above the ground against electrical grounding. The cell cable should be the maximum length obtainable, and automatic temperature compensation should be specified if the streams to be monitored routinely vary in temperature more than about 10° F.

Semiportable conductivity recorders are useful for preliminary surveys of waste systems and for troubleshooting. In addition, they are quite valuable in determining whether waste discharges are cyclic, sporadic, or continuous.

The semiportable instrument also is valuable when used as part of an operating plant. It can be quickly and inexpensively converted to operate on a 110 volt circuit as a permanent installation at a strategic point in the plant. It can be reconverted easily to battery operation for troubleshooting.

Temporary installations are most useful in making surveys of chemical sewers and drains to determine in which general areas of the plant pollutants are being discharged, and to detect sources of unsuspected contamination. Permanent installations usually are restricted to those plant areas where large amounts of possible pollutants are stored or processed. These installa-

Atmospheric well for conductivity cell



tions are designed for immediate detection of spills and consist of conductivity cells located in surface drainage ditches from storage tank areas (with each cell monitoring only a few tanks), and cells located in the discharge lines for cooling water from heat exchangers, reactors, and other units. Each cell is connected to a recorder, usually the multipoint type, equipped with an audible alarm.

Cell choice

The type of cell chosen and its installation for each application are critical if contamination is to be detected reliably. For use in surface drainage ditches where the effluent may contain a large proportion of suspended solids, especially during rains, the cell should be installed so as to minimize deposition of solids in the cell chamber, and should be readily removable for cleaning. This can be done with a settling chamber immediately upstream from the cell and by installing the cell facing the flow with open end pointing downward. To assure a flow through the cell when ditch flows are low, the ditch should be dammed and the cell installed through the dam an inch below the top with the vent below the dam. The cell should be of a type that can be cleaned easily and thoroughly without affecting the electrodes. Cells of one piece epoxy construction with platinum ring electrodes flush with the axial bore are rugged and dependable and

can be cleaned easily with a soft brush.

To monitor flows under pressure, it is best to bring a sample of the flow to a conductivity well containing the measuring cell at atmospheric pressure rather than to put the cell in the line under pressure. Inspection, calibration, and cleaning of a cell in an atmospheric well are much easier than for one installed in a pipeline.

Conductivity cells installed in drain lines have to be carefully located or suction and venturi effects may prevent a sample from entering the cell.

Location

Efficiency of the cell system depends heavily on proper location. The cells should be located in branch streams rather than in the main stream below the entering side streams: this makes the system more sensitive and pinpoints the source of contamination better. The cells should be located close to the points of potential contamination, but far enough downstream so that the contaminant will be thoroughly mixed with the waste water. Otherwise, the contaminant may slip by the cell undetected, especially in waste water streams where the flow tends to be laminar. Under laminar conditions, water soluble liquids having a specific gravity much greater than one (such as superphosphoric acid and concentrated fluid fertilizers) tend to travel along the bottom of sewers before becoming mixed well enough for detection.



If the water overflows from a large basin or a jacketed vessel over a weir in one side, the flow at each end of the weir will represent only the water coming from that side of the basin or jacket. The conductivity cell must be located in the jacket drainpipe at a point where these essentially separate streams are mixed, or a leak may go undetected.

Frequently, it is difficult to properly locate a conductivity cell in such drains. In this case, it may be expedient to install two conductivity cells wired in parallel in the jacket, one on each side of the discharge weir. This will result in the recorder indicating greater background conductivity for that point than one cell would indicate, but the response to contamination also will be greater. This arrangement will permit the detection of leaks into either half of the jacket. If the cells are wired in series, the indicated background and response will be less than that obtained from one cell. All cells should be located where they can be inspected and cleaned safely and conveniently.

A permanent installation usually is designed to serve a plant area where several points of possible contamination are relatively close. At TVA, the installation usually is limited to monitoring about 12 points, one of which is uncontaminated raw water to provide background measurements or baseline conductivity. Deviation from the baseline by any of the other points indicates contamination, except for small deviations that occur because of differences in nominal cell constants. Temperature differences in streams being monitored also will produce variations unless compensation is provided.

TVA's installation

A permanent conductivity installation is installed in TVA's fluid fertilizer manufacturing area where superphosphoric acid and ammonia gas are combined in a reactor to produce fluid fertilizer. The heat generated is removed by recycling the hot liquid through a water-cooled shell-and-tube heat exchanger which cools it further. The area contains storage tanks for phosphoric acid and the fluid fertilizer product. There is no storage for ammonia, since it is piped into the area.

The procedure we used to design the permanent conductivity installation in the area was as follows:

• The optimum number and location of the detection cells were determined. It was desirable to monitor small flows (less than 100 g.p.m.) so that small losses would cause high concentrations and, therefore, easily detected conductivities. A survey of the area showed that all points of possible loss could be monitored by installing detection cells at 10 locations; two were in the outlet water lines of the two heat exchangers, and eight were in surface drains. An eleventh cell was installed in a raw water stream to provide baseline information.

• Normal and maximum expected flow rates were determined for each stream to be monitored. Use of rainfall data enabled prediction of the flows in outside drainage ditches.

• The level of contamination to be detected was determined. In this area, phosphoric acid and mixtures of ammonia and phosphoric acid were the only possible contaminants. We decided that each of the 10 installations in the fluid fertilizer area should detect P_2O_5 loss at the rate of 200 pounds per day. The nitrogen loss would be less, because the $N:P_2O_5$ ratio of the fertilizer being manufactured was about 1:3.

• The net conductivity increase was calculated for each stream by use of these data, and the conductivity vs. concentration relationships previously determined for the contaminants involved.

• The type of instrumentation required was selected. Each of the eight streams in the surface drainage ditches had high conductivity ratios and remained within 10° F. of raw water temperature. Cells in these streams were connected to a multipoint recorder equipped with one manual temperature compensator that provided equal compensation for all cells. Cooling water leaving the two shell-and-tube heat exchangers required more precise instrumentation.

Usual variations of 5-10 micromhos/ cm. in the conductivity of the raw water would represent a significant change from the small net conductivities of 20 and 105 to be detected. The 35° F. temperature difference between the inlet and outlet water at each exchanger also required compensation. The temperature problem was eliminated by heating a sample stream of the inlet water to the temperature of the outlet water by conducting the sample stream of inlet water through several feet of tubing wound around the outlet pipe and covered with heat transfer cement; the pipe and tubing then were overlaid with insulation.



We did not use thermistor-type temperature compensation because it is impractical to insert both the second cell and thermistor in the Wheatstone bridge circuit. Variations in the conductivity of the raw water were compensated for by selecting an instrument which measures only the ratio of the conductivities of the inlet and outlet waters; this ratio will be one if there is no contamination of the outlet water and will be greater than one if contamination is present. Matched cells must be used because differences between cells can significantly decrease the sensitivity of the installation.

The conductivity ratio technique also can be used to monitor streams where phosphoric acid is the only possible contaminant and the net conductivity to be detected is in the inflected portion of the concentration vs. conductivity curve. In this case, contamination causes the conductivity ratio to be less than one. The physical layout of the system was designed for efficient inspection and maintenance. All conductivity cells were made readily accessible and easily removable from their mountings for inspection and cleaning.

Maintenance

To properly maintain a conductivity cell installation, each cell and recorder should be checked daily. The cells should be removed, checked, visually, and if necessary, cleaned. The cells may be carefully cleaned by using a soft brush. When the cell is removed from the monitored stream, the recorder should be checked to make sure that the indicated conductivity is zero. Once a week, or as often as necessary, each cell should be checked against a solution of known conductivity, such as raw water. Those cells which are located in surface drainage ditches should be inspected for stoppage at least once a shift by the chemical plant operator.

Data for design of electrolytic conductivity type contamination detection system for fluid fertilizer manufacturing area

| Stream No. | Source of flow | Possible contaminant | Estimated flow, g.p.m. | Parts per million P₂O₅ to give 0.1 ton per day | conductivity to be detected micromhos/ cm.a | Ratio, net conductivity of stream to conductivity of raw water ^b |
|---------------|------------------------------------|----------------------|---------------------------|---|---|---|
| 1 | Raw water (baseline) | | _ | _ | _ | 1 |
| 2 | Surface drainage north of building | Fluid fertilizer | 100 | 167 | 200 | 1.11 |
| 3 | Surface drainage north of building | Fluid fertilizer | 100 | 167 | 200 | 1.11 |
| 4 | Drainage from mixing tank area | Fluid fertilizer | 20 | 835 | 1200 | 6.67 |
| 5 | Drainage from west acid tanks | Phosphoric acid | 5 | 3335 | 5300 | 29.44 |
| 6 | Drainage from middle acid tanks | Phosphoric acid | 5 | 3335 | 5300 | 29.44 |
| 7 | Drainage from east acid tanks | Phosphoric acid | 10 | 1670 | 3100 | 17.22 |
| 8 | Drainage in west side of building | Fluid fertilizer | 10 | 1670 | 2200 | 12.22 |
| 9 | Drainage in east side of building | Fluid fertilizer | 10 | 1670 | 2200 | 12.22 |
| 10 | Water from primary cooler | Fluid fertilizer | 550 | 30 | 20 | 0.11 |
| 11 | Water from secondary cooler | Fluid fertilizer | 150 | 111 | 105 | 0.58 |
| | | | | | | |

 a At 25° C. b Conductivity of raw water was 180 micromhos/cm. at 25° C.

They also should be inspected after each rain and cleaned if necessary.

One point on the multipoint recorder should be wired so that it gives a calibration check reading. Any deviation from this constant check reading indicates recorder malfunction.

At the TVA National Fertilizer Development Center, we found that the electroconductivity technique is valuable for control of material losses. Five permanent installations are in use, as well as five semiportable and two portable units, for monitoring intermittent loss source. By showing when and where losses are occurring, this equipment has greatly simplified execution of our pollution abatement program, and savings that result from rapid detection of losses of valuable materials quickly repay the cost of installation and surveillance.



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Nat

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Factors Affecting the Use of Monomolecular Surface Films to Control Oil Pollution on Water

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■ Under suitable conditions, monomolecular surface films may be used to confine oily pollution on water. Since these materials spread spontaneously into one-moleculethick layers, very small quantities can be used to treat large surface areas. The surface-chemical characteristics of several potential pollutants were studied to determine their behavior at the air/water interface. A number of monolayer-forming materials with varying surface-chemical properties were examined for their ability to survive at an air/water interface and contain oil films. The following monolayer properties relevant to oil pollution control were determined: the monolayer spreading velocity, the ability to resist and spread against wind, and the thickness of an oil lens supportable by a particular monolayer. Optimum characteristics were demonstrated by "liquid" water-insoluble monolayers with high film pressures and low oil solubility. Surface films with high spreading pressures will compress thinly spread layers of pollutant oil to lenses 0.5-1.0 cm. thick, substantially reducing the area covered by pollution.

il of petroleum origin is constantly leaked or pumped into the ocean from ship bilges, coastal oil-drilling operations, and submarine geological faults. Recently, man has polluted the seas in vast quantities from oil tanker mishaps and valve-turning errors aboard ships carrying petroleum fuels. Once released onto the water, there are a number of dispersive forces which act upon this floating organic contamination (Figure 1). Low-molecular-weight and water-soluble components are lost from the surface by dissolution and evaporation. Other substances are returned to the sea by bacteriological attack (ZoBell, 1963; Pilpel, 1968), adsorption on nonbuoyant particulate matter, and the physical action of waves and breaking water. In addition, constituents of the surface are forced back into the sea by sinking water beneath wind-driven surface-film streaks (Kraus, 1967). Chemically unsaturated components are readily attacked by ultraviolet radiation. This photochemical oxidation ultimately breaks the unsaturated molecules into smaller, more soluble fragments which are easily displaced from the surface (Timmons, 1962). In addition to evaporation, organic material may be carried into the marine atmosphere by wind-generated sea spray or by fragments from bursting bubbles (Blanchard, 1964).



Figure 1. Partial cycle of organic material in the ocean-dispersive forces at the air-sea interface

Nature's compound attack upon the organic constituents of the sea surface prevents the ocean from becoming wholly slick-covered and partially destroys and disperses the vast quantities of oily pollution being injected into the marine environment. In spite of this, there is an immediate need for oil dispersion and control techniques in coastal areas, estuaries, and rivers where extensive petroleum pollution can be economically and esthetically harmful. Recent attacks on this problem have followed two general pathsphysical and chemical. Physical processes involves removal of the offending substance by burning, straw absorption, adsorption onto nonbuoyant solids, and various forms of surface skimming or rotating drum adsorption. The chemical approach utilizes surface-active material to emulsify the oil into the water. The pollution is temporarily displaced from the surface, but it remains in the water, and the pollutant oils may recur upon subsequent release from the solid adsorbers or upon breakup of the oil-water emulsions. The utility of these various methods depends upon the size of the petroleum spill, its location, and the meteorological and oceanographic conditions prevalent in the polluted site.

The subject of this paper is the use of water-insoluble, nontoxic, monomolecular films to guide or contain an unwanted oil slick. The confinement of the oil with a peripheral artificial slick would be useful in recovery operations on small spills. Obviously retrieval of the oil is preferable to dispersal since the offending material is removed from the environment. By compressing the spill into a thicker lens occupying a smaller surface area, retrieval would be facilitated. The use of water-insoluble piston films was first studied by Zisman (1943) as a possible technique to drive oil from the vicinity of sinking ships. The authors deemed the method to be of limited value because of the great oil-thickness in the vicinity of the ship subsequent to the spill. Sigwalt (1964) also proposed the use of a fatty acid to neutralize the spreading of oil, although no study was made of the limitations of the technique or of the chemical variables involved in selecting the most effective film. The validity of this approach and the conditions under which it is applicable to current oil pollution problems will be discussed in terms of (1) the surface chemistry of petroleum products on water bodies, and (2) the effects of oceanographic and meteorological parameters on the spreading properties and oil-confinement characteristics of the monomolecular control films.

Surface Chemistry of Petroleum Products on Water

In general, pure hydrocarbons do not spread spontaneously onto a water surface. Only the low-molecularweight hydrocarbons do not remain as a liquid lens but spread readily and exert a positive spreading pressure (Pomerantz, Clinton, *et al.*, 1967). The spreading pressure of the oil, F_{o} , is defined as

| $F_o = \gamma_w - (\gamma_o + \gamma_{ow})$ | where $\gamma_w = \text{surface tension of}$ water |
|---|---|
| | $\gamma_o = \text{surface tension of}$ |
| | $\gamma_{ow} = interfacial$ tension |
| | between the oil and water. |

Aliphatic hydrocarbons more volatile than *n*-nonane and most aromatics have small positive F_o 's (spread), while

none of the cyclic hydrocarbons spread spontaneously, i.e., their spreading pressures are negative. When petroleum spills occur, the volatile rapidly spreading components evaporate, leaving behind a complex mixture of the higher-molecular-weight hydrocarbons as well as compounds containing oxygen and sulfur. The principal hydrocarbon families in crude oils are paraffins, cycloparaffins and cyclic aromatics with smaller amounts of aromatics. The sulfur and oxygen-containing compounds are surface active, the hydrophilic polar portion of the molecule being associated with the water surface, while the nonpolar or hydrocarbon portion of the molecule is oriented toward the petroleum oil. It is these surfaceactive constituents which cause the otherwise nonspreading hydrocarbon oils to thin out into oil slicks which often show characteristic light interference colors. The extent of spreading is a function of the quantity and nature of the surface-active components of the oil.

If the water surface is already occupied by a surface film (sea slick), spreading of the oil may be retarded. Further, surface currents driven by wind, waves, and convectional cells determine the shape and direction of movement of the oil spill (Blokker, 1964). The spreading tendency of the oil against external forces (spreading pressure) is dependent upon the quantity of surface-active material in the oil. For example, 0.2, 0.5, and 1.0% dodecanol-1 dissolved in paraffin oil ($F_o < 0$) gave spreading pressure values for the respective mixtures of 3.0, 11.0, and 17.5 dynes/cm. (Zisman, 1941).

The sources and properties of three possible oily pollutants are listed in Table I. Spreading pressures of the oils were determined by the piston monolayer technique of Zisman (1941). Spreading pressure measurements of this kind should be performed with a fresh lens of oil because some of the hydrophilic components of the oil may interact irreversibly with the substrate. Furthermore, there is the possibility of dissolution of the piston monolayer into the oil lens. Repeat values on the same oil lens are unlikely because of irreversible changes which occur once the oil has spread. The rather high values of 25-33 dynes per cm. on seawater (Table I) were due entirely to the polar surface-active components in the oils. Thus, these pollutants will spread into thin films on a clean water surface unless external chemical agents or physical processes are present to exert a counter force against the spreading tendency of the oils.

| Table I. Sources and Surface-Chemical Properties of Potential Petroleum Contaminants | | | | | | | | |
|---|---|-------------|---------------------------|--|--|--|--|--|
| Туре | Source | Density | Spreading Pressure— F_o | | | | | |
| Light refugeo crude, Texas | Humble Oil Co. | 0.84 g./cc. | 33.0 dynes/cm. | | | | | |
| Lago crude, South American | Humble Oil Co. | 0.95 g./cc. | 28.1 dynes/cm. | | | | | |
| Navy special fuel oil | Cracked stock, Navy supply depot, Seattle, Wash. | 0.94 g./cc. | 25.0 dynes/cm. | | | | | |
| Marine diesel fuel | Navy | 0.84 g./cc. | 26.0 dynes/cm. | | | | | |



Figure 2. Spreading velocities of various monolayer-forming materials as a function of distance from spreading source

Properties of Monolayers for Oil Pollution Control

The effectiveness of water-insoluble monomolecular films to control or contain oil spills depends upon location and the geophysical conditions under which they are to be applied. Several liquid monolayer-forming materials were rated for their ability to spread rapidly and spontaneously into a monomolecular film, to spread against wind, and to contain oily pollution as a thick unspread lens.

The possibility of using monolayers to confine oil slicks on water required a knowledge of film-spreading rates. Monolayer-spreading velocities over short distances have been determined using small quantities of monolayerforming material (Frenkiel, 1965). However, under the conditions of application in the field, the surface film is supplied from unspread liquid lenses of material which are in equilibrium with the monolayer. Since the excess drops of liquid film-forming chemicals do not spread on their own monolayers, they act as reservoirs to replace losses from the control film and to expand its size. The following experiment was designed to provide information on the change of spreading velocity with distance from the point of application, a practical matter which must be considered in the application of this oil pollution technique.

Spreading velocities were determined for a series of liquid surface-active materials in a rectangular tank (3 m. long, 11.3 cm. wide, and 5.5 cm. deep). After the surface was cleaned by sweeping with sliding hydrophobic barriers, teflon powder was sprinkled on the water surface near the start end of the trough. A 20-mg. drop of mono-layer-forming liquid was added to this end of the trough which drove a straight line of powder normal to the tank sides as the monolayer front traveled down the length of the trough. The time of passage of the powder line was recorded at 30-cm. intervals up to 270 cm. Velocity v_s . distance plots are given in Figure 2 and summarized in Table II.

For most substances, the spreading velocity was a direct function of spreading pressure. In all cases, the velocity decreased as the monolayer front moved away from the liquid-drop source. The binary mixture of 0.78% dodecanol-1 in paraffin oil did not spread as rapidly as would have been expected from its spreading pressure. In this case, the spreading velocity was controlled by the rate of diffusion of the dodecanol to the air/water/oil drop interface from which the dodecanol could reinforce and supply its monolayer spreading down the trough. An overall rate for the entire 270 cm. travel path was compared

Table II. Comparison of Monolayer Spreading Velocities and Spreading Pressures

| Compound | Spreading Pressures Dynes/cm. | Spreading Velocity ^b cm./sec. |
|----------------------------|-------------------------------------|--|
| Dodecanol-1 | 41.1 | 13.4 |
| Sorbitan monooleate | 40.8 | 11.9 |
| Oleyl alcohol | 32.9 | 9.0 |
| Glyceryl trioleate | 17.0 | 8.5 |
| Cottonseed oil | 13.8 | 6.7 |
| Spreading oil ^a | 14.9 | 5.6 |
| Tricresyl phosphate | 9.0 | 3.9 |
| a 0.78% dodecanol-1 in non | enreading paraffin oil | |

a 0.78% dodecanol-1 in nonspreading parafin oil. b Based upon time to spread 270 cm.

with spreading pressure of the monolayer-forming material (Table II). With the exception of the synthetic twocomponent spreading oil, spreading velocity increased with increasing spreading pressure. Thus, one would choose a liquid with a high spreading pressure to rapidly cover a water surface with a monomolecular film.

Ability to Spread Against Wind

The movement of slicks and surface films on water bodies follows the motion of the surface water to which the molecules of the surface film are anchored. Of the many physical processes which cause motion of surface water, wind usually is the most influential. According to Fitzgerald (1964), a clean wave-covered water surface moves at a speed which is about 1/30 that of wind. This ratio of the rate of surface movement to wind velocity (μ_s/V) was independent of wind speed. By adding a watersoluble surface-active agent (detergent) to water in a laboratory wind tunnel, the capillary-wave structure was damped out and (μ_s/V) increased linearly with wind speeds at low V and tended toward a constant value of 0.045 for V greater than 5.5 m. per sec. The water-insoluble surface films which are being considered as oil-control agents damp capillary waves as intensively as concentrated detergent solutions (Davies and Rideal, 1963; Garrett and Bultman, 1963). It is reasonable, therefore, to apply Fitzgerald's wind coupling value of 0.045 (μ_s/V) to these water-insoluble films on a water surface.

The ability of the monolayer to spread against or resist wind are important factors in the determination of a suitable material. Wind resistance was measured in the small cylindrical wind tunnel depicted in Figure 3. A wax-coated hydrophil tray was constructed to fit inside the tunnel so that the tray water level was at the horizontal center line of the tunnel. The water-insoluble monolayerforming material was added to the downwind segment of the tray. An excess (20 mg.) was used to supply monolayer



Figure 3. Laboratory wind tunnel (top view) for determination of wind resistance of monomolecular films

to this portion of the tray in the event of loss due to the mechanical disturbances of the air stream. This experimental approach is consistent with the anticipated field technique, since control film will contain excess bulk material as liquid lenses in equilibrium with it. In the tray the monomolecular film was separated from the clean, upwind end by a floating teflon thread which bowed into the clean side due to the film pressure differential between the monolayer and that of the clean water. Wind velocity was increased until the spreading force of the film was balanced by the force of the wind, as indicated by the thread forming an S curve. Greater air velocities forced the thread to bow into the film-covered side of the tray.

The equilibrium wind velocities measured by this technique at 25° C. are listed for various monolayer-forming materials in Table III. The ability to oppose and spread against the wind increased with increasing spreading pressure. Thus, materials with high spreading pressure will not only spread rapidly but will move against and resist wind to a greater degree than low-pressure surface films.

When the spreading tendency of the film is in equilibrium with the wind velocity, the following expression can be written

$$u_m = \mathbf{k}(V) \tag{1}$$

where $k = \mu_s/V = 0.045$ for a fully damped, incompressible surface

V = air velocity $\mu_{\theta} = \text{surface velocity of water}$ $\mu_{m} = \text{initial spreading rate of surface film at } t = 0.$

From this expression and the measured equilibrium wind velocity, V, the initial spreading rate of the monolayer can be calculated. μ_m was not attainable from the previously described spreading rate experiments except by a crude extrapolation of the rate curves to zero distance. μ_m represents the maximum monolayer spreading rate in the vicinity of the monolayer source. Values of this parameter calculated from Equation 1 and equilibrium spreading pressures are listed in Table III for six liquid monolayer-forming substances. For comparison, extrapolated μ_m values have been reported for monolayers of oleyl alcohol (27 cm. per sec.) and a mixture of octadecanol-1, hexadecanol-1 and oleyl alcohol which had an

| Table | Ш | Equili | brium | Wind | Speeds | and S | Spreadin | g Pressures |
|-------|-----|---------|-------|--------|---------|-------|----------|-------------|
| | for | Various | Water | -Insol | uble Mo | nomo | lecular | Films |

| Monolayer | Equil. Wind Speed ^a (m./sec.) | Equil. Spreading Pressure ^b (dynes/cm.) | Initial Spreading Vel. (cm./sec.) |
|----------------|---|---|--|
| Tricresylphos- | | | |
| phate | 5.62 | 9.0 | 25.3 |
| Cottonseed oil | 7.51 | 13.8 | 33.8 |
| Glyceryl | | | |
| trioleate | 8.02 | 17.0 | 36.2 |
| Oleyl alcohol | 8.60 | 32.9 | 38.7 |
| Sorbitan | | | |
| monooleate | 8.71 | 40.8 | 39.2 |
| Dodecanol-1 | 9.26 | 41.1 | 41.7 |

^a Minimum wind speed which prevents spreading of monolayer. ^b Surface tension difference between clean water and water covered with monolayer in equilibrium with excess monolayer-forming material. initial spreading pressure of 32 cm. per sec. (McArthur and Durham, 1957). These values were determined at closely-spaced intervals in small hydrophil troughs near the monolayer source. The method described in this paper is a single-data-point technique for the measurements of μ_m and provides a measurement of the wind velocity at which the film is in spreading equilibrium with the opposing air motion.

Oil Thickness Supported by Monolayers

Perhaps the most important parameter relevant to this method is the thickness of oil which can be supported by a confining monomolecular film, as well as the area that will be occupied by a quantity of oil under confinement. If recovery methods are used on the confined oil pool, their design will depend upon the oil-layer thickness. According to Langmuir (1933), the thickness of a large lens of nonspreading oil ($F_o < 0$) on water can be calculated from

$$t^2 = \frac{-2F\rho_w}{g\rho_o(\rho_w - \rho_o)} \tag{2}$$

where t = oil lens thickness

 $\rho_o = \text{oil density}$

 $\rho_w =$ water density.

If an external spreading force is applied by a control monolayer (F_m) , it is possible to confine a pollutant oil containing surface-active components with a spreading pressure of F_o , as long as F_m is greater than F_o . In this case the oil lens thickness may be calculated from a modification of Equation 2.

$$t^{2} = \frac{-2(F_{o} - F_{m})\rho_{w}}{g\rho_{o}(\rho_{w} - \rho_{o})}$$
(3)

Oils with densities near that of water are confined in thicker lenses than less dense petroleum products. The lens thickness will also be greater when F_m , the spreading pressure of the confining monolayer, is high, and F_{α} , the spreading pressure of the spilled oil, is low. A test of Equation 3 was made by building up oil lenses on monolayer-covered distilled water surfaces until a constant thickness was attained. The oil lens thickness (t) was measured with a cathetometer to the nearest 0.01 mm. The wall of the transparent circular dish in which the experiment was performed was made hydrophobic with a clear inert perfluoroester resin. Thus, the water made a 90° angle of contact with the dish wall, and there was no meniscus to interfere with observation of the top of the oil lens. The laboratory data compared reasonably well with the modified Langmuir formula to justify its usefulness. This was particularly encouraging in view of the fact that the oil spreading pressures were difficult to measure exactly. Spreading pressures of the pollutant oil can, in fact, be obtained from Equation 3 once the oil thickness has been determined. Solutions to Equation 3 are shown in Figure 4, where the spreading pressure differential between the oil and control film $(F_m - F_o)$ is plotted against oil thickness for selected oil densities (ρ_0) . For a particular monolayer, knowledge of F_{ρ} and ρ_{ρ} will provide a close estimation of the oil thickness supportable by the monolayer.

Attempts to use dodecanol-1 as a control film in this confinement experiment met with curious failure. The solution rate of this low-molecular-weight alcohol was sufficiently high that strong surface tension gradients drove the oil lens and the excess drop of alcohol about the glass tray. In a short time the monolayer which had



dissolved into the oil increased the spreading pressure of the oil lens and reduced its thickness, since the spreading pressure difference $(F_m - F_o)$ was no longer as large. While this effect was not obvious with the higher-molecularweight, less-oil-soluble monolayers, it is clear that there is a requirement of low oil solubility for a monolayer used to confine oil spills.

Low solubility in petroleum products can be achieved by the inclusion of hydrophilic (hydroxyl) groups in the molecule of the film-forming compound. Sorbitan monooleate, which contains three free hydroxyl groups, is relatively insoluble in petroleum oils (Zisman, 1943) and does not dissolve rapidly in seawater. When a sorbitan monooleate monolayer was held at F = 20 dynes per cm. for 30 min. on a film balance, little film loss occurred by dissolution into a seawater substrate.

Optimum Properties of Control Monolayers

The studies of spreading rate, wind resistance, and oil lens thickness all indicated that control monolayers with high spreading pressure are most effective. In addition, low oil and water solubility are desirable for monolayer durability on a water surface in contact with an oil spill. The monolayer-forming material should be easily applied to the water to provide rapid, spontaneous surface coverage.

A chemically unsaturated alcohol, 9-octadecen-1-ol, (oleyl alcohol) has been studied as a useful compound for modifying air/sea interactions and meets most of these requirements (Barger and Garrett, 1968). However, its equilibrium spreading pressure, 33.8 dynes per cm. on seawater, is only slightly above that of some of the petroleum oil contaminants (Table I). Promising materials with film pressures in the neighborhood of 40 dynes per cm., which do not interact with alkaline substrates, include the solid saturated fatty alcohols and the fatty esters of sorbitol and glycerol. The solid fatty alcohol monolayers have been utilized extensively for evaporation control, but these materials must be dispensed as finely ground powder of from water emulsions. Their spreading rates from the solid state are quite slow and their monolayers are easily collapsed by wave action into multilayers which do not readily respread. On the other hand, many of the liquid surface-active agents spread rapidly, and their monolayers act like a two-dimensional liquid that will readily respread over a film deficient area caused by breaking water and wave-induced surface dilations.

Conclusions

The laboratory results indicated that a high-film-pressure monolayer would maintain itself against a wind of 8 m. per sec. However, in small-scale field tests, it was found that this method was not effective against onshore winds greater than 2 m. per sec. Although the film effectively compressed the oil into thick lenses, wind-generated surface currents in addition to the wind drag itself opposed the upwind spreading of the monolayer. However, the oil was readily confined, condensed, and driven from shore when winds were parallel to or away from the point of monolayer application. In open water, oil slicks were compressed to small thickened lenses by a peripheral control film. The oil was kept in a compressed condition; the oil-monolayer system moved with the wind.

These studies have indicated that surface films whose spreading pressures are 40 dynes per cm. or greater will operate effectively upon oil slicks whose thickness does not exceed 0.5-1.0 cm. Thus, it is anticipated that water-insoluble films will find greatest use against relatively minor spills along coasts or in rivers and harbors. The application of the one-molecule-thick piston film does not eliminate or disperse surface pollution, but acts as a confining barrier to compress and reduce the surface area occupied by the spilled oil. The "two-dimensional" surface film may be spread around the periphery of the spill to prevent its further spreading, pending removal or dispersal. Spreading the monolayer between the oil slick and the shore will prevent onshore drift and provide protection of waterfront property until the pollution has moved on to a less vulnerable location as long as the wind is not onshore. In addition, these films may be useful in driving oil out of inaccessible locations between ships and under docks so that retrieval techniques can be applied.

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Removal of Submicron Particles in Packed Beds

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• This study was undertaken to provide a better understanding of colloid removal in filter beds. The influence of physical parameters is evaluated and a model presented to correlate physical filtration parameters to removal efficiency. Removal of the virus *Escherichia coli* bacteriophage T_4 is studied in packed beds of activated carbon. The chemical characteristics of the system are maintained at optimum conditions for virus attachment, while the physical characteristics are varied. Virus removal is interpreted by a physical model based on particle transport by diffusion in a flowing fluid. Virus removal closely follows the transfer model, which can be used to predict the effects of flow rate, bed height, void volume, and bed grain size on removal efficiency.

Filtration has been extensively investigated, but much of the work concerning filtration was primarily empirical. None of the proposed empirical equations correlate all variables, making it impossible to evaluate the effects of variables on filtration efficiency. In recent years, innovations have altered the old concepts of filtration and theoretical advances have given impetus to the formulation of filtration theories.

Filtration efficiency depends on physical and chemical parameters which can be described by two steps-a particle transport and an attachment step. Particle attachment is brought about by colloid-chemical forces controlled by the surface properties of the respective materials and van der Waals forces (Ives and Gregory, 1966). In filtration, these forces result from interactions between the surface of the filter media and the suspended-aqueous phase particles. Chemical effects in filtration are supported by correlation between electrophoretic mobility of suspended particles and their removal (Jorden, 1963). Removal of clay colloids and bacteria by sand filters appears to depend on clay micelle orientation, diffusion, van der Waals forces, and electrokinetic forces (Edwards and Monke, 1967). It will be the purpose of this paper to consider the physical process of filtration, *i.e.*, the particle transport step.

Physical Filtration Theories

Physical filtration mechanisms include straining, sedimentation, inertial impingement, and diffusion. An excellent discussion of these has been presented by O'Melia and Crapps (1964). Traditional concepts of rapid sand filtration have assumed that suspended-particle removal is accomplished primarily by straining, sedimentation, or both, and have been generally described by various empirical equations. Ives and Sholji (1965) have recently developed a theoretical representation of physical filtration based on gravitational forces. They propose a model by evaluating the relationships between filter efficiency and the variables of media size, flow velocity, and water viscosity. Although the theory of Ives and Sholji is probably the most comprehensive in describing physical filtration, it is limited to particle sizes that are mainly influenced by gravitational forces.

The first attempts to explain filtration of small particles have originated from aerosol filtration data. Friedlander (1958) correlated data on aerosol filtration by fibrous filters operated at low Reynolds numbers to parameters based on diffusion and direct interception. O'Melia and Stumm (1967), using Friedlander's model, illustrated that diffusion and not direct interception was the major contributor to contact efficiency of suspended particles of 3 μ or smaller. For particles of 0.3 μ in size, diffusion almost solely governed contact efficiency. Traditionally, little importance has been given to diffusion models for water filtration, but studies presented by Robeck (1963) indicate that the great majority of the suspended particles in the influent to rapid sand filters are smaller than 3 μ in diameter. These studies indicate that diffusion is important, and the transport step in filtration may be limited by a diffusion process. A better model for filtration would then be obtained from consideration of diffusion in a flowing fluid.

This study examines the removal of viruses through packed beds and evaluates the theory of mass transfer, based on the thin boundary layer solution of the diffusion equation, for water filtration systems. The removal of bacteriophage T_4 by activated carbon beds is examined under varying conditions of bed length, grain diameter, bed porosity, and flow rate. Virus removal and filtration variables are interpreted by mass transfer theory. Although this study is devoted to virus removal in activated carbon beds, it should be emphasized that the model will apply to any colloid being removed in porous beds where diffusion is the limiting step. This study has many ramifications, since it will apply to the removal of color and other organics by filtration units and adsorption beds.

Viruses are transmitted by water, and the need for further knowledge on virus removal has been emphasized as a prerequisite to water quality control. Viruses are also very uniform in size and shape and can be assayed with a high degree of accuracy. One assays individual virus particles and not molar concentration.

Mass Transfer Theory

The goal of any filtration theory is to predict the effect of variables on removal efficiency. Particle removal in a filter can be related to a transfer coefficient, k. In a fixed bed, the rate of transfer between inlet and outlet conditions of the bed is described by the equation

$$G(C_1 - C_2) = k A_m \Delta C_{lm} V \tag{1}$$

In Equation 1, G is the flow rate, A_m the surface area per unit volume of packing, V the bed volume, ΔC_{lm} the log mean concentration, and C_1 , C_2 the inlet and outlet concentrations.

From the transfer coefficient, bed characteristics, and flow rate, Equation 1 can be used to predict filtration efficiency. Direct application of Equation 1, however, depends on the ability to calculate k from the theory of diffusional exchange between flowing fluids and surfaces.

Mass transfer coefficient is often expressed in the dimensionless Sherwood number, Sh. Mass transfer models can be expressed in terms of the Sherwood number and the dimensionless Peclet number, Pe. The Peclet number is a measure of the ratio of transport by convective forces to transport by molecular diffusion. The theory of heat transfer in a flowing fluid has been extensively investigated and can be directly applied to mass transfer. Theoretical approaches have used the boundary-layer theory and the von Karman integral relation. This approach involves the assumption that a concentration boundary layer exists. This boundary layer is a limited region of flow around the surface of the filter medium and is affected by the presence of this surface. Resistance to mass transfer is assumed to reside in this boundary layer. The driving force for mass transfer is the concentration difference across the boundary layer. The concentration of colloid or solute adjacent to the bed solid is the equilibrium concentration for adsorption systems or the saturation concentration for dissolution of solute. At the edge of the boundary layer, the concentration reaches the mainstream value. If a concentration distribution is assumed to exist across this boundary layer, and the concentration boundary layer coincides with the velocity boundary layer, then the mass transfer rate can be calculated by use of the known velocity distribution and a mass balance. Various alterations to the mass transfer problem have been developed.

Pfeffer and Happel (1964) extended mass transfer theory to include multiparticle systems. Their model is developed on the basis that two concentric spheres will describe a typical cell in a random assemblage consisting of many cells, each of which contains a particle surrounded by a fluid envelope. Each cell is assumed to contain a spherical fluid envelope whose relative volume to the particle volume is the same as that of the whole assemblage. The entire disturbance due to each particle is confined to the cell of fluid with which it is associated. Thus, the concentration of the forward moving fluid is that of the cell boundary.

From Pfeffer and Happel's (1964) derivation, the Sherwood number (Sh) is a function of the Peclet number (Pe) and void fraction, and at high Peclet numbers (Pe > 70), the Sherwood number can be expressed as a simple exponential function of the Peclet number

$$Sh = Be Pe^{1/3}$$
 (2)

(3)

Be is given by

where

$$W = 2 - 3\gamma + 3\gamma^5 - 2\gamma^6 \tag{4}$$

and the fractional void volume, ϵ , of a multiparticle system is directly related to γ , the geometry of the free surface model by the expression

Be = $1.26 \left[\frac{1 - \gamma^5}{W} \right]$

$$\epsilon = 1 - \gamma^3 \tag{5}$$

For a single particle in a flowing fluid, $\epsilon = 1$, Equation 2 reduces to

$$Sh = 0.997 Pe^{1/3}$$
 (6)

Mass transfer data for packed beds are usually correlated to the dimensionless *j*, or Colburn factor, which takes into account system characteristics and is defined by

$$j = \frac{\mathrm{Sh}}{\mathrm{Re}\,\mathrm{Sc}^{1/3}} = \frac{k}{u} \left(\frac{\nu}{\mathrm{D}}\right)^{2/3} \tag{7}$$

and since

$$Pe = Re Sc$$
 (8)

therefore

$$j = \operatorname{Be} \operatorname{Re}^{-2/3} \tag{9}$$

Thus, the Colburn factor is a function of the Reynolds number, Re, and a constant dependent on void fraction. This equation can be rewritten as follows:

$$j = 1.26 \left[\frac{1 - (1 - \epsilon)^{5/3}}{W} \right]^{1/3} \text{Re}^{-2/3}$$
(10)

In order to compare data taken at different void volumes, Equation 10 is written in terms of a pseudo-Reynolds number, N_{Re} , which depends on the void fraction.

$$j = 1.26 \left\{ \left[\frac{1 - (1 - \epsilon)^{5/3}}{W} \right]^{-1/2} \text{Re} \right\}^{-2/3}$$
(11)

$$j = 1.26 N_{\rm Re}^{-2/3} \tag{12}$$

The mass transfer coefficient, k, can be determined from Equations 7 and 9 and used in Equation 1 to predict filtration efficiency. This model was evaluated by correlation of experimental values of j and Reynolds number to the theoretical relationship expressed by Equation 9.

Experimental Procedure

Filtration columns of various diameters were made from plexiglas tubing (Figure 1). Columns were from 4.2 cm. to 25.2 cm. in length. The ends of each column were equipped with tubing connectors for the flow meter, pump, and manometer. A rubber or cork gasket and a copper screen (100 mesh) for supporting the bed media were placed between each flange. The column was packed by repeated addition of small amounts of activated carbon and tapping in order to obtain the greatest compaction. A peristaltic pump, consisting of a combination of masterflux pump heads and a servodyne power drive system provided excellent control of the flow rate. Flow rate was used to determine pressure drop in the packed beds during filtration.



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Table I. Physical Characteristics of Activated Carbon

| Mesh ^a size | Number of particles sized | Mean effective diameter $(\mu) D_m$ | Specific surface (cm. ² per cm. ³) Sv | Total surface ^b area (cm. ² per gm.) |
|---------------------------|---------------------------------|--|---|--|
| 20/30 | 1913° | 982° | 60.10° | 397° |
| 30/40 | 893° | 550° | 109.3° | 779° |
| 70/80 | 1918° | 248° | 241.6° | 1715° |
| 20/30 | | 992ª | 60.50^{d} | 357ª |

^a Particles passed a U.S. standard sieve No. 20 but were retained on No. 30, etc.

Determine by microscopic counting of number of particles per gram. Determine by microscopic examination.

^d Determine by pressure drop studies. Note: $D_m = 6/Sv$ for spherical particles.

In order to prevent the adsorption of viruses to glassware, positive charges were removed by washing in an alkalidetergent mixture. After washing, glassware was rinsed in tap water, rinsed with distilled water, and then sterilized in a hot air oven at 200° C. for one hour. The activated carbon was sterilized by autoclaving. Pumping equipment and accessories were sterilized before each test run with a mixture of penicillin (100 units per ml.), and streptomycin (0.2 mg. per liter). After a contact time of two hours, the pumping equipment was rinsed by passing sterilized distilled water through the system.

Application of mass transfer theory requires knowledge of the media particle size and the void fraction of the packed bed. Particle sizes were initially determined by microscopic examination and void fractions by immersion of the activated carbon bed in water. A Porton's Graticule was used to size the granular carbon microscopically. Three different mesh sizes of carbon were sized and used in the filtration studies (Table I).

The determination of void fraction by water immersion was found to be unrealistic for activated carbon beds. This discrepancy was revealed by pressure losses monitored during each filter run. Water immersion gave high void fractions, a result of the carbon's ability to sorb water in inner pores and other dead-end areas that do not constitute porosity related to the flow regime of the packed bed. If each particle is considered to be surrounded by an impervious envelope, the void volume needed is the space between the envelope particles; and the area of the enveloping surface per unit enveloped volume is known as the specific surface.

The effective void fraction (ϵ) of the activated carbon beds was calculated from experimentally determined values for the bulk density (ρ_B) of the packed column and the particle density (ρ) of the activated carbon.

$$\epsilon = 1 - \rho_B / \rho \tag{13}$$

The particle density of crushed porous materials can be determined from gas-flow rate, pressure drop and bulk density measurements in packed columns. This method was first outlined and discussed by Ergun (1951). The method is based upon the determination of the values a and b of the pressure drop Equation 14 at different bulk densities to which a given porous material may be packed:

$$\frac{\Delta P}{Lu}g = a + bU \tag{14}$$

where

$$a = 150 \frac{(1-\epsilon)^2}{\epsilon^3} \frac{\mu}{D_m^2}$$
(15)

$$b = 1.75 \, \frac{1-\epsilon}{\epsilon^3} \, \frac{1}{D_m} \tag{16}$$

The intercept, a, and slope, b, can be obtained by plotting g vs. U. The void fraction, ϵ , and the effective diameter, Lu D_m , are the only variables that a and b are dependent upon. Since the effective diameter is constant for a particle of a given size, the effect upon changing the intercept or the slope will make it possible to determine the void fraction.

A total of 118 flow rate-pressure drop measurements were made at 10 different bulk densities. Typical plots are given in Figure 2 from which values of a and b were determined by the method of least squares. An average particle density of



Figure 2. Typical plots of pressure drop equation at different bulk densities

Table II. Column and Bed Characteristics

Table IV. Experimental Values for the Equation $j = Be Re^{x}$

| | | | Colculated | Particle | | | Void Fra | ction Term | |
|-------------|------------|--------------------------|------------------|----------------------------|--|----------|--------------------------|------------|--------------------------------|
| Test no. | Height cm. | Area cm. ² | void fraction | diameter cm. $\times 10^2$ | A_m cm. ² /cm. ³ | Test no. | theoretical (Pfeffer) | Be | Reynolds number exponent |
| 1 | 8.60 | 0.375 | 0.345 | 9.87 | 50.0 | 1 | 3.8 | 4.3 | -0.53 |
| 2 | 8.59 | 0.405 | 0.296 | 9.87 | 53.4 | . 2 | 4.3 | 5.7 | -0.66 |
| 3 | 4.20 | 0.385 | 0.236 | 2.48 | 264.0 | 3 | 5.1 | 4.8 | -0.57 |
| 4 | 7.50 | 0.664 | 0.277 | 2.48 | 253.0 | 4 | | | |
| 5 | 12.40 | 1.330 | 0.330 | 9.87 | 50.8 | 5 | 39 | 4.6 | -0.58 |
| 6 | 25.20 | 2.010 | 0.315 | 9.87 | 52.2 | 6 | 4 1 | 4 1 | -0.64 |
| 7 | 25.20 | 2.010 | 0.299 | 9.87 | 53.0 | 7 | 4 3 | 4 1 | -0.57 |
| 8 | 25.20 | 2.010 | 0.278 | 9.87 | 54.9 | 8 | 4 5 | 4 1 | -0.50 |
| 9 | 12.40 | 1.330 | 0.413 | 5.50 | 91.6 | 9 | 3.3 | 4.4 | -0.54 |

| | Table III. Filtration Data | | | | | | | | |
|-------------|---|---|---|--|--|--|--|--|--|
| Test no. | Flow rate G. cm. ³ /sec. | $\frac{\Delta P}{Lu}g \times 10^{-3}$ dyne-sec./ cm. ⁴ | Inlet virus conc., virus/cm. ³ | Outlet virus conc., virus/cm. ³ | Transfer coeff., $(k \times 10^4)$ cm./sec. | Re | | | |
| 1 | 0.3020 0.1685 | Not measured | $1.4	imes10^8$ $1.4	imes10^8$ | $1.1	imes10^8$ $1.0	imes10^8$ | 4.66 3.52 | 7.92 4.43 | 1.44 1.95 | | |
| 2 | 0.1718 0.1533 | Not measured | $1.5	imes10^{6}$ $1.5	imes10^{6}$ | $\begin{array}{c} 1.0 \times 10^{6} \\ 9.6 \times 10^{5} \end{array}$ | 3.76 3.67 | 4.36 3.74 | 2.21 2.42 | | |
| 3 | 0.446 0.252 0.167 | 61.9 61.2 53.4 | 9.1×10^{5} 9.1×10^{5} 9.1×10^{5} | 2.7×10^{5} 2.0×10^{5} 1.1×10^{5} | 12.50 8.89 8.19 | 2.87 1.62 1.08 | 2.70 3.39 4.71 | | |
| 4 | 0.076 0.056 0.042 | 133.0 117.0 12.0 | 9.3×10^{5} 9.3×10^{5} 9.3×10^{5} | 0 0 | 4 52 | 0 158 | 17.85 | | |
| 5 | 0.636 0.550 0.467 0.380 0.292 0.210 0.122 | 63.4 62.2 61.9 61.8 64.5 62.2 54.9 | $\begin{array}{c} 1.1 \times 10^{6} \\ 1.1 \times 10^{6} \end{array}$ | $\begin{array}{c} 6.8 \times 10^{5} \\ 6.4 \times 10^{5} \\ 6.0 \times 10^{5} \\ 5.7 \times 10^{5} \\ 5.3 \times 10^{5} \\ 4.8 \times 10^{5} \\ 3.0 \times 10^{5} \end{array}$ | 3.54 3.46 3.29 2.90 2.47 2.01 1.84 | 4.71 4.09 3.47 2.82 2.16 1.56 0.91 | 1.87 2.09 2.36 2.53 2.81 3.18 5.01 | | |
| | Б <u>.</u> | | $S_c = \frac{\nu}{D} =$ | $1.25 	imes 10^5$ | | | | | |
| 6 | 4.370 3.770 3.170 2.750 2.000 1.400 0.867 | 5.14 5.56 5.21 5.26 4.53 5.37 5.18 | $egin{array}{c} 1.0	imes10^6\ 1.0	imes10^6$ | $\begin{array}{c} 6.7 \times 10^5 \\ 6.4 \times 10^5 \\ 6.5 \times 10^5 \\ 5.7 \times 10^5 \\ 5.7 \times 10^5 \\ 5.0 \times 10^5 \\ 4.0 \times 10^5 \end{array}$ | 6.60 6.33 5.17 5.80 5.72 3.65 3.00 | 21.45 18.50 15.55 13.50 9.80 6.85 4.26 | 0.76 0.84 0.82 1.06 1.43 1.31 1.74 | | |
| 7 | 0.292 0.210 0.122 0.058 0.018 | 8.51 8.31 8.18 6.45 6.82 | $1.0 	imes 10^{6}$ $1.0 	imes 10^{6}$ $1.0 	imes 10^{6}$ $1.0 	imes 10^{5}$ $1.0 	imes 10^{5}$ $1.0 	imes 10^{6}$ | $\begin{array}{c} 1.9 \times 10^{5} \\ 1.4 \times 10^{5} \\ 0.68 \times 10^{5} \\ 0.23 \times 10^{5} \\ 0.06 \times 10^{5} \end{array}$ | 1.81 1.55 1.22 1.15 0.49 | 1.44 1.03 0.60 0.285 0.089 | 3.12 3.69 6.12 9.96 13.45 | | |
| 8 | 3.770 2.890 1.720 1.130 | 7.31 6.38 5.81 6.63 | $1.4 	imes 10^{6} \\ 1.4 	imes 10^{6} \\ 1.4 	imes 10^{6} \\ 1.4 	imes 10^{6} \\ 1.4 	imes 10^{6} \end{cases}$ | 7.3×10^{5} 7.6×10^{5} 6.5×10^{5} 5.2×10^{5} | 8.87 6.43 4.73 4.03 | 18.45 14.20 8.43 5.50 | 1.18 1.11 1.37 1.79 | | |
| 9 | 0.151 0.217 0.302 0.373 0.482 0.565 | 5.56 6.18 6.11 6.28 6.95 6.84 | $\begin{array}{c} 1.2 \times 10^6 \\ 1.2 \times 10^6 \end{array}$ | $\begin{array}{c} 0.78 \times 10^{5} \\ 0.99 \times 10^{5} \\ 1.3 \times 10^{5} \\ 2.2 \times 10^{5} \\ 2.6 \times 10^{5} \\ 2.8 \times 10^{5} \end{array}$ | 2.56 3.13 4.12 3.96 4.55 5.06 | 0.62 0.90 1.25 1.55 2.00 2.34 | 5.62 4.86 4.54 3.63 3.15 2.98 | | |



Figure 3. Colburn factor vs. Pfeffer's pseudo-Reynolds number

Figure 4. Plot of je vs. Reynolds number

0.202 gram per cm.³ was obtained for the 20/30 size carbon. The range of values was 0.196 to 0.209 gram per cm.³. The 550- and 248- μ carbons were assumed to have the same particle density of 0.202 gram per cm.³. The average pore size of activated carbon is about 20 μ . The 550- and 248- μ particles should have about the same pore volume per weight as the 992- μ carbon, and, consequently, nearly the same particle density. Particle properties determined by the pressure drop technique confirmed those obtained by microscopic techniques (Table I). From the particle and bulk densities, the void fraction was calculated for each mass transfer test.

The procedures of Cookson and North (1967) were used for assaying and preparing bacteriophage T_4 stock solutions and *Escherichia coli* B. host cells. The filtration solution of virus was buffered at pH 7.0 with mono-dipotassium phosphate of ionic strength of 0.10. This pH and ionic strength provide the optimum condition for virus attachment to carbon. For each mass transfer test, samples were collected (1) from the buffered virus solution, (2) at the inlet of the filter column to determine any virus loss through the pump, and (3) at the outlet of the filter bed. Different flow rates were examined for each column by starting with the highest initial flow and then progressively decreasing.

Virus Removal Through Packed Beds

Since the packed bed removes a greater portion of the viruses upon initial contact with the bed, an average concentration value from the influent and effluent does not adequately describe the virus concentration of the flow through the bed. Consequently, a log-mean virus concentration value is used.

log-mean concentration, $\Delta C_{lm} =$

$$\frac{(C_1 - C^*) - (C_2 - C^*)}{\ln \frac{(C_1 - C^*)}{(C_2 - C^*)}} \quad (17)$$

The equilibrium concentration, C^* , at the surface of the carbon media is found by applying the Langmuir Isotherm, according to Cookson and North (1967).

In this study, tests were made under conditions where C^* was small (200 viruses per cm.³) compared to inlet and outlet virus concentrations of about 1×10^6 and 4×10^4 viruses per cm.³, respectively. In other words, the filter bed was operated well below its saturation point. Therefore, the equilibrium

concentration term has been neglected when determining the log-mean virus concentration.

Experimental Results

Virus removal was monitored through nine carbon beds, each bed being subjected to different flow rates. Physical characteristics were not identical for any of the nine columns (Table II). Parameters for mass transfer have been calculated for each column tested, incorporating the varying conditions of media size, column length, column area, void fraction, and flow rate (Table III). In mass transfer test 4, which used the $248-\mu$ carbon, all of the virus particles were removed, as none were detected in the effluent samples. The assay procedure requires a minimum of 2000 viruses per cm.³ for detection. For comparison with results of other tests, one virus per cm.³ was assumed to have passed through the column (Table III).

As discussed above, the theoretical correlation of Colburn factor to Reynolds number predicts an exponent of $-\frac{2}{3}$ for systems with a Peclet number greater than 70. All Peclet numbers in these tests were greater than 1000. The Reynolds number exponent varied from -0.50 to -0.66 (Table IV).

The experimental exponent may differ from the theoretical because of deficiencies in the basic mass transfer model. Application of mass transfer theory (Equation 9) requires knowledge of the equilibrium concentration; i.e., the virus concentration in solution at which the rate of virus adsorption equals that of desorption. A simplified equilibrium concentration, based on the total capacity of the carbon bed, was calculated from equilibrium studies of Cookson and North (1967). The maximum equilibrium concentration for each test was under 300 viruses per cm.3, which is negligible compared to the virus concentration in the bulk flow. Saturation is not expected to occur over the column length, but saturation may occur within the column. For gas flow in packed beds, saturation is nearly complete when the gas has passed a number of particles of the order of 10 (Theones, Kramers, 1958). One can also expect saturation of the first carbon particles of a packed bed with viruses. In this part of the column, the equilibrium concentration is equal to the concentration of viruses in the bulk flow, and the equilibrium concentration will vary in the direction of flow. The log-mean driving force (Equation 17), therefore, is an improper representation of the concentration profile. A second deficiency in the filtration model is that less than 100% particle attachment will result in values less than those theoretically predicted. Both particle attachment and equilibrium distribution are interesting aspects of the basic filtration model and merit further investigation by researchers in this field.

Virus removal is a function of void volume, and close correlation between different void volumes is obtained with Pfeffer's parameter Be (Table IV). Experimental data were plotted according to Pfeffer (1964), and the equation of best fit determined by the method of least squares (Figure 3).

$$i = 1.71(N_{\rm Re})^{-0.55} \tag{18}$$

The dependence of Colburn factor on void fraction is also examined according to Gupta and Thodos (1962). They recommend the correlation of $j\epsilon$ to Reynolds number. Wilson and Geankoplis (1966) used this correlation for Reynolds numbers of 0.0016 to 55 and recommend the following equation:

$$j\epsilon = 1.09(\text{Re})^{-2/3}$$
 (19)

From Figure 4 the experimental equation is:

6.0 5.0

$$j\epsilon = 1.50(\text{Re})^{-0.59}$$
 (20)

By correcting each test for void fraction by Pfeffer's method and $1/\epsilon$, the Colburn factor was found to vary with Reynolds number to the exponents of -0.55 and -0.59, respectively. McCune and Wilhelm (1949) obtained an exponent of -0.58for liquid phase mass transfer. The removal of viruses by packed beds correlates well with the simple version of the mass transfer theory used. Additional research, however, is needed to examine the back pressure due to desorption of viruses from the bed. This phenomenon appears to be significant, since Colburn factor, *j*, varies with bed height.

For column heights of 7.50 to 12.40 cm., very good correlation was obtained with Equation 19. The experimental equation for these columns is (Figure 5)

$$j\epsilon = 1.72(\text{Re})^{-0.65}$$
 (21)

For column heights of 25.40 cm., the best line through the data yielded the equation (Figure 6)

$$j\epsilon = 1.30(\text{Re})^{-0.53}$$
 (22)

Shorter columns gave *j* values 30% higher than the long columns. The Reynolds number exponent is also closer to the theoretical $-\frac{2}{3}$ for the shorter columns.



Figure 6. Plot of $j \in vs$. Reynolds number for column heights of 25.4 cm.

Wilson and Geankoplis (1966) report *j* values to be 15% higher for short columns compared to long columns. Bradshaw and Myers (1963) found j values 40% less for gases in 4-inch beds compared to 1-inch beds. They concluded that j was independent of bed height if the mean driving force used for the longer lengths was obtained by graphical integration, using the outlet concentrations from the shorter lengths.

In activated carbon adsorption columns and sand filters, the concentration gradient and mean driving force may differ from the log-mean driving force, ΔC_{lm} . Both the equilibrium concentration and mean driving force will vary with degree of saturation of the bed. This particular problem should be examined by determining the concentration profile in the bed based upon isothermal adsorption. This discussion indicates the need for getting internal samples, so that the true concentration gradient and mean driving force can be determined.

Conclusion

In summary, under optimum adsorption conditions, virus removal in packed beds of activated carbon closely followed mass transfer theory. Colburn factor, j, varied with fractional void volume of the bed, but j was constant if the void fraction corrections of Pfeffer and of $1/\epsilon$ were applied. Colburn factor also varied with bed heights. Greater deviation from theoretical equations occurred with longer column heights. This phenomenon is probably due to improper representation of the concentration profile through the column.

From this study, it appears that the particle transport mechanism in filtration can be described by application of the mass transfer theory when diffusion is the limiting process for removal. Application of mass transfer with information on isothermal adsorption may eliminate the effect of column height.

Nomenclature

- = surface area per unit volume of packing, cm.² per A_m cm.⁸
- = constant depending on void fraction Be
- C_1 = inlet concentration, viruses per cm.³
- C_2 = exit concentration, viruses per cm.³
- C_2 = exit concentration, viruses per cm.³ ΔC_{lm} = log-mean concentration, viruses per cm.³ C^* = equilibrium concentration, viruses per cm. D = diffusion coefficient, cm.² per sec. D_m = mean effective diameter of bed particles, G = flow rate, cm.³ per sec. g = gravitational constant, cm. per sec.² j = dimensionless Colburn factor k = transfer coefficient, cm. per sec. L = bed height, cm. N_m = nesudo-Rewolds number defined by [1] = equilibrium concentration, viruses per cm.³
- = mean effective diameter of bed particles, cm.

- = pseudo-Reynolds number defined by $[1 (1 \epsilon)^{\delta/\delta}/W]^{-1/2}$ Re $N_{\rm Re}$
- Pe = dimensionless Peclet number, $Re \times Sc$

- ΔP = pressure drop, gm. per cm.²
- = dimensionless Reynolds number, uD_m/ν Re
- Sc = dimensionless Schmidt number, ν/D
- Sh = dimensionless Sherwood number, kD_m/D
- Sv = specific surface area, cm.² per cm.³
- = superficial velocity based on empty column, cm. per u sec.
- U = mass flow rate of fluid, $U = \rho_1 u$, gm. per cm.² sec.
- V = volume of column, cm.³
- W = function of γ , $W = 2 - 3\gamma + 3\gamma^5 - 2\gamma^6$

Greeks

- = ratio of inner sphere to outer sphere radii, dimen-Y sionless
- = fractional void volume, dimensionless e
- = particle density, gm. per cm.³ 0
- = bulk density, gm. per cm.³ ρ_B
- = liquid density, gm. per cm.³ ρ_1
- = absolute viscosity, gm. per cm. sec. μ v
- = kinematic viscosity, cm.² per sec.

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Capture of Small Particles by London Forces from Low-Speed Liquid Flows

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The motion of a small particle near a much larger collector is discussed using realistic expressions for the London attraction and especially the hydrodynamic forces when the distance between particle and collector becomes comparable to the particle size. By inspection of the equation of motion, one can deduce the few dimensionless groups on which the single collector efficiency depends and, in certain limiting cases, determine this dependency.

he present work grew out of an experimental study of the coalescence of liquid-liquid dispersions by flow through fibrous media (Spielman, 1968; Spielman and Goren, 1970). Here, as in more conventional filtration, the solid and coalesced liquid matrix may capture droplets by a number of mechanisms: interception, Brownian diffusion, inertial im paction, gravity settling, and long-range attractive forces. Order-of-magnitude estimates indicated that interception should be the dominant mechanism under our experimental conditions. The existing theory of particle capture by interception from low-speed flows, largely developed for aerosol filtration, predicts the filter coefficients varies as the square of the particle size and the inverse cube of the collector size, and is independent of flow rate. In contrast, our experiments showed more nearly a first power dependence on particle size, inverse 2.5 power dependence on fiber size, and inverse 0.25 power dependence on flow rate. Other recent liquid filtration experiments where interception is expected to be the dominant capture mechanism also give a first power dependence of the filter coefficient on particle size. We were therefore led to re-examine the existing theory of particle capture by interception from low-speed flows.

The classical model for particle capture by interception assumes the center of a small particle to follow exactly an undisturbed fluid streamline near a larger collector until the particle and collector touch, whereupon the particle is retained by molecular adhesion. Fluid motion is considered to enable collision and molecular attraction to prevent reentrainment. However, a particle in close proximity to a collector must deviate from the undisturbed streamline. The continuum description of fluid motion with "no slip" at solid boundaries becomes invalid for describing fluid movement in the gap between particle and collector when the gap becomes comparable to the mean free path of fluid molecules. For such small gaps the hydrodynamic resistance to closer approach of the particle is lower than that predicted by continuum theory with no slip. The mean free path of air molecules at standard conditions is about 0.1 μ ; thus, the capability of describing capture of micron and smaller particles from air by classical interception, which neglects viscous interactions between particle and collector altogether, should be promoted by the breakdown of the no slip continuum flow model. For liquids, however, the mean free path is of the order of the molecular dimensions; hence, the no slip continuum description should remain valid virtually to contact and the classical model for interception appears doubtful as an accurate description of capture from liquids. In fact, from a no slip continuum point of view, a spherical particle cannot truly contact the collector as a result of hydrodynamic forces alone because the rate of drainage of fluid between particle and collector would become infinitesimally small as the gap narrows. However, London-van der Waals forces increase very rapidly as the particle approaches the collector and becomes strong enough to overcome the otherwise slow drainage.

In this paper an equation is established describing the trajectory of a very small spherical particle in close proximity to a much larger cylindrical or spherical collector, and subject to hydrodynamic and London forces. Knowledge of the particle trajectory permits calculation of the efficiency of collection by individual obstacles which, in turn, is related to the filter coefficient of the macroscopic medium. Collection by simultaneous interception and Brownian diffusion is also discussed.

Motion of a very small particle in proximity to a much larger cylinder

The undisturbed low-speed flow field near a cylinder is given by the stream function

$$\Psi = 2A_F U a_F^{-1} (r - a_F)^2 \sin \theta \tag{1}$$

where A_F is a parameter characterizing the flow model. For isolated cylinders A_F is found from Lamb's solution:

$$A_F = \frac{1}{2} \left[1 - \ln \left(\frac{2\rho a_F U}{\mu} \right) \right]^{-1}.$$

For fibers in a fibrous mat, A_F is a function of the fraction solids α and is given as

$$4_F = \frac{1}{2} \left[-\frac{1}{2} \ln \alpha - \frac{1}{2} + \frac{\alpha^2}{2(1+\alpha^2)} \right]^{-1}$$

by Happel (1959),

$$A_F = \frac{1}{2} \left[-\frac{1}{2} \ln \alpha - \frac{3}{4} + \alpha - \frac{\alpha^2}{4} \right]^{-1}$$

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$$A_F = \frac{1}{2} \frac{ZK_1(z)}{K_0(z)}$$

where $\alpha = z^2[z + 2zK_1(z)/K_0(z)]/8$ by Spielman and Goren (1968).

We assume inertial impaction, sedimentation, and Brownian diffusion to be negligible. In many practical cases, the suspended particles are much smaller than the cylinder. It is then a good approximation to assume that the flow field past the cylinder is undisturbed by the particles except in the latter's immediate vicinity, and that at separations greater than several particle diameters, particle centers move along the undisturbed fluid streamlines given by Equation 1. At closer approaches it is necessary to take more realistic hydrodynamic interactions into account. Here we make the further approximation that the particles are so small compared to the cylinder that within separations where a particle trajectory deviates significantly from an undisturbed fluid streamline, the cylinder can be treated as a plane wall (except insofar as its size and shape determine the flow field far from the particle). The flow field in the neighborhood of a small moving particle is governed by the incompressible creeping flow equations

$$\nabla p = \mu \nabla^2 \vec{u}$$

$$\nabla \cdot \vec{u} = 0$$
(2)

In addition to giving the particle trajectory at large distances from the collector, Equation 1 also determines the boundary conditions far from the particle for the solution to Equations 2 for the locally disturbed flow field. With y = $r - a_F$ and $x = a_F(\theta - \theta_F)$, where θ_F is the angular displacement of the particle from the forward stagnation point, the undisturbed flow field far from a particle can be resolved into two flows, one a planar stagnation flow \vec{u}_{st} (arising from that velocity component at infinity along the line of centers of the cylinder and particle) and the other a shear flow \vec{u}_{sh} (arising from the flow normal to the line of centers).

$$\vec{u}_{st} = 2a_F^{-2}A_FU\cos\theta_P(2xy\ \vec{i}_\theta - y^2\ \vec{i}_R) \tag{3}$$

$$\vec{u}_{\rm sh} = 4 \, a_F^{-1} A_F \, U \sin \theta_P y \, i_\theta \tag{4}$$

These formulas for the undisturbed fluid velocity are valid for $a_F \gg (x^2 + y^2)^{1/2} \gg a_P$ and are correct to second order in x and y. Denoting the minimum gap between the particle and the assumed "flat" surface by h, the particle center is located at x = 0 and $y = y_P = a_P + h$.

The particle movement and accompanying flow disturbance can be obtained by considering radial and angular motions of the particle separately, since the linear Equations 2 apply and the boundary conditions at the particle surface, cylinder surface, and far from the particle are additive (Figure 1).

The radial (y-directed) motion of the particle may be resolved further into two separate flows. In one flow, the particle moves under the influence of an externally applied force F_n , consisting of a molecular component and a hydrodynamic component, the fluid velocity vanishing far from the particle and on the "flat" surface of the cylinder. Since the y-directed particle velocity, v_R , depends only on the quantities which enter into the equation of motion and boundary conditions of the problem,

$$v_R = \frac{dy_P}{dt} = \frac{dh}{dt} = f_1(\mu, F_n, a_P, h)$$

and dimensional analysis gives



A. Particle moving under applied force



Figure 1. Resolution of induced particle motion

$$p_R = \frac{dy_P}{dt} = \frac{dh}{dt} = \frac{F_n f_1(H)}{6\pi\mu a_P}$$
(5)

 $f_i(H)$ being a universal function of the dimensionless gap width $H = h/a_P$. For large H, the function $f_i(H)$ becomes unity, since far from the obstacle the particle obeys Stokes' law:

$$f_1(H) \cong 1 \quad \text{for} \quad H \gg 1 \tag{5a}$$

For small gaps the fluid motion has been solved by Charles and Mason (1960), who used the lubrication approximation to describe flow in the gap and obtained

$$f_1(H) \approx H \quad \text{for} \quad H \ll 1.$$
 (5b)

Happel and Brenner (1965) give numerical values for f_1 obtained from an exact solution to the equations of motion in bispherical coordinates.

The hydrodynamic component, F_{st} , of the force F_n is obtained by considering a second flow in which the particle is held stationary. The fluid velocity vanishes on both the particle and "flat" cylinder surfaces, but far from the particle becomes the undisturbed planar stagnation flow field of Equation 3. F_{st} can depend only on the quantities which enter into the equations of viscous flow and boundary conditions of this second hydrodynamic problem. Thus,

$$F_{\rm st} = f_2(\mu, a_P, h, a_F^{-2} A_F U \cos \theta_P)$$
 (5c)

where the last quantity in parentheses is the only parameter entering into the boundary condition far from the particle. Dimensional analysis then gives

$$F_{\rm st} = -6\pi \ \mu \ a_P{}^3 a_F{}^{-2} A_F U \cos \theta_P f_2(H) \tag{6}$$

where $f_2(H)$ is a universal function of H = Y - 1, $Y = y_P/a_P$ being the dimensionless location of the particle center. Far from the cylinder the force is given by Stokes' law, using the local fluid velocity so that

$$f_2(H) = f_2(Y-1) \cong 2Y^2$$
 (6a)

for $a_P \ll h \ll a_F$. As the gap width approaches zero, the function $f_2(H)$ approaches some positive numerical constant. That is,

$$f_2(H) \cong \kappa_2 \tag{6b}$$

for $h \ll a_P \ll a_F$. The constant κ_2 was determined by Goren (1970) by solving the hydrodynamic problem outlined above, using tangent sphere coordinates. For the planar stagnation flow of Equation 3, he found $\kappa_2 = 6.46$. The problem of the hydrodynamic forces on two spheres of arbitrary size and spacing in a uniform flow field has been solved by Stimson and Jeffery (1926), but their result is not convenient for computation for small gaps or great disparity in the sphere sizes. The hydrodynamic force F_{st} , given by Equation 6, is seen to be directed inward normal to the cylinder on the upstream side and outward on the downstream side.

The component, F_{Ad} , of F_n resulting from London attraction between a plane and a sphere neglecting the retardation effect has been calculated by Hamaker (1937); the result is

$$F_{Ad} = -\frac{2}{3} \frac{Q}{a_P} \frac{1}{(Y^2 - 1)^2}$$

$$= -\frac{2}{3} \frac{Q}{a_P} \frac{1}{(H + 2)^2 H^2}$$
(7)

where Q is known as Hamaker's constant and is typically of the order 10^{-12} to 10^{-13} ergs. Far from the obstacle, Equation 7 becomes

$$F_{Ad} \simeq -\frac{2}{_3} \frac{Q}{a_P} \frac{1}{Y^4}$$
(7a)

for $H \gg 1$. Near the obstacle, Equation 7 becomes

$$F_{Ad} \cong -\frac{Q}{6a_P} \frac{1}{H^2} \tag{7b}$$

for $H \ll 1$. When retardation is taken into account, F_{Ad} is expected to be of the form

$$F_{Ad} = -\frac{2}{3} \frac{Q}{a_P} \frac{1}{(H+2)^2 H^2} f_{\rm ret} \left(\frac{2\pi a_P}{\lambda}, H \right)$$
(8)

where λ is typically of the order 10^{-5} cm. The function f_{ret} is expected to approach unity for small h/λ and to approach $\kappa_{\text{ret}}\lambda/h \approx \kappa_{\text{ret}}\lambda/a_P H$ for large h/λ . Kruyt (1965) discusses the form of f_{ret} and the value of the numerical coefficient κ_{ret} . The hydrodynamic and attractive components of the force F_n may be added to give

$$F_n = F_{\rm st} + F_{Ad} \tag{9}$$

and substitution of Equations 5, 6, and 8 into Equation 9 yields an expression for the y-directed particle velocity:

$$v_R / a_P = \frac{dH}{dt} = -\frac{a_P A_P U}{a_F^2} \left[f_i(H) f_2(H) \cos \theta_P + \frac{N_{Ad_P} f_1(H) f_{ret}(2\pi a_P / \lambda, H)}{(H+2)^2 H^2} \right]$$
(10)

in which the dimensionless group

$$N_{Ad_F} = \frac{Qa_F^2}{9\pi\mu A_F Ua_F^4}$$
(11)

is termed the adhesion number.

The particle velocity v_{θ} tangential to the surface of the obstacle is obtained by considering the spherical particle as freely rotating and translating under the boundary conditions that far from the particle the flow field is the uniform shear flow given by Equation 4, while on the surfaces of the cylinder and sphere there is no slip. v_{θ} must depend only on the parameters entering into the equations of motion 2 and the boundary conditions; thus

$$v_{\theta} = f_3(a_P, \mu, h, a_F^{-1}A_FU\sin\theta_P)$$

The last quantity in parentheses is the single parameter entering into the condition 4. Dimensional analysis gives

$$v_{\theta} = a_F \frac{d\theta_P}{dt} = a_P a_F^{-1} A_F U \sin \theta_P f_{\mathfrak{s}}(H)$$
(12)

For large gap widths, the particle follows the fluid motion and $f_{a}(H)$ becomes

$$f_3(H) = f_3(Y-1) \cong 4Y$$
 (12a)

for $a_P \ll h \ll a_F$.

The behavior of $f_3(H)$ for very small gaps is in question. Goldman, Cox, and Brenner (1967) have recently solved the creeping flow equations for the motion of a sphere close to a plane wall. Those authors conclude that the translational velocity of the particle approaches zero as the gap approaches zero, *i.e.*, $\lim_{H\to 0} f_{\mathfrak{Z}}(H) = 0$. This prediction, however, is in conflict with the observations of Carty for the terminal velocity of spheres rolling down a plane in a viscous liquid. Combining Carty's empirical expression for the drag coefficient, as reported by Goldman, Cox, and Brenner, with the expression for the drag on a sphere touching a plane in a uniform shear field given by Goldman, Cox, and Brenner or by O'Neill (1968), one can show that the tangential velocity for zero gap is of the form of Equation 12 with $f_3(0) = 0.76$. Goldman, Cox, and Brenner suggest that the most likely explanation for the discrepancy between their theory and Carty's observations is that cavitation occurs near the point of contact. The former authors demonstrate cavitation to be possible only when the dimensionless gap width H is smaller than approximately 4×10^{-4} , which for experimental spheres with radii of order 1 cm. corresponds to gaps of a few μ . For spheres with radii smaller than a few μ , however, cavitation can occur only when the gap is at most a few angstroms and, at such small separations, hydrodynamic forces are overwhelmed by London forces. Therefore, if cavitation is, in fact, the only explanation for the observed discrepancy with experiments in which larger spheres were used, the motion of particles having colloidal dimensions should not be so influenced, and the cited theoretical expressions are expected to apply. For our analysis we shall assume that $f_3(H)$ approaches a finite constant as H approaches zero:

$$f_3(H) \cong \kappa_3 \tag{12b}$$

for $h \ll a_P \ll a_F$. In view of the slow rate at which f_3 approaches zero, according to the theory of Goldman, Cox, and Brenner, compared with the very rapid increase of the London forces, our conclusions should not be greatly affected by this assumption. Differences between the following and a more exact development may be taken into account through adjustment of the constant κ_3 .

Elimination of the time t between Equations 10 and 12 yields the equation describing the particle trajectory,

$$-\sin\theta_P \frac{dH}{d\theta_P} = \frac{f_1(H)f_2(H)\cos\theta_P}{f_3(H)} + \frac{N_{Ad_P}f_1(H)f_{ret}(2\pi a_P/\lambda, H)}{f_3(H)(H+2)^2H^2}$$
(13)

From Equation 13 and the limiting forms of f_i , f_z , f_s , and f_{ret} it follows that $(-dH/d\theta_P) \rightarrow \infty$ as $H \rightarrow 0$, which implies that there are no "grazing" trajectories. Consequently, the limiting trajectory for capture intersects the line $\theta_P = \pi$ at the rear of the obstacle. At the point of intersection dH/dt =0 and the value of $H = H^*$ corresponding to the intersection satisfies Equation 13 for $\theta_P = \pi$, giving

$$\frac{N_{Adg}f_{ret}\left(\frac{2\pi a_P}{\lambda}\cdot H^*\right)}{f_2(H^*)(H^*+2)^2H^{*\,2}} = 1$$
(14)

Figure 2 schematically depicts the particle capture. The collection efficiency η can be determined by tracing a particle back along the limiting trajectory to a point where the gap width is sufficiently large that the trajectory thereafter effectively coincides with a fluid streamline. For small interception numbers this is taken to occur sufficiently near the cylinder that Equation 1 still accurately describes the undisturbed flow field. The efficiency is thus given by

$$\eta = \frac{\Psi_{\lim}}{Ua_F} = \lim_{\theta_P \to 0} \left[2A_F \left(\frac{a_P}{a_F} \right)^2 Y^2 \sin \theta_P \right]$$
(15)

The limiting trajectory is determined by that solution of Equation 13 which passes through the point (H^*, π) as given by Equation 14. The only parameters which enter into these equations are the groups N_{Ad_P} and a_P/λ . The quantity $\lim_{\theta_P\to 0} (Y^2 \sin \theta_P)$ of Equation 15 therefore must be a function

of N_{Ad_F} and a_P/λ only (as an example, see Equation 20 below) and the efficiency is given by

$$\frac{\eta}{2A_F R^2} = f_F(N_{Ad_F}, a_P/\lambda) \tag{16}$$

for small interception numbers where $f_F(N_{Ad_F}, a_P/\lambda)$ is a universal function of the adhesion group N_{Ad_F} and a_P/λ . If the retardation effect can be neglected, we have

$$\frac{\eta}{2A_F R^2} = f_F(N_{Ad_F}) \tag{17}$$

Equation 16 or 17 is important in that it suggests a possible method for correlating experimental data. Comparison with the classical expression $\eta/2A_FR^2 = 1$ shows the more rigorous result 16 to be quite different, in general, from that predicted by simple interception. Not only are the particle and fiber diameter dependences different, but the more rigorous treatment also implies a decrease of efficiency with increasing velocity and intervening fluid viscosity which are predicted by classical interception to have no influence.

For very large values of N_{Adp} and with the retardation effect neglected, H^* also becomes large and Equation 14 simplifies to

$$Y^* = (2N_{Adp})^{1/6} \gg 1 \tag{18}$$

where $Y^* = H^* + 1$. The limiting trajectory $(\theta_P = \pi)$ then lies in the range of large Y where Equation 13 may be approximated as



Figure 2. Particle path lines in capture by molecular attraction (not to scale)

$$-\sin \theta_P \cdot \frac{dY^6}{d\theta_P} = 3Y^6 \cos \theta_P + \sqrt[3]{2}N_{Ad_P}$$
(19)

Integrating this equation along the limiting trajectory gives

$$Y^6 \sin^3 \theta_P = \sqrt[3]{2} N_{Ad_F} \int_{\theta_P}^{\pi} \sin^2 \theta \ d\theta$$

or

$$Y^{2}\sin \theta_{P} = \left[\sqrt[3]{2} N_{Ad_{P}} \int_{\theta_{P}}^{\pi} \sin^{2} \theta \ d\theta \right]^{1/3}$$
(20)

Substitution of Equation 20 into 15 gives the efficiency as

$$\eta = 2A_F R^2 \left[{}^{3}/_2 N_{Ad_F} \int_0^{\pi} \sin^2 \theta \ d\theta \right]^{1/3^{27}}$$
$$= 2A_F R^2 \left[{}^{3\pi} N_{Ad_F} \right]^{1/3}$$
(21)

for small interception numbers and large adhesion numbers, but not so large that particles are attracted from the area of uniform velocity. Natanson (1957) obtained the result given by Equation 21 by a somewhat different procedure and specified its validity for $N_{Adp} \ge 2$. Natanson assumed, however, that formulas which apply only for $H \gg 1$ were applicable for all H.

It can be shown that for a retardation correction of the form $f_{\text{ret}} \approx \kappa_{\text{ret}} \lambda/h$, the single fiber efficiency is given by

$$\frac{\eta}{2A_F R^2} = f\left(N_{Ad_F} \cdot \frac{\lambda}{a_P}\right) \tag{22}$$

Examination of Equations 13 and 14 for small adhesion numbers under the assumption 12b and neglecting the retardation effect leads to the expectation that

$$\frac{\eta}{2A_F R^2} = \kappa_5 N_{Ad}^{\kappa_6} \tag{23}$$

where

$$\kappa_6 = \kappa_3/2\kappa_2$$

For details see Spielman (1968). Using the values of κ_2 and κ_3 obtained from the work of Goren and Carty, respectively, as discussed above, $\kappa_6 = 0.059$. With this value of κ_6 , the right hand side of Equation 23 would be very nearly constant as with classical interception, but not necessarily unity, depending on κ_5 . As pointed out above, there is some uncertainty concerning the proper value of κ_3 .

The function $f(N_{Ad_{P}})$ defined by Equation 17 is thus expected to be an increasing function of its argument, going over to the form 21 for very large $N_{Ad_{P}}$ and the form 23 for very small $N_{Ad_{P}}$. We remark that data on the coalescence of emulsions by flow through fibrous mats was correlated by Equation 17 (Spielman, 1968; Spielman and Goren, 1970). In the range of N_{Ad_F} from about 10^{-6} to 10^{-1} roughly, a 1/4 power dependence on the adhesion number was observed.

Motion of a very small spherical particle in close proximity to a spherical obstacle

An analogous calculation can be performed for a spherical collector. The local flow field in the vicinity of the particle can again be resolved into a stagnation flow tending to move the particle radially and a shear flow tending to roll the particle toward the rear of the obstacle. In this case the stagnation component of the undisturbed flow analogous to Equation 3 has axial symmetry about the line of centers and is given in local cylindrical coordinates as

$$u_{\rm st} = \sqrt[3]{2} \frac{A_S U \cos \theta_P}{a_S^2} \cdot [r z \, \vec{i}_{\rm r} - z^2 \, \vec{i}_{\rm z}] \qquad (24)$$

The local shear component analogous to Equation 4 is

$$u_{\rm sh} = \left[\sqrt[3]{_2} \frac{A_S U}{a_S} \sin \theta_P \right] z \vec{i}_{\theta}$$
 (25)

Arguments corresponding to those leading to Equation 13 can be invoked and an equation having the same form is obtained for the particle trajectory. The efficiency is found to be given by

where

$$\frac{\eta}{{}^{3}/_{2}\mathcal{A}_{S}R^{2}}=f_{S}(N_{Ad_{S}},a_{P}/\lambda)$$
(26)

$$N_{Ad_S} = \frac{Qa_S^2}{9\pi\mu a_P{}^4A_SU}$$
(27)

For very large N_{Ad_s} and retardation neglected the result analogous to Equation 21 is

$$\frac{\eta}{{}^{3}/{}_{2}A_{S}R^{2}} = {}^{4}/{}_{3}\left[{}^{9}/{}_{5}N_{Ad_{S}} \right]^{1/3}$$
(28)

For very small N_{Ad_s} , the result analogous to Equation 23 is

$$\frac{\eta}{\sqrt[3]{2}A_{S}R^{2}} = \kappa^{s'} N_{Ad_{S}}^{\kappa_{b'}}$$
(29)

The function $f_s(N_{Ad_s})$ of Equation 26 is different from $f_F(N_{Ad_F})$ of Equation 16. For large values of N_{Ad} both equations predict a power of 1/3 on N_{Ad} . For small N_{Ad} the equations predict a simple power dependence on N_{Ad} but the powers are expected to be somewhat different, since the stagnation flows given by Equations 24 and 3 determining the normal force on the particle are different. Using the values for stagnation force and rolling velocity given by the work of Goren (1970) and Carty, one would expect $\kappa_6' \approx 0.022$. Under this circumstance, as with Equation 23, the right hand side of Equation 29 would be very nearly constant, in accord with classical interception, but not necessarily unity, depending on κ_5' .

Collection by simultaneous interception and Brownian diffusion

For sufficiently small particles, Brownian diffusion might be an important capture mechanism. Owing to the smallness of the Brownian diffusivity, particle concentration changes will be confined to a thin boundary layer adjacent to the collector, within which Equations 10 and 12 are good approximations for the average particle velocity. It is usual to neglect diffusion compared to convection tangential to the collector surface. If *n* denotes the number concentration of particles, n_{∞} being the number far from the collector, then the flux of particles tangential to the collector surface is

$$j_{\theta} = v_{\theta} n \tag{30}$$

with v_{θ} given by Equation 12. The flux normal to the collector has both a convective and diffusive part:

$$i_R = v_R n - \mathfrak{D} \frac{\partial n}{\partial y} \tag{31}$$

with v_R given by Equation 10.

A balance on the number of particles in a differential volume at steady state gives

$$\frac{1}{a_F}\frac{\partial j_{\theta}}{\partial \theta} + \frac{\partial j_R}{\partial y} = 0$$
(32)

or upon substitution from Equations 10, 12, 30, and 31 and rearrangement we find

$$\frac{\partial}{\partial \theta} \left[\sin \theta f_{3}(Y)n \right] - \frac{\partial}{\partial Y} \left\{ \left[f_{1}(Y)f_{2}(Y) \cos \theta + \frac{N_{Ad_{F}}f_{1}(Y)f_{ret}(2\pi a_{p}/\lambda, Y)}{5(Y-1)^{2}} \right] n \right\} = \frac{\mathfrak{D}_{w}a_{F}^{2}}{A_{F}U a_{F}^{3}} \frac{\partial}{\partial Y} \left[f_{1}(Y) \frac{\partial n}{\partial Y} \right]$$
(33)

 \mathfrak{D}_{∞} is the Brownian diffusion coefficient far from the collector surface; the decrease in Brownian diffusion coefficient due to hydrodynamic interactions with the collector surface are accounted for through the $f_1(Y)$ term on the right-hand side of Equation 33. The boundary conditions on the equation are

$$\begin{array}{ll} Y \to \infty & n \to n_{\infty} \\ Y \to 1 & n \to 0 \end{array} \tag{34}$$

Following the procedure of Friedlander (1967) who treated the case of simultaneous interception and Brownian diffusion, assuming the average particle velocity at any point to be the undisturbed local fluid velocity, it may be shown that the solution to the diffusion equation must be of the form

$$\frac{n}{n_{\infty}} = f(Y, \theta, N_{Ad_F}, a_P/\lambda, A_F U a_P^3/\mathfrak{D}_{\infty} a_F^2)$$
(35)

and the efficiency is of the form

$$\frac{\eta}{2A_F R^2} = f(N_{Ad_F}, a_P/\lambda, A_F U a_P^3/\mathfrak{D}_{\infty} a_F^2)$$
(36)

Future work in this area should include numerical solution for the trajectory using accurate representations for the various universal functions discussed above and extension to include other forces acting on the particle, such as gravity and double-layer repulsion.

Nomenclature

| a | = particle or collector radius |
|------------------|--|
| A | hydrodynamic factor depending on flow model |
| D | Brownian diffusion coefficient |
| f1, f2, f2, fret | = universal functions of their argument |
| f | = function giving efficiency of capture |
| FAd | = London-van der Waals force |
| Fat | = hydrodynamic force on particle |
| h | = gap thickness between particle and collector |
| H | = h/a_P , dimensionless gap thickness |
| NAdF | $= Qa_{F}^{2}/9\pi\mu A_{F}a_{F}^{4}, \text{dimensionless} \text{ad-} \\ \text{hesion number}$ |
| Q | = Hamaker's constant |

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| r | = | radial coordinate | ; | | | | | | |
|------------------------|---|---|------------|-------|-----------|--|--|--|--|
| U | = | fluid velocity far from collector | | | | | | | |
| $v_{	heta}$ | - | particle velocity surface | tangent | to | collector | | | | |
| v_R | - | particle velocity surface | normal | to | collector | | | | |
| x | = | distance coordina surface | ate tanger | nt to | collector | | | | |
| У | = | distance coordina surface | ate norma | al to | collector | | | | |
| Y | = | y/a_P , dimensionless distance coordinate normal to collector surface | | | | | | | |
| η | = | collector capture | efficiency | ' | | | | | |
| θ | = | angular coordina | ite | | | | | | |
| Kret | = | retardation coeffi | cient | | | | | | |
| K2,K3,K4,K5,K6,K5',K6' | = | numerical consta | nts | | | | | | |
| λ | = | wavelength in re- | tardation | fund | ction | | | | |
| μ | = | fluid viscosity | | | | | | | |
| Ψ | = | stream function | | | | | | | |
| Subscripts | | | | | | | | | |
| F | = | fiber collector | | | | | | | |
| Р | = | particle | | | | | | | |
| S | = | spherical collecto | or | | | | | | |

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Accumulations of Lead in Soils for Regions of High and Low Motor Vehicle Traffic Density

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Accumulation of lead in soils over a period of approximately 40 years was compared for areas of high and low motor vehicle traffic densities. Where motor vehicle traffic density was less than 80 motor vehicles per square mile, no lead accumulations were observed, but where the motor vehicle traffic density was greater than 580 motor vehicles per square mile, the concentration of lead in the surface 2.5 cm. of soil increased by a factor of two to three times. Although large percentage increases were observed in the surface soils from the areas of high motor vehicle traffic density, the amount of lead found in the surface soil did not exceed 52 p.p.m., a level which is common to many soils from areas of low motor vehicle traffic density and not subjected to atmospheric or industrial lead contaminations.

ecent reports have demonstrated that atmospheric pollution of lead (Pb), caused principally by combustion of leaded gasoline and liquid and vapor wastes from coal-burning and metal-melting establishments, has contributed to the increased Pb content of waters (Johnson, Rossano, et al., 1966; Tsaihwa, 1966), plants (Cannon and Bowles, 1962; Everett, Day, et al., 1967; Lagerwerff, 1966), and soils (Cannon and Bowles, 1962; Lagerwerff, 1966; Marten and Hammond, 1966) in industrial and urban areas. But information relative to accumulations in soils is fragmentary and inadequate.

Bashirova (1966) reported the content of Pb at depths from 9 to 30 cm. in city soils as 8000 p.p.m. (mgm. of Pb per Kgm of soil) compared to 25 p.p.m. at similar depths for virgin soils. Cannon and Bowles (1962) found an average of 515 p.p.m. of Pb with a range of 100 to 1000 p.p.m. of Pb in six soil samples collected 15 meters from a street in the city of Canandaigua, N.Y. Near a battery smelter in Minnesota, Marten and Hammond (1966) found 680 p.p.m. of Pb in the surface 2.5 cm. of soil, and 95 p.p.m. of Pb at a depth of 15 cm. The surface 2.5 cm. of soil from the bank of a well-traveled four-lane highway contained 59 p.p.m. of Pb (Marten and Hammond, 1966).

The previously cited references provide only scanty information and are not sufficiently detailed to evaluate possible accumulations of Pb in soils in regions subjected to abnormally high levels of Pb in the atmosphere. The objective of the present study was to evaluate lead contents and accumulations of Pb in regions of high and low motor vehicle traffic density in southern California.

Experimental

The Department of Soils and Plant Nutrition, University of California, Riverside, has kept soil samples from field experiments which date back as early as 1919. The samples are stored in closed containers, and records providing the date, location, and depth sampled are on file. The Pb contents of a number of these soils, which were collected from 35 to 50 years ago, were determined.

Soil samples were collected from the same locations and

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depths in 1967 and their Pb contents determined. The locations sampled were selected from areas of high and low population and motor vehicle traffic density.

Total Pb content of the soils was determined as follows. The bulk soil sample was air dried at room temperature and passed through a 1-mm. plastic screen. A representative subsample was then passed through a 40 mesh (0.42 mm.) screen and ground to a fine powder in an agate mortar. Duplicate samples of 0.250 gram of the finely powdered soil were weighed into platinum dishes and ignited at 450° C. to destroy the organic matter. The samples were decomposed using a mixture of HClO₄ and HF (Bradford, Pratt, et al., 1965). The residue was dissolved in about 40 ml. of 0.003N HCl. Two and one-half milliliters of 5% ammonium pyrrolidine dithiocarbamate (APDC) were added and the mixture adjusted to pH 2.8 with HCl. This pH was maintained throughout the entire Pb extraction process. The mixture containing the APDC was warmed to a temperature of about 70° C. for 1 hour and then transferred to a separatory funnel. After the contents of the funnel had cooled to room temperature, 5 ml. of chloroform were added. The mixture was shaken and the Pb separated in the chloroform phase. Extracting with chloroform was repeated two additional times. The chloroform phase was taken to dryness using heat from an incandescent lamp. The residue was dissolved in an appropriate volume of 4N HNO₃ and the Pb content determined using an atomic absorption spectrometer. Using the procedure described, the recovery of Pb added to soils ranged between 95 and 105%; so the methods used were sufficiently quantitative for our purposes.

The soils collected were virgin alluvial soils, slightly acid to slightly alkaline (pH saturated paste ranged between 5.4 and 7.4) and, except for the surface samples, contained less than 1% organic matter. All locations sampled were one mile or more from a major highway.

Motor vehicle traffic densities were computed by taking the total 1967 population within a 10-mile radius from the location sampled, and dividing by 1.9, the average number of persons per motor vehicle for southern California.

The total Pb content of the soils was expressed on the basis of the weight of the soil dried at 110° C. for 48 hours.

Results and Discussion

Lead Contents in Surface Soils as Related to Motor Vehicle Traffic Density. In Table I, the Pb contents of soil samples collected 35 to 50 years ago are compared to the Pb contents of soil samples collected from the same location in 1967. The data show no direct relation between motor vehicle traffic density and Pb accumulation in soils, but do show much greater accumulations in soils from areas of high motor vehicle traffic density (i.e., >580 motor vehicles per square mile as compared to <80 motor vehicles per square mile).

The cities of La Verne, Puente, Whittier, La Habra, and Tustin are within the Los Angeles metropolitan area. The Los Angeles metropolitan area includes parts of both Los Angeles and Orange counties. Its area encompasses some 3200 square miles, with an estimated population, in 1967, of 8,500,-000 (Commercial Atlas & Marketing Guide, 1968). The average number of persons per motor vehicle in southern California is 1.9 (Dept. of Motor Vehicles, Riverside, Calif.) so the traffic density for the Los Angeles metropolitan area is about 1400 motor vehicles per square mile. The atmospheric Pb concentration in the city of Los Angeles in 1963 averaged 5.08 μ g. per m.³ with a low and high of 2.91 and 9.05 μ g. per

| Table I. | Accumulation | s of Pb in the | Surface 2.5 cm. of |
|----------|---------------|----------------|--------------------|
| Soils | as Related to | Motor Vehicle | Traffic Density |

| Location | Pb Content Year Sa Between 1919 and 1933 ^b | Motor Vehicle Traffic Density, Motor Vehicles per Sq. Mi. | | |
|----------------|---|--|------|--|
| La Verne | 17 | 52 | 735 | |
| Puente | 16 | 52 | 1525 | |
| Whittier | 16 | 39 | 2475 | |
| La Habra | 17 | 50 | 1475 | |
| Tustin | 16 | 31 | 1370 | |
| Riverside | 17 | 38 | 580 | |
| San Bernardino | 12 | 24 | 630 | |
| Hemet | 19 | 21 | 25 | |
| Santa Paula | 21 | 23 | 80 | |
| Meloland | 26 | 25 | 50 | |
| | | | | |

Oven dry weight basis, 110° C. for 48 hours.
 Year sampled: Whittier and Riverside, 1919; Santa Paula, 1926; San Bernardino, 1927; La Verne, Puente, Tustin, 1928; Hemet, 1930; Meloland, 1931; La Habra, 1933.
 Computed by taking total 1967 population within a 10-mile radius from the site sampled and dividing by the average number of nersons

from the site sampled, and dividing by the average number of persons per motor vehicle for southern California.

m.3, respectively (Robinson and Ludwig, 1967). Our data (Table I) show a maximum accumulation of Pb in the surface 2.5 cm. of soils from the metropolitan Los Angeles area to be 40 p.p.m. over a period of about 40 years. Lead concentrations of soils throughout the world which are not subjected to atmospheric pollution vary widely with a normal range of 10 to 200 p.p.m. (Mitchell, 1964). Extreme values considerably in excess of 200 p.p.m. are found near Pb ore deposits. Under the conditions outlined above, the data point out that, on a regional basis, Pb accumulations for the area tested do not exceed Pb contents of soils from many parts of the world which have not been subjected to excessive atmospheric pollution from Pb.

Others (Cannon and Bowles, 1962; Lagerwerff, 1966) have shown that Pb contents of soils collected within 30 meters from well-traveled highways are considerably greater (100 to 1000 p.p.m.) than those we have observed. Our study was not designed to evaluate this factor but was designed to examine accumulations of Pb over long periods of time. All locations sampled in our study were 1 mile or more from major highways, so comparing our results to those of others suggests that the more excessive accumulations of Pb in soils caused by heavy motor vehicle traffic are localized near the point where the Pb is discharged into the atmosphere.

In Los Angeles County, for the period 1940 through 1967, about 47 billion gallons of leaded gasoline were combusted (Fuller, 1968). If we assume that 75% of the Pb in this gasoline was released to the atmosphere and deposited uniformly over the surface of Los Angeles County (area 4083 square miles), that the proportion of regular and premium gasoline used are 70 and 30%, and taking the Pb contents of regular and premium gasoline as 1.5 and 2.1 grams per gallon, respectively, then the amount of Pb accumulated on the surface of Los Angeles County for the 27-year period would be about 15 metric tons per square mile. This figure neglects atmospheric transport of Pb outside of the county, as well as transport into the county. The above figure would be quite conservative for the heavily populated areas of Los Angeles and Orange Counties. However, on this basis, if we assume that Pb contamination is concentrated in the surface 2.5 cm. (the data in Table II show this to be the case) then Pb accumu-

Table II. Amounts of Pb in Contaminated Soils at Various Depths in the Soil Profile

| Location | 0–2.5 | Depth Sam 2.5–15 Pb con p.p | npled (cm.) 15–30 ntent ^a .m. | 30-45 |
|-------------------------------------|------------|--------------------------------------|---|-------|
| La Verne | 52 | 19 | 12 | 16 |
| Puente | 52 | 15 | 13 | 16 |
| Whittier | 39 | 20 | 15 | 15 |
| La Habra | 50 | 19 | 16 | 15 |
| Tustin | 31 | 15 | 14 | 16 |
| Riverside | 38 | 18 | 16 | 20 |
| San Bernardino | 24 | 11 | 13 | 16 |
| Hemet | 21 | 15 | 13 | 15 |
| Santa Paula | 23 | 15 | 13 | 20 |
| Meloland | 25 | 18 | 14 | 15 |
| ^a Oven dry weight basis, | 110° C. fo | r 48 hours. | | |

lation for the soils in Los Angeles County for the 27-year period would be about 150 p.p.m. (mgm. Pb/Kgm. soil). The observed accumulation for the Los Angeles metropolitan area was about 40 p.p.m. for a 40-year period.

Riverside and San Bernardino, showing an accumulation of 21 and 12 p.p.m. of Pb for a period of 49 and 40 years, respectively, are about 60 miles east of the center of Los Angeles. The 1967 population for the Riverside-San Bernardino metropolitan area (1513 square miles) is estimated as 605,000 (Commercial Atlas and Marketing Guide, 1968). The area to the north, south, and east of the metropolitan area is sparsely populated, being either mountains or deserts.

The soils sampled near Hemet, Santa Paula, and Meloland showed no accumulation of Pb over the period observed (about 30 years). Hemet is an agricultural community located about 30 miles southeast of Riverside, at the base of the San Jacinto Mountains. The only large population area within a 30-mile radius is Riverside. Meloland is a desert agricultural community in the Imperial Valley. The nearest centers of population are Yuma, Ariz., about 50 miles to the east, and San Diego, Calif., about 120 miles to the west. Santa Paula is in Ventura County about 50 miles north of Los Angeles city. The Ventura-Oxnard metropolitan area, with a population of 182,000 (Commercial Atlas and Marketing Guide, 1968) is between 15 and 20 miles from the location where the soil samples were collected.

Lead Concentrations of Contaminated Soils at Various Depths in the Soil Profile. Results presented in Table II give the distribution of Pb as a function of depth in the soil profile. They show that practically all of the Pb which has accumulated remained in the surface a few centimeters. The soils investigated were virgin soils and, as far as we are aware, were not disturbed over the period of time tested. Consequently, the accumulations observed should represent maximum accumulations because periodic cultivation of soils will serve to dilute the surface concentration.

In those locations where little or no accumulation of Pb occurred (Hemet, Santa Paula, and Meloland), amounts of Pb in the surface 2.5 cm. are slightly greater than the amounts of Pb found at lower depths. This increase in the surface may be due to plant cycling of Pb which has been observed by others in other areas (Mitchell and Reith, 1966).

Summary and Conclusions

Amounts of Pb accumulated in the surface of 2.5 cm. of soils from the Los Angeles metropolitan area, over a period of about 40 years, ranged between 15 and 36 p.p.m. of Pb. These amounts are considerably below levels which may cause toxicities to economic plants, or which may cause abnormally excessive accumulations of Pb in the plants. Therefore, immediate problems associated with soil pollution of Pb caused by high motor vehicle traffic density for this area are not anticipated.

Soils from regions of low motor vehicle traffic density did not accumulate Pb over a period of about 40 years.

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Hydrocarbon and Carbon Monoxide Analysis by the Selective Combustion Method

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An instrument involving heat effects in catalytic beds has been developed and applied to measurement of carbon monoxide and hydrocarbons in an air stream. The temperature rise from slug sample injection into an air stream with constant flow rate has been found to give a linear and selective measure of "total" HC injected with a vanadia catalyst and of total CO with a Hopcalite catalyst at the levels normally encountered in exhaust gases. The response to hydrocarbons in vehicle exhaust gas which is substantially additive can be tailored to correspond reasonably well with either photochemical reactivity or nondispersive hexane-sensitized infrared, although response for olefins and aromatics relative to paraffins is higher than for the infrared method. Response and recovery times allow rapid measurement and depend primarily on catalyst bed diameter. Although the major use of the instrument appears to be for vehicle exhaust analysis, suitable modification would make it useful for air monitoring and chromatography detection.

he role of reactive hydrocarbons in photochemical smog formation, the over ten-fold variations in hydrocarbon emission levels between vehicles (*e.g.*, Brubacher and Raymond, 1967), the importance of combined HC-CO measurements in diagnosing causes of such emissions (Cline

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and Tinkham, 1969) all indicate the importance of simple instrumentation for vehicle exhaust inspection.

The primary objective of this work was to develop an instrument that would meet federal specifications for this application (Sigsby, 1967) which in summary include:

• Independent measurement of both carbon monoxide and hydrocarbons

• Results correlatable with established methods (infrared and flame ionization)

• Method amenable to modification so as to correlate with reactive hydrocarbons when standards are put on this basis

• Operation simple, nonhazardous and fail/safe with no specialized knowledge or equipment required

• Precision adequate for pass/fail determination. Time requirement per test less than one minute.

Experimental

HYDROCARBON ANALYSIS

The hydrocarbon instrument developed to meet these requirements is shown in Figure 1.

Water saturated air supplied by a diaphragm type pump and water saturator continuously flows through the storage coil and into the preheater and catalyst bed at a fixed rate of about 1 liter/min. A syringe port is used for injecting a 5–75 ml. sample in 3–8 sec. into the air stream. Constant flow is maintained during injection by the action of the water bubbler pressure regulator, which maintains a constant pressure drop across the reactor element. The hydrocarbons in the sample



Figure 1. Simplified schematic of model 10 SELCOM analyzer

are oxidized by the catalyst as they flow through the bed, resulting in a temperature rise which is detected by differential temperature probes, amplified by the electrical system and read out on a meter or recorder to an accuracy of about 0.01 °C.

The preheat-reactor sections, which are inside a common metal block, are maintained at near constant temperature by control of block temperature. The reactor and reference elements shown in Figure 2 are in the form of removable plugs which screw into the block. The gas passes through a screen, granular catalyst in contact with a thermocouple element, a borosilicate glass wool cush oning agent, and out through an exit port.

CARBON MONOXIDE ANALYSIS

The principle and apparatus employed for carbon monoxide measurement is the same as for hydrocarbon analysis, except for use of a Hopcalite oxidation catalyst and a charcoal scrubber (5 cc.) ahead of the reactor to remove interfering hydrocarbons. The two measurements are combined as shown in Figure 1. The flow split with lesser flow to the CO unit, together with the volume of charcoal scrubber (not shown), serves to delay the CO peak until after the HC peak, so that both measurements can be conveniently read on the same readout system by electrical switching.

SAMPLING

The sampling probe and metal syringe system shown in Figure 3 was developed for this purpose and found to be very convenient for rapid sampling. Syringe pumping to flush the small dead space is obviously desirable because of wide variations in HC levels in exhaust samples.

STANDARDIZATION

The unit needs to be standardized first for selectivity and then for gain. However, except when high precision is needed, infrequent standardization appears satisfactory.

For selectivity standardization, the ratio of butene to butane response appears most suitable, since it is a very sensitive indicator. Adjustments can be made by changing flow rate or block temperature set.

For span standardization where auto exhaust is involved, a mixture simulating exhaust containing highly reactive butene, moderately reactive propene, and slightly reactive butane, as well as CO and air, has been found most suitable. Response change with changes in instrument parameters correspond closely with response changes for exhaust gas, and accurate standards can be readily prepared since these components are not subject to condensation or adsorption.

Since hexane is the basis of primary gain standards for other HC instruments, it was used for this instrument and the readout scale has ranges from 0-1000 and 0-10,000 p.p.m. hexane. Propene is another good secondary standard not subject to condensation or adsorption phenomena, and which gives substantially the same C basis response as hexane.

Because of response linearity with concentration, smaller samples of more concentrated gases can be used. Thus, 5 ml. of 1% hexane is the equivalent of 50 ml. of 1000 p.p.m. hexane. This makes it practical to use $1/_2$ liter pushbutton can standards, since one can will supply several hundred samples. Samples can be conveniently withdrawn by use of a smallbore Tygon tubing connector. The syringe tip (without needle) is pressed against the can valve for transfer from can to syringe. Span adjustment is made by appropriate amplifier gain adjustment.





Figure 2. Cross section of reactor element



---TIME----Figure 4. Idle exhaust response

-1 min.-+

t tratra

te





Figure 5. Peak linearity with mols. carbon from hydrocarbons

REPRODUCIBILITY AND ACCURACY

With ten-fold variations in levels, high precision would not seem very important, so that no major effort was made to achieve precisions greater than a standard deviation of 2%. Possible sources of error and estimated values are shown in Table X. All these errors, except readout, are believed reducible with better temperature control. Improper standardization can affect the accuracy, but this source of error can be minimized by repetition, preferably interspersed between regular testing.

Results and Discussion

HYDROCARBON ANALYSIS

Response Curves. Response curves are shown in Figure 4. The left curve shows response for continuous injection at a rate less than total flow rate, while the right curve shows response for slug injection by the procedure described above. The time to peak for slug injection is largely determined by the injection time. While the slug passes, it undergoes oxidation believed to be proportional to the individual hydrocarbon concentration and the oxidation rate constant at any point in the bed. The temperature rises linearly, levels, then passes through a peak as the slug passes and then decays logarithmically as a result of heat transfer to the air stream and block.

Theoretical maximum temperature rise is achieved only under ideal conditions because of heat transfer. Neglecting heat transfer and assuming also that reaction rate is directly proportional to hydrocarbon reactant concentration and heat capacity of the catalyst is much greater than the gas heat capacity, the following idealized expression can be derived for a uniform surface where only one oxidation step is involved:

$$\Delta T = C_1(K/F) \exp -(K/F)V \tag{1}$$

where

- ΔT = temperature rise from injection at some point in the bed, °C.
- V = volume of catalyst prior to this point in the bed, cc.
- K = first order oxidation rate constant for combustible, min.⁻¹ (the transient rate constant may differ from steady state values)
- $C_1 = \frac{\text{mols. reactant injected} \times \text{molar heat of oxidation}}{\text{catalyst heat capacity per cc. of bed}}$

$$F =$$
flow rate in cc./min.



Figure 6. Hydrocarbon response vs. temperature for 0.05 cc. catalyst volume prior to probe 0.8 CFH flow, $\frac{3}{16}''$ bed diam.

The expression should be considered only as a useful upper limit guide in estimating parameter effects, since the assumptions are applicable only to instantaneous effects with negligible heat capacity temperature probes.

Linearity of Peak Values. The peak values from slug injection have been found to be directly proportional to the product of sample size and concentration over a wide range of conditions; *i.e.*, to the number of mols. of individual hydrocarbons injected, regardless of injection times, up to about 8 sec. This is partially illustrated by Figure 5, and is in line with Eq. 1.

Major Parameters and Their Effects. The temperature rise depends also on the molar heat of oxidation, the amount oxidized, and the catalyst system heat capacity. If injection is prolonged, heat transfer would be expected to decrease peak values, which would then be substantially influenced by heat transfer to gas and wall. The region where the oxidation occurs, relative to the probe position, also would be expected to have an effect. The major parameters, therefore, would appear to be as shown in Table I.

The catalyst affects both the degree and selectivity of the response. A vanadia composition proved to give both high response and a high degree of selectivity for combustion of smog-forming hydrocarbons *vs.* carbon monoxide and hydrogen.

The effect of temperature on response was investigated for a variety of hydrocarbons at fixed probe positions and flow rate. Illustrative results for the probe near the porous disk inlet are shown in Figure 6 for a reactive, a moderately reactive, and a slightly reactive hydrocarbon. Relative responses approach constant relative values at low temperatures which appear to correlate with oxidation rate constants. For any compound, the general behavior over the proper temperature range is first an increase in response with temperature in-

| Table | I. | Major | Parameters | and | Practical | Ranges |
|-------|----|-------|------------|-----|-----------|--------|
| | | | | | | |

| Parameter | Practical ranges |
|-----------------------------|--------------------------|
| Nature of catalyst | Vanadia composition |
| Block temperature | 250–375° C. |
| Flow rate | 0.3-1.5 CFH |
| Probe placement in catalyst | 0.02-0.50 cc. from inlet |
| Catalyst bed diameter | 0.15-0.60 in. |





Figure 7. Hydrocarbon response vs. temperature for 0.20 cc. catalyst volume prior to probe, 0.8 CFH, 1/4" bed diam.

| | - | 1 | |
|-----------|---------|------------|---------|
| Table II | Ontimum | Parameter | Values |
| Table II. | Optimum | 1 arameter | 7 aiuco |

| Parameter | Best correlation with both FI and HSNDIR HSSC ^a | Best correlation with smog effects LSSC ^b |
|---|--|--|
| Block temperature, °C. | 375° | 300° |
| Flow rate, CFH | 0.8 | 0.8 |
| Catalyst volume, cc. prior to probe | 0.20 | 0.05 |
| Butene/hexane carbon basis response ratio | 1.2 | 4.5 |

Abbreviation for high-severity selective combustion. Abbreviation for low-severity selective combustion. Values are 75° C. lower for an improved catalyst at 0.5 CFH.

crease, then a leveling off, and finally a gradual decrease as shown, for example, by butene. The decrease is believed to be due to lower hydrocarbon concentration in the bed where the probe is located because of reaction ahead of the probe. Figure 7 shows data obtained where the probe is placed, so that there is 0.2 cc. of catalyst ahead of the probe and the flow rate is the same as for Figure 6. Lower responses are observed than with the probe near the inlet, and there is also greater decrease in response of reactive hydrocarbons with temperature than for the 0.05 cc. catalyst volume case.

Flow changes in general were found to have about the same effect on relative peak response as temperature change. That is, for example, increase in flow rate from 0.8 to 1.4 CFH was found to be equivalent to lowering the temperature by about 20° C. Therefore, a 4% increase in flow rate in this case was equivalent to 1° C. temperature decrease.

The results indicated a wide variety of possible relative responses. To meet the federal requirements given above, two conditions (high- and low-severity selective combustion, designated as HSSC and LSSC) were chosen as defined in Table II, although it now appears that none of the individual parameters are important if the indicated butene/hexane relative response prevails. Responses for a variety of hydrocarbons under these conditions are given in Table III.

Values for various isomers were about the same, so that values were averaged in the table. Cyclohexane and methyl cyclohexane also gave values fairly close to the normal paraffins for the same carbon number.

Correlation of Responses with Smog Effects. Table IV is an attempt to estimate how well the responses correlate with photochemical reactivity, as well as flame ionization (FI) and hexane-sensitized nondispersive infrared (HSNDIR) for classes of hydrocarbons with similar photochemical reactivity.

The selective combustion responses for the various classes are obtained from weighted averages of the compounds in their classes. The weighting is based on exhaust analysis reported on cars using 35-40% aromatic fuel (Innes and Tsu, 1963).

According to Table IV, LSSC response relates fairly well to the smog-forming effects. Responses for HSSC are in good agreement with the infrared, except for somewhat greater response to smog formers and lower response to low-mol.-wt. paraffins. HSSC agrees with flame ionization, except that it gives lower response to low-mol.-wt. components and aromatics.

Correlation of Selective Combustion with Infrared. Results of limited direct comparison of HSSC with HSNDIR are given in Figure 8. The data show a reasonable correlation which varies with fuel octane, which is presumably related to the greater aromatic content of high octane fuel, together with greater aromatics response for HSSC than for HSNDIR.

Correlation of Flame Ionization with Selective Combustion. Comparisons were made with FI at several severity levels, as summarized in Figure 9. The ratio of FI/SC decreases markedly with severity increase in line with decreased relative response to the more reactive hydrocarbons at higher temperatures.

| | | Low-Severity Combustion | Selective (LSSC) ^b | | | High-Severit Combustion | y Selective (HSSC) ^e | |
|---------------|------------|-----------------------------|-------------------------------|-----------|------------|-----------------------------|------------------------------------|----------|
| Carbon No. | Acetylenes | Diolefins and olefins | Paraffins | Aromatics | Acetylenes | Diolefins and olefins | Parafins | Aromatic |
| 1 | | | 0 | | | | 0 | |
| 2 | 15 | 6 | 0 | | 51 | 10 | 0 | |
| 3 | | 100 | 0 | | | 100 | 15 | |
| 4 | | 450 | 14 | | | 120 | 35 | |
| 5 | | | 35 | | | 95 | 70 | |
| 6 | | | 100 | 19 | | 95 | 100 | 50 |
| 7 | | | 120 | 375 | | 90 | 80 | 50 |
| 8 | | | | 410 | | 90 | 80 | 50 |

| A MOLE ATT CARDONICATION OF THE AND A MOLE A | Table | IV. | Classification | of Hydro | carbons by | Smog | Effects and | Estimated | Instrument | Response |
|--|-------|-----|----------------|----------|------------|------|-------------|-----------|------------|----------|
|--|-------|-----|----------------|----------|------------|------|-------------|-----------|------------|----------|

| | | | R_n = Response Normalized ^a to <i>n</i> -Hexane = 100 | | | | | |
|--|------------------------------|------------------------------|---|----------------|----------------|--------------|--|--|
| Class | % in exhaust ^b | Smog effects ^b | HSNDIR % as C | LSSC % as C | HSSC % as C | FI % as C | | |
| C1-C5 paraffins, acetylenes, and benzene | 28 | Negligible | 40 | 20 | 40 | 115 | | |
| Ethylene | 10 | c | 8 | 6 | 10 | 100 | | |
| C6 + paraffins | 23 | Slight | 90 | 120 | 85 | 100 | | |
| C7 + aromatics | 23 | Moderate | 25 | 250 | 50 | 100 | | |
| C3 + olefins and diolefins | 16 | High | 50 | 500 | 100 | 100 | | |

• Relative response of class calculated from exhaust composition where $R_n = \sum (n_i R_i)$ response for *n*-hexane, n_i = fraction of compound *i* in b Con a carbon basis as given in Innes and Tsu, 1963. ^b Forms no PAN, slow reacting, forming some ozone and formaldehyde-visibility effects not established.

Most of the data were obtained at the high severity conditions believed optimum for correlation with both HSNDIR and FI (i.e., as defined by a butene/hexane C basis response of 1.2). Illustrative results are given in Tables V and VI, which indicate a generally linear correlation between FI and HSSC.

Although more work, particularly under loaded engine conditions, is needed to establish the best overall value for FI/HSSC, it appears to be in the range 1.8-2.1. Fuel effects would be expected to be generally small, except where substantial raw fuel is present in the exhaust. Since fuel paraffins



Figure 8. Correlation with hexane-sensitized nondispersive infrared



Figure 9. Correlation factors for selective combustion vs. flame ionization

give more than 50% HSSC response relative to FI, their presence in the exhaust would lead to a lower ratio for FI/ HSSC. At low severity, where aromatics give about the same response as paraffins, raw fuel effect on FI/HSSC should be slight.

Recovery Time, Equilibrium Time and Maximum Sensitivity. These items, defined in Figure 4, both depend on heat transfer and, therefore, are greatly influenced by the tube diameter, as shown in Table VII.

Table V. Comparison of HSSC with FI for a Car without Exhaust System

| 19 | 65, 6-Cyl. Cl | nevrolet,ª 81 | .000 Mi. | |
|-------------------|---------------|-----------------------------|---------------------------|-------------------------------|
| Mode | % CO | HSSĆ ^e p.p.m. | FI ^e hexane | Ratio FI/HSSC ^e |
| Idle ^b | 3.8 | 680 | 1200 | 1.79 |
| | 3.8 | 600 | 1150 | 1.92 |
| 1500 RPM, | 2.5 | 424 | 1050 | 2.46 |
| no load | 2.4 | 474 | 1170 | 2.25 |
| 2500 RPM, | 4.7 | 474 | 1120 | 2.36 |
| no load | 6.5 | 586 | 1300 | 2.22 |

Used for taxi service with frequent maintenance (11.5 mi./gal.). ^b After warmup.

^c Parts of identical 50 ml. sample tested. Tests made rapidly with limited precision (estimated at $\pm 5\%$ for both FI and SC and ratio at $\pm 0.2)$

Table VI. Comparison of HSSC with FI for a Car with **Exhaust System**

| 1966 Valiar | nt V-8, 24,000 Mi | Autom | atic Trans | mission |
|-------------------------|-------------------|-------|------------|---------|
| Mode | Fuel | FI | HSSC | FI/HSSC |
| | | p.p.m | . hexane | |
| Idle | Reg. | 600 | 300 | 2.0 |
| | | 575 | 282 | 2.0 |
| 2000 RPM, | Reg. | 238 | 130 | 2.4 |
| no load | | 263 | 125 | 2.1 |
| Idle | Amoco | 634 | 325 | 1.95 |
| | premium | 452 | 250 | 1.8 |
| | | 650 | 290 | 2.2 |
| 1000 RPM, | Amoco | 600 | 330 | 1.8 |
| in gear with braking | premium | | | |

| Table VII. Equilibrium and Recovery Time vs. Bed Diameter | | | | |
|---|--|---|--|--|
| Tube diameter, inches | Equilibrium time, ^a minutes | Recovery time, ^b minutes | | |
| 0.189 | 0.3 | 0.3 | | |
| 0.250 | 0.7 | 0.7 | | |
| 0.33 | 1.5 | 1.0 | | |
| 0.62 | 2.5 | 1.7 | | |

^a Time to reach 90% of equilibrium level. ^b Time to decrease 90% of peak value at 0.5 to 1.0 CFH.

Table VIII. Additivity Studies

| Propene | <i>n</i> -butane | 1-butene | n-hexane | theory ^a |
|---------|------------------|----------|----------|---------------------|
| | | Low se | verity | |
| 0.143 | | | 0.135 | 101 |
| 0.143 | | 0.100 | | 102 |
| | | 0.100 | 0.135 | 99 |
| | | High se | verity | |
| 0.30 | | 0.20 | | 94 |
| | 0.20 | 0.20 | | 96 |

Assuming test data for pure compounds and additivity.

The results indicate that use of small diameter beds can reduce recovery and equilibrium time to low values, although the peak becomes more difficult to read. Pressure drop appears to be the limiting factor if a diaphragm pump is used. Equilibrium response times as low as 5 sec. are attainable at moderate forepressure (\sim 5 p.s.i.) for applications requiring continuous "fast" response readings, such as chromatographic analysis.

For continuous atmospheric monitoring application where maximum sensitivity is primary and fast response secondary, large bed diameter would seem preferable, since maximum response is realized with adiabatic conditions. Assuming a 1 μ V. microvolt sensitivity for the electronic system, a 10junction thermocouple element, 50% oxidation, and a bed large enough to be essentially adiabatic, the theoretically computed sensitivity is about 50 p.p.b. as hexane.

Hydrocarbon Additivity. Although peak additivity would generally be expected as a first approximation when surface sites are far in excess of reactant molecules, there are reasons for expecting minor exceptions, particularly in the case of hydrocarbons differing in reactivity when catalyst volume ahead of the probe is appreciable. Reactive hydrocarbons react primarily ahead of the probe, and heat can be transferred through the bed to the probe, thus delaying peak appearance. Measurements on mixtures of "reactives" and "nonreactives" (hexane + butene) (butane + butene) indicate that mixture values are only slightly less than additive, as shown in Table VIII. At low-severity conditions, no departure from hydrocarbon linearity would be expected, and none was found.

Water Vapor Interference. Significant interference has been observed from water vapor under some conditions. Water vapor is adsorbed by the catalyst and produced immediate positive response, presumably due to heat of adsorption followed by negative effect due to heat of desorption. This problem, which is important in testing water-saturated exhaust gas, has been solved by humidifying the inlet air so

that it has essentially the same moisture content as the sample. Taking the inlet air into the system via a water bubbler appears to be the best humidification method. Recent work has led to further refinement involving routing of the line, after the injection port through the water saturator with a small piece of porous stainless steel inside the tubing at this point to act as a water reservoir to completely eliminate effects due to differences in moisture content between sample and carrier gas. Thermostating of this section is also advisable where ambient temperatures are variable, in order to eliminate minor changes in catalytic activity associated with changes in air water content which can affect selectivity.

Carbon Monoxide and Hydrogen Interference. The response of carbon monoxide and hydrogen, relative to exhaust hydrocarbons, increases markedly with temperature, so that whereas carbon monoxide and hydrogen can be neglected even for rather high levels at low severity, the interference can be significant at high severity.

Response for carbon monoxide, relative to hexane on a carbon basis at high-severity conditions, (i.e., HSSC) is 0.3% or less. Response per mol. for hydrogen is about half that for carbon monoxide. Both give linear response with mols. injected when pure.

In general, low hydrocarbon levels are not found with high carbon monoxide in exhaust gas, so that maximum interference (which causes higher values) should not exceed 5% of the hydrocarbon level.

CARBON MONOXIDE ANALYSIS

The effects of temperature and flow rate on peak response are shown in Figure 10. The nature of the response is similar to that of a very reactive hydrocarbon on vanadia catalyst, in that response which is linear with mols. CO goes through a maximum with temperature increase and/or flow rate change.

Comparisons with continuous infrared values have shown expected agreement in considering sampling differences and experimental error involved in the two methods. Table IX illustrates the degree of agreement realized.

No significant interferences have been found except for slow, reversible changes in response with water vapor content of carrier gas. By operating at plateau response level conditions, and controlling water saturator temperature, interference from this source can be neglected. Otherwise, precise measurements require frequent standardization. Plateau response is illustrated by the 76° C. plot between 1.5 and 2.0 CFH in Figure 10.



Figure 10. CO unit response vs. temperature and flow rate in cu. ft./hr.

| Table | IX. | Ca | rbon | Monox | ide | Determination |
|-------|-------|-----|-------|-----------|-----|---------------|
| J | Infra | red | US. S | Selective | Co | mbustion |

| NDIR | SC | NDIR | SC | NDIR | SC |
|------|------|------|-----|------|-----|
| % C | XO O | % 0 | 20 | % 0 | CO |
| 2.5 | 2.5 | 0.9 | 1.1 | 3.3 | 2.7 |
| 2.6 | 2.5 | 0.4 | 0.4 | 3.3 | 3.2 |
| 2.6 | 2.5 | 0.5 | 0.6 | 3.2 | 3.2 |
| 0.9 | 0.8 | | | 4.0 | 3.5 |
| 4.1 | 3.7 | 5.1 | 4.2 | 2.0 | 1.5 |
| 1.0 | 0.9 | 5.2 | 4.2 | 2.0 | 1.5 |
| 0.4 | 0.4 | 3.2 | 3.3 | 0.6 | 0.6 |
| 0.4 | 0.2 | 3.3 | 3.5 | 0.5 | 0.6 |

OTHER APPLICATIONS

This type of analyzer offers significant advantages over other methods for analyzing various exhaust streams from petroleum products:

Correlation of response with harmful effects

No cylinder gas requirement

Little if any maintenance

No sample train or treatment required

Versatility, since other components (*e.g.*, aldehydes, carbon dioxide, etc.) can be measured "simultaneously" or by replacing the hydrocarbon reactor plug with one suitable for other requirements.

VEHICLE EXHAUST INSPECTION

Field application studies have been reported recently (Innes, 1969).

Conclusions

• The selective combustion approach is well suited for analysis of hydrocarbons and carbon monoxide in automotive exhaust gas and should be a very useful tool for economically detecting and correcting improper engine operation, which is a major factor in air pollution.

• It can be tailored either to correlate roughly with the

Table X. Sources of Error and Estimated Magnitudes

| Sources of error | |
|------------------------------|-----|
| Read-out | 1 |
| Amplifier noise | 0.5 |
| Amplifier drift | 1 |
| Sample size | 1.5 |
| Gas temperature and pressure | 1 |
| Catalyst bed temperature | 1 |
| Flow rate | 0.5 |
| Overall | 2.8 |

^a For prototype model with manual block temperature control used for most of this work. Values higher at low hydrocarbon levels.

current flame ionization or infrared methods, or to give good correspondence with probable future standards based on photochemical reactivity.

• The method has good potential for analysis of other exhaust streams containing hydrocarbons and for air monitoring.

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Direct Gas Chromatographic Analysis of Low Molecular Weight Substituted Organic Compounds in Emissions

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• This paper describes an automated, gas chromatographic method for direct analysis of C_2 through C_4 aldehydes, C_3 and C_4 ketones, and various other oxygen-, nitrogen-, and halogen-containing organic compounds present in combustion effluents. Retention times are given for a great variety of compounds this system is capable of analyzing. Examples of chromatograms from analysis of samples of auto exhaust, trench incineration effluents, and ambient air are included. The limit of detection for the system is 0.05 p.p.m. of acetaldehyde.

Gas chromatographic analysis of oxygenated hydrocarbons in auto exhaust and other combustion effluents is a complex problem. Hydrocarbons in combustion effluents are at least 10 to 100 times more concentrated than their oxygenated homologs. Gas chromatographic columns reported in the literature provide little or no resolution between the hydrocarbons and oxygenates commonly present in automotive emissions.

Although selective detectors for aldehydes have been reported (Cremer, 1967), they are not commercially available, nor do they appear sufficiently sensitive for analysis of combustion emissions. For these reasons few significant oxygenate data can be collected by a standard direct gas chromatographic analysis. An approach to solving these problems is to form a derivative of the oxygenated material by passing the gaseous sample through a reagent mixture of 2,4-dinitrophenylhydrazones (Camin and Raymond, 1967; Oberdorfer, 1967). The material of interest reacts with the reagent and is retained in the solution, while the insoluble nonreacted hydrocarbons are vented. The reacted compounds are then transferred quantitatively to a gas chromatograph for analysis. This method, however, entails some problems. Only a limited group of oxygenated compounds form suitable derivatives. Quantitative transfer of the derivative from the collection medium to the gas chromatograph is difficult. Formation of the derivative under varying environmental conditions is unpredictable. Pyrolysis of the derivative within the gas chromatograph can occur.

Procedure

Hollis (1965) first described the unique separation obtained by using columns packed with porous polymer beads (Porapak). These separations can be utilized for analyzing light oxygenated hydrocarbons if the interfering C_1 to C_8 hydrocarbons can be removed (Table I). In sharp contrast to these separations, many commonly used packed columns elute

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these light hydrocarbons long before the first aldehydes appear. One such liquid phase is 1,2,3-tris(2-cyanoethoxy)propane. Figure 1 indicates the time from injection to peak maximums for various compounds eluting from a column packed with this liquid phase. The figure shows that if a sample were injected and allowed to flush through this column for 5.45 min., most of the C₁ to C₈ hydrocarbons would be vented, while most of the organic compounds that contain oxygen and nitrogen would be retained. Any compound eluting within the time interval between 4.75 and 6.15 min. would be only partially retained within the column.

The approximate per cent of any given compound retained by the column can be calculated by placing the 50% point on the gaussian curve scale at the point of the peak and then reading the per cent retained at 5.45 min. For instance, assume a peak at 5.70 min. Application of the gaussian curve scale indicates that more than 82% of the compound would be contained in the column at 5.45 min. This calculation entails the assumptions that all the peaks are gaussian and exhibit polarities similar to that of ethylene oxide.

All of the compounds that are quantitatively retained within this column at 5.45 min., if ideally transferred to a Porapak Q column (analytical column), would be rapidly and efficiently separated with no interfering hydrocarbon peaks. To transfer the retained fraction from the cutter column to the analytical column, the flow to the cutter column is

Table I. Retention Times of Selected Compounds Eluting from a Porapak Column

| 12 feet long, 0.105-inch ID 50 to 80 mesh Temperature: 160° C. Flow rate: 50 cc./min. |
|--|
| Carrier: helium Retention time (min.) |
| 1.10 |
| 2.43 |
| 3.98 |
| 4.68 |
| 8.53 |
| 9.56 |
| 10.06 |
| 16.00 |
| 19.43 |
| e 21.50 |
| 22.65 |
| |



MINUTES





Figure 2. System schematic

reversed (backflushed) at 5.45 min. All of the compounds that are not irreversibly absorbed will emerge from the cutter column in about 5.45 min.

The components constituting the backflush peak emerge over a relatively long period of time and cannot be presented directly to the analytical column. To eliminate this problem, these components are retained in a short section of packed column (trap) at a reduced temperature. After transfer into the trap is complete, the temperature is rapidly programmed to about 100° C. efficiently presenting the components of the backflush peak as one slug to the analytical column. This method of presentation allows use of the relatively high number of theoretical plates per foot characteristic of porous polymer columns.


Experimental

Figure 2 shows schematically the system designed to perform the functions described. The cutter column is constructed from 1/4-inch-O.D. tubing. With this column one can inject gaseous samples as large as 25 cc. without seriously affecting the geometry of the fore flush peaks.

The port on the seven-port linear valve (valve 2) marked "fore flush vent" can be monitored with a suitable detector to determine the retention times for various compounds emerging from the cutter column. The backflush point for any particular analysis can be determined from these data.

Critical internal volumes are kept at a minimum by use of $\frac{1}{16}$ -inch-O.D. tubing between the trap, valve 3, and the analytical column. An auxiliary gas sampling valve is placed before the trap inlet for introduction of qualitative gas mixtures for peak identification.

The trap (Figure 3) is constructed from 16 inches of 0.105inch-I.D., 1/s-inch-O.D., 304 stainless steel tubing. Two-inch segments at each end are packed with siliconized glass wool. The central 12 inches of the trap contain 10% sucrose octaacetate on 60- to 80-mesh Gas-chrom Z. At reduced temperatures this substrate quantitatively retains all the oxygenated materials reported in this paper. The lower packed part of the trap is cooled by expanding liquid CO₂ around it. Short bursts of CO₂ (about 0.1 sec. long) every 4 sec. cool the packed area to -55° C. Trapped materials are efficiently desorbed by rapidly temperature-programming the trap at a rate of 12° C. per sec. to 100° C. The trap is heated by its own resistance with a low-voltage high-current source. Care must be taken in construction of the trap so that all metal surfaces become hot enough to desorb all of the condensed materials instantly. Generally a cool spot is characterized by excessive tailing of the polar materials eluting from the analytical column. Two 50-watt heaters, located on the top of the trap container, keep the trap tubing constantly hot where it passes through the container.

Each step of the analysis must be timed precisely to assure quantitative accuracy. An automatic programmer incorporating Automatic Timing Controls, Inc., cascading timers was constructed to initiate each step. Figure 4 shows the wiring diagram and the equipment. The functions controlled are as follows.

From start to 30 sec. valve 1 is energized, allowing the sample to purge the calibrated injection volume at 100 cc. per min.

At 30 sec. the gas sample valve injects the sample into the cutter column.

At 60 sec. the injection valve returns to the fill position and valve 1 is de-energized purging the calibrated injection volume with clean air.

At 5.45 min. from injection (function 2) the two automatic seven-port valves (valves 2 and 3) switch simultaneously, backflushing the cutter column through the trap and venting the trap exit to atmosphere. Simulta-



Figure 4. Programmer wiring diagram



Figure 5. Rotary gas sampling valve automation

neously a cam timer starts pulsing liquid CO2 at thep rescribed rate. To compensate for any flow variations, the backflush step is held for the length of the foreflush step plus 2 min.

At 12.9 min. the two seven-port valves (valves 2 and 3) are returned to their original position. The pulsating CO2 is stopped and power is applied to heat the trap for 12 sec.

At 13.1 min. the recorder is started to record the chromatogram.

At the end of the chromatogram, about 35 min. from function 6, the recorder is stopped. When needed, the analytical column backflush valve can be activated to backflush any components remaining in the column. This step can be performed either automatically or manually by selection of the proper switch position. Figure 5 shows the method of automating the Perkin-Elmer gas sampling valve by use of 90-degree-turn Trok-more air-operated actuators.

Hydrocarbon Interferences

Since the compounds of interest are generally 10 to 100 times more dilute than the hydrocarbons vented by the cutter column, it is obviously necessary to insure that at least 99.9 + % of these hydrocarbons are vented. In practice, this is a difficult task because the shapes of peaks emerging from the cutter column are gaussian. In addition, diffusion in the



Figure 6. Chromatogram of auto exhaust diluted 13.7:1 with Air

| | Compound | Full scale response equal to | Concentration, p.p.m. |
|----|--------------------|---------------------------------|--------------------------|
| 1 | Methanol | 1 × 10 ⁻¹¹ | 0.69 |
| 2 | Acetaldehyde | amps | |
| 3 | Unknown | 5 × 10 ⁻¹² | |
| 4 | Unknown | 5×10^{-12} | |
| 5 | Unknown | 5×10^{-12} | 2.22 |
| 6 | Acrolein | 5×10^{-12} | 0.38 |
| 7 | Propanal | 5×10^{-12} | 0.13 |
| 8 | Acetone | 5×10^{-12} | 0.25 |
| 9 | Unknown | 5×10^{-12} | 1.212 |
| 10 | Unknown | 5×10^{-12} | |
| 11 | Unknown | 5×10^{-12} | 4 7 9 |
| 12 | Unknown | 5×10^{-12} | 1.227 |
| 13 | 2-Methylpropanal | 5×10^{-12} | 0.13 |
| 14 | Unknown | 5×10^{-12} | |
| 15 | Butanal | 5×10^{-12} | 0.082 |
| 16 | Methylethyl ketone | 5×10^{-12} | 0.090 |
| 17 | Unknown | 5×10^{-12} | |
| 18 | Benzene | 5×10^{-12} | |



Figure 7. Chromatogram of incinerator effluent

gas phase and other physical phenomena (Kaiser, 1963) cause the peaks to tail. Experiments indicate the following venting efficiencies, in per cent, at initial concentration of 10,000 p.p.m.: ethane, 100; propane, 100; butane, 99.999+; pentane, 99.987; and hexane, 99.81. Fortunately, in auto exhaust, the hydrocarbons in the C₅ to C₆ range are dilute enough to cause no detectable interference.

Analytical Columns

If the Porapak Q is not sufficiently conditioned, a large response is obtained early in the chromatogram that generally interferes with the peaks of methanol, acetaldehyde, ethylene oxide, and methyl formate. This response is probably due to water preferentially desorbing impurities from the polymer. Usually this condition can be corrected by placing the Porapak Q in a Soxhlet extractor, extracting these impurities with methyl alcohol for about 2 hrs, and drying. The column described here was packed with this dried, extracted Porapak Q, and conditioned with dry, oxygen-free nitrogen for about 60 days at 175° C. Conditioning periods vary among batches of Porapak Q.

Applications

A chromatogram of a sample obtained by a variable dilution sampler (Broering, *et al.*, 1967) from a car operated on a chassis dynamometer is shown in Figure 6. A hydrogen flame detector was used to obtain maximum sensitivity. Samples must be collected in such a manner that absorption of oxygenated materials is minimized. An ice bath commonly used with proportional samplers to remove excessive H_2O vapor cannot be used in the line, since the oxygenated materials are very water-soluble. Samples must be analyzed rapidly after collection, even though they are diluted, since aldehydes are products of many of the photochemical and dark reactions of oxides of nitrogen and olefins.

Figure 7 shows chromatograms of the effluent from an incinerator burning wood under two conditions. The samples were taken before and after forced air was introduced. For the sample taken without forced air, the chromatogram shows a much wider range of products. With forced air added, the lower-molecular-weight materials, in particular the alcohols, are the main products shown. The incinerator samples show a considerably higher ratio of alcohols to aldehydes than auto exhaust does, a reflection of the differences in type of combustion and source.

Figure 8 represents chromatograms of ambient air collected at various sites. The trace for the traffic sample shows a simplified exhaust pattern, whereas that for the open-field sample shows very small amounts of oxygenated materials.

These chromatograms of samples collected from various sources suggest the broad applicability of the technique. Since most oxygenated and nitrogen-containing materials of approximately the same molecular weight are seen by this technique in complex mixtures, the difference in each source is readily apparent.

Table II lists retention times for various compounds detected in trace quantities in the presence of relatively abundant hydrocarbons by the system described.

Table III lists the operating conditions for the various columns incorporated throughout the instrument.



Figure 8. A chromatogram of ambient air

Table II. Retention Times of Various Compounds Eluting from the Analytical Column-Trap Combination

| Compound | Time (min.) | Compound | Time (min.) |
|-----------------|----------------|----------------------|----------------|
| Methanol | 3.63 | Allyl alcohol | 15.50 |
| Acetaldehyde | 4.05 | 2,3-Butylene oxide | 16.31 |
| Ethylene oxide | 4.21 | Methyl acrolein | 16.95 |
| Methyl formate | 5.11 | 2-Methylpropanal | 17.82 |
| Ethanol | 7.17 | Isobutylene oxide | 17.88 |
| Furan | 8.05 | Propionitrile | 18.28 |
| Propylene oxide | 8.32 | 2-Methylfuran | 18.78 |
| Acetonitrile | 8.51 | 1,2-Butylene oxide | 20.11 |
| Acrolein | 8.92 | 2-Methylpropane-2-ol | 20.68 |
| Propanal | 9.35 | Tetrahydrofuran | 22.23 |
| Dichloromethane | 9.56 | Butanal | 22.27 |
| Methyl nitrate | 9.71 | Vinyl methyl ketone | 22.38 |
| Acetone | 10.45 | 2,3-butanedione | 22.84 |
| Ethyl formate | 11.23 | Methylethyl ketone | 24.60 |
| Acrylonitrile | 11.78 | Cyclobutanone | 31.29 |
| Methylal | 12.42 | 2,2-dimethylbutanal | 31.53 |
| 2-Propanol | 12.80 | Benzene | 31.60 |
| Methyl acetate | 12.89 | Crotonaldehyde | 34.50 |
| Nitromethane | 13.44 | 2-Methylpropanol | 35.55 |

Table III. Operating Conditions for Chromatographic Columns

Cutter column 0.25-inch OD 0.18-inch ID 304 stainless steel 12 feet long 20% 1,2,3-Tris(2-cyanoethoxy) Propane on 45-60 mesh N.A.W. Chromosorb-W Temperature: 22°C Carrier: helium Flow rate: 100 cc./min. Analytical column 0.125-inch OD 0.105-inch ID 304 stainless steel 12 feet long 50-80 mesh Porapak O Temperature: 156° C. Carrier: helium Flow rate: 50 cc./min. Soxhlet extracted with methanol for 2 hours. Packed and conditioned at 175° C. for 60 days

Summary

Automated analysis capable of direct quantitative determination of a great variety of oxygenated and nitrogencontaining hydrocarbons from auto exhaust and other air pollution sources has been developed in this laboratory. The method employs two columns; the first (the cutter column) vents the hydrocarbons and retains the compounds of interest; the retained compounds are then transferred to the second column (the analytical column) for analysis.

By taking advantage of the wide variety of gas-chromatograph columns reported in literature, the investigator can increase the range of possible analyses. He can select combinations of cutter and analytical columns that exhibit widely differing properties such as polar, nonpolar, solid adsorptive, irreversible adsorptive, and chemisorptive characteristics. In our laboratory the use of two-column systems has simplified analyses; for example, removal of C1 to C8 paraffins and analysis of the remaining fraction of olefins (Bellar, et al., 1964; Smith, 1962), and removal of paraffins and olefins up to C13 and analysis of the remaining aromatic fraction (Lemoine, 1965). The technique described here measures C2 through C5 oxygenates in samples from both emission sources and the ambient atmosphere.

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COMMUNICATION

Possible Source of Atmospheric Pollution of Selenium

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■ A method of tracking down a source of elemental atmospheric pollution is based on the determination of pertinent elemental ratios in the samples of interest. As a first approach, in an attempt to study a source of selenium pollution in the atmosphere, selenium to sulfur ratios were determined in the samples of some fuels, rubbers, and soil samples by analyzing sulfur and selenium with ultraviolet-visible spectrophotometry and turbidimetry, respectively. The ratios thus obtained were compared with those of the atmospheric precipitation and particulate samples, which were found to be in the same order of magnitude as those of fuel oils and rubber products. The present study, therefore, indicates that the fuel oils can be an important source of selenium pollution in the atmosphere.

he use of selenium in industry is growing. One of the major uses of selenium compounds is in the glass industry to color glass a deep red and to neutralize iron color. It was also found lately by West (1967) that various papers contain significant amounts of selenium of physiological and toxic importance. The incineration of paper, therefore, should be an important source of selenium. However, importance of fuel as a possible source of selenium in the atmosphere has been neglected until 1967, when selenium in atmospheric samples was first analyzed by Hashimoto and Winchester (1967). They reported that the average ratio of selenium to sulfur in those samples collected in the greater Boston area is about 1×10^{-4} with an apparent positive correlation between sulfur and selenium. It was for this reason that selenium was considered as a possible atmospheric pollutant along with sulfur, which mostly originates from fuel burning.

The materials analyzed are listed in Table I. Raw petroleum, coal, heavy petroleum, and petroleum were chosen because

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| Raw petroleum | Nippon Petroleum Co. | | |
|-------------------|---|--|--|
| Heavy petroleum A | Arabian Petroleum Co., and others | | |
| Heavy petroleum B | Arabian Petroleum Co., and others | | |
| Heavy petroleum C | Arabian Petroleum Co., and others | | |
| Petroleum | Nippon Petroleum Co., for oil heater | | |
| Coal | Sumitomo Mining Co., for coal heater | | |
| Soot | Collected at a power plant using heavy petroleum | | |
| Soil | Collected in Tokyo, Japan, and its vicinity | | |
| Rubber | Various automobile tires used in Tokyo area | | |

they are the main source of sulfur pollutants in the atmosphere. Rubbers were also analyzed as they are the major components of automobile tires, to which sulfur is added in the production line. Simple analysis of sulfur and selenium in those samples, however, will provide no useful information as to the source of pollution, unless the elemental ratios of a pair of elements which have similar chemical and physical properties are studied.

Procedure

The method developed by Forrester and Jones (1960) was used to decompose the samples of petroleum, coal, and rubber, while the method by Chaudry and Cornfield (1966) was utilized for the decomposition of soil samples. Separation of selenium was made as described by Hashimoto and Winchester (1967). Analytical methods are based on the procedure by Cheng (1956) and ASTM procedure (1964) for selenium and sulfur, respectively. A Model EPU-2 spectrophotometer (Hitachi, Japan), was used throughout the experiment.

Results and Discussion

The analytical results of selenium, sulfur, and their ratios are summarized in Table II. Raw and heavy petroleum contain



ATMOSPHERIC SAMPLES

Figure 1. Variation of Se/S ratios of atmospheric samples (collected in the greater Boston area) and comparison of their ratios with those of possible pollutants

| Table II. Analytical Results of the Samples Analy |
|---|
|---|

| Samples | Se(µg./g.) | S(mg./g.) | Se/S ratio $(\times 10^{-4})$ | Sample | Se(µg./g.) | S(mg./g.) | Se/S ratio $(\times 10^{-4})$ |
|-----------------|------------|-----------|-------------------------------|---|------------|-----------|-------------------------------|
| Raw petroleum 1 | 0.95 | 20.9 | 0.45 | Rubber tires 4 | 2.00 | 15.1 | 1.33 |
| Raw petroleum 2 | 0.89 | 21.3 | 0.42 | Rubber tires 5 | 1.45 | 14.0 | 1.00 |
| Raw petroleum 3 | 0.50 | 16.1 | 0.31 | Rubber tires 6 | 1.55 | 14.0 | 1.10 |
| Raw petroleum 4 | 0.80 | 18.1 | 0.44 | | Av. 1.33 | Av. 13.0 | Av. 1.01 |
| Raw petroleum 5 | 0.95 | 19.6 | 0.49 | Coal 1 | 1.30 | 2.38 | 5.50 |
| | Av. 0.92 | Av. 18.4 | Av. 0.42 | Coal 2 | 1.05 | 2.50 | 4.20 |
| Heavy pet. A-1 | 0.95 | 12.0 | 0.79 | | Av. 1.18 | Av. 2.44 | Av. 4.85 |
| Heavy pet. A-2 | 1.05 | 8.6 | 1.22 | Petroleum 1 | 0.50 | 3.45 | 1.50 |
| Heavy pet. A-3 | 1.30 | 12.2 | 1.09 | Soot 1 ^a | 4.30 | 138 | 0.31 |
| | Av. 1.10 | Av. 10.9 | Av. 1.03 | Soot 2 ^b | 0.50 | 30 | 0.17 |
| Heavy pet. B-1 | 0.50 | 16.5 | 0.55 | Soil 1 | 1.10 | 1.70 | 6.47 |
| Heavy pet. B-2 | 0.70 | 17.6 | 0.63 | Soil 2 | 1.30 | 1.60 | 8.13 |
| Heavy pet. B-3 | 1.05 | 16.5 | 0.46 | Soil 3 | 1.30 | 2.40 | 5.42 |
| | Av. 0.75 | Av. 16.9 | Av. 0.55 | Soil 4 | 1.00 | 1.50 | 6.67 |
| Heavy pet. C-1 | 1.65 | 18.9 | 0.87 | Soil 5 | 1.20 | 1.60 | 7.50 |
| Heavy pet. C-2 | 0.89 | 20.2 | 0.44 | | Av. 1.14 | Av. 1.76 | Av. 6.84 |
| Heavy pet. C-2 | 0.80 | 18.9 | 0.42 | Soil extract 1 | 0.50 | 0.10 | 50 |
| •• | Av. 1.12 | Av. 19.3 | Av. 0.58 | Soil extract 2 | 0.50 | 0.11 | 45 |
| Rubber tires 1 | 0.70 | 11.6 | 0.60 | | Av. 0.50 | Av. 0.11 | Av. 48 |
| Rubber tires 2 | 0.95 | 12.8 | 0.74 | | | | |
| Rubber tires 3 | 1.40 | 10.7 | 1.31 | ^{<i>a</i>} Mechanically c ^{<i>b</i>} Electrically coll | ollected. | | ¥. |

consistent amounts of both elements, while petroleum appears to have much less sulfur. The amounts of selenium in the automobile tires, coal, and soil samples are fairly comparable, even though soot, when collected electrically, and soil extract contain slightly less amounts of selenium. Amounts of sulfur, however, vary significantly depending on the samples of soot, coal, soil, and soil extract.

The wide spread in amounts of sulfur necessitates, therefore, analysis of selenium to sulfur ratio to detect the source of selenium pollution. Figure 1 shows that selenium to sulfur ratios of the fuel samples analyzed here are in the same order of magnitude as found in the atmospheric precipitation and particulate samples. Particularly, the ratios of raw and heavy petroleum samples are in good agreement with those of the atmospheric samples. It would, therefore, be safe to assume that both raw and heavy petroleum can be a source of selenium in the atmosphere.

Further study on V/Se and Te/Se ratios on the atmospheric samples and the possible pollutants will refine the analytical results so that a firm conclusion may be drawn.

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bookshelf

Report of the Secretary's Commission on Pesticides and Their Relationship to Environmental Health. 696 pages. Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402. 1969. \$3.00, paper.

This report is the result of extensive examination of studies on more than 600 active pesticidal chemicals in use in this country. Based on findings and evaluations of all available data on uses and benefits of pesticides, environmental contamination, human effects, and effects on nontarget organisms other than man, the study emphasizes the need for ecological research.

USDA Summary of Registered Agricultural Pesticide Chemical Uses. Volume II, Fungicides, Nematicides. 212 leaves. Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402. 1969. \$3.50, paper.

Chemical Fallout: Current Research on Persistent Pesticides. Morton W. Miller and George G. Berg. 560 pages. Charles C. Thomas, Publisher, 301-327 E. Lawrence Ave., Springfield, Ill. 62703. 1969. \$22.50, hard cover.

1969 Proceedings of the American Society for Testing and Materials. 488 pages. American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103. 1969. \$12.00, hard cover.

Proceedings of the 1969 Conference on Animal Waste Management. Edited by Raymond C. Loehr. 414 pages. Agricultural Waste Management Program, Riley-Robb Hall, Cornell University, Ithaca, N.Y. 14850. \$10.50, hard cover.

Tobacco, Sensitive Monitor for Photochemical Air Pollution. 23 pages. Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402. 1969. 25 cents, paper.

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No. 13 Pesticides in Tropical Agriculture. Use of pesticides on basic tropical food crops—sugar cane, cotton, cacao, rubber, coffee, rice, and bananas—in weed control, and on stored products. 102 pages Paper (1955) \$5.00

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CLEVELAND, OHIO 44105: 6200 HARVARD AVENUE BUFFALO • CHICAGO • DETROIT • NEW YORK CITY PHILADELPHIA • PITTSBURGH • LAKELAND, FLORIDA LICENSEES THROUGHOUT THE WORLD **CRC Handbook of Analytical Toxicology.** Edited by Irving Sunshine. 1104 pages. Chemical Rubber Co., 18901, Cranwood Pkwy., Cleveland, Ohio 44128. 1969. \$26.00, hard cover.

Scientific and Technological Communication. Sidney Passman. x + 151 pages. Pergamon Press, Inc., Maxwell House, Fairview Park, Elmsford, N.Y. 10523. 1969. \$6.00, hard cover.

Functioning of Terrestrial Ecosystems at the Primary Production Level. 616 pages. A UNESCO Publication. Unipub, Inc., P.O. Box 433, New York, N.Y. 10016. 1969. \$19.00, hard cover.

Clean Air for Your Community. 12 pages. Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402. 1969. 25 cents, paper.

Opportunities in Oceanographic Careers. Odom Fanning. 160 pages. Universal Publishing and Distributing Corp., 235 E. 45th St., New York, N.Y. 10017. 1969. \$3.75, hard cover; \$1.95, paper.

Quality of Surface Waters in the United States, 1964—Parts 7 and 8, Lower Mississippi River Basin and Western Gulf of Mexico Basins. 602 pages. U.S. Geological Survey, Distribution Section, 1200 S. Eads St., Arlington, Va. 22202. 1969. \$2.50, paper.

The Universities and Environmental Quality—Commitment to Problem Focused Education. 80 pages. Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402. 1969. 70 cents, paper.

Air Pollution Publications, A Selected Bibliography with Abstracts, 1966-1968. 522 pages. Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402. 1969. \$4.50, paper.

new products digest



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The AirPol Basic Venturi Scrubber for industrial dust and fume removal is especially designed for iron and steel, chemical, cement, and lime plants, pulp and paper mills, and foundries, as well as other industrial facilities emitting dust, gas, or fumes. The unit features water-film scrubbing-controlled distribution of water-providing water injection through a few large diameter pipes, and elimination of jets and nozzles. These pipes also allow recirculation of dirty liquids containing high solids, the company says. The new scrubber can be built to handle to 1 million c.f.m. in a single unit, and is capable of providing ultrahigh efficiency for plus and submicron particulates. Air Pollution Industries, Inc. 61

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The Pipeline De-Lumper Chopper, which chops lumps in liquid streams to increase flow rates and break up stoppages, is available. Units are designed to suit many applications, for example, where mixing of the product is not desirable, the device is supplied to operate at a low r.p.m., avoiding agitation while expediting product flow; where mixing is preferred, a high speed unit is supplied. The manufacturer claims that the De-Lumper prevents blockage of pumps, valves, and the pipe itself, is self cleaning, clogproof, and pressure tight. The device can handle sludge in oil lines, wastes in liquid streams, such dry materials as caked up cane and beet sugar, corn sugar, and flour, and wet solids as centrifuge, filter press, and expeller chunks. Franklin P. Miller & Son, Inc. 63

Air monitor

The Air Pollution Monitor (or NOX Box) for sampling and measuring sulfur dioxide or oxides of nitrogen is available as an instrument or a complete system. The lightweight compact unit features an electrochemical longlife faradaic cell for fast response time. portability, easy calibration, and low maintenance cost. Dynasciences Corp.

64

Oil pollution detector

An as yet unnamed oil-on-water detector is floated on the surface of the water, using the reflectivity of the stream to measure degrees of water pollution. Any oil on the surface-as close as 30 feet away-causes an increase in the intensity of a beam of reflective light, according to the manufacturer. Hallikainen 65



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Home waste disposal

The Waste Tamer-a home unit sanitary disposal plant which will replace cesspool and septic tank systems-is available. The company claims that the unit is designed as an aerobic digestion system, providing both primary and secondary treatment of home sanitary waste and producing a clear odorless effluent. Each unit consists of two packages connected by pipes-a corrosion resistant tank containing four chambers and no moving parts, and a mechanical assembly with controlsrequires no costly chemicals, and produces no offensive odors, while providing pollution reduction to 95%. Environmental Services, Inc. 66

Gas analyzer

The MT 150G Gas Chromatograph is designed for high performance in trace gas analysis, according to the manufacturer. An ultrasonic detector (which may be used with any carrier gas) has linearity of at least 10^7 and sensitivity of better than 1 p.p.m. to all gases. Tracor, Inc. **67**

Digital dust indicator

All dust particles in the range 0.5μ , and dust concentrations from 0.02-500 mg./m.³ can be measured by a new dust indicator. The portable device features pushbutton, battery operation, and samples air at the rate of 10L. per minute. Counts are displayed on a dial or can be accumulated in the digital counter. WeatherMeasure Corp.



Residual gas analyzer

The EAI Quad 1100 residual gas analyzer is available. The low-cost device features solid-state electronics for improved performance, according to the company. Mass range of the instrument is 1-300 amu; partial pressures on the order of 5×10^{-14} for N₂ are detectable. An interchangeable, throw-away plug-in unit contains two ion source filaments. This ion source is designed to eliminate the need for a separate electron extractor and focus electrode. Varian **68**

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Instruments catalog. Technical help and application examples for uses of low pressure gages, flowmeters, manometers, and air operated electric control switches are offered in a new catalog. Prices and description of differential pressure, air velocity, and combustion testing instruments are included in the more than 100 page publication. Dwyer Instruments, Inc. 91

Combustion control instrumentation. Bulletin 4099, "Beckman Steam Plant Instrumentation for Combustion Control and Water Purity Analysis" describes the full range of the company's electronic and pneumatic combustion control instrumentation and shows typical systems. The 20 page brochure includes specifications, principles of operation, special features, and applications of instruments, and is illustrated with photographs, diagrams, and flow charts. Beckman Instruments, Inc. 92

An approach to water pollution problems. The company's pollution control consulting services are outlined and described in a 4 page bulletin (PCS2). Two key steps for minimizing water treatment costs are discussed, as well as some tips for cutting pollution control costs. Nalco Chemical Co. 93

Articles on activated carbon. The sixth issue of "Activated Carbon Abstracts," summarizing articles (from 163 U.S. and foreign periodicals, plus patents and nonpublished papers and theses) on theoretical and practical applica-



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Circle No. 1 on Readers' Service Card 164 Environmental Science & Technology tions that utilize the adsorptive qualities of activated carbon, is available. Subjects covered in the 15 page publication include process design, stream pollution, environmental health, radioactive containment, and chemical processing. Witco Chemical Corp. 94

Automatic nitrogen system. Design features, specifications, and applications of an on-site automatic nitrogen system are described in a new bulletin. The compact air separation plant is available in a range of producing sizes from 14,000-100,000 standard cubic feet per hour of high purity nitrogen, the company says. Foòd processing, semiconductor and float glass manufacture, as well as chemical, petrochemical, and metallurgical processes are some of the industrial applications of the system. Airco Industrial Gases. 95

Instruments for water analysis. The company's line of CR2 Water Instrumentation is described in a 6 page folder. "A New Way of Looking at Water" provides complete specifications for continuous reading analyzers, as well as a discussion of effective water management. Hach Chemical Co. 96

Wet scrubbing device. The Petersen Separator, a wet scrubbing device that removes submicron liquid and solid impurities from gas and air is described in a 4 page bulletin. Other features of the unit are discussed, as well as operating design details, performance data, and typical applications. Union Carbide Corp. 97

Water-borne waste treatment. A 12 page brochure is fully illustrated, and, in layman's language, highlights the features of the company's system for treatment and purification of municipal sewage and industrial water-borne wastes. Flocor systems are designed for waste water biological oxidation, are engineered to increase unit efficiency and loading capacity of sewage and waste treatment units, and may be

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used to replace conventional packing or to create new tall biological oxidation towers, the company claims. Ethyl Corp. 98

Solid wastes projects. A compendium of 42 projects undertaken from July 1, 1965-June 30, 1968 with funds appropriated under the Solid Waste Disposal Act is available. "Summaries of Solid Wastes Program Contracts" covers such topics as appraisals of current solid waste practices in Europe and the U.S. and development of a new solid waste technology. Objectives, approach, and summary of progress, as well as contractor, project director, cost, and inclusive dates are included for each project. Bureau of Solid Waste Management, Environmental Control Administration, 5555 Ridge Ave., Cincinnati, Ohio 45213 (Write direct)

An alternative disposal method. The "Tezuka Refuse Compactor System" is a report on and analysis of the major elements, operations, and cost of the Japanese developed system. The report is part of an American Public Works Association waste railhaul study, which suggests that refuse compression is the key to successful waste railhaul operations. Bureau of Solid Waste Management, Environmental Control Administration, 5555 Ridge Ave., Cincinnati, Ohio 45213 (Write direct)

Flow studies in Texas rivers. Report 97, "Base-Flow Studies, Leon and Lampasas Rivers, Texas, Quantity and Quality, January 16-17, 1968" describes an investigation of the Bell County rivers. By measuring discharge and collecting water samples for chemical analysis, the authors found that both generally gained flow in the research area. Concentration of dissolved solids, chloride, and sulfate were within limits suggested by the U.S. Public Health Service for municipal water supplies. The water also was found of a satisfactory quality for many industrial and agricultural uses. Texas Water Development Board, P.O. Box 12386, Austin, Tex. 78711. (Write direct)





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meeting guide

February 11 and 12 Illinois Department of Public Health, and Department of Civil Engineering, University of Illinois

12th Sanitary Engineering Conference Urbana, III.

The conference is aimed toward engi-neers and scientists in government, industry, or private practice, as well as water works managers and operators. Sessions will include papers and dis-cussion topics under the general theme Nitrate and Water Supply: Source and Control. and Control.

March 2-6 **National Association of Corrosion** Engineers

26th Annual Conference

Philadelphia, Pa.

Among the more than 100 technical papers to be presented at the conference, a number will consider disposal of chemical cleaning wastes. Industrial water pollution control research and development programs; evolution in chemical cleaning waste disposal; and deep well disposal-pollution answer or pollution problem-are among topics to be discussed.

March 12 and 13

American Society of Civil Engineers Specialty Conference on Water Quality Enhancement

Sheraton-Park Hotel, Washington, D.C. Participants at the 2 day conference will attempt to find some answers to the question, "Is water quality enhancement feasible?" Divergent views of federal, state, and local policy makers, regulatory agencies, conservationists, and the public will be debated. The sponsors hope new policy ideas and recommenda-tions for the national pollution control effort will result.

March 18 and 19 U.S. Bureau of Mines and IIT **Research Institute**

2nd Mineral Waste Utilization Symposium

Chicago, III.

Chicago, III. This year's symposium will be divided into four sections, covering utilization of mining wastes; industrial wastes; municipal refuse; and scrap. Papers will be presented by investigators rep-resenting research centers, resources centers, and contractors. For informa-tion: Murray A. Schwartz, IIT Research Institute, 10 W. 35th St., Chicago, III. 60616 60616

March 24–26 University of Houston and Environmental Control Administration

National Industrial Solid Wastes Management Conference

University of Houston, Tex.

Papers will be presented on such topics as research and development on organic and mineral industrial wastes characterizations; collection, handling, processing, conversion, or utilization; byproduct production processes from wastes; secondary material processes; economics; and resource recovery techniques from urban and industrial solid wastes. For further information: H. Nugent Myrick, Cullen College of Engineering, University of Houston, 3801 Cullen Blvd., Houston, Tex. 77004

March 30-April 1 California Air Resources Board, University of California, and California State Department of Public Health

11th Conference on Methods in Air Pollution and Industrial Hygiene Studies

University of California, Berkeley Primarily intended for individuals knowledgeable in the basic aspects of air pollution measurement, the conference aims to increase basic understanding, heighten awareness of the scope and limitations of different methods and instruments, and develop knowledge of instruments' potential use in monitoring programs. Atmospheric contaminants for which new air quality standards have been set will be focal point for technical sessions and workshops.

March 31-April 3 International Association for Great Lakes Research

13th Conference on Great Lakes Research

Statler Hotel, Buffalo, N.Y.

The program consists of five half day sessions of technical papers on Great Lakes of the World. Purpose of the meeting is the promotion of all aspects of research and dissemination of research information on the Great Lakes and their basins.

April 1–3 Houston Junior Chamber of Commerce

3rd Annual National Pollution Control Conference and Exposition

Fairmont Hotel, San Francisco

Theme of this year's meeting is The Environment 1980: Management, Cost, Technology. The 3 day conference will explore programming, planning, and budgeting necessary for government and industry to achieve environmental goals of 1980. Air pollution, water pollution, solid waste problems, noise, and thermal pollution will be considered and discussed at panel sessions and technical meetings.

(Continued on page 168)

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MEETING GUIDE (continued)

Courses

March 17–19

Technical Forum Associates, Inc. Short Course on Water Pollution Control

Boston, Mass.

Recent research activities in water pollution control—sources, types, and effects of water pollutants—will be explored, in addition to basic biological and chemical aspects of water pollution, changes in ecological patterns, and principles of pollution control. Waste water treatment, waste water reuse, thermal pollution, and industrial wastes also will be discussed.

April 16-18

Institute of Environment Sciences Short Course on Thermal Pollution

Sheraton-Plaza Hotel, Boston, Mass.

Purpose of the 3 day seminar is to acquaint attendees with the problem of thermal pollution and its impact, and to discuss methods of controlling the problem for preservation of our natural resources. Lectures and discussion will cover such topics as the nature of the problem; analysis of the problem; potential solution. Enrollment limited. For information: Institute of Environmental Sciences, 940 E. Northwest Highway, Mt. Prospect, Ill. 60056

Call for papers

March 16 deadline Instrument Society of America

25th Annual Conference

Civic Center, Philadelphia, Pa. Papers are invited covering all major sectors of instrumentation and automatic control, including pollution control, marine sciences, and pulp and paper. Forms may be obtained from: Sal F. Luna, Instrument Society of America, 530 William Penn Pl., Pittsburgh, Pa. 15219

Special notice

February 15 deadline University of Arizona

Summer Institute in Systems Hydrology The institute—for undergraduate college teachers of hydrology, engineering, agriculture, geology, or soil science will be conducted June 15–August 7. Courses to be presented include operations research in water resources systems, and computer aided experimentation in probabilistic and deterministic modeling of hydrologic and water resource systems. Applications may be obtained from Chester C. Kisiel, Hydrology and Water Resources Office, University of Arizona, Tucson 85721

University of Illinois, Urbana

U.S. Public Health Service Traineeships in Solid Wastes Management

An interdepartmental effort, this program leads to an M.S. degree in sanitary engineering, food science, or agricultural engineering, while specializing in solid waste management. Stipend for the one calendar year program is \$2400 plus \$500 for each dependent. Applicants should contact: R. S. Engelbrecht, 3239 E. Civil Engineering Bldg., University of Illinois, Urbana 61801

professional consulting services directory



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