

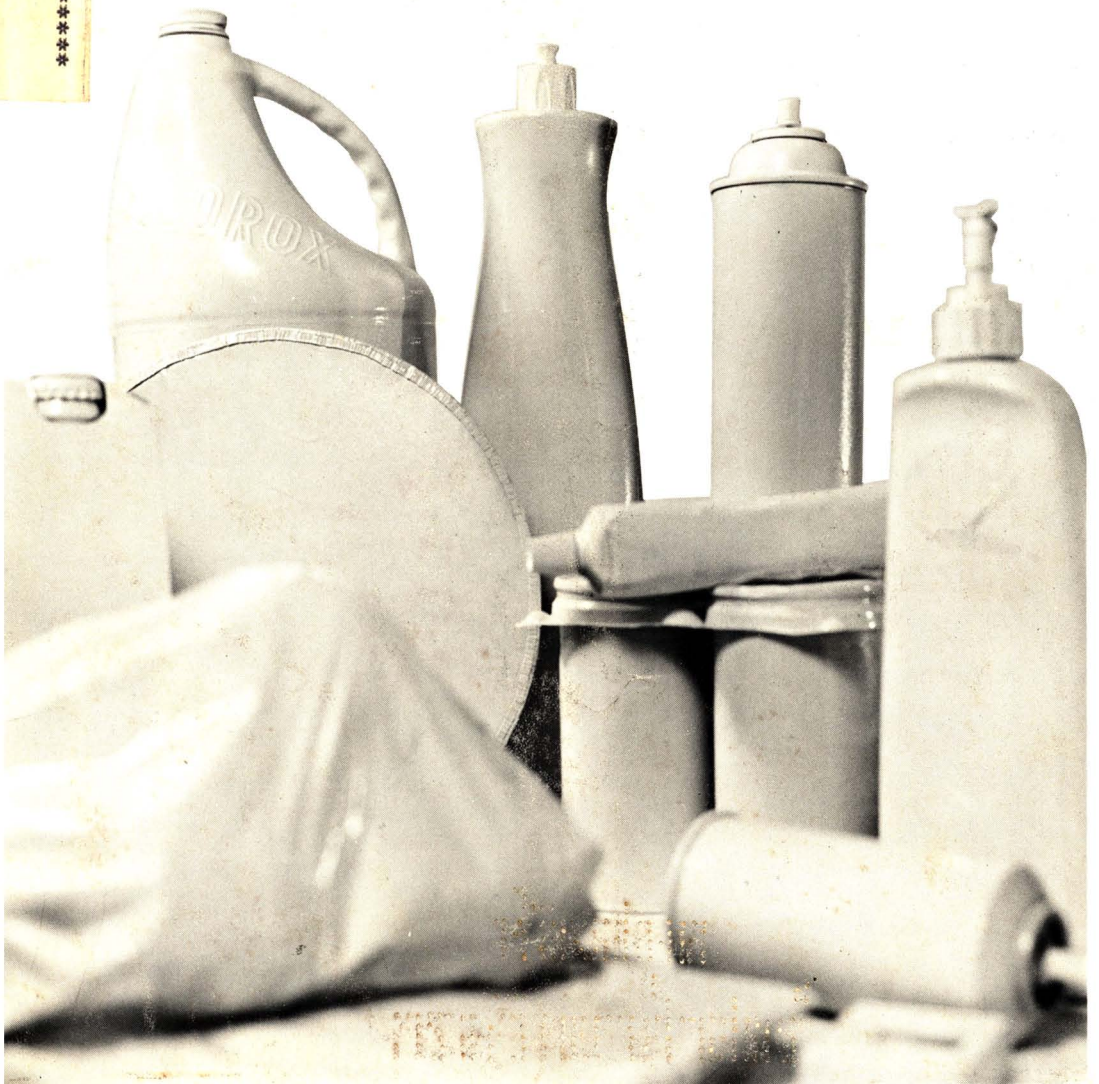
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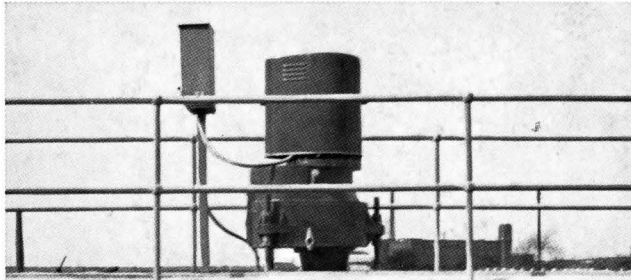
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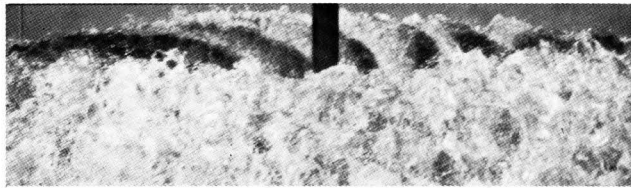
*Houston's
Pollution Control Show 343*

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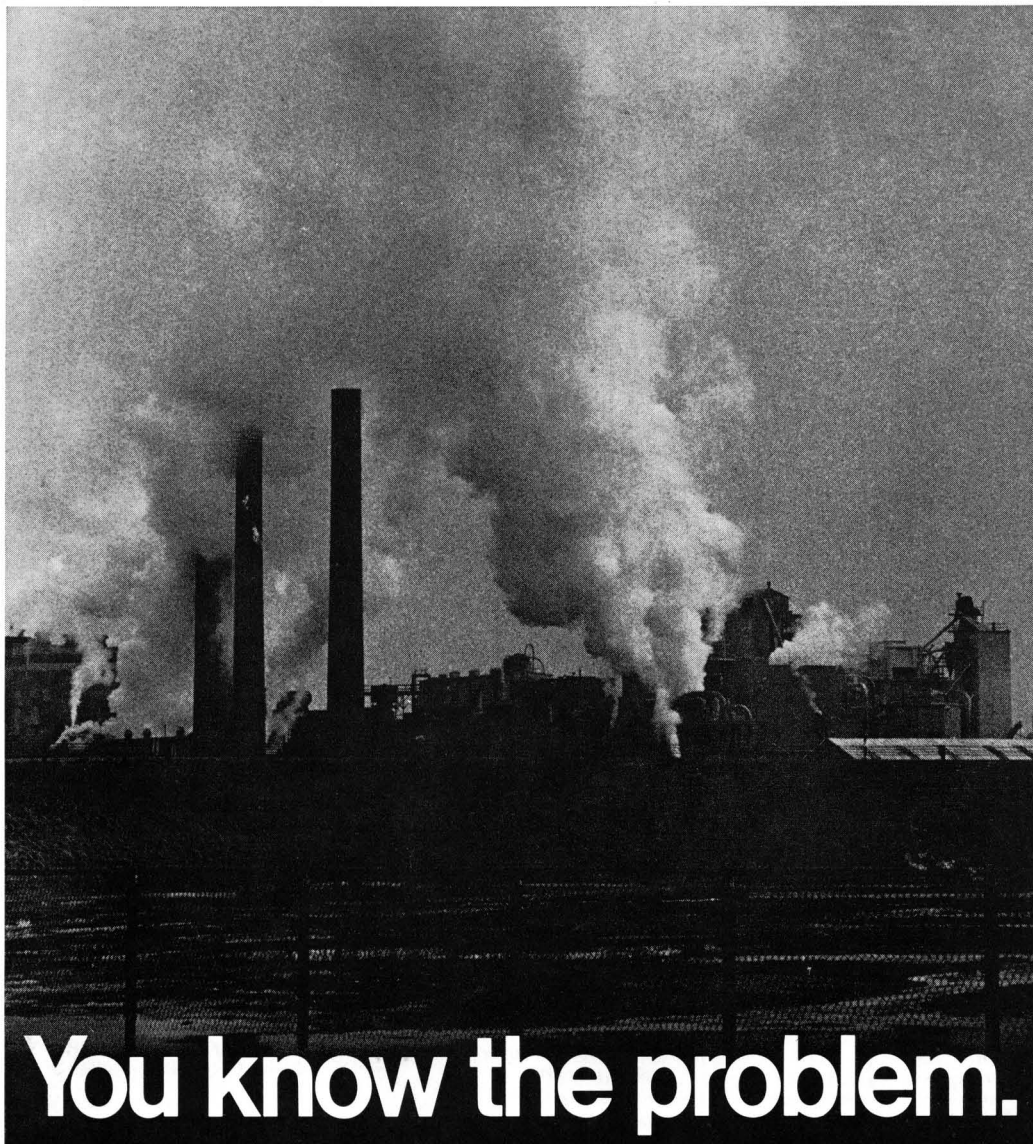
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Volume 3, Number 4

April 1969

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Published monthly by the American Chemical Society, from 20th and Northampton Sts., Easton, Pa. 18042 and additional mailing offices. Executive Offices, Editorial Headquarters, and Subscription Service Department, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Advertising Office: 430 Park Ave., New York, N.Y. 10022. Second class postage paid at Easton, Pa. 18042 and additional mailing offices.

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ESTHAG

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contents

Current Research

- Variation in the composition of brine from the Sylvania formation near Midland, Michigan 367

G. C. Egleson and C. W. Querio

The geochemistry of brines are further understood by recent analyses of samples from 51 wells in Dow Chemical Co.'s brine field. The bulk of the total dissolved solids comprises the ions—Ca, Mg, Na, Sr, Cl, and Br. Dolomitization is probably the most important mechanism in determining the Ca, Mg, and Sr content of the brine. Also, the relative amounts of Li, I, and NH_3 are too high to have been derived from sea water evaporation.

- Components of wood pulp bleach effluents 371

J. W. Collins, A. A. Webb, H. P. Didwania, and B. F. Lueck

The sources of BOD and color, two of the more undesirable properties of bleaching wastes, have been tracked down by further analysis of concentrated wood pulp bleach effluents. The concentrated effluents contain highly colored organics and solids with high ash content. Much of the color in kraft chlorination effluents are of carbohydrate origin. The stable end products of sulfite chlorination effluents are organics with catechol groups.

- Effects of various fluoride sources on citrus growth and fruit production 378

R. F. Brewer, F. H. Sutherland, and F. B. Guillemet

Spraying of citrus trees with dilute aqueous solutions of sodium fluoride or hydrofluoric acid (0.00125-0.0025 N) produces toxicity symptoms similar to those of citrus plants which have been exposed to low concentrations of gaseous hydrofluoric acid. In both cases, the citrus trees show gradual fluoride accumulations in citrus foliage. The reduction in top growth of citrus trees—in this case Lisbon lemon trees on *Macrophylla* rootstocks—was closely correlated with reduced photosynthetic area resulting from smaller leaves and increased leaf fall.

- Comparative size measurements of monodisperse liquid aerosols by electrical and optical methods 381

B. Y. H. Liu, V. A. Marple, and H. Yazdani

A new electrical method is available for sizing monodisperse aerosols in the 0.03-10 micron diameter range. In this method, the liquid or solid aerosol is charged at atmospheric pressure, and then the ratio of electric mobility of the charged aerosol is measured at two lower pressures. Then, the particle size is calculated by Millikin's equation. The electrical method compares favorably with other methods such as that using the Royco PC 2000 single particle optical counter. A major limitation of the new method is that the aerosol must not evaporate in the vacuum environment of the system.

- Measurement of mass flow and density of aerosols in transport 386

S. L. Soo, J. J. Stukel, and J. M. Hughes

Two extremely important parameters which must be measured accurately before any aerosol sampling probe can be fabricated are local mass flow and density of aerosol particles. Two probes were assembled: the first uses a filtration method for measuring the particle flux, and the second probe—based on the attenuation of light passing through a suspension—involves fiber optic measurement of the density of particles. The two probes can be combined into one probe to measure these important parameters.

Communications

- Concentration of dilute aqueous phenol solutions utilizing methylsulfinylmethane (DMSO) 393

J. S. Tranquillo and G. F. Lee

The loss of volatile compounds from dilute aqueous solutions now can be minimized by adding an organic solvent to the dilute solution and distilling the mixture under reduced pressure. Using this technique and DMSO, for example, phenol recoveries of 64% can be achieved, whereas only 13% recoveries were achieved by proceeding with vacuum distillation alone. Another organic solvent, N-methyl-2-pyrrolidone, accomplishes similar results.

- Colorimetric determination of carbonyl compounds in automotive exhaust as 2,4-dinitrophenylhydrazones 397

L. J. Papa

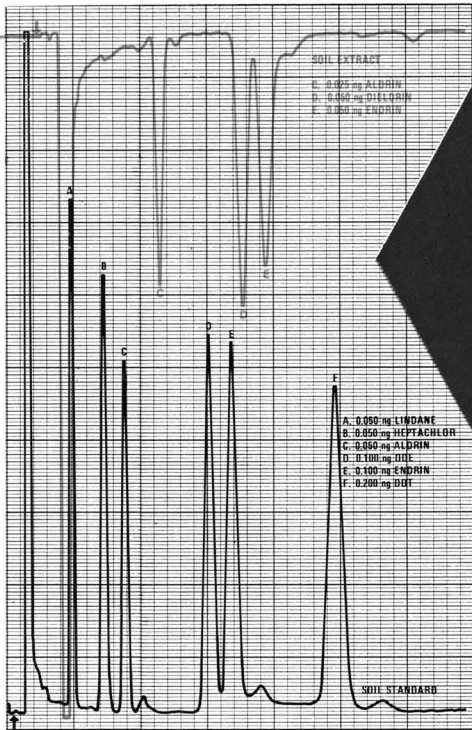
The presence of different carbonyl compounds, such as those present in automobile exhaust, can be shown by a colorimetric technique, based on 2,4-dinitrophenylhydrazones of the carbonyl compounds. The minimum detectable quantity is 0.5×10^{-8} moles. The colorimetric procedure is rapid and saves considerable time over competitive gravimetric procedures.

Correction

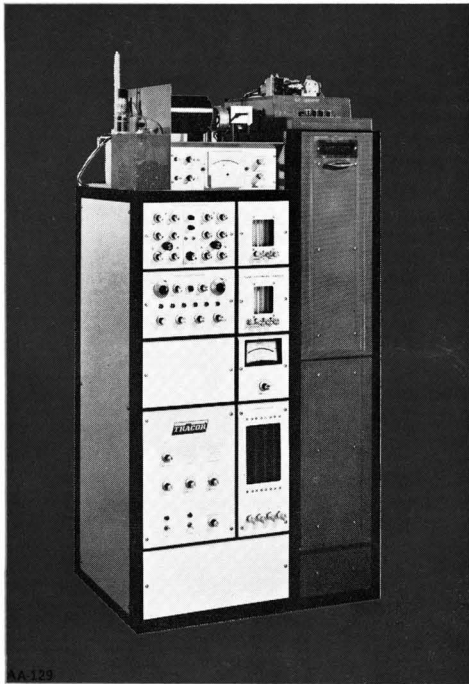
- Determination of sulfate and phosphate in water by ion exchange-titrimetric method 396

G. W. Dollman

This article appeared originally in ES&T, November 1968, page 1027.



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Environmental awareness demands divers inputs

The various disciplines and activities involved in environmental understanding remain discreet but draw strength from each other

ENVIRONMENTAL SCIENCE & TECHNOLOGY, for several years has been practicing and preaching the concept that the best approach to solving many environmental problems is to consider the environment as a whole, i.e., a single integrated system in which the sequence of evolution is a cycle—technology, research, science, development, technology. Where technology employed in solving problems, large and small, reveals new needs for knowledge and lays out the course for research. Where research shows new opportunity, new direction, new relationships, and grows at various speeds into a body of science that, through trial and development, leads to new technology that can be applied to the solution of problems. The old or present problems may not be fully solved, and new ones may crop up. But in any event, the cycle continues.

There are other cycles involved, too; for example, the wheel of various disciplines involved in environmental understanding, control, and management, that moves in a circle from engineering through the geological, soil, marine, atmospheric, medical, and social sciences to biology, ecology, and even economics and politics. Each is a spoke in a huge wheel that helps move all civilized activities forward. The strength of the wheel rests on the mutual support and strength of each of the spokes which, only together with the continuity of a compiling rim, can complete the wheel.

There are cycles within cycles, wheels within wheels. And to achieve significance each one must be treated alone, yet in concert with the others. It is as if each system were but a single ingredient in

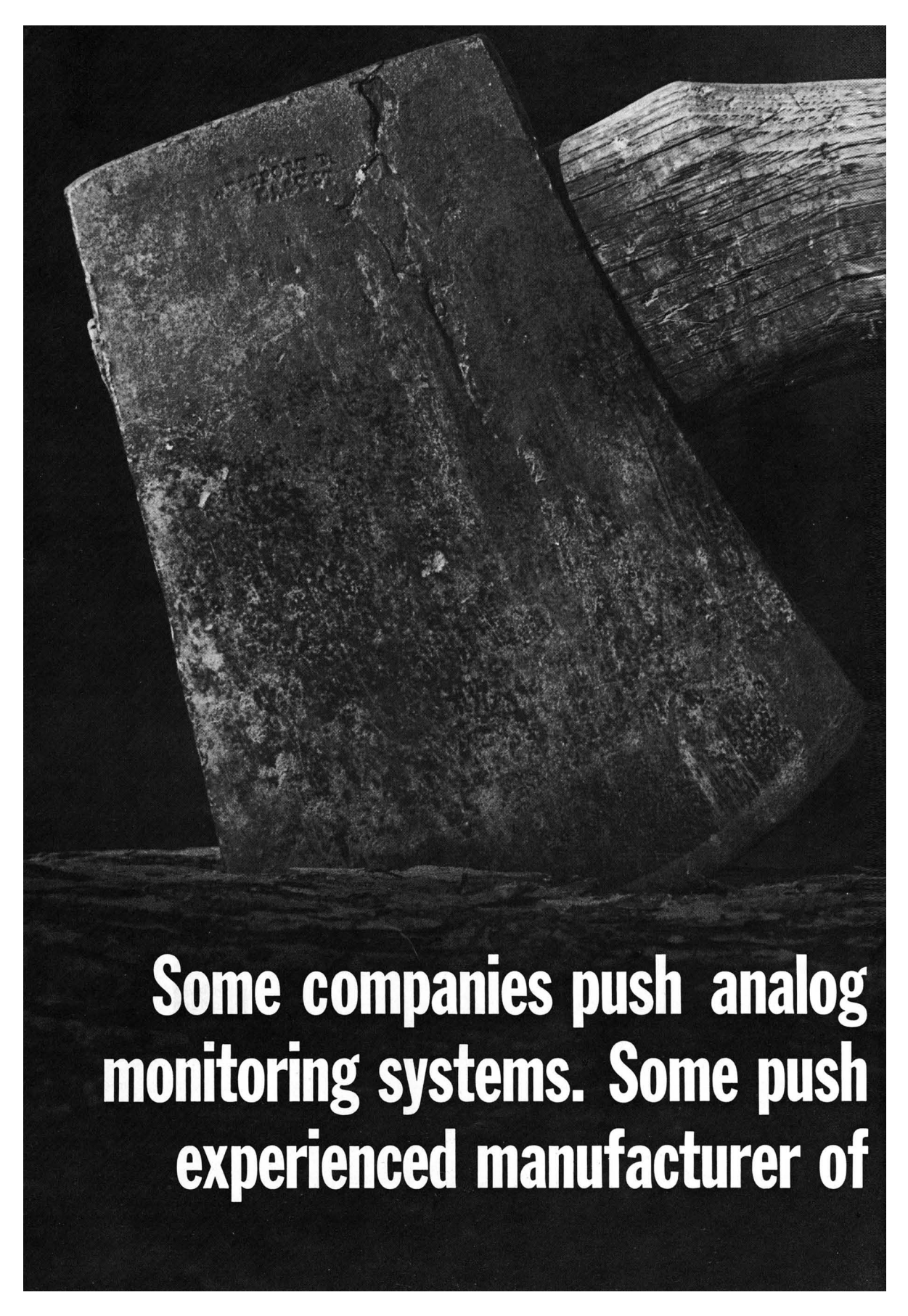
a huge pot of stew. Each ingredient maintains its discreetness while contributing to the special overall effect of combination.

What ES&T has tried to do is to provide the serving dish for the agglomeration of many critical, individual, and discreet ingredients to be presented to as many as care to feed at the table of full environmental awareness. Not all participants need partake of the entire offering; one need only take that portion or combination which satisfies or fulfills.

The need for a single forum in which environmental matters may be discussed alone and with other relevant items seems obvious, and it is certainly demonstrated by the reception accorded ES&T in its 28 months of existence. Likewise, the value of the whole or integrated approach is evident in another success—that achieved by the Houston Junior Chamber of Commerce's National Pollution Control Conference and Exposition. First held a year ago, the exposition is having its second run this year (see page 343) before what promises to be a much larger audience than last year's 2500 attendees.

We wish the exposition's sponsors well in their program for, in many ways, they have embraced within their own context the concept of an integrated environment responsive to each of its many parts, where pressures on any one part lead to bulges somewhere in the overall system, and where the interrelated nature of the individual parts permits each unit to draw strength from the others while contributing to the common success.

William J. Josephs

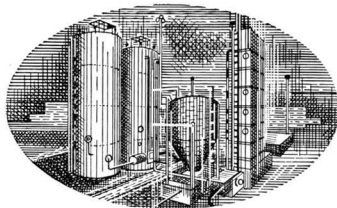


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environmental currents

Water management program to curb estuary pollution

With a \$40,400 planning grant from the Federal Water Pollution Control Administration (FWPCA), Maryland's Department of Water Resources plans to develop a comprehensive management program for the entire Patuxent River Basin. "The planning program at this time represents more of a preventive effort than a corrective one," FWPCA Commissioner Joe G. Moore noted. "The estuary's water quality has not yet been significantly degraded to the point where it has interfered with sport and commercial fishing or recreation activities which produce an estimated annual income for the area of \$6.5 million." Maryland's final study is due before June 30, 1970.

All 50 states are brought in on Air Quality Act

Last month, the National Air Pollution Control Administration (NAPCA) announced a second list of 25 proposed air quality control regions. These 25 regions plus the earlier list of 32 will involve air quality control regions in all 50 states, covering more than 70% of the U.S. urban population. Whereas the original list of 32 covered 60% of the urban population, it involved only 28 states. Now, with the second list of 25, bringing the total to 57, all 50 states will become involved with the national air quality control program specified by the Air Quality Act of 1967 (ES&T, November 1967, page 884).

NAPCA also issued guidelines last month to help state officials interpret and establish air quality standards based on earlier criteria and control technology documents (ES&T, February 1969, page 99). The implementation schedules in the standards will probably not specify compliance before the next 5-7 years, according to a NAPCA spokesman.

Air pollution control equipment for gray iron foundries

Continuing its industrial air pollution surveys, the Business Defense and Supply Agency (BDSA) (Department of Commerce) surveyed 1376 gray iron foundry melting furnaces and found that 1232 (90%) operate cupolas for air pollution control in the foundry. The survey notes that cupola foundries are found in every region of the U.S., but four fifths of them are located east of the Mississippi River. Only 180 of the cupolas, or one out of every seven, are equipped with air pollution control systems including, for example, wet cap control devices, fabric filters, and scrubbers. Earlier, BDSA, which has other surveys in preparation, surveyed the industrial gas cleaning equipment industry (ES&T, October 1968, page 728).

Reverse osmosis process uses new membrane

A new membrane of cellulose acetate butyrate has been announced jointly by Universal Water Corp. (Del Mar, Calif.) and the Office of Saline Water (Department of the Interior) for the conversion of saline and brackish waters using the reverse osmosis process. Ease of fabrication, excellent strength and greater resistance to chemical attack are several advantages of this membrane, according to Serop Manjikian, vice president of Universal Water Corp. "The development should enhance substantially the posture of reverse osmosis as an economically feasible process for seawater conversion," says Manjikian.



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- L&N Thermocouple Assemblies, to detect gas temperature in the stack.

Speedomax[®] recorders, used with such detectors, provide permanent, day-to-day records of the factors of the mass-flow equation. A simple analog computer can provide a direct, on-the-spot analysis of your plant's SO₂ characteristics, in terms of pounds of sulphur per hour, for example.

Equipment is also available for the measurement of other gases significant to air pollution, and of other factors related to the problem; for example, the L&N Smoke Density Recorder and its associated Smoke Sampler can give you a continuous

record of smoke density in the stack—and a prompt warning if a pre-set limit is accidentally exceeded.

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environmental currents

Chemical industry's investment in pollution abatement

(All figures in millions of dollars)

	Air 1967	Water 1967	Total 1967
Capital expenditures	\$287.9	\$385.3	\$673.2
Research expenditures	9.1	9.3	18.4
Annual operating expense	41.7	59.6	101.3
Expenditures (Canadian companies)	9.3	11.2	20.5

Source: Manufacturing Chemists Association

Manufacturing Chemists Association updates pollution survey

MCA's survey of 129 U.S. and 12 Canadian major chemical companies show that air and water pollution abatement continues to be a major consideration in the industry's cost of doing business, and that the chemical manufacturing industry has made substantial progress toward abating pollution. "In 1962, five-year projections for capital investments in this field were only \$119 million. In 1967, the same projections had risen to \$405 million, and we regard this as very conservative," says Gen. George H. Decker, MCA president. Entitled "Toward A Clean Environment," the 1967 survey, which also covers solid waste disposal, notes the following: • Facility investments of \$673 million—\$287.9 million for air and \$385.3 million for water—through 1966. • Operations and maintenance of \$100 million annually through 1967. • Projected commitments for facilities alone of more than \$400 million through 1971. • Research expenditures for abatement of air pollution tripled, and for abatement of water pollution doubled 1962 figures. • Of the 9000 separate chemical manufacturing processes surveyed, 80% had air pollution control devices installed. The survey also noted that, in 1967, less than 3% of the water withdrawn by this portion of the chemical industry was discharged in an unsatisfactory condition.

Water use in U.S. (billions of gallons per day)

1950	200
1955	240
1960	270
1965	310

U.S. water use increased 15% in the past five years

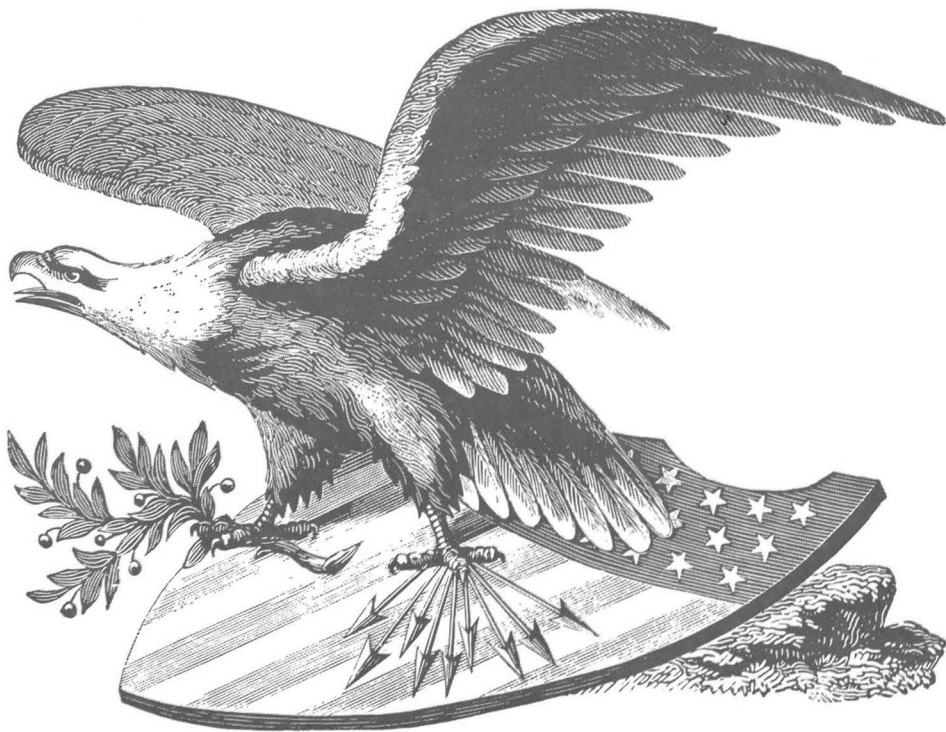
The U.S. used an average of 310 billion gallons of water per day—equivalent to 1600 gallons per day per person—according to a 1965 study by the Geological Survey. The 310 billion gallons is a 15% increase in water use since 1960. The survey notes that hydroelectric power withdrew and returned seven and one half times this amount (2.3 trillion gallons per day) after developing hydroelectric power. Of the 310 billion gallons for 1965, 78 b.g.d. were lost due to evaporation, and 233 b.g.d. (75%) were returned to water supplies in an unclean condition.

Natural gas eases New York's air pollution . . .

Since 1966, more than 22,200 buildings in New York City have converted their heating plants to natural gas, according to Austin N. Heller, the city's Commissioner of Air Resources. In the past two years, natural gas was chosen for more than 11,000 new buildings for heating purposes. The use of natural gas has resulted in a reduction of 2100 tons of particulates and 5500 tons of sulfur dioxide which would have otherwise entered New York's air, according to Heller's estimate. Furthermore, all new buildings require a dual heating system—one for conventional fuel and the other for temperature controlled gas, a system which shifts boilers from oil to gas when the outside air reaches a pre-set temperature.

. . . and legislation helps New Jersey's burden

New Jersey's air pollution control code was recently upheld in a decision by the Appellate Division of the State Superior Court. One chapter of the code regulates permissible levels of sulfur in coal, another regulates permissible levels of sulfur in oil. The oil regulation became effective in May 1968 and has resulted in a 40% reduction of SO₂ emissions in the state, according to Richard J. Sullivan, Director of the Division of Clean Air and Water. With the recent court decision, the coal regulation holds further promise of clean air in New Jersey.



Is anyone screaming at you?

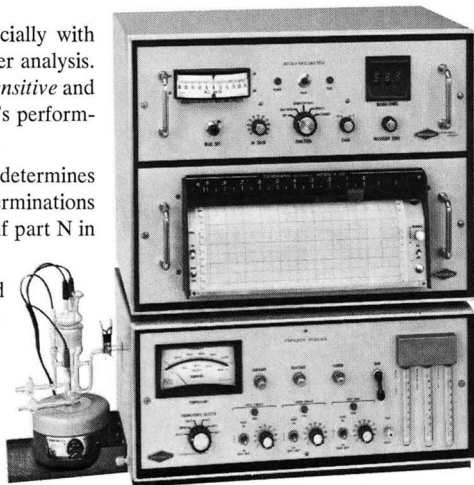
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environmental currents

Ohio areas plan city water systems for year 2010 . . .

With a \$201,333 grant from the Department of Housing and Urban Development (HUD), Cleveland and 60 neighboring urban areas are designing a water system to meet their needs till year 2010. Charles M. Haar, HUD's assistant secretary for metropolitan development, says, "The opportunity to apply the technology provided by the systems engineering approach has exciting implications for programming, planning, and managing public service facilities and systems." The project, under HUD's newly established Urban System Engineering Program, will consider funding, land acquisition, land utilization, design, tax structure, and social influences.

. . . while Nebraska areas make similar moves

Similarly, Nebraska plans a comprehensive system of water and waste disposal services in 74 rural counties, with a grant of \$317,080 from the Department of Agriculture. "The grant will assure statewide planning for modern water and sewer systems wherever they remain to be developed in the towns and countryside of rural Nebraska," says Clifford M. Hardin, Agriculture's Secretary.

National Water Commission plans ahead five years

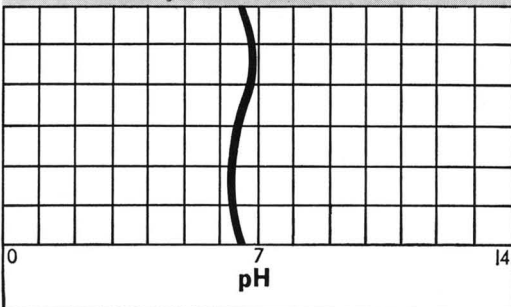
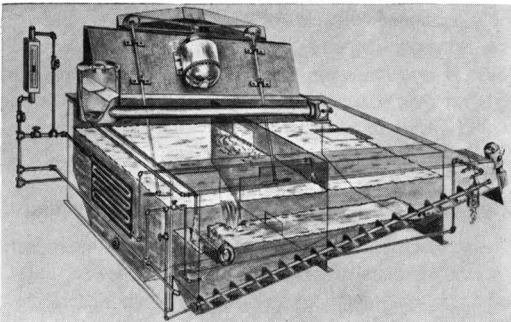
Charles F. Luce, chairman of the seven-man National Water Commission (NWC) (ES&T, November 1968, page 991) told attendees at the Water Supply and Wastewater Seminar (Washington, D.C.) last month that the commission is an advisory commission of citizens from different walks of life. NWC has already named a panel of consultants and plans to release a program of studies soon. With a \$5 million authorization from Congress for the next five years of operation, NWC will solicit comments from its consultants, federal agencies, and, then, in late summer, conduct a series of public hearings around the U.S. to select the meaningful areas of study that NWC will conduct in the remaining 4½ years of its planned five year life. One priority item for study is interbasin transfer of water, among others, according to Luce. The commission has one vacancy at present—created when Russell E. Train left to become Undersecretary of Interior. NWC's executive director is Theodore M. Schad, formerly with the Library of Congress.

Electric utilities must focus attention on air and water pollution

In the next 20 years, electric utilities will have to quadruple their electrical capacity in 11 northeastern states if the region's electric power demands are to be met, according to a recent report of the Federal Power Commission's Northeast Regional Advisory Committee. "Attention must be focused on such considerations as the siting of generating plants, transmission line routing, and the problems of air and water pollution," says Lee C. White, chairman of the advisory committee. These findings will be integrated into a revision of the national survey, which is planned for release by May 1970.

This 11-state region includes the New England states, New York, New Jersey, Pennsylvania, Delaware, parts of Maryland and Virginia, and the District of Columbia. The report concludes that nuclear power will account for 58% of the area's generating capacity by 1990 and predicts that the remainder will consist of 3% conventional hydroelectric, 7% pumped storage, 8% diesel or gas turbine, and 24% fossil-fuel thermal.

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environmental currents

Need for an environmental committee resolved

Whether to establish a select committee on technology and the human environment or not was the subject of recent hearings by the Senate Committee on Government Operations. Many senators and the witnesses recognize the need for such a committee but are not resolved on a workable plan for its establishment. Herbert A. Simon of Carnegie-Mellon University (Pittsburgh, Pa.) testified, "early warning systems for technological and social change are only useful if they are priority-setting systems." Harvey Brooks, of Harvard University, said that he would prefer to see a joint committee of both houses rather than a committee of the Senate alone.

According to S. Res. 78, which is Sen. Edmund S. Muskie's (D-Me.) proposal for the select committee, the select committee would be a study group where scientists and legislators can gather to discuss the gravity of environmental problems to be faced and what science and technology can do to solve these problems in cooperation with the federal, state, and local governments. This committee would not have any jurisdiction over legislation or powers of legislative oversight. Rather, its purpose would be to provide a source of information and analysis not now available in the Senate. The select committee would comprise three members from each of the following senate committees—agriculture, banking and currency, commerce, government operations, interior and insular affairs, labor and public welfare, and public works. The committee would expire on Jan. 31, 1972; but before termination, the group would render a final report, which would provide a base for the development of national goals for the environmental betterment of man, not only in the U.S., but throughout the world.

BOMEX plans are firmed

Beginning next month, the Barbados Oceanographic Meteorological Experiment (BOMEX), the first field experiment in the Global Atmospheric Research Program (ES&T, May 1968, page 321) aims to investigate the mechanism of sea-air interaction to better understand the energy transfer steps in a large tropical ocean area, according to Joachim P. Kuettner, director of BOMEX. Ultimately, the understanding may lead to a world weather watch with prediction capabilities. A main objective of this scientific investigation is to find how the primary storage of the sun's heat energy resides in the tropical oceans. BOMEX will study the first two of the following three energy transfer steps which account for the transfer of 10 trillion tons of water from the tropical ocean to the atmosphere; in term of steady state operation, the transfer requires 10 days. The steps are: • Evaporation of water from the ocean to a boundary layer about 5000 feet high. • Transfer of the energy from the boundary layer to the troposphere. • Transfer of the energy from tropical to other latitudes by the troposphere. The May 1-July 28 experiment will cost \$18.2 million, according to Charles E. White, of the Environmental Science and Service Administration, U.S. agency for BOMEX.

Air pollution threatens dried food processors

Ozone from automobile exhaust causes off flavors in powdered milk. Confirming earlier suspicions and preliminary data (ES&T, July 1968, page 487), Agricultural Research Service scientists now conclude that polluted air containing automobile exhaust fumes, and specifically ozone, was the culprit causing off flavors in dried milk processed at its laboratory (Washington, D.C.) last summer.

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Waste water treatment costs for organics, 1969-73

Engineering consultants assess five-year cost estimate for organic chemicals industry to achieve levels of water pollution abatement

How the organic chemicals industry treats its waste waters is the subject of a recently released technoeconomic report. Representing approximately 60% of the entire chemical industry, organic chemicals was singled out by the Federal Water Pollution Control Administration (FWPCA) for an extensive study to provide estimates of the costs of treatment needed to bring the organic chemicals industry's waste waters up to today's water quality standards (ES&T, February 1969, page 120). The estimates also can be used to arrive at some cost assessments for removal of specific pollutants at six different quality levels.

During the period 1969-73, the organic chemicals industry will require \$234-331 million for the construction and operation of waste treatment facilities to treat their effluents, according to the report. Also, during the five-year period, the industry's average large plant, which exists only in a statistical sense, will treat 3.2 million gallons of waste waters each day.

The organic chemicals industry takes in a total of 1.8 trillion gallons of water per year, and discharges close to 2.4% (45 billion gallons) of its industrial waste waters to municipal sewers, according to Census of Manufacturers data (1963).

The cost estimates in this year's addition to the basic "Cost of Clean Water" issued last year (ES&T, March 1968, page 257) were developed under contract by four engineering consulting firms—Cyrus Wm. Rice and Co. (Pittsburgh, Pa.), which served as coordinator for three other firms; W. Wesley Eckenfelder, Jr., and Assoc.

(Austin, Tex.); Roy F. Weston, Inc. (West Chester, Pa.); and Resource Engineering Associates, Inc. (Stamford, Conn.). Cost data on waste water treatment by the organic chemicals industry are based on information developed by the four U.S. companies that studied 53 operating organic chemicals plants. These costs will have to be incurred by the organic chemicals industry if current water quality standards are to be met by 1973.

Cost rationale

Of the 245 large organic chemicals plants in the U.S., only 53 (nearly 22%) of the plants, distributed throughout the U.S., were included in the survey. The industry's plants are located in more than 29 states, but those surveyed are in 13 states—Delaware, Illinois, Louisiana, Massachusetts, Michigan, Minnesota, New Jersey, Ohio, Pennsylvania, Tennessee, Texas, Virginia, and West Virginia.

The cost estimates in the study have been developed for construction and operation of waste treatment plants for the organic chemicals industry as a whole. These estimates do not include costs for process changes, disruption of plant operations, sewer segregation, monitoring and reporting of waste treatment efficiencies, and the like. In the survey group's opinion, these additional costs may add 40% to the basic costs.

Although each company did not furnish complete data, all information—obtained by use of a data form—was used to the maximum. To supplement the data obtained from the form, the survey group based cost assessments on material collected from confidential reports, private communications, and pertinent literature.

Developed specifically for this study of the organics chemicals industry, the industrial waste treatment practices data form is useful in gathering information which can be translated into engineering costs, according to the study group. The data form also can be used as generalized methodology for similarly continuing cost estimates for other major water-using industries. Although the form is useful in establishing and projecting costs for one industry or for groups of industries, its use is limited since it cannot be used for an individual plant.

Basically an apertured card which can be machine sorted, the data form can—and probably will—be used for other major water-using industries to provide an insight on how industries can handle their water pollution abatement costs.

For the organic chemicals industry, waste water generation may range from 100 gallons to as much as 100,000 gallons of waste water per ton of product. On the basis of 1963 production—71 billion pounds of

Costs for treatment of organic chemicals industry's waste waters, 1969-73

Level of treatment	Removal of critical pollutants			Capital costs (average plant of 3.2 m.g.d.)	Operating cost per year (3.2 m.g.d.)	Operating cost (dollars/yr./1000 g.p.d.)
	BOD ^a	COD ^b	SS ^c			
1	Removal of gross pollutants			\$ 470,400	\$ 22,400	\$ 7
2	10%	10%	65%	563,200	27,200	8.5
3	83	13	71	800,000	41,600	13
4	98	30	89	2,240,000	336,000	105
5	99	33	99	2,403,000	384,000	120
6	100	100	100	5,273,600	1,120,000	350

^a Biological oxygen demand

^b Chemical oxygen demand

^c Suspended solids

Source: Cyrus Wm. Rice and Co.

goods—the organic chemicals industry discharged nearly 1400 gallons of waste water per ton of product.

The principal contaminants of the waste process water are biological oxygen demand (BOD), chemical oxygen demand (COD), oil, suspended solids, acidity, heavy metals, color, taste- and odor-producing compounds, residual organic products, and byproducts. Throughout the industry, biological treatment is used widely to treat waste waters because the relatively high BOD values of these waters can quite easily be reduced by secondary treatment systems such as the familiar activated sludge process.

The industry has found that in-plant, separate treatment of its waste waters generally has certain economic advantages. These methods include both physical and chemical treatments. Coarse suspended matter, floating oils, and scums often are removed by sedimentation or filtration. Filtration also is used for certain reusable waste water and pretreatment for deep well injection. Chemical treatment is used mainly as pretreatment prior to sedimentation, filtration, or biological treatment.

In the plants surveyed, the level of engineering technology was judged to be average or advanced, and the median age of the plants was 18 years, according to the report. The relatively short lives of chemical processes and equipment explains the apparent anomaly in plant age and the state of the technology. The replacement equipment and new processes, which often are installed in even the older plants, tend to be of the latest design.

Scope of study

Although not readily definable in terms of the Standard Industrial Classification (SIC) numbers, the organic chemicals industry lists its important products as:

- Cyclic and acyclic organic chemicals and chemical products.
- Plasticizers.
- Flavor and perfume materials.
- Rubber-processing chemicals.
- Pesticides.
- Other synthetic chemicals.

Ordinarily, the production of monomers is included in the organic chemicals industry's products, but the polymers produced from these monomers are not included. Approximately 75% of the industry's total shipment of products in 1967 was classified as

miscellaneous acyclic chemicals, generally designated as petrochemicals.

Accounting for nearly three fourths of the total shipments by the organic chemicals industry, petrochemicals are characterized by complicated interrelationships between processes before their products have consumer identity. But a limited number of processes account for a significant portion of this industry. So, an important insight can be gained into an evaluation of this industry's waste water treatment problems by understanding petrochemicals' basic processes.

The sources of contaminated waste waters from petrochemical operations are threefold:

- Wastes containing a principal raw material or product arising from stripping a product from a solution.
- Production of byproducts during a specific reaction.
- Spills, slab washdowns, and vessel cleanouts. (From a process point of view, these are uncontrollable.)

Profiles of products

Industrial profiles for 34 products of the organic chemicals industry (in-

cluding some 30 petrochemicals) are included in the report. The products covered range from acetaldehyde, acetic acid, and acetic anhydride to urea and xylenes. The report summarizes and tabulates the waste loads associated with the manufacture of each product. The survey group has anticipated changes in processes for some products and has offered a discussion of the waste reduction which would result with each change of process. The plants surveyed provided data on such chemicals as acetone, ammonia, benzene, butadiene, butanol, cumene, cyclohexane, ethanol, ethylbenzene and styrene, ethylene, ethylene oxide, isopropanol, phenol, polyethylene propylene, toluene, urea, and xylenes.

From basic chemical raw materials, the organic chemicals industry manufactures a variety of intermediates that finally are converted to plastics, elastomers, resins, solvents, and other materials. The industry can be segregated into six major product groupings—primary petrochemicals, primary intermediates, secondary intermediates, primary polymers, dyes and pigments, and miscellaneous organics.

Correlation of cost parameters

The consulting firms have singled out six parameters which can be interrelated to provide some insight into the economics of treating waste waters from the organic chemicals industry. With these six items and data from 37 surveyed plants, the following relationships were found to hold:

Item

1	Capital cost of treatment facilities	(dollars/1000 g.p.d.)
2	Operating costs of treatment facilities	(dollars/yr./g.p.d.)
3	Efficiency of critical pollution removal	(percent)
4	Capital cost of treatment facilities	(dollars/ton of annual production)
5	Operating costs of treatment facilities	(dollars/yr./ton of annual production)
6	Volume of waste water	(g.p.d./ton of annual production)

Capital costs of waste treatment facilities in a plant (a function of waste water volume):

$$\log P_4 = 1.1145 + 1.1559 \log P_6$$

Operating costs of treatment facilities in a plant

$$\log P_5 = 1.8977 + 0.9293 \log P_4$$

Unit operating costs

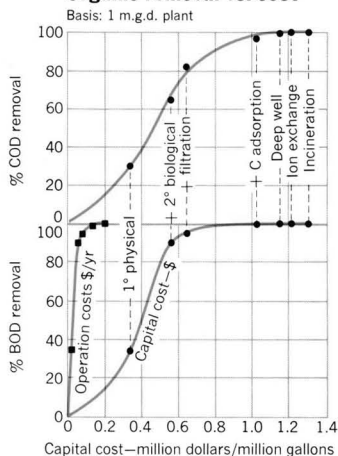
$$P_2 = -76.7181 + 0.2611 P_1$$

Overall, the following mathematical relationship holds for an evaluation of this industry's costs for waste water treatment. This relationship is limited for flow capacities ranging from 30,000 g.p.d. to 15 million g.p.d. and BOD values ranging from 150 mg./l. to 6000 mg./l.

$$C = KQ^m S_0^n$$

C = Capital cost (thousands of dollars—1968 replacement value)
K, m, and n = Constants
Q = Flow (m.g.d.)
S₀ = BOD of waste water (mg./l.)

Organic removal vs. cost



Summary of bases for unit cost functions

Pretreatment or primary treatment

Equalization—Cost vs. volume (gal.)

Neutralization—Cost vs. flow rate (m.g.d.)

Oil separation—Cost/m.g.d. vs. flow rate (m.g.d.)

Sedimentation—Cost vs. surface area (sq. ft.)

Biological treatment

Lagoons—Cost vs. surface area (acre)

Aerated lagoons—Cost vs. volume (m.g.)

Activated sludge—Cost vs. volume (m.g.)

Aeration basin—Cost vs. volume (m.g.)

Final clarifier—Cost vs. surface area (sq. ft.)

Tertiary treatment

Filtration—Cost vs. flow rate (m.g.d.)

Ion exchange—Cost vs. flow rate (m.g.d.)

Adsorption (carbon)—Cost vs. flow rate (m.g.d.)

Sludge handling and disposal

Total sludge disposal—Cost vs. flow rate (m.g.d.)

Thickening—Cost vs. volume of thickener (gal.)

Flotation thickening—Cost/m.g.d. vs. flow rate (m.g.d.)

Vacuum filtration—Cost vs. area of filter (sq. ft.)

Ultimate disposal

Deep well injection—Cost vs. flow rate (m.g.d.)

Waste water characteristics for each have been prepared by two members of the survey group, Roy F. Weston, Inc., and Resource Engineering Assoc. These characteristics include such distinguishing major features as volume of waste water per ton of product, flow volumes for each product, BOD loads (mg./l.), COD loads (mg./l.), and others such as oil, acidity, phenol, suspended solids, and nutrients.

Biological treatment

Activated sludge processes for the removal of soluble biodegradable matter is the predominant waste water treatment used by the organic chemicals industry. Many of the plants surveyed used activated sludge processes for which they claimed as average 88% removals of BOD₅ (five-day BOD). Generally, such treatments start by aerobically digesting water

sludge, then thickening, dewatering by vacuum filtration, and disposing the residues in landfills. The report, however, discusses variations of this general system and offers other examples and cost data for such process steps as contact stabilization, aerated lagoons, and deep well disposal.

In addition to biological treatment, other treatment techniques can be used to treat the organic chemical industry's waste waters. Invariably, pretreatment is required for its waste waters, regardless of the combinations used to reduce its BOD levels.

For example, lagoons can be used where large land areas are available. (Anaerobic lagoons reduce BOD levels to 100 mg./l.; and aerated lagoons achieve even greater reductions to as little as 50 mg./l.) Ultimately, the activated sludge (biological treatment) reduces BOD levels to 25 mg./l.

However, pretreatment processes always precede the main BOD reducing processes. These pretreatment steps usually include oil separation, neutralization, and, in case of high load variations, equalizations. Also, primary waste waters having high concentrations of suspended solids often require primary sedimentation.

Design criteria

The basis for design of a waste water treatment facility for the organic chemicals industry depends mainly on four items—flow (m.g.d.), BOD (mg./l.), COD (mg./l.), and suspended solids (mg./l.). The study group evaluated 20 different combinations of these plant variables and established some engineering fixes, shown in an accompanying table.

In-plant control is but the first step in instituting cleanup practices, which include the following:

- Salvage of unreacted chemicals.
- Recovery of byproducts.
- Multiple reuse of water.

• Good housekeeping to reduce leaks and spills.

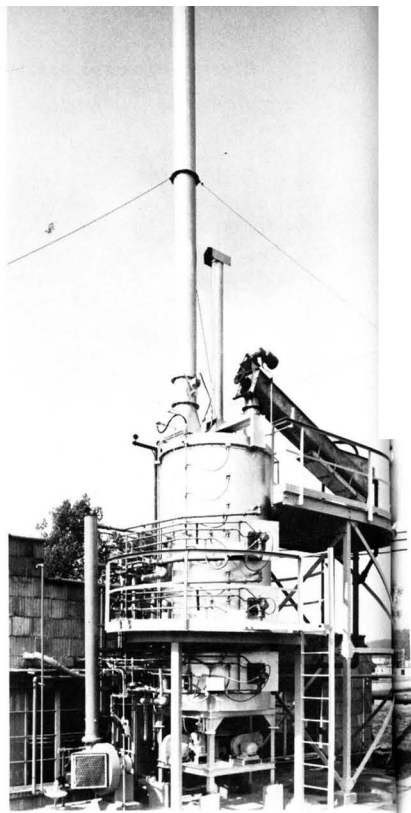
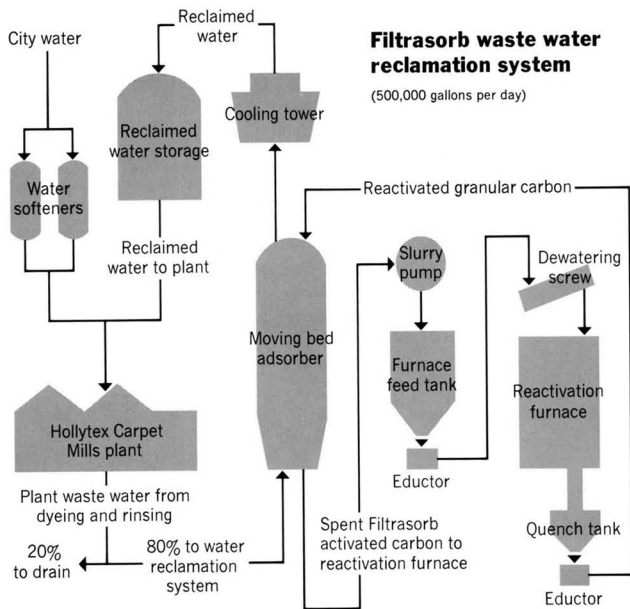
- Changes in processing methods.

Trend

The organic chemicals industry will grow at an annual rate of 8-12%, according to the study group. In 1973, total sales for this industry will probably reach \$15.6 billion, for 201.6 million pounds of product, up from \$3.7 billion for 66 million pounds of products in 1969.

Growth in the industry will not be uniform, the report notes, because some of the areas in which the industry operates will grow faster than others. In the petrochemicals portion of the organic chemicals industry, growth will be sparked by an increased demand for fibers, coatings, plastics, and elastomers, the report observes. In the cyclic intermediates portion, growth probably will be caused by increased production of ethylbenzene, styrene, and phenol. But growth rates in dyes and coal-based materials, probably will be low.

No major increase should occur in the amount of the organic chemicals industry's waste water treated by joint municipal-industry treatment systems, the report claims. The portion of the industry's waste waters that are handled in joint municipal-industry treatment facilities should remain at the same level, 2.4%, as today.



Furnace. Activated carbon is regenerated in multiple hearth furnace

Activated carbon reclaims textile industry's waste waters

Process waters for dyeing and rinsing operations can be reused

Calgon Corp. has received a contract for an industrial waste treatment unit that marks a significant departure for the company's activated carbon adsorption process: reclamation of industrial waste water. The system is being installed at a new plant being built by Hollytex Carpet Mills, Inc., a large California-based carpet manufacturer, at Southhampton, Pa. Initial capacity of the unit, which will treat as much as 80% of the plant's waste effluent for eventual reuse, will be 500,000 gallons per day, with provisions for a planned expansion to one million gallons per day. Under terms of the turnkey contract, Calgon will be responsible for the engineering,

installation, and startup of the treatment system.

Calgon's granular activated carbon system, around which the treatment facility has been designed, was developed about six years ago and originally was intended to replace use of conventional filter media, such as sand or coal, in the purification of municipal water supplies. The company has since installed about half a dozen activated carbon systems for water purification, including a 15 million gallon per day advanced version of the process at Nitro, W.Va. In addition, two activated carbon tertiary municipal waste treatment plants are in operation, at Pomona, Calif., and Lake Tahoe, Nev. However, the Hollytex unit will be the first of the company's units to be installed for treating industrial waste water for inplant reuse.

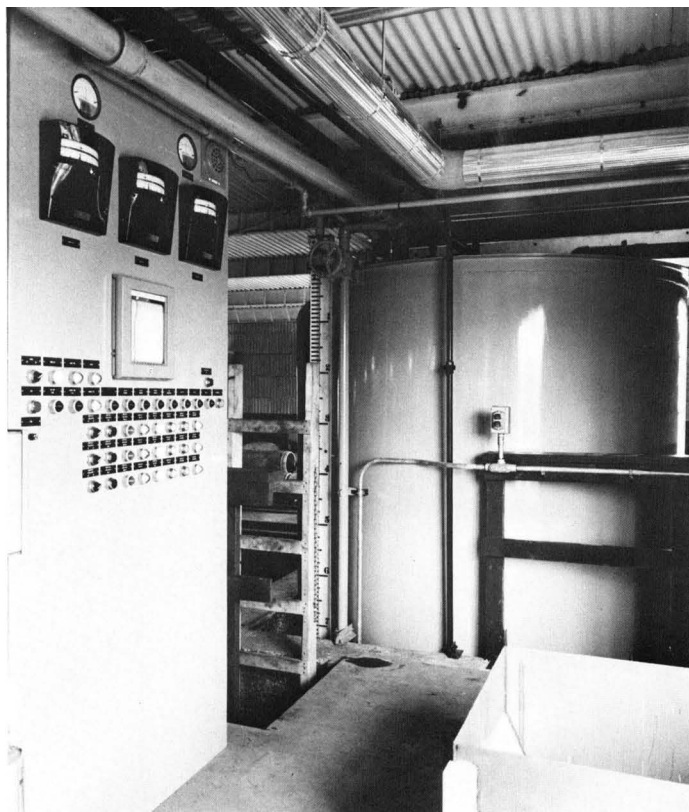
Knotty problem

The availability of a system for recovery of the waste water solved a particularly knotty problem for Hollytex, and, incidentally, for the Bucks County Industrial Corp. and the Southhampton Land Development Co. When

the carpet manufacturer, whose operations have been concentrated primarily in the western states, began negotiating with these two groups on a Southhampton site for an eastern plant, an early, major stumbling block was the need for large quantities of process water, which is typical of most textile finishing operations.

Specifically, the water requirements for the new plant would be one million gallons per day, and a sewer capacity to handle a like amount of industrial waste water.

Neither the Southhampton municipal water supply system nor the local sewage authority had such capacity available; to install such additional capacity would require a major expansion, and involve a considerable capital expenditure. Part of the costs would have to be passed on to the company, Hollytex was told. At the million gallon per day level under consideration, the plant's share of the water system and sewer expansion costs would have amounted to more than \$100,000 per year. Because these costs seemed prohibitive, Hollytex retained a consultant in an attempt to



Quench. Reactivated carbon is received as slurry in quench tank, where make-up carbon, usually less than 5%, also is fed into system



Slurry. View of control panel shows slurry tank and carbon hopper

discover a less costly solution. Discussions between the company, the consultant, and Calgon resulted in the design and development of the reclamation system for an installed cost of about \$300,000.

Process water

The major requirement for process water at the Hollytex plant will be for use in the plant's textile dyeing and rinsing operations. When the system is put in operation, 80% of the effluent from these processes will be treated in the water reclamation system. The system itself will consist of the carbon adsorption unit, carbon handling system, the regeneration furnace, a cooling tower, and storage facilities.

The process waste water will be treated in a moving bed carbon adsorption unit, the most efficient type of adsorber for plants of this size, according to Calgon. The moving bed adsorber is a refinement of the counter-current operating principle. Water flow is upward through the bed with portions of the bed removed periodically from the bottom of the unit for regeneration.

From the adsorption unit, the treated waste water is sent through a cooling tower, and then on to storage and eventual reuse in the plant. Makeup water for the plant water system, which is drawn from the municipal water supply, is pretreated in two 280 gallon per minute water softeners built by Calgon's Bruner division. The reclaimed water does not require this pretreatment, and bypasses the water softening step.

Carbon regeneration

Reactivation of the spent activated carbon from the adsorption system is achieved in a multiple hearth furnace. In the basic operation sequence, the granular activated carbon is pumped from the adsorption unit as a water slurry to the reactivation area. The carbon then is dewatered and fed to the furnace for reactivation by heating to between 1500-1800° F. to volatilize and oxidize the adsorbed impurities. The hot reactivated carbon then is quenched in water and pumped back to the adsorption unit to complete the carbon cycle. Fresh carbon is added to the top of the adsorption unit to

compensate for the loss of carbon during the reactivation, which is usually less than 5%.

Calgon says that the reactivation costs vary with the size of the unit involved, but generally fall in the range of 2-5 cents per pound. This figure takes into account fuel cost, power, labor, and the cost of makeup carbon.

Spokesmen for both Hollytex and Calgon view the Southampton water reclamation system as an important development in the field of industrial waste water treatment. Ralph Mishkin, Hollytex chairman, says his firm is "proud to put into practice this unique system. It demonstrates that industry does have alternatives [to effluent discharge] that can be more economical over an extended period. It shows, also, that a manufacturer can be a good neighbor and still save money in the process." William Weitzel, vice president of Calgon's water management division, adds that "although the design concept for the Hollytex plant is not the answer to all waste water problems, it can be the answer for many firms that find themselves in similar situations."

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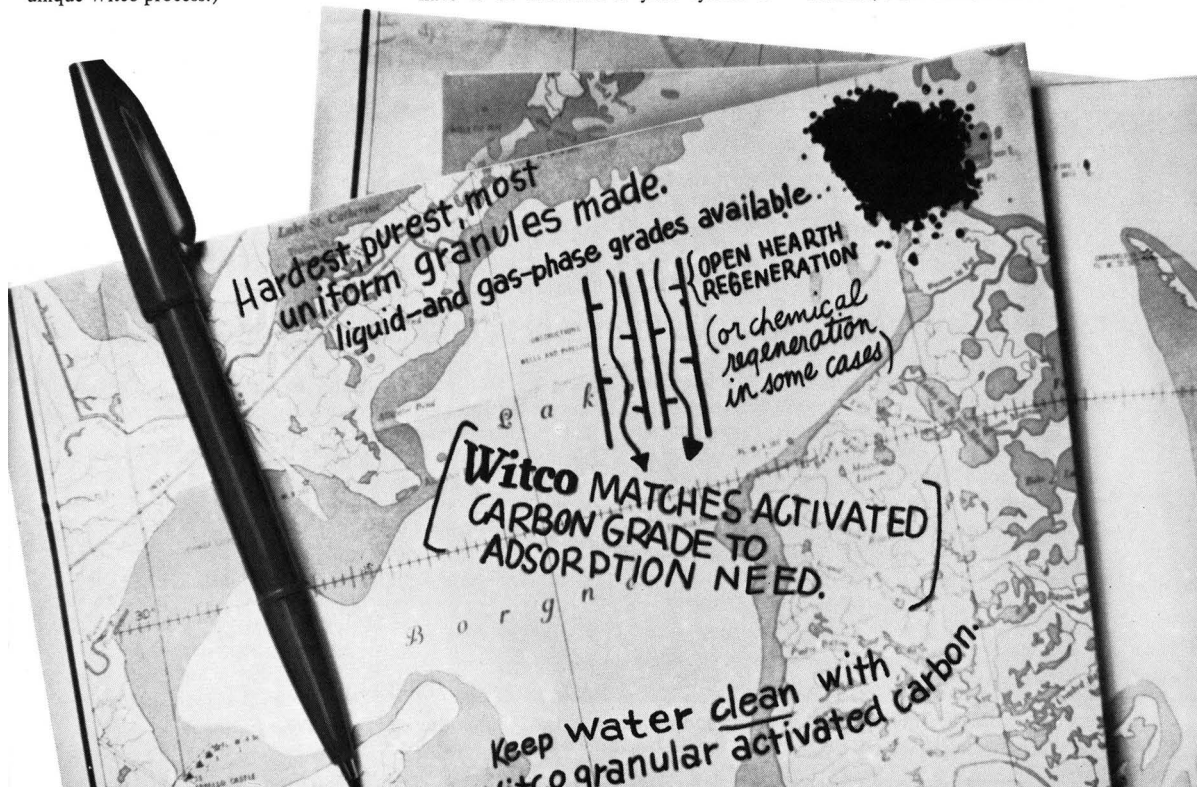
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Illinois moves along in fight for clean air

Legislative study committee recommends air quality standards

Illinois, one of the first states to take the initiative for control of its air pollution, continues to seek ways to implement and improve its present law. Recently, the state's Joint Air Pollution Study Committee, a legislative committee of the Illinois General Assembly, issued a final report calling for the following courses of action:

- Establish a Department of Environmental Pollution Control.
- Abolish the present nine man air pollution control board.
- Appoint a superintendent of air pollution control.
- Endorse nine recommendations for air quality standards.

Legislation to implement the findings of the study committee already has been prepared. The speaker of the Illinois House of Representatives, Ralph T. Smith, cosponsored a bill specifying more rigorous control of air pollution and including the endorsements of the study committee.

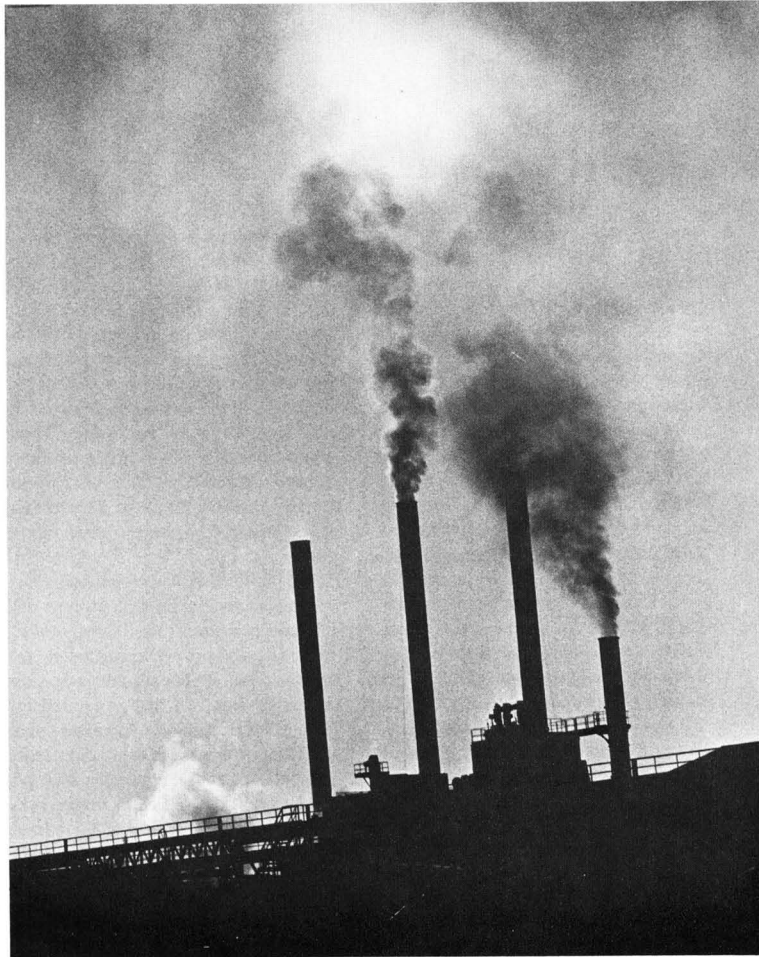
Created by legislative state authority which comprises 10 elected legislators—five state senators, and five state representatives—the study committee began work in late 1967. The committee made its present findings and recommendations on the basis of public hearings, expert testimony, and review of pertinent records and reports since that date, according to Charles J. Ryant, Jr., the committee's technical consultant.

Fault finding

The study committee finds fault with the present Illinois Air Pollution Control Board on several counts, alleging that the present board was remiss in providing adequate safeguards for the health and welfare of state residents and, further, that the board was dilatory in the enforcement of promulgated rules and regulations. More specifically, the study committee found that the board granted open burning variances in what the committee calls

“virtual total disregard of the intent of the law.” The committee also charges that “the board exercised questionable judgment in granting exceptions to some political subdivisions and then arbitrarily denying an exemption to an obviously qualified political subdivision.” The committee recommends that all certificates of exemption issued by the present board be revoked.

On the other side, John Warren, speaking last December for the Illinois Air Pollution Control Board, and commenting on a draft of the study committee's report, noted that only 28 variances are active under the authority of the board. These 28 are 20.8% of the board's total number of applications for variances. Of the 28, open burning is permitted by 22, which is



Recommended air quality standards for Illinois

SO₂. Annual 24-hour average concentration of less than 0.02 p.p.m. The 24-hour average should not exceed 0.10 p.p.m. on more than 1% of the days in any six month period.

H₂S. One half hour average of 0.05 p.p.m. no more than twice a year. The one half hour average of 0.03 p.p.m. should not be exceeded more than twice in any five consecutive days.

Total oxidant. Not to exceed 0.10 p.p.m. for any one hour period; to be determined by the potassium iodide colorimetric method of measurement.

Dustfall. Not to exceed 30 tons per square mile per month (Averaged for any period of three consecutive months).

Oxides of nitrogen. Not to exceed 0.10 p.p.m. for any one hour period.

CO. One hour average concentration of less than 100 p.p.m. The eight hour average should not exceed 30 p.p.m. and the 24-hour average should not exceed 25 p.p.m.

Haze. The coefficient of haze (Coh) should not exceed 0.4 Coh unit (annual geometric mean).

Suspended material. Less than 75-micrograms of suspended particles per cubic meter of air (annual geometric mean).

Odor. An objectionable odor is specified as any odor which is objectionable to at least 15% of the registered voters in a political subdivision. The superintendent of air pollution control division should enforce any laws enacted by local political subdivisions pertaining to the emission of objectionable odors within its jurisdiction.

10.8% of the board's total applications for open burning variances.

To remedy some of the problems, the committee favors establishment of a broad-based environmental quality control board which would consider not only air pollution but water pollution, noise pollution, solid waste pollution, and the like. Director of the proposed department would be appointed by the governor, Richard B. Ogilvie.

The present nine man air pollution control board would be replaced by an air pollution control division superintendent, who also would be appointed by the governor. Then, the current air pollution control board and its resources would become part of the newly proposed department of environmental pollution control.

Nine recommendations for air quality standards also are proposed by the study committee, including limits for sulfur dioxide, hydrogen sulfide, total oxidant, dustfall, oxides of nitrogen, haze, carbon monoxide, suspended matter, and odor.

Consumer costs

The cost of burning coal to produce electricity amounts to 10% of the average householder's electric bill of \$10 per month, the study committee notes. Thus, if the cost of removing sulfur from coal increases the cost of coal by an additional 10%, then the overall increase in the electric bill for burning low sulfur coal would be 1%.

In the same \$10 electric bill, 7 cents represents the cost and operation of the most sophisticated air pollution abatement equipment now available

for use with coal combustion systems, according to Ryant.

"We should proceed, in a stepwise manner, to limit the sulfur content of flue gas to 10 grains per 1000 B.t.u. of gross heating value," Ryant says. The committee agrees that such a limit is an ultimate but achievable goal. However, the committee believes that the limit should be set first at a release of 30 grains per 1000 B.t.u.; within three years, at 20 grains; and within five years, at 10 grains.

All automobiles purchased by the state of Illinois, or its political subdivisions, would have to be fitted with antipollution equipment, according to Ryant. He goes on to specify that the release of hydrocarbons in exhaust gases would have to be less than 0.1 pound per hour, and carbon monoxide, less than 1 pound per hour. These emission levels are identical to those already adopted by the Los Angeles County (Calif.) Board of Supervisors, Ryant observes.

Evaporation losses

Evaporative losses of gasoline and related petroleum distillates during transfer also should be regulated, the report says. A vapor collection and disposal system would be required for bulk gasoline facilities handling more than 20,000 gallons per day, with proper storage tanks specified for petroleum products. For example, storage tanks of 40,000 gallons capacity, having a vapor pressure of 1.5 pounds per square inch absolute or greater, would have to be equipped with a vapor-loss control device. Oil-water separators also are recommended if the

facility handles more than 200 gallons of petroleum products per day.

Photochemically reactive organic solvents would be limited to the same levels as those specified in Rule 66 for Los Angeles County (ES&T, March 1968, page 221). Moreover, storage facilities would have to limit certain solvent emissions to less than 40 pounds per day. For those plants employing processes involving contact with a flame, or baking, heat-curing, or heat polymerizing in the presence of oxygen (unless controlled by incineration, absorption, or equivalent technique), emission limits of 15 pounds per day are specified.

But other recommendations may be more difficult to effect. For example, the study committee recommends uniform state standards rather than different standards for different areas; and there are problems of conflicting areas of jurisdiction. Although the state or superintendent of the air pollution abatement division can set uniform standards, any political subdivision can set and enforce standards equal to, or more severe than, those set by the board, state, or superintendent, according to Ryant. For example, in the national air quality control program, HEW may designate two air quality control regions, which would include portions of Illinois. HEW already has designated the first region around Chicago (ES&T, February 1969, page 99). A second region may be designated for East St. Louis, Illinois-Indiana, and Illinois-Missouri, Ryant notes.

Penalties

The present \$100 fine for each day of violation of the air pollution abatement law is no deterrent to business operations, according to Ryant. The fine should be increased to \$2500 per day of violation, a stronger inducement for compliance with the state's air pollution statute, he continues. Also, the proposed superintendent of air pollution could obtain an injunction to halt operations, in certain adverse situations.

The time lag is great. Even after the Illinois General Assembly passes the bill which has been endorsed by this study committee, and the governor appoints a superintendent for the air pollution control division, it will take three years for the people of Illinois to finally become aware of the state's effort to prevent and abate Illinois' air pollution, the report concludes.



Growing menace. *Smog settles down over remote area of New Mexico*

Electric utility plans to control its air pollution

In spite of remote location, thermal generating units arouse public concern

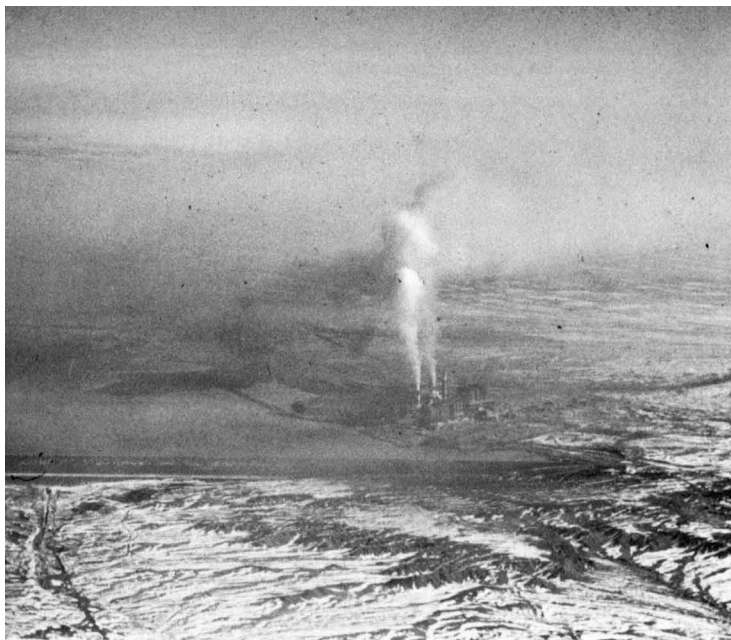
Recently, an air pollution complaint about an electric utility in New Mexico reached the headquarters of the National Air Pollution Control Administration (NAPCA) in Arlington, Va. The complaint is aimed at the Arizona Public Service Co. for air pollution caused by its thermal electric generating units. Its present units, which are not equipped with electrostatic precipitators, have been in operation for the past several years.

Normally, a local air pollution complaint about an electric utility's operation at a remote site would rarely be aired nationally. But this complaint is an important one since two other units with increased electrical generating capacity are planned for the area in the near future. Located at Fruitland, N.M.—about 20 miles west of Farmington—in the four-corner area of the state, where New Mexico, Utah, Colorado, and Arizona meet—the utility company operates three units with a combined generating capacity of 575

megawatts. All three units have inadequate collection devices for fly ash removal.

The control devices on the operating units are mechanical separators, whose theoretical efficiency for fly ash removal is only 80%, according to a spokesman for NAPCA. What is more, NAPCA says that it is probable that these mechanical devices operate at an even lower efficiency. These generating units use low-grade coal from nearby strip mines—coal that is low in B.t.u. and sulfur content, but high in silica content. Without adequate controls, the operation has been creating a severe air pollution problem for residents in distant communities—as far away as 100 miles.

In this remote area of New Mexico, there is no air pollution control regulation, according to Aaron Bond, chief of the air pollution division of New Mexico's Health Services Department. "Actually, we are in the process of writing the regulation and drafting



Electric utility. *Situated at Fruitland, N. M., Arizona Public Service Co.'s units eventually will be equipped with electrostatic precipitators*

ambient air quality standards," Bond says. The regulation and standards will be in existence by July of this year, Bond observes.

It was Bond's letter requesting technical assistance from NAPCA that first called wide attention to the air pollution problem. Bond, who wants to set up a monitoring and surveillance team to identify and quantify the area's air pollution problem, suggests, "The data would help write a better regulation."

Responding to Bond's call and realizing the need for action, NAPCA sent a three-man survey team—an engineer, a meteorologist, and a third—to New Mexico to assess the complaint.

The nearest residents to the utility are located in Los Alamos, nearly 100 miles downwind. They have been aware of the problem and have been trying to do something about it for the past two years.

Viewpoint

On the scene is Joseph J. Devaney, a physicist at the Los Alamos Scientific Laboratory. Devaney is no newcomer to the recent complaint. He serves as chairman of the Los Alamos Antismog Federation, an organization of citizens and conservation minded groups that includes the Sierra Club. The federation was formed to inform the citizens and to serve as an information vehicle

for potential air pollution problems, according to Devaney.

One of Devaney's special concerns is the very finely divided particles that do not fall out at all or fall out extremely slowly, particles approximately 1 micron in size. According to the Los Alamos scientist's calculations, the utility emits approximately something in the order of 10^{20} particles per day to the atmosphere. Devaney notes that the particles from these large capacity units persist in the atmosphere for long periods due to lack of rain. Opacity is one problem; loss of beauty at nearby national parks is another consideration. Together, they add up to considerable loss in regional values, notes Devaney as he awaits the findings of the NAPCA survey team.

Planned expansion

The West Power Consortium, a cooperative of about a half dozen electric utilities in the west, plans to put on line soon two additional units, each with a generating capacity of 750 megawatts. This expansion would nearly quadruple the present generating capacity at Fruitland. The first new unit is scheduled for operation in midsummer 1969, the second unit for 1970. According to the utility planners, the consortium probably will be the largest electric generating power complex in the U.S. Other planned

capacity includes new units in nearby states—for example, at Mohave in southern Nevada and at Kaiparowits Plateau in southern Utah. Apparently, all would use the indigenous supply of very low-grade coal. But air pollution problems may not develop into a serious matter since, eventually, all units will be equipped with electrostatic precipitators.

One purpose of the West Power Consortium's expansion is to test underground long-range transmission lines for electrical power. When unit 4 goes on line in midsummer 1969 and unit 5 in 1970, their electricity will be transmitted to the Southern California Edison Co. Meanwhile, today's production from the three units of the Arizona Public Service Co. goes mainly for the electrical requirements of nearby Phoenix, Ariz.

Today's three units, which form the basis for the complaint, are scheduled to be fitted with electrostatic precipitators. Only recently, William R. Reilly, president of the Arizona Public Service Co., announced the utility's intent to accelerate planning for the installation of electrostatic precipitators for the first three units at the Fruitland station. But, the actual order for precipitators will be placed only after an evaluation of unit 4's efficiency late this summer, according to Jack F. Swift, a spokesman for the utility company. Swift observes that precipitators routinely take 19 months from the date of order to the date of actual operation. Thus, today's units probably would not be equipped with precipitators before 1971. But the utility, Swift notes, has not been remiss in its planning. Originally, even before the present complaint, Swift says that the utility had agreed with the Secretary of the Interior and the Navaho tribe to order the necessary precipitators for existing units 14 months after unit 5 goes into operation in 1970.

Meanwhile, residents in the Los Alamos scientific community, as well as other residents as far away as Albuquerque, want reassurance that future generating units will be equipped with the best available air pollution control devices when these units become operational. More importantly, they want better control devices on the units already operating. They await the installation of electrostatic precipitators and look forward to cleaner air in that area of the U.S.

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Ice fields. During Lake Erie project, ACV encountered massive ice fields and pressure ridges, but maintained average speed of 30 m.p.h.

Air cushion vehicle

One U.S. aerospace company and Canada's Centre for Inland Waters have teamed up on an experiment designed to evaluate the use of air cushion vehicles (ACV) for gathering water data from icebound Lake Erie. The month-long experiment was conducted in February utilizing an SK-5, the ACV developed by Textron's Bell Aerosystems Company of Buffalo, N.Y. Aboard the craft, which was operated by two Bell pilots, a team of three scientists from the center were able to conduct water monitoring operations covering approximately 2700 square miles on the eastern section of the lake. Ice cover on the lake normally makes these stations inaccessible during the winter months.

The Canada Centre for Inland Waters was established in 1967, under the auspices of the Department of Energy, Mines and Resources, the Fisheries Research Board and the Department of National Health and Welfare. As part of its overall Great Lakes program, the center is charged with monitoring the chemical and biological status of Lake Erie. Normally, the center checks each of its 80 Lake Erie monitoring stations with its 600 ton research ship, *C.S.S. Limnos*. But the lack of winter time data has left the center with a serious gap in its knowledge of the lake's ecology. For instance, little is known about the effects



Pilot. Canadian Centre scientists consult with one of two Bell pilots who operated ACV during 2700 sq. mi. operation

Profile. One phase of test involved temperature profile of lake



hwarts barrier to winter water data

of water temperature and ice cover on polluting substances, and how these substances affect the plankton and other marine life of the lake during the cold weather months. The need for such year-round data prompted the center's evaluation of winter time transportation methods. In addition to ACV's, helicopters also are under consideration.

The eight ton ACV used by the center is owned and operated by Bell Aero-systems. It rides on a four foot cushion of air created by a turbine-powered lift fan which forces air into chambers beneath the craft. The air is captured by a flexible bag-like container underneath the vehicle and supports the craft when it is in motion. The vehicle is capable of speeds up to 60 m.p.h., and can travel over water, land, and marshes, as well as ice.

For the Lake Erie tests, the Bell ACV was rigged with a bow-mounted platform from which scientific instruments were lowered through holes drilled in the ice. Samples were extracted to determine the chemical and thermal content of the water at varying depths. The interior of the ACV was equipped to handle some of the spot analyses of water samples extracted, but the majority of the sample analyses were carried out at a temporary laboratory at Bell's ACV base near Buffalo and at the center in Burlington, Ont.




Bow platform. Special platform on ACV facilitated lowering of instruments through the ice cover and recovery of water samples



Operations. Centre's experimental program, under operations officer Derek J. Cooper, covered 25 monitoring stations in eastern Lake Erie

Sounding. Instrumentation for lake study included sounding device





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Throwaway packages—a mixed

The rising national concern about pollution emphasizes an aspect of life that most of us would just as soon forget—the problem of solid waste disposal. The discussions about solid waste in our newspapers and magazines are not so much a sign of progress as an indication that one activity which we had taken for granted is failing. And this fact intrudes on our consciousness. However irritating that may be, only one sane course is left: the ailment must be diagnosed and some sort of remedy prescribed.

In 1967 and 1968, Midwest Research Institute (MRI) took part in such a diagnostic endeavor. MRI economists spent nine months attempting to discover the role that packaging materials play in solid waste disposal in a study undertaken for the Solid Wastes Program, U.S. Department of Health, Education, and Welfare.

Packaging materials are only one part—and a relatively small one—of the total solid waste problem. Food wastes (garbage), lawn trimmings and leaves, ashes, newspapers and magazines, discarded toys and tools, rags, and furniture, and a variety of other items such as Christmas trees, old tires, aged swingsets, and an occasional washer or drier, account for about 80% of all residential wastes. Packaging accounts for about 20%. Materials other than packaging wastes repre-

sent 92% of total industrial and commercial discards; packaging represents the remainder.

A discussion of packaging in relation to solid waste handling necessitates a review of the entire solid waste disposal problem. What emerges is the fact that no one specific group—solid waste handling agencies, packaging companies, merchants, and the like—can be blamed for the problems we face. Rather, the problems result from the many individual activities pursued in ignorance or innocence of the ultimate consequences.

What are the solid waste problems? To say that solid wastes cause environmental pollution is too simple a characterization of the situation. In my view, solid waste handling presents six clearly distinct aspects, each of which constellates a different set of difficulties. Packaging relates to each of these aspects and contributes to each difficulty in a greater and lesser degree. Furthermore, each set of problems suggests a set of solutions.

Several general observations are worth noting:

- Solid waste disposal, viewed as an art or technique, is very much behind the times. Our waste collection practice is analogous in many ways to water distribution practice on the American frontier in the mid-19th century. With few exceptions, dis-

posal techniques in use today are indistinguishable from the techniques used by the Romans. We do not fight, communicate, build, or educate as they did, but our smoldering dumps are very much like theirs.

- The materials flowing into this antique waste processing system are the products of sophisticated industries—fiber-processing, chemicals refining, metal shaping, and glass making. In short, the kinds of waste are changing.

- The availability of goods at throwaway prices, the rapidly rising economic well-being of a large segment of the population, and the growth in population are increasing the quantity of wastes. At the same time, very little money seems to be available for so mundane an activity. Ghettos, inadequate housing, a burgeoning crime rate, archaic water treatment and sewage disposal systems, crowded airways, decaying downtowns—all vie for municipal dollars. Little remains to expand and modernize waste disposal facilities.

Collection

Ninety cents of each dollar spent on solid waste disposal is spent picking up and transporting wastes to disposal sites. Of the \$2.8 billion spent on collection in 1966, about 80% was for labor. In that year, 46.5 million tons of packaging materials were discarded,

feature

In the years to come, discarded packaging materials will strain present disposal systems

blessing

and subsequently collected at a cost of at least \$373 million.

The role of packaging materials in this connection is significant because consumption of these materials is rising steadily—absolutely and in terms of per capita use. In 1966, each person threw away 121 pounds more of such materials than in 1958; by 1976, we shall be discarding 136 pounds more per person than we did in 1966. This per capita increase, coming on top of the normal population increase, will mean that in 1976—when packaging consumption has risen to 73.5 million tons per year, or nearly 23 million tons higher than in 1966—nearly 15 million tons of the additional tonnage will be accounted for by increased per capita consumption, and only 7 million tons by normal population growth. However, these figures are for total packaging consumption; only about 90% of the total enters the solid waste stream, the remainder is recycled.

Collection labor costs are rising, too, as well as the prices of collection vehicles. Moreover, as disposal sites near population centers are filled and engulfed by expanding subdivisions and industrial parks, collection vehicles must travel farther. This, in turn, adds to collection costs. But even if unit costs are the same in 1976 as they were in 1966, to collect and



Consumer demand. Fed by consumer prosperity, the demand for specialized products is increasing the total amount of packaging wastes; at the same time, funding for new disposal technology is not keeping pace

haul the *increase* in packaging materials alone will cost \$157 million, or nearly half of the amount spent on collecting *all* packaging wastes ten years earlier. The increase in waste will necessitate nearly 4.75 million more collection trips than were required in 1966, and some 9500 more collection vehicles (costing about \$265 million currently) would have to be added to the present fleet of about 150,000 trucks.

Clearly, packaging materials will cause serious strains on waste disposal systems. For one thing, total residential waste tonnage will increase by 34% in the 1966-1976 period, according to Public Health Service estimates.

At the same time, packaging materials thrown away by residential sources will increase by 42%.

Forecasts also indicate that packaging materials will be less dense in 1976, and will require more space in collection vehicles. The reason for this is that packaging materials in 1976 will contain more paper, more plastics, and less metal than in 1966.

The solution to collection problems in solid waste handling is not to be sought in the reduction of tonnages to be collected, but through automation of the collection process. Processes worth examination are on-site reduction by grinding, and pipelining of wastes to collection or separation sites.

Piping of solid wastes could be piggy-backed on sewer systems, especially in areas where new storm or sewer lines are being built or where underground tunneling is being used for subway construction. Some development work along these lines is underway.

Waste processing

Once collected, wastes usually are transported to one of four basic types of disposal operations—open dumps, landfills, municipal incinerators, or composting plants. In addition, there are a number of other disposal routes which need to be mentioned. Among these are the various on-site burning installations, such as backyard burners, tepee burners, and apartment house burners. Ocean dumping is another technique; wastes are dumped at sea either unburned or as ashes. The feeding of swill to swine is still practiced, but it is generally an activity on the way out.

The one characteristic marking all these disposal processes is the lack of sophisticated equipment and techniques. Roughly 75% of all wastes end up in open dumps. Sanitary landfills, which sound good on paper, frequently are quite unsanitary. The average incinerator, in the words of one federal official, is "nothing more than a dump roofed over." And composting plants, usually started up amidst optimism, tend to fail with regularity, either because their prod-

ucts cannot be sold or because the plant attracts undue public interest by its odor.

Against this backdrop, an attempt at serious analysis of the disposability of packaging materials is handicapped at the start. Packaging materials may cause difficulties in a few well-operated incinerators, landfills, or composting plants, but, for the most part, their final destination is a facility which does no processing and accepts a paper carton as readily as a polyethylene bottle, a kraft bag as readily as an aluminum can, a pop bottle as readily as a pressurized CO₂ container.

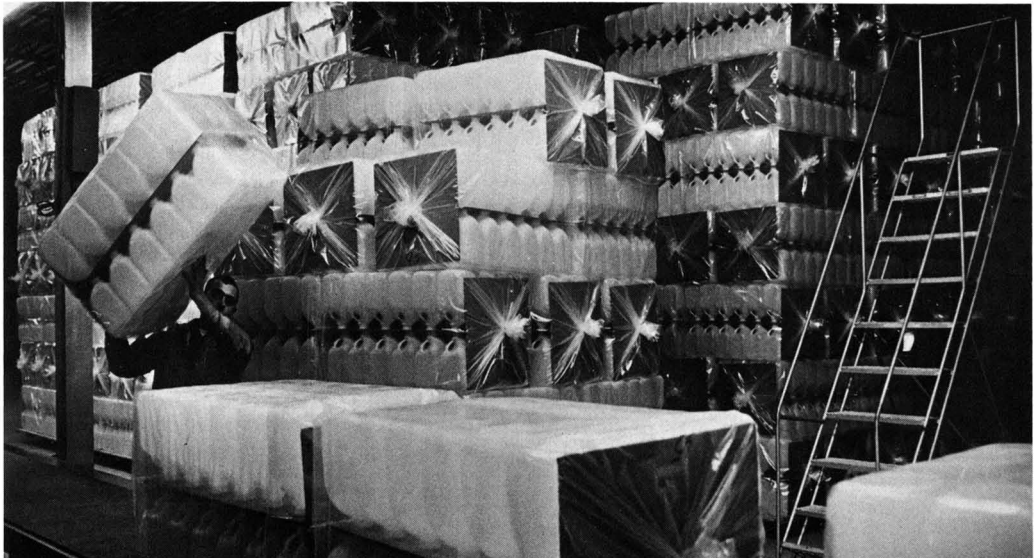
There is a vast gulf in waste disposal technology between the leading practitioners and the rank-and-file that forces one to a schizophrenic approach, in which it is impossible to generalize. The literature on solid waste handling is produced by the avant-garde—people who worry about plastics in incinerators because grate-fouling can result, or about liquefied glass deposits on refractory walls. These are people who are concerned about plastic and aluminum containers which persist in landfills and, when the fills are put to some other use, may rise to the surface. These are also the people who dislike film plastics because these materials are difficult to remove mechanically in composting. Over against these leaders are many others who have fewer or no problems with packaging because they do not

operate at the leading edge of technology.

The result of this general situation is that you can assert, in the same sentence, that some packaging materials are troublesome and that they aren't—it depends on your point of vantage. More curious, however, is the fact that even advanced practitioners do not have at their command the best technology available, either in their own field or in related fields. There is, for instance, the materials handling expertise of such companies as American Machine and Foundry, which has developed a fully automatic short-order kitchen; Link-Belt; and Union Tank Car. Computer-controlled chemicals processing is a multimillion dollar reality. A score or so companies making farm equipment have made giant strides toward the elimination of hand-picking in fruit, berry, and vegetable harvesting. Numerical controls have been used for some years now in guiding machine tools. And, finally, sensing technology has been advanced as aerospace and medical electronics have developed under government sponsorship.

All these techniques could be harnessed to breach the barrier to sophisticated solid waste processing—that of material mixing and contamination. Proper control of incinerator operations, for instance, could be achieved by segregating waste into its components, batch-loading wastes of the

Plastic. One of the latest packaging trends is plastic bottles, such as polyethylene milk containers



How packaging relates to aspects of solid waste problems

Aspect	Basic problem	Packaging contribution	Possible solution
Waste collection	<ul style="list-style-type: none"> Collection is labor-intensive, thus costly 	<ul style="list-style-type: none"> Proportion of packaging materials in municipal waste growing 	<ul style="list-style-type: none"> Automation of collection On-site volume reduction and disposal
Waste processing	<ul style="list-style-type: none"> Disposal technology is relatively backward Insufficient support of research and development Land available for waste disposition is dwindling 	<ul style="list-style-type: none"> Packaging materials are usually nondegradable by natural processes 	<ul style="list-style-type: none"> Retooling of financial support for waste processing Development of new disposal technology Modify packaging materials to make them more degradable
Aesthetic blight from littering	<ul style="list-style-type: none"> Public carelessness and/or indifference 	<ul style="list-style-type: none"> Packaging is major component of litter 	<ul style="list-style-type: none"> Intensive anti-litter publicity Rigorous anti-litter law enforcement Economic incentives for returning containers
Soil and groundwater pollution from decomposition of organics	<ul style="list-style-type: none"> Inadequate waste processing Poor selection of disposal sites 	<ul style="list-style-type: none"> Packaging plays indirect role; some materials may contain organic residues 	<ul style="list-style-type: none"> Relocation of adequate sites Replacement of dumps by incinerators
Air pollution from waste combustion	<ul style="list-style-type: none"> Existence of burning dumps Poorly operated or designed incinerators 	<ul style="list-style-type: none"> Role of packaging same as for solid waste in general 	<ul style="list-style-type: none"> Elimination of burning dumps and inadequate incinerators R&D on improved combustion equipment High quality pollution abatement equipment for incinerators
Loss of potentially valuable raw materials	<ul style="list-style-type: none"> Solid waste has low value because of contamination by intermixing Low cost of virgin material reduces demand for secondary materials 	<ul style="list-style-type: none"> Many high value raw materials combined in single package Exploitation of concept of throwaway containers 	<ul style="list-style-type: none"> New technology for low cost automated separation of heterogeneous solid waste Incentives for wider industrial use of secondary materials Modifications in package design which would utilize more homogeneous materials

same combustion characteristics, and bypassing noncombustibles around the incinerator. Waste reduction techniques—shredding and grinding—could reduce all landfill materials to a uniform consistency. Small bits of aluminum or plastics would be far less objectionable than full-sized containers.

Such techniques, however, suggest more processing and processing adds value. In this case, the value is added to a material which has no value; it is waste by definition. It might appear that any increment of solid waste processing is an increment of money thrown away. Indeed, such seems to be the prevailing attitude, and it translates into an absence of funding for solid waste disposal activities.

This attitude—insofar as it is general, and I have little doubt that it is—stems from an era of abundance: abundant land, abundant water, abundant clean air. The American Indian moved his campsite periodically when the wastes of his daily activity began to get underfoot. We inherited his lighthearted ways. Today, however, the unwillingness to add value to our

wastes perpetuates open burning dumps, creates black plumes atop office buildings of large cities at 5 p.m., permits municipal incinerators to violate laws which private citizens break at their peril, and adds to the pollution of groundwaters.

Given this general state of affairs, the contribution to the problem presented by packaging materials is slight. Waste processing must be upgraded, and the only way to do so seems to be a retooling of the financial infrastructure on which solid waste disposal rests. In one area of the nation with which I am particularly familiar, the average householder's expenditures on water services are \$10 a month, compared with \$1.75 for waste disposal. Both are vital utilities, and their costs should be much closer than they are.

Litter is one of the signs of affluence, a phenomenon corresponding to belching smokestacks in the 19th century that were viewed as so many badges of prosperity. However, litter is a nuisance. Unlike the dump, which is probably on the other side of the tracks, litter is everywhere, and is a

reminder that we have a solid waste problem.

This is one aspect of solid waste handling in which packages play a dominant role. On a tonnage basis, packages may not be the greatest contributors to litter. A few discarded tires, bumpers and bedsprings—all actually found along a mile-long stretch of a Kansas highway surveyed for litter—easily outweigh a large number of cigarette packets and aluminum cans. On the other hand, discarded packages account for the majority of items in litter.

In spite of efforts by civic organizations, there is good reason to believe that littering will intensify in the future, fed by a powerful expansion in the production of one-way beverage containers. Looking only at beer and soft drink containers—bottles and cans—10 billion nonreturnable units were produced in 1958, 25.6 billion units in 1966, and 58 billion units will be produced in 1976 unless legislative dampers are placed on this growth.

A good part of the reason for expansion in nonreturnable containers

rests on their appeal to both consumer and merchant. The consumer need not return the empties, and the merchant need not receive, store, and handle them. Another part of the reason derives from the fact that beverage packaging is a last growth frontier for package makers, especially glass makers. Each deposit-type bottle displaced from the market means the sale of 20 one-way containers, since deposit bottles make an average of 20 trips to the home before they are broken. In 1966, for instance, 65 billion containers were filled, but only 28 billion containers were produced. If all containers were of returnable type, a market for 37 billion units would have been up for the taking, and that's a lot of bottles or cans.

All this, of course, would not mean more litter if the population would be more thoughtful or conscientious. Littering cannot be blamed on industries which produce the ammunition, even though in future wars against the litterbug, the first casualties may turn out to be can and glass makers. Laws limiting the use of such containers have been introduced by the score in state legislatures, and some may pass in coming years. In 1967, 32 proposed bills were presented in 19 states, but none survived as law.

Such laws may well act, indirectly, to make the population aware of the extent of littering and create strong incentives to buy returnable containers by touching off discussions in the press and on radio and TV. A look at bills already put forward suggests that future legislation probably will take the form of outright bans, taxes on one-way containers to make them less attractive to purchase, or deposits on cans and bottles. The difficulties inherent in a regulation requiring a deposit on cans can be imagined. Such a law, for instance, suggests that merchants would have to store empty beer cans. This, in turn, would mean special collection bins that would contain the odor of fermentation. Also, would the thousands of cans thrown away before passage of such a law be redeemable?

Just how effective such laws would be in curbing litter is an open question. The state of Vermont, which banned one-way bottles for a brief period in the mid-1950's, found that the ban had little effect on collection costs.

Soil and groundwater pollution

Soil and groundwater pollution can be caused by solid wastes. Pollution of this type occurs predominantly because the disposal site is at an elevation below that of the surrounding terrain and, thus, becomes a natural collection basin for runoffs, or because the site is placed in an area where the groundwater table is relatively high and pollution is likely to take place. Another situation that tends to bring about such pollution is establishment of a dump or landfill in a region where heavy rainfall is usual or soil conditions are not favorable to landfilling. By and large, such pollution is preventable. Packaging materials play an indirect role in this aspect of solid waste handling. In themselves, packaging materials are not very degradable, and are unsuitable for composting but harmless to underground storage.

Air pollution

In addition to gaseous effluents generated as wastes are burned, solid waste handling also results in unpleasant odors and dust at all points where wastes are transferred or processed.

How do packaging materials relate to air pollution from solid waste handling operations? First, the various materials involved—paper, metal, glass, wood, plastics, and textiles—do not contain sufficiently high percentages of hazardous compounds to rate as dangerous fuels. One packaging material, polyvinylchloride (PVC) decomposes into undesirable chlorine compounds; about 36,000 tons of this material were used in packaging in 1966. However, more than one million tons of PVC were sold in the same year in the form of garden hoses, rainwear, shoe soles, floor coverings, construction materials, and the like, indicating that PVC occurs in solid waste at a much higher rate than a look at the packaging component alone would suggest.

The sulfur content of packaging materials is lower than that of most hydrocarbon fuels. Test results developed by Elmer R. Kaiser, and MRI estimates of packaging materials markets, show that a typical ton of packaging materials in 1966 contained 1.80 pounds of sulfur, or 0.9%. Our estimates also indicate that sulfur content will increase only slightly by 1976, to 2.02 pounds.

Solid wastes leave considerable residue when burned—ash, noncombustible components, and unburned leftovers. These must, of course, be disposed of in a landfill or dump. In some operations, incinerator residues are sufficiently free of unburned organics to be sold as clean fill. Handling of these residues may cause air pollution, and some particulates escape through incinerator chimneys.

In the usual case, incinerator residues account for 20–40% of the original weight. Calculations conducted on a typical ton of packaging materials in 1966 indicated that about 35% by weight of these materials is left over, a percentage close to the maximum. However, more than 90% of these leavings consists of cans and glass containers, not fine ash, leading to the conclusion that particulate air pollution from packaging sources is relatively low.

Loss of valuable raw materials

In 1966, materials valued at \$16.2 billion entered the packaging market, and, of this total, probably 90% was thrown away. This illustrates the nature of the final aspect of solid waste handling to be discussed here. We may ask ourselves why it is that we find uses for the bark of trees, process trash fish to make nutritious fish meal, are able to utilize every component of an animal carcass to produce valuable goods, and squeeze high-priced commodities from every fraction of crude oil, but are unwilling to prevent the squandering of valuable natural resources after they have been converted into finished goods. The answer seems to be that whereas we have perfected the technologies necessary to harvest, separate, refine, and convert virgin materials—no matter how complicated their chemical structure or how heterogeneous the mixtures in which we find them—we have not made any strides toward using secondary materials resources because we have had no need to do so.

If one takes a sober and unemotional look at the situation, there is, indeed, no immediate need to be concerned about our wasteful behavior. We have sufficient timber in the U.S. and Canada to supply domestic needs for many decades without any strain. (We are, however, a large exporter of paper, and shortages may occur within

30 years if we put export demand on top of domestic demand.) Our resources of hydrocarbon stocks will last for a long time, and we have yet to tap tar sands and shale oils. There is no foreseeable shortage of iron ore. Our aluminum is derived largely from imports (about 80% is imported), and aluminum conservation would make good sense, if for no other reason than to limit the outflow of gold.

Only if we look well beyond the year 2000 does it seem as if shortages may begin to be felt, especially if an across-the-board industrialization of backward nations is assumed and current population growth rates persist. Although the 21st century is still a long way off, we should be working on reuse and recovery of secondary materials in anticipation of faroff eventualities. We should now be creating the technologies, distribution networks, and financial structures that will give us flexibility in the next century. Nevertheless, the opposite trend is perceptible, especially with reference to packaging materials.

Paper

Let's look at paper supplies. Right after World War II, 35% of all U.S. paper fiber requirements was met by waste paper (or paperstock, as it is called in the trade). In 1956, paperstock accounted for slightly more than 26%; in 1966, for 21%; and by 1980—extending the trend—paperstock should supply only 17.5% of total paper required. The decline in percentage figures does not mean that tonnage of paperstock used has been declining. On the contrary, it rose from 7.3 million tons in 1946 to 10.2 million in 1966. But, proportionately, secondary paper fiber consumption is trending down when—to anticipate shortages in the long term—it should be trending up.

The declining popularity of waste paper as a raw material may ultimately be traced to cost. On one hand, pulp-tree harvesting and processing have been improved by new technology, driving down virgin pulp prices. On the other hand, costs of handling secondary paper have been rising, partly because labor costs are increasing, but, more significantly, because the waste papers are more and more contaminated. Papers are coated with plastics, printed with inks that resist

de-inking, and are laminated to metals. To separate the useful and useless components of waste paper takes hand labor, and the more sorting that is required, the higher the price. Not surprisingly, paperstock dealers prefer to buy from sources such as printing shops and binderies, where the waste is already fairly clean, rather than from office buildings or residential sources where paper wastes are frequently mixed with organic materials.

Much the same situation characterizes salvage of other materials used in packaging. To give one last example, to make a ton of cullet (broken glass of uniform color), a dealer has to handle between 1900–4600 bottles; and for a ton, he can obtain \$15, at best. In some cities, sorting costs exceed \$30 a ton, and consequently cullet is not handled at all.

The composite picture which emerges from even a cursory look at waste salvage is one where this activity slowly is being squeezed out of existence because of adverse economics. In other words, we are once more faced with the need to add value to something that seems to have no value.

Thus, increased use of secondary materials can be brought about only by an indirect tax on virgin materials—for instance, by subsidizing secondary materials handlers, giving tax incentives to potential users, or investing in research and development on automated processing of wastes for reuse. To ban the use of one-way beverage containers would also be an indirect tax on bottle and can makers. Yet, to turn about at this time and reorient various industries from a virgin-materials focus to a secondary materials focus may well be the thing to do—in the long run. In the short run, it may not be justifiable.

There is no doubt that the contribution of packaging to solid waste problems cannot be assessed without also passing some judgment on current practices for handling solid wastes. Large inputs of packaging materials into the solid waste system cannot be blamed for all the distress signals which are perceptible. Rather, the problems illustrate that the entire field of solid waste handling is a neglected area and should now be overhauled.



Arsen J. Darnay, Jr., is industrial economist in the Washington, D. C., office of Midwest Research Institute (MRI). Since joining MRI in 1965, he has participated as analyst, researcher, and project leader, in such projects as design study for a national urban information clearinghouse network, 10-year forecast of technological developments affecting gasoline, and dissemination of NASA generated technology to private industry. Previously (1961-65), Darnay was with J. F. Pritchard & Co., and served as civil affairs specialist with the U.S. Army (1956-61). He attended Rockhurst College and the University of Maryland.

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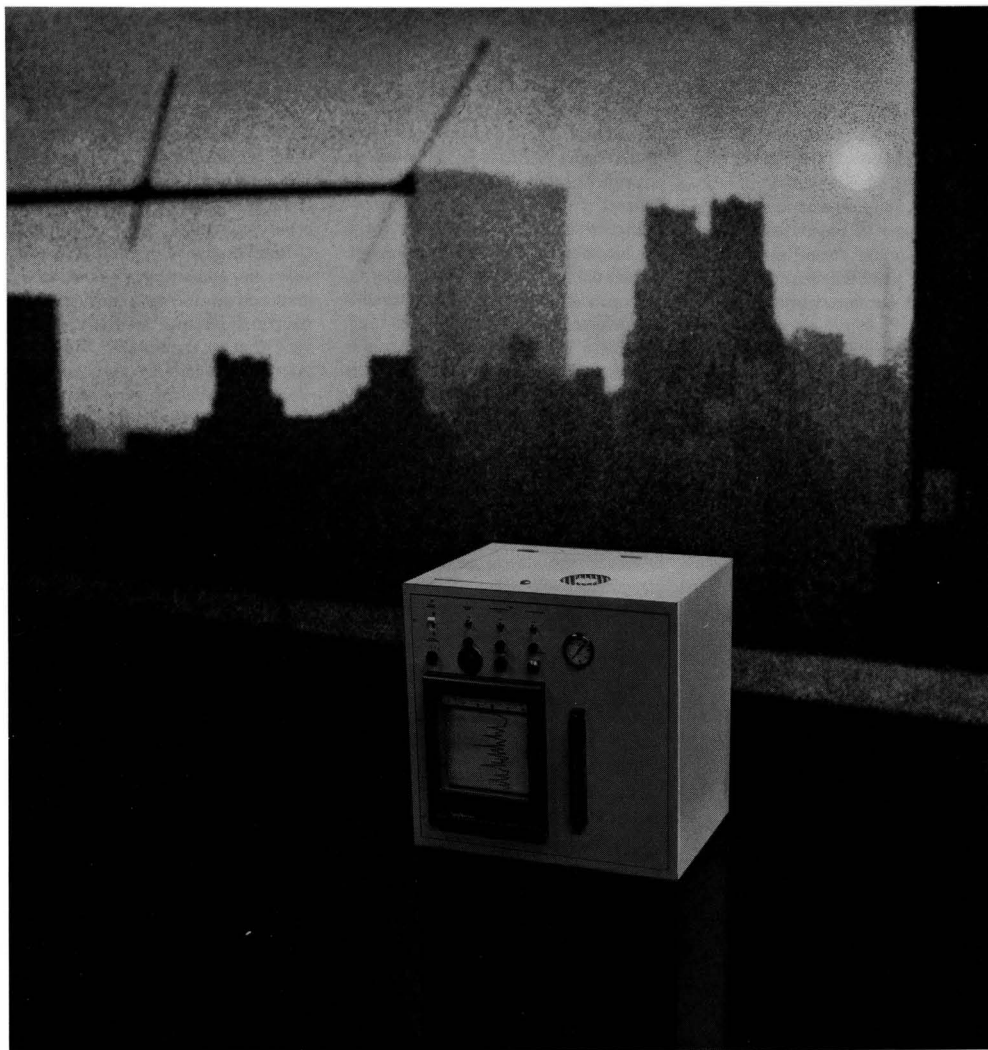
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Ion exchange is feasible for desalination

For waste waters with low amounts of total dissolved solids, ion exchange is more economically feasible than chemical regeneration

Although ion exchange has been used widely for many years in various water treatment practices, it has not been actively studied as a desalination technique until fairly recently, primarily because chemical regeneration costs are excessive in terms of the relatively small amount of high solids water that exhausts the resins. As the total dissolved solids (TDS) of the water drops, the regeneration costs per unit volume of water treated tend to become more reasonable, and, eventually, a point is reached at which the technique becomes worthy of consideration.

Another inherent restriction on the use of ion exchange for desalination lies in the requirement for using water (usually product water) to rinse the regenerating solutions away from the resin. When operating with a high TDS water, which produces a relatively small volume of deionized water, the rinse water often consumes an appreciable percentage of the product water.

There has been a recent revival in consideration of ion exchange as a desalination process. This trend may be attributed to three factors:

- The development of high capacity ion exchangers for the demineralization process.

- The development of ingenious techniques for efficient use, recovery, and reuse of resin regenerants.

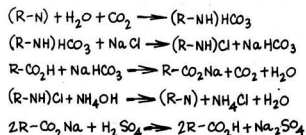
- The introduction of exotic, non-resin, ion exchange techniques.

New processes using these approaches include the Desal process, Sul-bi-Sul process, Sirotherm process, Continuous Ion Exchange process (Graver C.I. process), and a liquid ion exchange process for concentrating and removing magnesium selectively from

brackish waters. Other variations of ion exchange, such as electro dialysis and transport depletion, are not discussed in this article.

Desal process

The Desal process, developed by Dr. Robert Kunin and his associates at the Rohm & Haas Co., is based on a number of new concepts. Its primary concept is that a weak base anion exchange resin has the ability to form the bicarbonate salt from solutions of carbon dioxide. Having formed the bicarbonate salt, the resin then is capable of undergoing salt (NaCl) splitting reactions. Used in this manner, the high capacity of such weak base resins is in sharp contrast with the low capacity of the strong base anion exchange resins that normally are used for deionization. In addition, the weak base anion resin has an unusually high selectivity for chloride over bicarbonate. The result of this discovery has been the development of a reversible deionization system using weak electrolyte ion exchange resins. Moreover, a carboxylic cationic exchanger can fully utilize the high capacity of this resin. The sequence of reactions in the process is:



The actual process involves a series of three columns: anion resin (carbonate form), cation resin (hydrogen form), and anion (free base). In practice, almost quantitative recovery of CO₂ is possible and only small amounts of makeup CO₂ are required. After

the first and second resin beds are exhausted, the third bed is fully regenerated. Regeneration of the first and second columns is carried out with acid and base, and the cycle is complete. Deionization is accomplished by passage of the saline water in the opposite direction, that is, through the third column first. In this way, the first and third columns alternate as anion exchange columns and CO₂ recovery columns.

Regeneration efficiency is high for a system employing weak electrolyte ion exchange resins. Such resins require only a small excess of regenerants, usually about 10% to approach 100% efficiency. By contrast, strong electrolyte resins often require three or four times the theoretical amount of reagents for adequate regeneration.

The chloride:bicarbonate selectivity ratio of the weak base resin is about 50 at a 25% chloride saturation, and is still 20 at 50% chloride saturation. Other anion resins have less favorable selectivity ratios. Thus, the saline water is converted to alkaline water with a very low chloride leak, and the subsequent product water is of high purity. On the other hand, there are still some disadvantages to this process. For example, since both anion and cation regenerants are required, the advantage of a third column to recover the carbon dioxide is less than might be expected. In addition, extra resin and facilities for adding the makeup carbon dioxide are required for the third column.

The Desal process was evaluated in a pilot plant in Italy for more than a year, with a fair degree of success. The columns were about two feet in diameter and slightly more than six feet long. The tests were performed on

water containing from 150-10,000 p.p.m. of salts. Because of its low cost, lime was used as the anion resin regenerant. Under conditions of the study, solutions with 4000-5000 p.p.m. salts could be desalinated economically; for higher salt concentrations, other systems might be more competitive. One advantage of the Desal process is that the product water is quite low in salinity, often reaching 50-100 p.p.m.

Plant designs for this system can include four, five, or six columns. The six-column design consists of two separate three-column units, one of which is exhausted while the other is being regenerated. In a five-column system, one of the carbonization units is eliminated, and while two anion carbonate columns are being deionized, one is being carbonated. In the four-column approach, one carbonate column is replaced by a degasifier and CO₂ is injected into the feed stream.

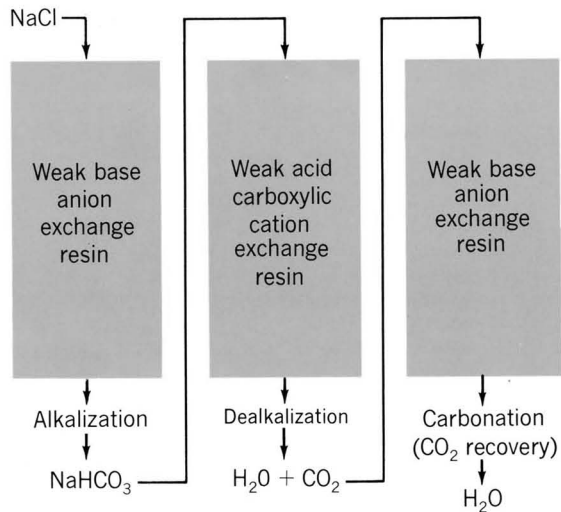
Cost estimates provided by Rohm & Haas show that, depending upon the TDS content, price of ammonia, and plant configuration, operation costs of water plants of from 5-10 million g.p.d. capacity will vary from 13-78 cents per 1000 gallons.

Sul-bi-Sul process

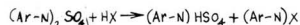
Another novel ion exchange approach to the demineralization of water has been developed by Nalco Chemical Co. and is being marketed by the Elgin Water Softening Co. This process is based upon the fact that an anion exchange resin which has been exhausted with sulfate may be in either the divalent sulfate ion form or the monovalent bisulfate form, depending upon the pH.

The Sul-bi-Sul process uses a conventional, strongly acidic, sulfonic cationic exchange resin for cation removal. The resin is regenerated with sulfuric acid. When the water to be demineralized passes through the cation exchange resin bed, all its salts are converted to acids. The second bed in the system consists of a strongly basic quaternary ammonium anion exchange resin that has been converted to the sulfate form, perhaps by waste regenerant from the cation exchanger. As the acids produced by cation ex-

Desal process



change pass through the anion exchanger, the sulfate that occupies two exchange sites on the anion exchanger is converted to monovalent bisulfate, and one exchange site becomes available to pick up an anion from the acid mixture:

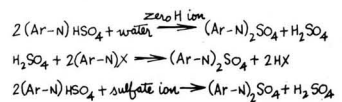


The hydrogen from the acid that has come out of the cation exchange bed is removed by conversion of sulfate to bisulfate, and the strong acid anion is also removed. Thus, the strong acids are removed in toto by the anion exchange bed. This is in contrast to the conventional anion exchange reaction in a two-bed system, where the quaternary ammonium anion exchanger is in the hydroxyl form. The anion of the strong acid replaces the hydroxyl on the resin and this free anion then reacts with the hydrogen left in the solution to form water.

The anion exchange resin in the Sul-bi-Sul process reacts in this manner because of the highly acidic environment. The low pH makes possible the creation of a large concentration of bisulfate ions due to the conversion of sulfate to bisulfate. Being monovalent, the bisulfate ion is held much less strongly by the resin.

Obviously, the capacity of the anion exchange resin in this process is low. First of all, the strong base exchanger has a relatively small capacity. Even under ideal conditions, the Sul-bi-Sul process would allow only one half of the exchanger capacity to be used; in practice, less than this theoretical capacity actually is used. In view of this limited resin capacity, the use of this system must be justified on the basis of extremely small regeneration cost.

The cheap, efficient regeneration of the anion exchange resin is the heart of the Sul-bi-Sul process. The resin can be regenerated with the water supply itself, or any neutral or alkaline water. Neutralization is accomplished more rapidly by applying lime water or a lime slurry directly to the bed. This regeneration technique is especially applicable to waters containing substantial amounts of sulfate ions. With low-sulfate water supplies, the rinse regeneration is conducted upflow:



In this manner, the sulfuric acid produced by regeneration with water acts

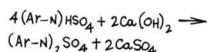
as a regenerant for anions other than sulfate which have been absorbed by the bed during exhaustion.

Some objections to this regeneration technique are:

- Large volumes of rinse water are required. This can be a critical problem where product water is used for rinsing, and where the water supply is low in sulfate.

- Large volumes of dilute acid are produced, and waste disposal could be a critical problem.

An alternate method of regeneration involves alkaline neutralization of the acids. Obvious choices are sodium hydroxide, sodium bicarbonate, ammonia, and lime; each has technical problems associated with it and a price differential to complicate or compensate for these problems. Of the first three listed, ammonia appears to be the most attractive on a cost basis. In fact, the use of lime as a neutralizing agent is even more economically appealing. Hydrated lime, probably one of the cheapest sources of alkali, has a limited solubility in water. It cannot be applied at high concentrations except in the form of a slurry. However, since the acidity of the exhausted anion bed is extremely high, and since the acid is discharged from the resin and into the water phase, regeneration with a lime slurry is quite feasible:



While the resin is not regenerated by lime per se, the lime quickly neutralizes the acid outside the resin bead, speeding up the conversion of bisulfate ions to sulfate. The obvious advantages of this regeneration procedure are reduced water requirements, low cost, and less acid wastes.

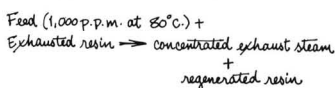
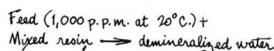
The Sul-bi-Sul process is claimed to be economically competitive with electro dialysis in small installations, or where chemical costs are low and power costs are high. In addition, the capital costs are claimed to be lower. However, from available information, the Sul-bi-Sul process does not appear able to produce water of the quality available from the Desal process.

Sirotherm process

Dr. D. E. Weiss and his coworkers in Australia have developed a unique process for the regeneration of the spent resins with heat rather than chemicals. They have found that low grade heat sources (under 90° C.) of

the type usually discarded can become a cheap regenerant. Temperature has a marked influence on the equilibrium between a solution of sodium chloride and a mixed bed of weak base and weak acid resins. Heating promotes the hydrolysis of the resin salts, and the reaction is driven in the direction of regenerated resin and concentrated salt solution.

Consider, for example, a mixed bed used to deionize a feed solution of 1000 p.p.m. total dissolved solids at 20° C. Raising the temperature to 80° C. reverses the equilibrium and regenerates the resin with accompanying elution of a concentrated exhaust stream:



The regeneration efficiency of any particular mixed bed system can be determined by a comparison of the resin titration curves at the two temperatures involved. A simple pH-ionization plot is prepared, containing curves for each resin of a mixed bed at each of the two temperatures chosen. The intersection of the low-temperature curves shows the equilibrium point for the two resins under conditions of exhaustion. The intersection at the higher temperature is the equilibrium point for regeneration. The difference in the ionized fraction represents the amount of regeneration that has been obtained by heating.

Certain conclusions become apparent from a study of this technique:

- The greater the difference between the points of intersection of the curves at the two temperatures, the greater the effectiveness of the technique.

- Monofunctional resins are preferred to those which have polyfunctional groups. The broad plateau exhibited by a monofunctional resin demonstrates a greater utilization of exchange capacity over a narrow pH range.

- The degree of demineralization may be varied by changing either the pH or cation-anion ratio.

The optimum resin ratio is usually not 1:1. Analysis of ionization curves indicates that the overlapping will be increased if one of the component resins is present in excess. However, increasing the resin ratio also increases

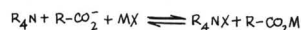
the total weight of resin per unit of resin capacity so that the effectiveness passes through a maximum on a weight basis and the optimum resin ratio is different at each pH level.

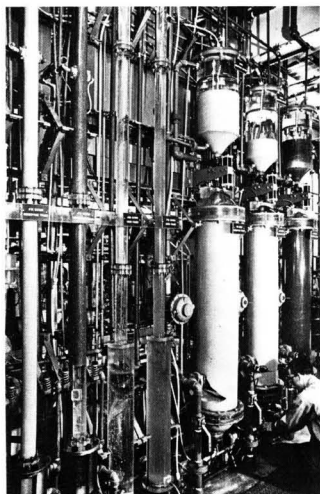
A question may be raised as to the utility of this process in view of the high temperature to which the resins must be subjected in each cycle. Dr. Weiss states that he and his coworkers have subjected a mixed bed of microbeads of Deacidite G and Zeokarb 226 (particle diameters from 10-20 microns) to 6500 successive cycles between 32° C.-70° C. Changes of solutions were made at each adsorption and desorption cycle. Examination of the resins after the 6500 cycles showed that the only beads which cracked were the few of particle diameter exceeding 20 microns. Apparently, any degrading effect of temperature can be overcome by a careful selection of the resins to be used.

There are some obvious drawbacks to this process. For example, because much of the exchange takes place in the pH range 5-7, the reaction rate is quite slow. The carboxylic cation exchanger, which is the one most commonly used in this procedure, is relatively dissociated in that region. Another drawback is the slow rate of heat transfer in thick resin beds. Very low liquid flow rates prevail because of the use of microbeads. These microbeads are required because the reaction rate increases as the resin size decreases. More exchange groups become more readily available and the detrimental effect of the substantially smaller hydrogen volume compared to the resin sodium volume is mitigated. The optimum sizes for the commercial resins that have been examined for this purpose are from 5-20 microns in diameter. There are other difficulties in making the Sirotherm process practical. For example, a plant 250,000 g.p.d., which would treat water with 1000 p.p.m. TDS and yield a product with 500 p.p.m. TDS and a 4000 p.p.m. waste, would require about eight cubic feet of resin spread out over an area of approximately 200 square feet.

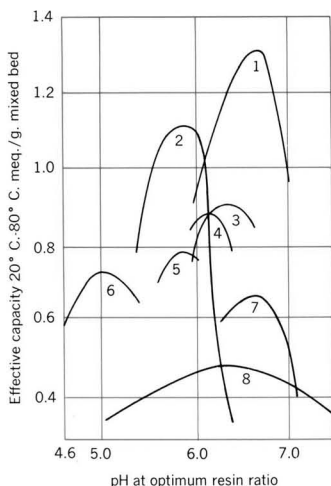
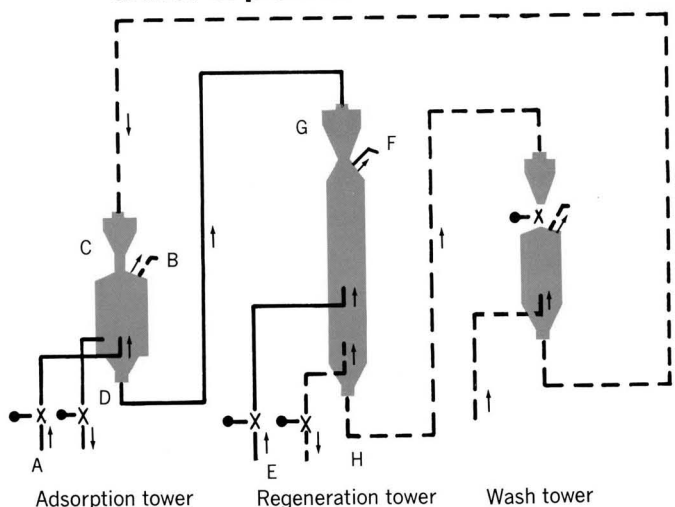
Liquid ion exchange

Liquid ion exchange also is being studied for use in desalination. In this process, organic amines and long chain acids are mixed together in toluene. The toluene then is contacted with the water to be treated:





Graver CI process



Predicted effective capacity (20° C.-80° C.) vs pH at optimum resin ratio for mixed beds of various amine resins with Zeo-Karb 226 in 1760 p.p.m. saline. The optimum resin ratio at maximum effective capacity is shown in parentheses.

1. 3-5% cross-linked polyvinylbenzylethylamine (1.9)
2. De-Acidite G containing 2.6% quaternary ammonium groups (2.5)
3. 7-9% cross-linked polyvinylbenzylidimethylamine (119)
4. Amberlite IRA-93 (2.5)
5. As in 2, but with Amberlite IRC-50 as the acid resin (4.0)
6. 7-9% cross-linked polyvinylbenzylpropylamine (4.0)
7. De-Acidite G containing 2.6% quaternary ammonium groups (1.5)
8. De-Acidite M (1.0)

Both long chain primary amines and quaternary amines may be used for the metal ion removal, but the use of the primary amines together with the carboxylic resins appears to give a more favorable equilibrium.

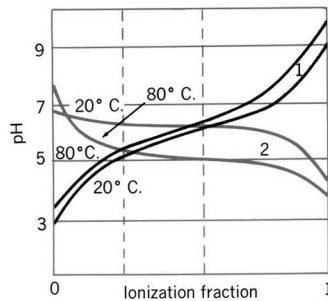
The complete transfer of all the salts present in a typical system, and their subsequent recovery, appear to be uneconomical at this time. However, magnesium can be removed feasibly by this process, since the system can be made highly selective for that ion. The process thus lends itself to a pretreatment technique prior to complete deionization, and has the added advantage of obtaining a favorable by-product. At present, the Office of Saline Water is sponsoring Dow Chemical Co.'s work on this process.

More than 90% of the magnesium chloride available in the feed may be recovered from the brine by the liquid ion exchange process. Through the use of 4-6 washing stages, a solution containing roughly four times the magnesium concentration of the feed solution, plus some calcium chloride, can be obtained.

Continuous ion exchange

The previous discussion has been directed toward processes which depend on different types of ion exchange materials for success. The mechanics of these systems are built around the nature of the exchanger. The final system to be discussed works indepen-

Matching of titration curves in 1760 p.p.m. saline (resin ratio unity)



1. 2.5% cross-linked poly(acrylic acid)
2. De-Acidite G

dently of the exchange material used. This continuous ion exchange system was developed initially by the Asahi Chemical Co. of Japan, and further refined in this country by Graver.

The traditional philosophy of ion exchange as a unit operation entails the use of a single vessel as a combined service and regeneration chamber, even though this is a compromise of the optimum configuration for flow in each of the individual operations. By separating the two steps and optimizing the vessels designed for each operation, chemical efficiencies are improved. This, of course, reduces the cost of the operation.

Jacob I. Bregman is Deputy Assistant Secretary, Water Quality and Research, U.S. Department of the Interior, a position he has held since 1967. He is also Commissioner, Ohio River Valley Water Sanitation Commission. Previously, he was with IIT Research Institute (1959-67) as director, chemical sciences division (1965-67); manager, water research center (1965-67); assistant director, chemistry research (1963-65); and manager, physical chemistry research (1959-63). Bregman received his B.S. from Providence College (1943), his M.S. (1948) and Ph.D. (1951) from Polytechnic Institute of Brooklyn. The author of "Corrosion Inhibitors," "Surface Effects in Detection," "The Pollution Paradox," and many papers, and holder of numerous patents, Bregman is a member of ACS, American Water Resources Association, Water Resources Research Council, N.Y. Academy of Sciences, Sigma Xi, Phi Lambda Upsilon, and American Institute of Chemists.

James M. Shackelford is Chief, Pollution Control Technology Development Section, Federal Water Pollution Control Administration, a position he has held since 1967. Previously, he was chemist, U.S. Department of the Interior, Office of Saline Water, as well as chemist, E. I. Dupont (1952-63), and Melpar, Inc. (1960-62). He received his B.S. (1949), M.S. (1951), and Ph.D. (1955) from the University of Missouri, and served in the U.S. Marine Corps (1944-46; (1951-52). Coauthor of "Bibliography of Membrane Technology Pertaining to Saline Water," "Recommended Procedures for the Testing and Evaluation of Candidate Reverse Osmosis Membranes for Desalination," as well as many papers and articles, Shackelford holds several patents. He is a member of ACS, Water Pollution Control Federation, New York Academy of Sciences, Alpha Chi Sigma, and Sigma Xi, and a fellow of the American Institute of Chemists.



Jacob I. Bregman



James M. Shackelford

In the accompanying flow diagram of the Graver process, let us consider the process used as a cation exchanger, operating in the hydrogen cycle. Water to be treated enters at A and exits at B, while the resin enters at hopper C and exits at D. The spent resin is circulated through a hopper leading to a regenerating column entering at G, where it is regenerated by contact with a solution entering at E and exiting at F. The regenerated resin exits at H. The wash tower is used to remove the last traces of regenerant, dirt, and fine resin and, finally, the regenerated resin is recycled to the hopper C. A similar system is used for the anion exchange cycle.

The adsorption tower has a number of interesting features. A specially designed distributor insures optimum contact for the water with the resin bed. Most of the ion exchange takes place within the first six inches above the influx distributor. The remaining depth of resin above it serves to polish out the leakage. The fact that the bed is filled allows for more intimate con-

tact at the exchange sites. In addition, high cross sectional area flow rates, from 30-40 g.p.p. per square foot, can be obtained with no diminution of effluent quality.

The exhaustion cycle requires 15-45 minutes. As the process continues, fresh resin is introduced into the vessel from the wash tower while exhaust resin is being removed and transferred to the regeneration tower. The timing is such that the new resin going into the adsorption tower moves downward uniformly, thus assuring no intermingling of the various exhaustion bands in the resin bed.

The regeneration tower is optimized for the removal of the ionic contaminants that were picked up by the resin during the service cycle. To accommodate the wide band characteristics of desorption ion exchange, sufficient height and transfer units are provided by a large height to diameter ratio. A typical column height is 22 feet with diameters in the range of 16-18 inches.

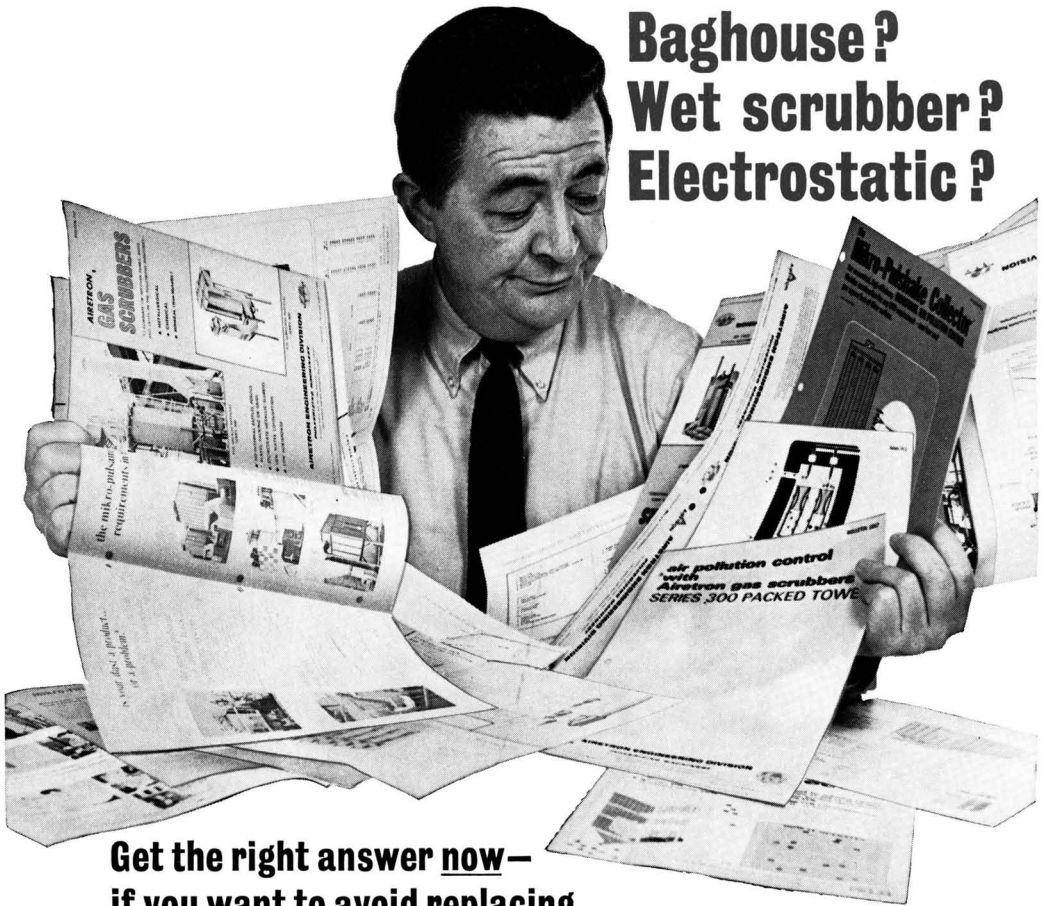
This regeneration column also func-

tions in a countercurrent manner. The fresh regenerant contacts the resin as it leaves the desorption zone, and the spent regenerant contacts the most exchanged resin which enters at the top of the column. This countercurrent function ensures maximum use of the available regenerant.

Resin from the regenerant column then is transferred to the hopper above the resin wash tower. This tower is a fluidized bed system with water entering the lower portion of the vessel and flowing upward continuously while the resin flows downward.

The installation costs of this process are 20% lower than conventional bed units, and space requirements are up to one third less. With water containing 250 p.p.m. TDS, one such unit is reported to have produced water containing 2 p.p.m. TDS at a cost of approximately 10 cents per 1000 gallons. According to predictions, a unit of this type, if put to work on 1000 p.p.m. TDS water, would produce quality water at a cost of 25-35 cents per 1000 gallons.

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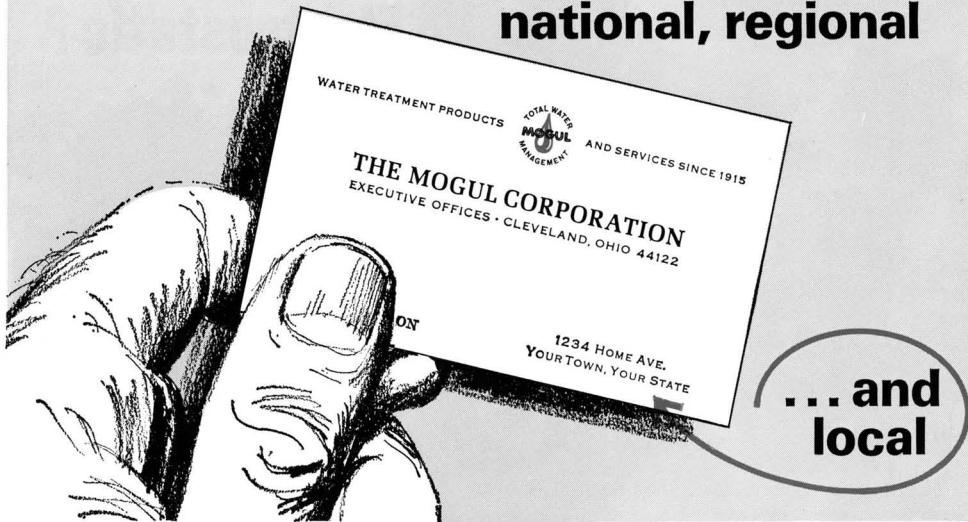
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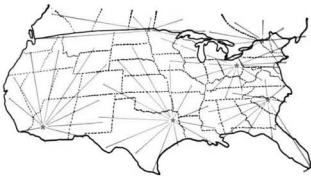


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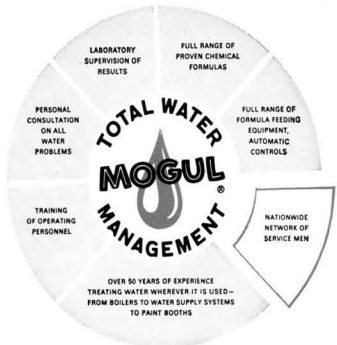
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Pollution Control Show:

**A second visit Houston's national conference
and exposition gains momentum**

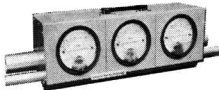
The National Pollution Control Conference and Exposition returns to Houston for another show. The second show at the Astrohall promises to be larger than the first, more than 4500 attendees in comparison with last year's 2200. Exhibitors will present their equipment and services for the control of air pollution, water pollution, solid waste disposal, and noise pollution. Conference speakers from government and industry will summarize the U.S. commitment for pollution abatement. Special emphasis will be placed on the criteria and cost assessments for pollution abatement in the U.S.

Environmental Science & Technology, which will be in Booth 80, offers a preview of the equipment and products from approximately 50 exhibitors. Each exhibitor is listed with his booth number at the Houston show.

Companies	Booth Number	
American Standard	28	Maurice A. Knight Co.
Armco Steel Corp.	57a	Lab-Line Instruments, Inc.
Ashbrook Corp.	83	Litton Systems, Inc. ESC
Bacharach Instrument Co.	49	Monsanto Co.
Betz Laboratories, Inc.	81	National Loss Control
Brailsford & Co., Inc.	168	North American Rockwell Corp.
Brinkmann Instruments, Inc.	60	Pan/Tech Engineering Co.
Brown & Root, Inc.	33	Phipps and Bird, Inc.
BSP Corp.	57	Process Analyzers, Inc.
Centri-Spray Corp.	56s	Reliance Chemicals Corp.
Continental-Emsco Co.	62	Rhodia, Inc.
Coulter Electronics Ind. Div.	17	Robertshaw Controls Co.
Davco Manufacturing Corp.	1a	Scranton Publishing Co., Inc.
Delta Scientific Corp.	82	Sonford Products Corp.
Dempster Bros., Inc.	47	Technical Fabricators, Inc.
DHEW, Public Health Service	27	Technicon Corp.
Dover Corp.—OPW Div.	53	Texas Electronics, Inc.
E. I. duPont deNemours & Co.	54	Texas Engineering Corp.
Environmental Science & Technology	80	UOP-Air Correction
Halliburton Co.	32	UOP-Johnson Div.
Heil Process Equipment	46	United Air Specialist, Inc., S & C Mfg. Div.
Homestead Valve Manufacturing Co.	1a	Western Precipitation, Div. of Joy Mfg. Co.
Howell Engineering Corp.	31	Westvaco Corp.
Ionics, Inc.	85	Wilkins-Anderson Co.
ITT Barton	70	Zurn Industries
Kem-Tech Laboratories, Inc.	79	

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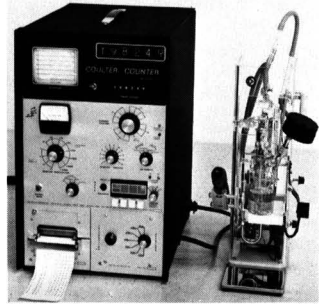


The pesticide sampler is designed to specifications of the United States Public Health Service and is in use by the USPHS at various sites throughout the United States at the present time. It is designed to collect extremely low concentrations of all major pesticides.

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Coulter Electronics will display its Model T counter, a 16-channel, fully solid-state, particle size analyzer. The unit is capable of not only counting and sizing a sample, but presenting a high-speed tape-printer readout of a complete particle size distribution, by size or weight percent, in less than 20 seconds. No data reduction is necessary. The unit is capable of counting fine particles from 1/2-400 microns at speeds up to 4000/second.

Another unit to be shown is the Model B Coulter Counter, which is used in conjunction with the Model M Volume Converter. The Model B Coulter Counter was the first counter produced for the Industrial Division and is suitable for research work. Both the Model T and Model B Coulter Counters operate under a principle that permits one-by-one counting and sizing of particles. Each particle is measured according to its three dimensional size-volume, which is the most precise measurement. The Coulter Counter's response is independent of particle shape, color, and density. Information regarding Coulter's particle size analysis service also will be displayed.

**Coulter Electronics Ind. Div.,
Booth 17**

Kem-Tech will display a trailer-mounted air sampling station the company has developed, as well as a panel depicting the various services offered in the areas of air and water pollution. The sampling station consists of a 20-head suspended particulate sampler, programmed to collect 24-hour samples sequentially; tape samplers for determination of coefficient of haze values and hydrogen sulfide concentrations; and a sulfur dioxide atmospheric sampler.

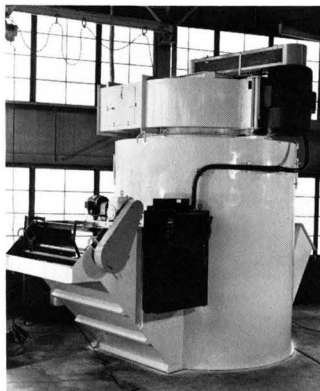
Aside from mobility and compactness, an outstanding feature of the

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sampling station is that it can operate for extended periods without servicing. If a 24-hour suspended particulate sample is desired every day, the unit need be serviced only every 19 days. If less than daily samples are required, longer periods without servicing are possible.

Other services offered by Kem-Tech Laboratories will be shown pictorially on a display panel with appropriate descriptions, and brochures will be available.

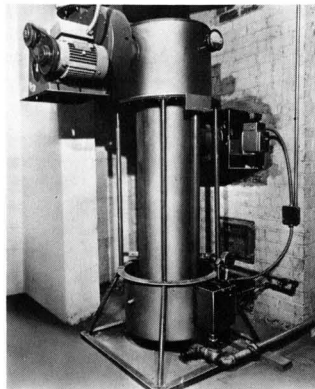
**Kem-Tech Laboratories, Inc.,
Booth 79**



Centri-Spray Corp. will be showing both air and water pollution control equipment at Houston. Among these is the company's centrifugally-generated water air spray, which is designed to remove airborne particulate matter from plant discharge air. In many installations, it is possible to recirculate plant air back to the work area by passing it through the Centri-Spray air washing system, with savings in air heating costs. Applications for Centri-Spray air systems include removal of airborne contaminants from the stack discharge of foundry cupolas, paint spray booths, plating facilities, or other industrial operations. Capacities from 300-500,000 c.f.m. are available. One piece of water treatment equipment to be shown is an oil recovery unit, which will remove up to 120 g.p.h. of surface tramp oil. These units may be installed in rivers, in weatherproof housings in lagoons, or liquid stratification areas. The oil recovery unit is also part of a complete industrial filtration system that will be on display, which includes a horizontal drum filter and an automatic charging pre-coat filter. The complete system is capable of reducing the undissolved solid par-

ticles of waste water to less than 0.5 parts per million, at capacities of more than 5000 g.p.m.

**Centri Spray Corp.,
Booth 56s**



American Standard's exhibit at the Houston exposition will feature the Leckenby wet gas scrubber, for which American Standard has the exclusive U.S. marketing rights. The scrubber has been used predominately for upgrading incinerators to comply with local air pollution ordinances, but has also found use in new incinerator construction for apartment buildings, school, hospitals, shopping centers, and, more recently, in industrial applications. The Leckenby scrubber is available in 100-3000 c.f.m. sizes. The exhibit itself will demonstrate the simplicity of design and efficient operation of the all stainless steel construction, and the patented features that add to scrubbing effectiveness and low maintenance. Vacuum impellers eliminate slurry damage or clogging; water is recirculated, so there is no need for costly fresh water. Impingement plates and baffles eliminate the need for vent holes which could be plugged by grease vapors, and the homogenizing effect of the cyclonic flow keeps the unit clean. American Standard manufactures other air pollution control equipment such as mechanical collectors and electrostatic precipitators which, though not on display, will be described by literature available at the booth.

**American Standard,
Booth 28**

Ashbrook-I (50 HP) Aerator. A cut-away model of the new 50 HP Ashbrook-I pump-type floating aerator,

which has been designed to eliminate icing problems, is to be shown at the exposition. This unique design is the result of float geometry and motor elevation. The Morse-Morflex radial coupling, B. F. Goodrich marine cutless bearing and glass fiber float, integral parts of this equipment, are viewed easily in the cut-away model.

**Ashbrook Corp.,
Booth 83**

Ashbrook BLOxidizer (Black Liquor Oxidation). A model of the Ashbrook BLOxidizer, recently installed by a kraft pulp mill to oxidize black liquor and, thus, reduce air pollution, will be on display.

**Ashbrook Corp.,
Booth 83**

The complete consulting services complex of Betz will be featured at the company's exhibit at the Houston exposition. The corporate exhibit will show how the Betz Consulting Services Division offers total assistance in waste water and air pollution control. These services include feasibility studies, optional treatment recommendations, engineering design, waste reuse and water conservation studies, client representation with regulatory authorities, and coordination programs.

Betz recently announced a merger with Albright & Friel, Inc., a consulting engineering firm that specializes in the engineering, design, and supervision of construction for municipal and industrial water supply, sewage, and waste water treatment systems. The merger has further extended the capabilities of the Betz Consulting Services Division to be all inclusive in the environmental and pollution control area.

The exhibit also will display a few of the corporate total capabilities as related to the solution of water pollution problems. A modular automated cooling water control system, designed and manufactured by Uni-Loc, a Betz subsidiary, will be shown. Information will be presented to demonstrate the superior performance of high molecular weight polyelectrolytes. The 1100 Series Polymers have wide application. They are used in plant influent water clarification, industrial process water clarification, industrial waste treatment in-line clarification, and sewage treatment.

**Betz Laboratories, Inc.,
Booth 81**

Brailsford Instrument Co. will exhibit a line of effluent samplers at the Houston show. The samplers are designed for collecting liquid samples from industrial outfalls, streams, and sewers. Three of the units are completely portable and are enclosed in wood cases designed for field operations; a fourth is designed for continuous sampling of liquid wastes under explosive conditions likely to be encountered in chemical process plants or petroleum refineries. The units, all of which weigh less than 20 pounds, are battery operated with a six volt lantern battery, with the exception of the Model EV sampler, which is equipped for use with either a 12 volt rechargeable nickel-cadmium cell or a 115 volt, 60 cycle power source. Prices of the samplers range from \$255-\$525; two of the models, the EV and DU-1, can be converted to true proportional samplers by means of an accessory head detector, which is available at additional cost.

**Brailsford & Co., Inc.,
Booth 168**

Porteous Process: automated, continuous, dewatered sludge without corrosive and costly chemicals, digesters, or large land areas for drying beds. Not affected by weather; odor-free; no air pollution; minimal labor, power, fuel, and water required. (Existing plants report utility costs as low as \$2 per ton of dry solids.) Steam injection is the key to this process. Raw sludge is pumped into a heat exchanger, mixed thoroughly with steam in a reaction vessel; conditioned sludge passes back through heat exchanger giving up heat to incoming raw sludge, then enters decanting vessel. Solid material settles; supernatant water is drawn off top. Treated sludge, reduced to one-third original volume, product is a sterile, easily handled cake undergoes final dewatering. Final which is auto-combustible in a BSP system or used for compost or fill.

**BSP Corp.,
Booth 57**

BSP Ecologix Systems, as developed at South Lake Tahoe, Calif., are an important part of an advanced waste

water treatment project and low-cost phosphate removal, incorporating the following original processing concepts:

- 1) use of lime as an economical coagulant for removal of solids from effluent;
- 2) means of recovering lime for re-use through incineration of chemically treated sludges;
- 3) stripping tower for wholesale removal of ammonia-nitrogen;
- 4) carbon columns capable of complete removal of taste, odor, color, trace organics and inorganics, and detergents from effluent;
- 5) means for regenerating carbon in large quantities for reuse, thus economically warranting the employment of carbon adsorption as a large-scale sewage treatment process. Treated water is extremely clear, of drinking water quality, and suitable for natural uses or marine life environment.

**BSP Corp.,
Booth 57**

Activated Carbon Regeneration is accomplished in a BSP Carbon Regeneration System at one tenth the cost of buying new material. Spent carbon is withdrawn from the bottom of carbon columns, dewatered, then fed into a six-hearth gas-fired BSP furnace. Regeneration is accomplished by heating carbon to 1,650 -1,700° F. in a steam atmosphere. Heat volatilizes adsorbed impurities on the carbon and drives them off as gases. The regenerated carbon discharges into a quench tank, then is pumped to two carbon defining tanks. It is washed to remove fine carbon particles, then moved hydraulically to the top of the carbon columns for reuse. The regeneration process is controlled by hourly measurements of the apparent density of the carbon and by tests of the iodine number at 4-hour intervals.

**BSP Corp.,
Booth 57**

Lime Reclamation system developed by BSP Corp. is highly economical and eliminates waste-storage problem. Main features of the system are: minimization of CO₂ content to prevent recarbonation while maintaining proper atmosphere for calcination; extreme control on light burned lime; operation by central control with a panel at the furnace for key functions; and a high degree of automation. System is applicable to all industries using lime, as well as to waste water treatment where lime is used as flocculant. For example, lime sludge from a chemical clarifier is dewatered, then regenerated

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I.P.C.I.'s basic approach to industrial waste control is evaluation of waste quantities and characteristics, reduction of waste through in-plant changes, formulation of treatment requirements and determination of optimum system for disposal or utilization.

The full scope of disposal methods are employed by I.P.C.I. in the design, construction and operation of pollution control systems through sub-surface disposal wells, chemical treatment, landfill, incineration, biological treatment and combinations of these methods. Learn more about I.P.C.I.'s "total performance" concept of pollution control. Write for literature, or call your nearest I.P.C.I. office.



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CONTRACTS RECENTLY COMPLETED:

Abbott Laboratories
Barceloneta, Puerto Rico
Construction: Drilled and constructed water supply and waste disposal wells for new multi-million dollar pharmaceutical plant.

General Electric Co.
Mt. Vernon, Indiana

Design: Did engineering design for 3 million gallon-per-day municipal-type water treating system for chemical plant on Ohio River.

Bareco Wax
Kilgore, Texas

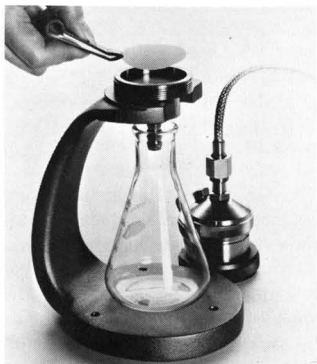
Analysis, Design, Construction: Constructed facility for separating oil and paraffin material from waste brine stream. Drilled waste disposal well for injection of brine; built incinerator for disposal of oil and paraffin materials.

for reuse by calcining. Reclaimed lime is then introduced as flocculant in primary treatment or is used in tertiary clarifiers.

**BSP Corp.,
Booth 57**

Thermal Disc Processor, an indirect-type heat exchanger for cooling, drying, and heating free-flowing solids, is installable at any angle from verticle to horizontal. It provides higher heat transfer coefficients than conventional heat exchangers, needs minimum floor space, requires minimum maintenance and is highly economical, needing no dust collection equipment, no feeders, no troughs nor auxiliary equipment. The Thermal Disc Processor has many applications, including a cooler in lime calcining, one of the BSP Ecologix Systems for waste water treatment. It also has proved 100% effective in bacteria control in the processing of high protein materials.

**BSP Corp.,
Booth 57**



The Sartorius Membrane Division of Brinkman Instruments plans to display the following items: • A new line of membrane filters with two essential differences from all others. Sartorius filters have up to a 10% faster flow rate and have practically no extractables. • A new line of all stainless steel filtration apparatus with many new innovations. This line is unique in that all are available with optional Teflon coatings, have quick change connections, exclusive volume filtration versions, many come with a support stand especially designed to hold the apparatus, and is the most modern line available. • A special modern industrial multiplate filtration apparatus is available making use of a new design that permits handling by a

single man by eliminating the heavy housing. Prefilters are superimposed on individual filters with built-in pre-and post-filtering test valves.

**Brinkman Instruments, Inc.,
Booth 60**

The National Supply Division of Armco Steel Corp. is exhibiting equipment necessary for an injection well—one of the most effective methods for controlling water pollution. Injection wells are used to route pollutants deep into the earth instead of discharging them into rivers and lakes. With long experiments in supplying equipment and materials for injection wells in the oil industry, Armco has developed especially adapted equipment for pollution wells.

One example is the Armco J series of plunger pumps, used to inject waste fluids down the injection well and into the earth. Special titanium-palladium alloys protect the pumps from highly corrosive fluids such as acids. Other pumps of standard steel construction are available for use with noncorrosive fluids. At the Houston exposition, Armco is showing equipment for a typical well, including the National pumps and wellheads and Armco casing and tubing. Wellheads are used to control the pressure of the fluids being injected. The casing and tubing prevent waste from escaping into the wrong geological formation.

**Armco Steel Corp.,
Booth 57a**

Automotive Exhaust Gas CO Analyzer. This is a new instrument being introduced to provide service stations exhaust emissions to conform to federal and state regulations regarding air pollution and smog that develops from automobile usage. This instrument will give quick, convenient measurements of the CO content in automobile exhaust which will aid in the adjustment of carburetors to keep them at an efficient combustion level.

**Bacharach Instrument Co.,
Booth 49**

SS-P Super-sensitive Indicator for Combustible Toxic Gases. This is a precision instrument that detects concentrations of combustible toxic gases. It is being used currently in some areas for air pollution work in connection with measuring the toxic gas content of exhaust fumes emanating from industrial smoke stacks. It is particu-

larly useful for measuring emissions in plants and factories that work with organic compounds and a variety of toxic combustible products.

**Bacharach Instrument Co.,
Booth 49**



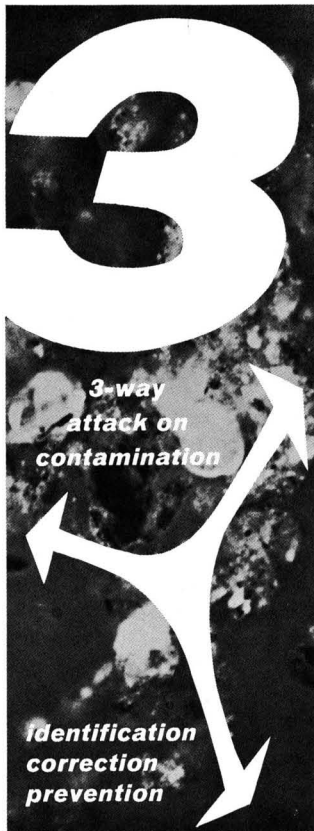
Fyrite Combustion Test Kits. The Bacharach Instrument Co. makes a variety of instruments that are used for the checking of industrial and residential heating systems to assist servicemen and installers in achieving good clean combustion. It includes items such as Smoke Testers and CO₂ Indicators which aid in adjusting the heating systems to provide clean efficient combustion. In recent months, these Combustion Kits have been recognized as important in the role of assisting industry towards curtailment of air pollution that is caused by heating with fuel oil.

**Bacharach Instrument Co.,
Booth 49**

Johnson-Williams Combustible Gas Monitoring Systems. A number of Johnson-Williams Combustible Gas Monitoring Systems have been put to use in refineries and chemical plants to provide outdoor measurements of combustible vapors that may be escaping from the processing of combustible fluids. In some cases, refineries have experienced contamination of sewers and manholes which give off vapors that are considered a nuisance and also an explosive hazard.

**Bacharach Instrument Co.,
Booth 49**

Monoxor and Gas Hazard Indicator Kits. These are small portable hand instruments that are used for detecting concentration of toxic gases including carbon monoxide, carbon dioxide, hydrogen sulfide and sulfur dioxide, chlorine, and nitrogen dioxide. Several



Photomicrograph of typical city fallout.

Walter C. McCrone Associates is uniquely qualified, by training, experience and equipment, to track down in-plant sources of contamination and pollution. A survey of your plant or operation by a trained McCrone engineer, plus detailed laboratory analysis, pinpoints the nature, amount and source of contaminants.

Identification

McCrone Associates provide detailed advice on corrective measures. Recommendations extend to types, sizes and costs of necessary equipment. Recommendations are thoroughly objective, aimed at producing best results at lowest cost to you.

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Our staff will engineer corrective measures based on our laboratory findings. We provide comprehensive drawings and bids from equipment manufacturers.

prevention

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of these gases are known contributors to air pollution and are considered detrimental when experienced in both indoor and outdoor areas.

**Bacharach Instrument Co.,
Booth 49**

Mist Eliminators of Teflon FEP-Fluorocarbon Fiber for very fine mists in corrosive atmospheres. A highly efficient, low-cost knitted mist eliminator of Teflon fiber has been developed to remove micron and sub-micron particles of fog or mist from stack gas emissions. Originally developed for Du Pont's sulfuric acid plants, the units are now available for use by others. The corrosion-resistant properties of Teflon fiber make this mist eliminator ideal for hot acid exposure in sulfuric acid plants. Mist is collected by inertial impaction and direct interception by fibers of Teflon uniformly distributed throughout the specially knitted coalescer pads. Acid is removed from the gas stream without dilution and may be drained directly to the acid mix tanks.

- a. As vapor disengages from liquid, it carries fine liquid droplets with it.
- b. When the vapor stream passes through the FEP mesh, entrained liquid droplets impinge on the monofilament surfaces; they coalesce into large drops, which fall off.
- c. Vapor leaving mesh is free from entrained liquid.

**E. I. duPont de Nemours & Co.,
Booth 54**

Filter Bags of Teflon FEP-Fluorocarbon Fiber. Filter bags of Teflon fiber work far longer than filters they replace. Filter fabrics of Teflon TFE fiber are inert to virtually all chemical attack over the entire pH range and can withstand temperatures up to 500° F. In addition, they have excellent cake release and zero moisture absorption. Bags of Teflon fiber now are used for dust collection in many applications: carbon black, organic chemicals, titanium dioxide, clay and copper smelting. Fabrics and felts of Teflon fiber are offered for dust bags.

**E. I. duPont de Nemours & Co.,
Booth 54**

The Total Oxygen Demand Analyzer measures within three minutes the oxygen demand exerted by impurities in water, thereby making the analyzer an important new tool for the control of water pollution. The instrument originally was developed by the Dow



Chemical Co., and now is licensed exclusively to Ionics. It is the result of two years of testing and is aimed at the automatic monitoring and control of industrial organic processes and waste treatment plant effluents. Other potential applications include stream surveillance and water pollution research and development. The total oxygen demand or TOD method is based on the rapid, automatic, quantitative measurement of the amount of oxygen used to combust the impurities in a water sample. The TOD measurement is achieved by continuous analysis of the concentration of oxygen in a combustion process gas effluent.

**Ionics, Inc.,
Booth 85**

The Maurice A. Knight Co., manufacturer of chemical equipment, will show by photographs and material samples some typical examples of pollution control of chemical wastes. One illuminated drawing shows a system where both incineration and gas scrubbing are used for disposal of chlorinated organic chemical wastes. Another lighted diagram illustrates a typical acid waste neutralizing system. Each Knight system and piece of equipment is engineered, using proper materials of construction, to best meet customers chemical fume or acid waste problem.

**Maurice A. Knight Co.,
Booth 35**

Lab-Line Instruments, Inc., plans to exhibit Soluvisor Electrolytic Conductivity Controllers and Water Purity Monitors, for continuous, fully automatic control of solution strength within narrow limits. Soluvisors are easy to install, adjust, and operate; and they also feature Sproule Conductivity Cells that are virtually indestructible in acids, alkalis, and

heat; require no skilled maintenance, and the electrical characteristics are permanent.

**Lab-Line Instruments, Inc.,
Booth 61**

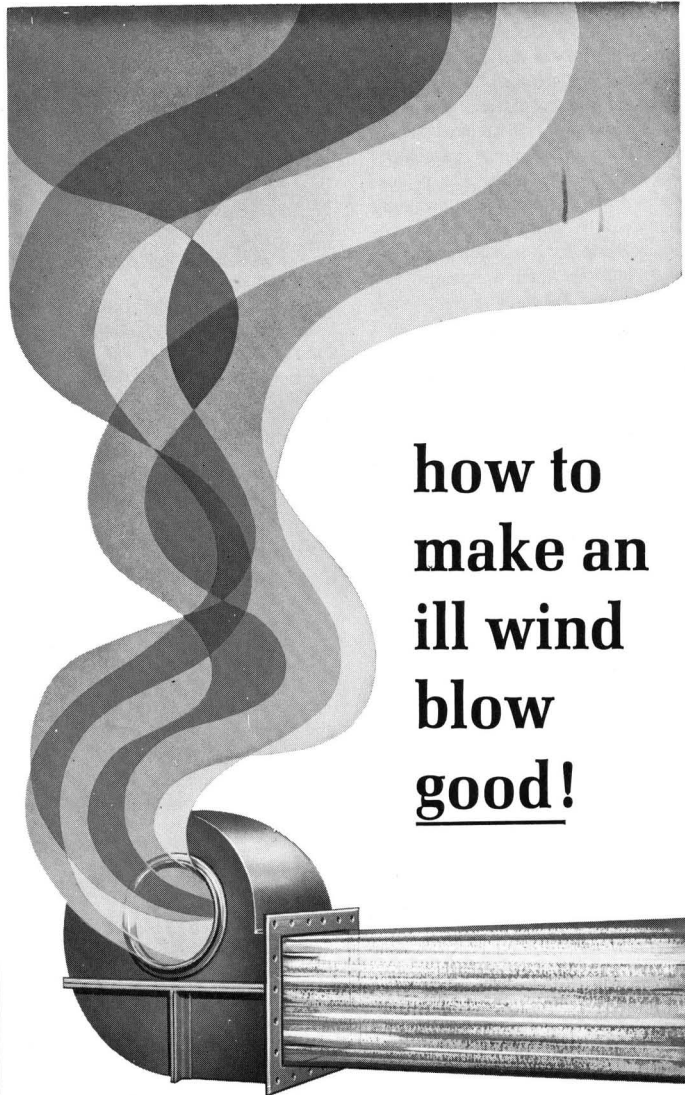


Lab-Line Instruments, Inc., plans to exhibit the Lectro-Mho-Meter Mark IV, a portable battery-operated conductivity instrument with exclusive, unbreakable conductivity cells. The Lectro Mho-Meter is an advanced, general purpose instrument. It is designed for long, trouble-free service in laboratory, plant, or field. The patented Sproule Conductivity Cells are virtually indestructible. They are molded of extremely hard, mica-impregnated, epoxy resin. Annular, impervious carbon composition electrodes are molded in flush with the tubular bore, allowing the cell to be scrubbed clean with a brush simply by removing the snap-in bottom plug.

**Lab-Line Instruments, Inc.,
Booth 61**

Monsanto Co., through its subsidiary, Biodize Systems, Inc., plans to exhibit two environmental control approaches for water and air pollution abatement. Monsanto Biodize Systems offers complete water pollution abatement facilities and services. This includes systems capable of removing BOD (organic pollutants) in excess of 90% from effluents of industrial and municipal installations, as well as deep well injection systems. Services include design, engineering, fabrication and construction of turnkey plants, with performance guaranteed. Capabilities of Biodize are illustrated at the Monsanto booth by an animated flow chart of a typical treatment plant, showing the flow of waste material through the biological system. Also on exhibition are cutaway models of the oxidation tank and the oxidation tower used in Biodize systems.

**Monsanto, Co.,
Booth 1**



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ill wind
blow
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When you find yourself eyeball to eyeball with a tricky air handling job — one involving extremely high or low temperatures, corrosives, abrasives or handling difficult materials — call in the Garden City experts.

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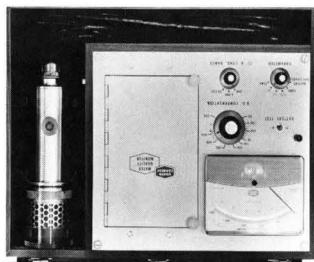


Monsanto also is displaying information on Brink Mist Eliminators, a series of mist eliminators designed to remove mist particles from process flow streams and stack effluents. The Brink Mist Eliminator will remove essentially 100% of all mist particles 3 microns or larger, and 99.8% of those smaller than 3 microns. On display is a comparative chart showing various classifications of particle sizes and equipment used to remove them.

**Monsanto Co.,
Booth 1**

Model 1100 Dissolved Oxygen Analyzer. This instrument, which measures the parts per million of dissolved oxygen in water or aqueous solutions, features a unique nonfouling probe. It requires no membrane or electrolyte gel used in all other instruments of this type, but, rather, uses an exposed thallium electrode which reacts with oxygen. The Model 1101 Dissolved Oxygen Analyzer has operated in raw sewage for months without maintenance or even cleaning of the probe.

**Pan/Tech Engineering Co.,
Booth 13**



Union Carbide Model 1400 Portable Water Quality Monitor. The Model 1400 is a compact, laboratory quality instrument for measuring five significant parameters of water quality—pH, dissolved oxygen, chloride ion concentration, conductivity, and temperature. The instrument and probe are contained in a rugged light weight carrying case, containing rechargeable nickel cadmium batteries, making it ideally suited for field or boat use. In contrast to old sampling methods, the Model 1400 offers a rapid, precise, in-situ measurement for spot testing areas of suspected pollution.

**Pan/Tech Engineering Co.,
Booth 13**

Union Carbide Model E Total Carbon Analyzer. This instrument is unique in that it is designed for continuous use in process for determining total carbon in an aqueous solution. It will automatically sample, make a measurement, and record it as quickly as once every two minutes. It is being used successfully to continuously monitor plant water and waste streams in order to detect spills, leakage in heat exchangers, and the like. Other features of the Model E Total Carbon Analyzer are: • The use of nitrogen as a carrier gas instead of high purity oxygen. • Automatic zero is provided to eliminate drift even when the instrument is exposed to wide ambient temperature changes. • Long-term operation without maintenance or attention.

**Pan/Tech Engineering Co.,
Booth 13**

Davis Instruments Air Pollution Monitor for Detecting Sulfur Dioxide. This instrument, designated as the Model 11-7000 Series described in Bulletin 5171, uses a simple, low maintenance electroconductivity bridge circuit to

Sample shown
10,000 times
actual size.

1 Micron

NEW AEROSOL SAMPLER

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With Thermo-Systems' Aerosol Sampler Model 3100, a sample of airborne particles can be evaluated without sampling bias due to particle size, shape or composition. Particles are deposited directly onto a variety of surfaces, including glass microscope slides and/or electron microscope grids.

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The sampler augments a growing line of aerosol research equipment, including the Whitby Aerosol Analyzer for indicating size distribution of submicron sized particles. Thermo-Systems also performs independent research in aerosol and fluid flow areas. We welcome your inquiry.

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High frequency flow measuring equipment for liquids and gases, aerosol particle analyzers and samplers.

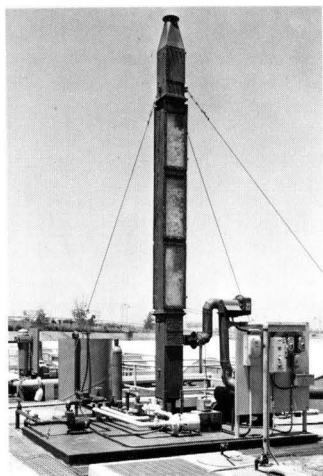
determine the quantity of sulfur dioxide in air. It can be provided as an automatic sampling monitor for continuous unattended use, or can be used as a portable instrument. The sulfur dioxide monitor can be used to provide an alarm when the measurement exceeds a preset limit, or it can be used with a recorder to provide a continuous record of air pollution.

**Pan/Tech Engineering Co.,
Booth 13**



Process Analyzers, Inc., makers of analytical process instruments, plans to exhibit the PAI Titrilog II, an automatic instrument for the determination of oxidizable sulfur compounds such as hydrogen sulfur, sulfur dioxide, mercaptans, thiophene, and organic sulfides and disulfides. This instrument offers an effective and economical means of continuously, automatically, and quantitatively recording the concentration of these compounds in the atmosphere, in gas streams, and in stack gases.

**Process Analyzers, Inc.
Booth 2**



U.O.P. Air Correction Division's Houston exhibit will feature its turbulent contact absorber, a wet scrubber which uses a mobile packing of hollow spheres to improve the contact between the gas and the liquid. It provides an efficient method for removing sticky particulates, or particulates which form a gummy slurry, from gas streams. Information on other types of wet scrubbers will be available, both with and without the use of mobile packing spheres. This unit on display will be a portable pilot

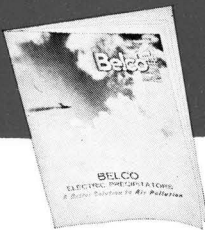
plant model. It is used to run tests on such parameters as mass transfer rates, liquor flow rates, effluent appearance, and the effects of particulate loading in the gas stream, before a final design for a permanent unit is settled.

**UOP-Air Correction,
Booth 4**

Texas Electronics, Inc., is showing a complete New Series 5000 Data Acquisition System; for sensing, transmitting, and logging such air pollution

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**BELCO Electric
Precipitators
are designed to
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any industrial
gas volume to
4,000,000 CFM**



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The Name to Remember!

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Processes for Removal of
Water and Air Pollutants



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Volume 3, Number 4, April 1969 351

data as wind speed and direction, ambient temperature, barometric pressure, rainfall, and the like. This new concept allows a custom designed system to be assembled from production elements, and it can be reconfigured or expanded at any time with no performance compromise or economic loss due to equipment obsolescence. For example, the output is a simple function of inserting the proper output module, and obtaining interface with any output device such as a printer, tape perforator, magnetic tape, or on-line to a computer.

**Texas Electronics, Inc.,
Booth 167**

A complete line of wind speed and wind direction recording systems are also available from Texas Electronics, Inc. There are six models available for direct analog recording of these parameters and descriptive literature on the Models 445, 446, 450, 451, 452, and 453 for the specifications on each system is available.

**Texas Electronics, Inc.,
Booth 167**



All solid state wind direction control and alarm system is being shown by Texas Electronics. A simple cam adjustment gives the choice of any control sector angle over a 345° range. A dependable solid-state time delay eliminates unnecessary on-off cycling of equipment. The delay period is dial adjustable between 1 and 50 seconds. The systems can be used to control high volume air samplers, factory fresh air venting systems, production processes such as incineration, or any

other sampling or control equipment. Optional equipment includes a control circuit running time indicator and/or control circuit closure indicator.

**Texas Electronics, Inc.,
Booth 167**

A wind speed control system which offers the user all solid-state controllers with dial adjustable set-points for the wind alarm point and time delay is offered by the company. Also available is descriptive literature on the WVT-3.

**Texas Electronics, Inc.,
Booth 167**

A wind speed control system for turning on or off other pieces of equipment in relationship to the wind speed is available from the company, which also supplies descriptive literature on the Model WVT-4.

**Texas Electronics, Inc.
Booth 167**

Texas Engineering Corp. plans to exhibit Yeomans Bros. Surface Aerators, both floating and pier mounted. These

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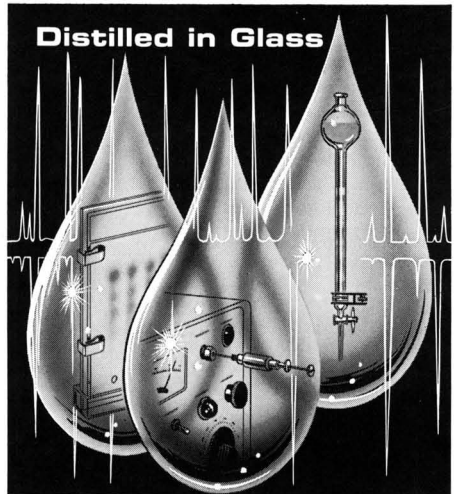


NATIONAL POLLUTION CONTROL CONFERENCE AND EXPOSITION

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Ask for Bulletin BJ-13K U.S. Agencies use F.S.S.

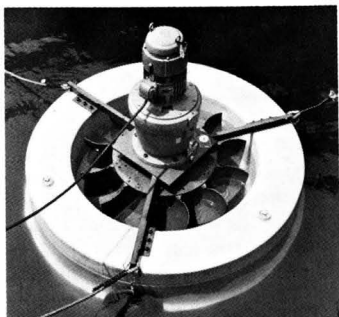
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photometric analysis



units are used in the control of water pollution for both industrial and domestic waste.

Texas Engineering also plans an exhibit on Aer-O-Flo Corp.'s package waste treatment plants. These units are for treatment of domestic waste and recently have been used in Texas for treating waste from schools, subdivisions, highway rest stations, recreation areas and industrial facilities.

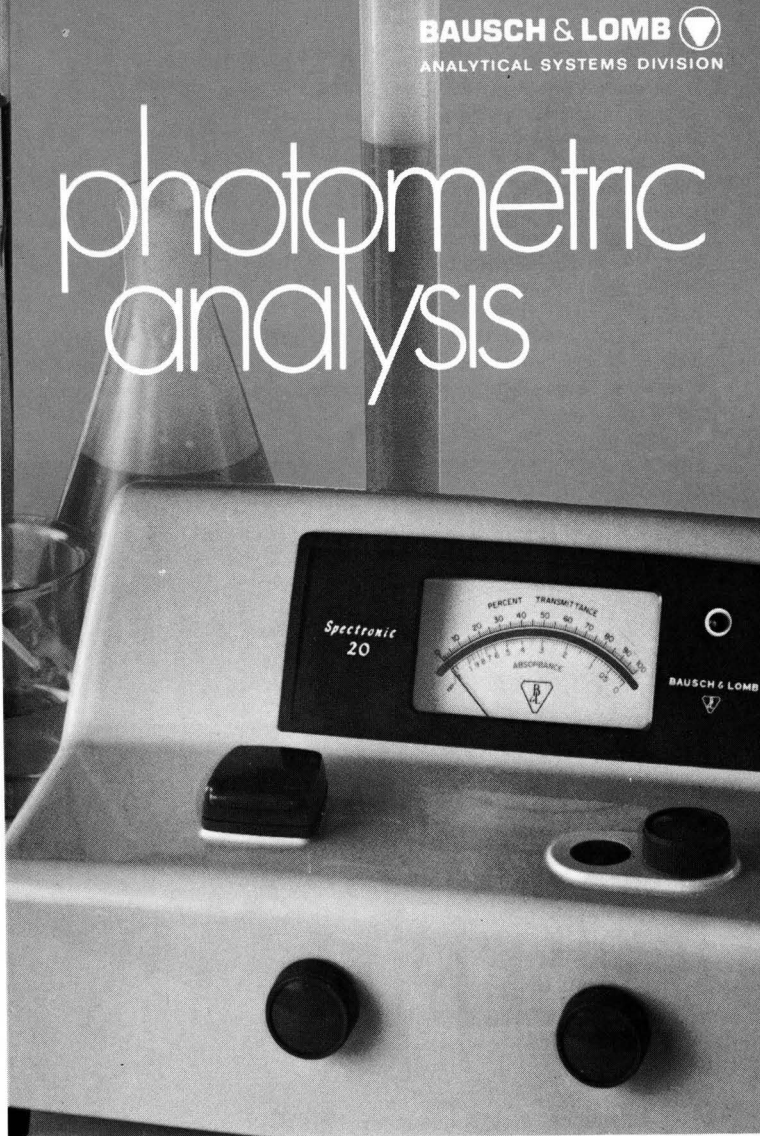
**Texas Engineering Corp.,
Booth 51**

Texas Gulf Coast industrial and municipal waste treatment plants are being offered a new service by Reliance Chemicals Corp. of Houston. Reliance has liquid bacteria cultures available for specific waste problems. These liquid cultures are delivered by tank truck and applied directly into the waste treatment plant or lagoon by highly trained personnel. By Reliance assuming the responsibility of application, regular plant employees are released for other important duties. Research has shown that the liquid biological treatment is many times more potent and starts to function six to eight hours sooner than the dry product. This service is supplied on a contract basis and at a reasonable cost.

**Reliance Chemicals Corp.,
Booth 50**



Completed in design and field tested in 1968, the Rocketdyne Organic Analyzer provides in one minute the organic content in water, an analysis



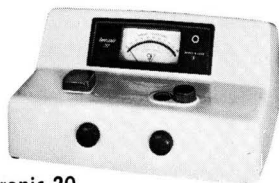
the ubiquitous Spectronic 20

It's everywhere . . . doing so many photometric tests faster and at a lower instrument cost per sample than any other make.

Over 60,000 Spectronic 20® users around the world have field proven and approved it. They know it has the wide continuous range of a spectrophotometer (340-950nm with optional

IR phototube and filter). It's the only instrument in its price class (as low as \$425) using B&L Certified Precision Gratings. And it has a long list of accessories to extend its versatility. You can even attach our Concentration Computer and get direct concentration readings.

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Spectronic 20

Circle No. 48 on Readers' Service Card

ATLAS ANALYZERS and CONTROLLERS

for

O_3

IDOMETRIC METHOD

SO_2

IDOMETRIC

and

COLORIMETRIC METHODS

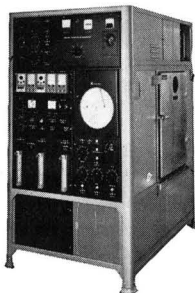
NO_2 and NO_x

COLORIMETRIC METHOD

for use wherever specific concentrations of gases are to be measured or controlled.

- New Schulze Methods of Analysis (Patented)
- Accurate analysis with high sensitivity
- Variations of 0.001 ppm/v can be detected
- Extremely fast response
- Built-in electronic calibration
 - Continuous recording
- Unattended weekly operation
 - Shipped complete, ready to operate

Write for complete technical information

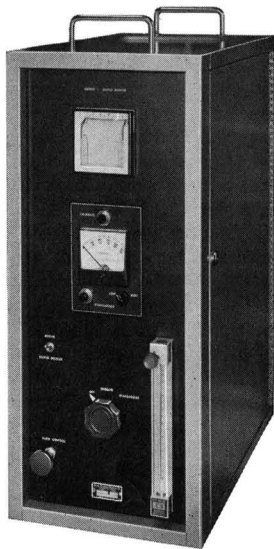


ATLAS 600 Series

Weather-Ometer® and test chamber

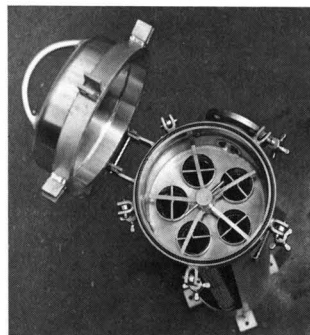
Atmospheric contaminants can be controlled automatically in combination with temperature and humidity with or without simulated sunlight. Basic models available with variations of controls.

For over 40 years manufacturers of testing machines for Weathering and Fading.



which formerly required five days. This compact instrument can be used for analysis of any aqueous system including raw municipal waste water, waste treatment effluents, industrial waste, and commercial process streams, and provides the information needed to make changes in the process to correct for changes in the effluent stream. The principal of operation of the instrument involves the direct pyrolytic fragmentation of the organic constituents of the water sample followed by detection of the total quantity of volatile organic fragments with a flame ionization detector. The advantage of the instrument over current measurement technology derives from coupling rapid analysis capability with specificity for organic carbon.

North American Rockwell Corp.,
Booth 52



Technical Fabricators, Inc., plans to show TC in-line filter, the head of which is the top loading tube sheet and hold-down assembly. This innovation in cartridge filters has eliminated all internal parts except the cartridge. Thus, center posts, spacers and gaskets used in conventional housings are not needed. TC filters are in service on polishing, pre-coating, bulk-loading, straining and air applications. In all of these, the advantages of easy cartridge access, quick media change, and low cost operation prevail. One special application regarding pollution control is the use of TC filters as final polishing filters for effluents to be pumped into deep-well disposal systems.

Technical Fabricators, Inc.,
Booth 64

Twistloc cartridge filters made of 100% PVC for handling corrosive chemicals will be shown by Technical Fabricators. The salient features of this rugged production sized filter are:

ATLAS ELECTRIC DEVICES COMPANY / 4114 N. Ravenswood Ave.
Chicago, Illinois U.S.A. 60613
Phone: 312-327-4520

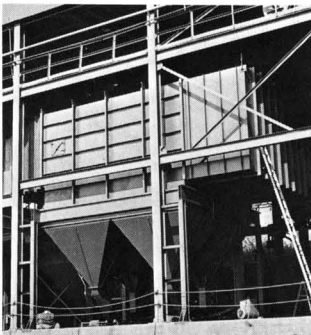
Circle No. 13 on Readers' Service Card

Tiger polypropylene filter cartridges providing separations in the range from 2-100 microns; swingbolt hold-down for easy access to the long length cartridges; heavy, outside, steel reinforcement; leak-proof O-ring seal, and the design features of operation to 35 p.s.i. at 170° F.

**Technical Fabricators, Inc.,
Booth 64**

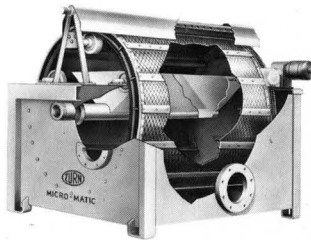
The new, unique Tech Fab Snap-Set centrifuge liner is available from Technical Fabricators. A complete line of polypropylene filter liners to cover virtually all centrifuge applications from the standpoints of retentive characteristics, cake discharge, and particle retention, are coupled with an extruded polypropylene backing screen by means of snap strips which are sewn to both the liner and screen. This new idea is particularly suited to handling ECM sludges because the low cost media and long life backing screen substantially reduce costs in this rough service application.

**Technical Fabricators, Inc.,
Booth 64**



Fly Ash Arrestor Corp., a subsidiary of Zurn Industries, Inc., will be exhibiting a working model of a high energy venturi scrubbing system illustrating the advantages of using a single supplier who manufactures all items of a scrubbing or collecting system. The company will also display a recently developed high efficiency T.A. Mechanical Collector which affords complete accessibility, high efficiency, long life, and installation flexibility. Fly Ash Arrestor Corp. manufactures scrubbers, collectors, ducts, dampers, fans, expansion joints, stacks and related elements on a turnkey, delivered, and erected basis.

**Zurn Industries,
Booth 30**



The Water Pollution Control Div. of Zurn Industries, Inc., will display an operating Micro-Matic Straining Sys-

tem. The new Micro-Matic Straining Systems are engineered for use in removing small particles from plant influent, effluent or in process lines to meet specific demands in steel mills, paper mills, textile and woolen mills, food processing or canning plants, meat processing plants, tanning plants, municipal disposal plants, raw river and cooling tower water, sugar industry, grain industry, pigment industry and chemical industry. Micro-Matic Straining Systems may be used wherever small particles are to be removed

A Revolutionary New Concept!

INSTANT ODOR ABATEMENT

Rhodia's Chemscreen® System **instantly** eliminates the toughest odor problems arising from waste disposal plants, feed lots, pulp and paper mills, chemical processing plants, stock yards, petroleum plants, canneries, fertilizer plants, etc.

NO INVESTMENT in capital equipment required

We can prove it! Ask for a demonstration right on your own premises. No obligation!

Write for Name of Local Representative



RHODIA INC.

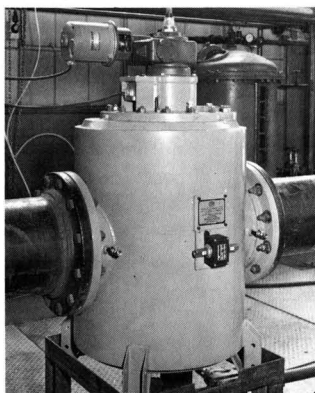
600 MADISON AVE.
NEW YORK, N.Y. 10022
PHONE (212) 753-4850

and an adequate flow rate is to be maintained in a nonpressurized liquid flow.

**Zurn Industries,
Booth 30**

Erie City Iron Works, a subsidiary of Zurn Industries, Inc., will be exhibiting the unique design waste heat energy recovery system now being offered to the process industries for combatting air pollution. Erie City Waste Heat Recovery Systems are designed to control air pollution caused by high-temperature gases which escape through the stacks of smelters, acid plants, power plants, and petroleum industries. Left uncontrolled, these waste gases damage human and vegetable life, and in combination with other gases in the atmosphere contribute to various smog conditions. The system basically entraps these valuable sources of energy and uses them as primary fuel in a combustion chamber. When main fuel is insufficient to produce the required steam output, auxiliary fuels are fired singly or in combination to assure complete combustion. Open pass convection design utilizes maximum boiler heating surface with low gas velocity to prevent tube erosion from dirty gases. All waste gases are transformed into useful energy for generating steam with the proper application.

**Zurn Industries,
Booth 30**



The Water Pollution Control Div. of Zurn Industries, Inc., will exhibit the Zurn Strain-O-Matic, an automatic, self-cleaning straining system, completely automated for continuous or intermittent operation. Ideal for protection of vital metering, measuring, and pumping equipment used in cool-

ing, air conditioning, quenching, descaling or other process use; in soluble oil or emulsion lines; fuel oil, jet fuel and gasoline transfer lines; lube oil lines; paper and paper mill processes; and in sugar and oil refineries or other plants handling process liquors; and to insure continuous, clean flow to critical components. Available complete with electro-mechanical master control console.

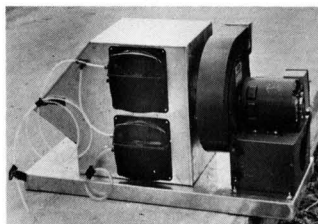
**Zurn Industries,
Booth 30**

Westvaco will provide information on its Waste Water Treatment Consulting Service. This is a specialized consulting service which, first, explores the potential for using an activated carbon adsorption system at an industrial installation (this initial part of the service is offered at no cost or obligation). Then, if carbon appears feasible, Westvaco provides the necessary skills, facilities, pilot plant operations and experienced consultation with the clients' engineers to design and construct an efficient system at the installation. Westvaco has had more than 45 years of experience with activated carbon and is expert in the field of adsorption on activated carbon.

**Westvaco Corp.,
Booth 66**

Westvaco's Nuchar activated carbon includes a complete line of activated carbon, both powdered and granular grades, for both liquid and gas phase applications. Nuchar granular active carbon is now shipped in a new "bags-in-a-box" package. This is a telescoping box containing the bags of Nuchar on a pallet. It saves space by allowing skids to be stacked three pallets high; and it protects against spillage. Nuchar granular active carbon provides a wide range of grades and mesh sizes.

**Westvaco Corp.,
Booth 66**



In assisting plant management to operate within an atmosphere of better and more pleasant community rela-

tions, the Chemscreen system offers the following major advantages: • Available on a loan basis. Eliminates investing in capital equipment. • Isolates plant malodors from the community. • Installation proven, fully integrated system, employing Rhodia vaporizer equipment in conjunction with scientifically formulated chemical counteractants which effectively neutralize specific industrial malodors. • It's efficient, effective, economical, and easily maintained.

The Chemscreen system for odor control is based on the principle that only gases can register an odor impression on the nose. Consequently, malodors are noticed only to the extent that they are gases mixed with the air that we breathe. Thus, the only really effective way to counteract malodors is by using chemical counteractants that are also in a gaseous state. Using this principle, the Rho-D-Air equipment acts to convert Rhodia's chemical counteractants into a gaseous state in continuous and predetermined quantities. After vaporization, the counteractants are induced through a custom-designed duct system, and released into the air from regularly spaced orifices in the ducts. This process creates a chemical air screen through which malodors must pass and be neutralized before continuing on into any nearby residential area.

**Rhodia, Inc.,
Booth 209**



Delta Scientific Corp. has announced a new line of water monitoring instruments, many of which will be on display at the Houston exposition. Included in these are the new Model 75 and 85 dissolved oxygen meters for rapid oxygen analysis of potable and industrial process water, sewage, and

BROWNBIT IN NINETEEN MONTHS . . . from groundbreaking to paper production: Southland Paper Mills' new plant at Sheldon, Texas.

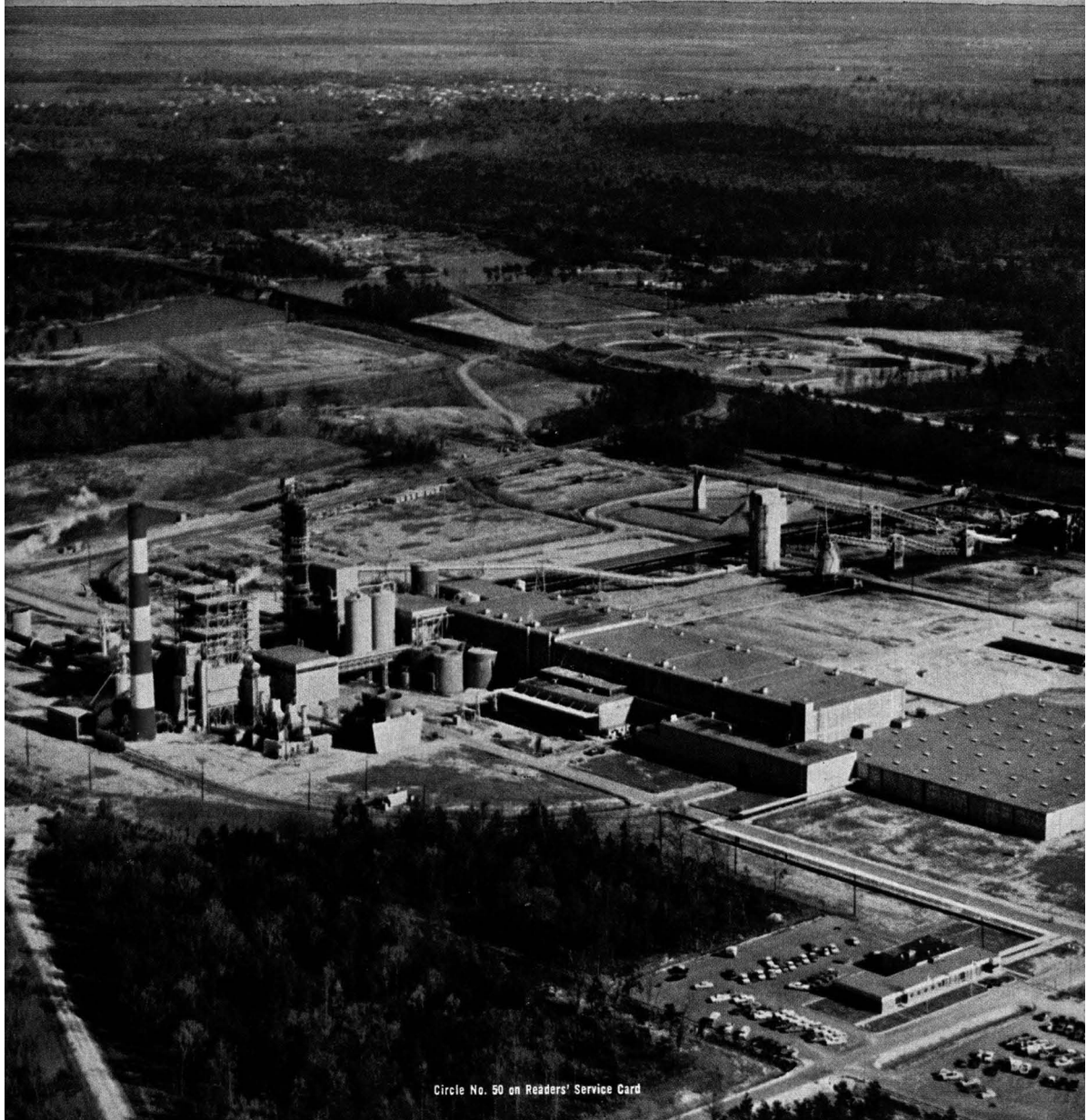
An unusual feature of this job is the waste treatment plant, designed and built by Brown & Root. The plant site is 12½ miles from the Houston Ship Channel, the designated water outlet. Solving the problem efficiently and economically, Brown & Root installed 66,000 feet of 42-inch concrete pipe requiring 1200 feet of tunneling through industrial and residential areas, rice fields and forests, highways and bayous, to the outlet. On budget, on time—the Brownbilt way. (For detailed information on our capabilities, write on your corporate letterhead for our Pulp and Paper Brochure).

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Brown & Root, Inc.
Engineers / Constructors / Houston, Texas
P.O. Box 3 / (713)-672-3011 / Cable: Brownbilt
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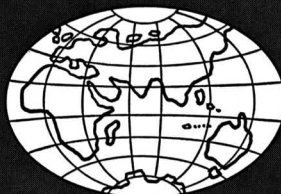
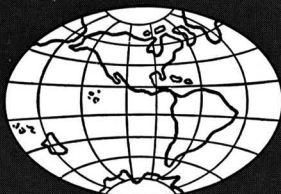


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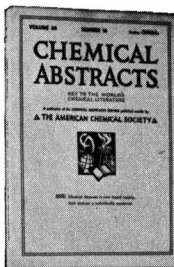
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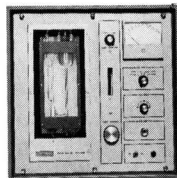
Beckman

INSTRUMENTS, INC.
PROCESS INSTRUMENTS DIVISION
FULLERTON, CALIFORNIA • 92634

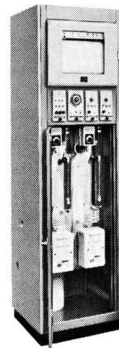
INTERNATIONAL SUBSIDIARIES: AMSTERDAM; CAPE TOWN; GENEVA; GLENROTHES, SCOTLAND; LONDON; MEXICO CITY; MUNICH; PARIS; STOCKHOLM; TOKYO; VIENNA



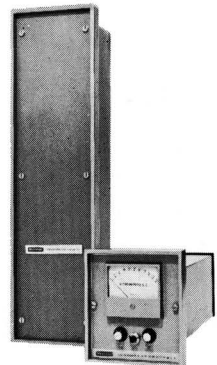
Mobile Monitor: monitors all primary air contaminants. Ask us about our lease plan.



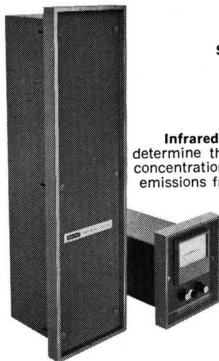
SO₂ Analyzer: analyzes and records trace concentrations of SO₂ in ambient air.



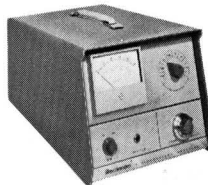
Acrylizers: monitor and record low concentrations of oxidants and oxides of nitrogen in the atmosphere.



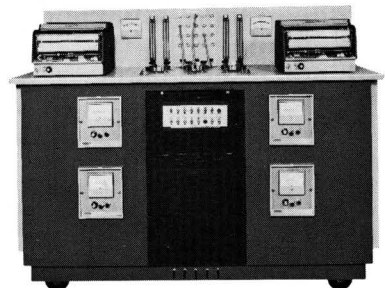
Ultraviolet NO₂ Analyzer: measures NO₂ emissions in automotive exhaust.



Infrared Analyzers: determine the atmospheric concentration of CO or SO₂ emissions from a source.



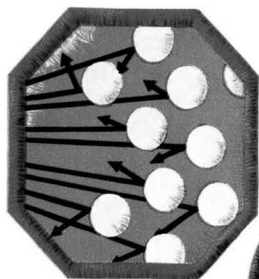
Hydrocarbon Analyzers: detect and measure trace concentrations of hydrocarbons in the air.



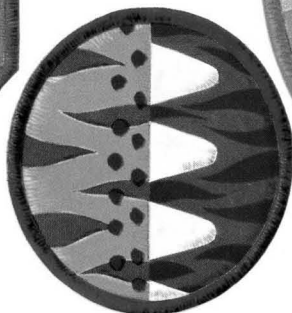
Vehicle Emissions Analysis System: analyzes vehicular exhaust emissions.

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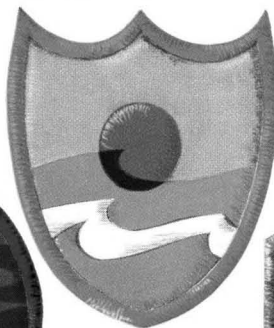
THE UOP CORPS OF ENVIRONMENTAL ENGINEERS IS WINNING THE WAR ON POLLUTION



UOP AIR CORRECTION
DIVISION



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UOP WATER SERVICES
DIVISION



UOP PROCESS DIVISION

UOP has four divisions marshalled to attack pollution on several fronts.

In air correction, this is the one company offering the broadest selection of systems and equipment, in world-wide use. **UOP Air Correction Division** relieves you of the technical burdens of air pollution control, and provides you with the best equipment at the most economical cost. It offers eight basic types of control equipment, plus a complete range of services, from stack gas analysis to field start-up.

To deal with water management problems, **UOP Johnson Division** manufactures screens and filtering equipment. These are widely used in water treating, water conditioning, slurry screening, water filtration, de-watering, odor, color and suspended solids removal. There are many other anti-water pollutant uses for Johnson-brand screens, including disposal well applications.

A variety of water treating chemicals, for both process and make-up, are offered by **UOP Water Services Division**. They are used for treating algae and slime, preventing scale and corrosion, providing oxygen scavenging, sludge conditioning, and foam suspension.

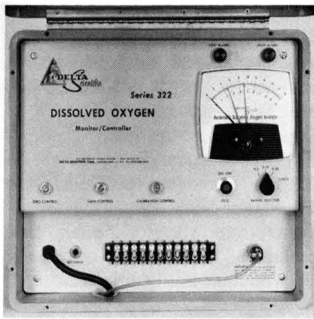
UOP works to alleviate pollution in many ways. One new UOP refining process is an efficient and economical method of desulfurizing heavy fuel oil, so that fuel oils burn cleaner. Another new development from **UOP Process Division** is an effective counter-measure against water contamination. It eliminates problems caused by detergents that do not break down by bacterial action, by improving biodegradable detergents.

It is easy to see how UOP's environmental engineering competence can help you with your air and water pollution problems. And new concepts are on the way. Universal Oil Products Company, 30 Algonquin Road, Des Plaines, Illinois 60016, U.S.A.

better ideas from 

Visit us at the Houston Pollution Control Expo—Booth 4, UOP Air Correction/Booth 65, UOP Johnson

Circle No. 60 on Readers' Service Card



factory waste. Both models make use of a unique patented membrane probe which eliminates the need for Winkler titrations; model 85 has a built-in thermistor. A dissolved oxygen meter, the 322-P, is designed for continuous measurement of dissolved oxygen in aeration tanks, ponds, or streams, and automatically controls accessory equipment for optimum BOD removal efficiency. The unit also can be used in pollution control, fisheries studies, and

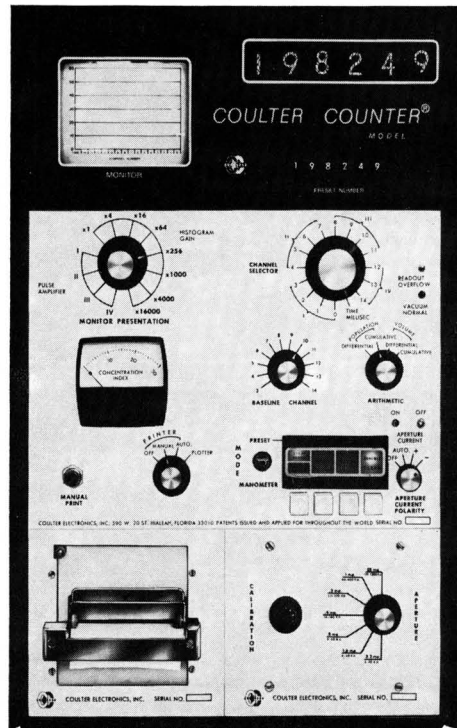


to monitor the oxygen content of cooling water for power plants and atomic reactors. Another new line, on display will be the series 3000 self-powered analyzer/recorders, for continuous monitoring of such parameters as pH, dissolved oxygen, conductivity, turbidity, temperature, and oxidation-reduction potential. Models are available with dual channels. Other major displays will be the Model 50 portable laboratory for water and waste testing, that uses a photometer to perform 20 different tests; and the new series 260-1 analysis systems for individualized water and waste analysis.

Delta Scientific Corp.,
Booth 82

take T* and see...

Who else gives you complete particle size distribution in only 20 seconds?



*The Coulter Counter® Model T

The new Model T Coulter Counter® is all action. Capable of counting air pollutants, pesticides, emulsions, foods, sediments, metals, pigments, pharmaceuticals, hydraulic oils, crystals and other fine particles from 0.5 to 400 microns.

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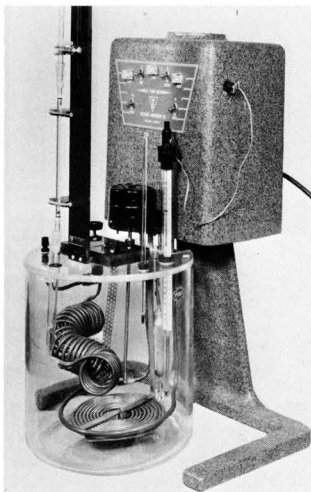
A Division of Coulter Electronics, Inc.

590 West 20th St., Hialeah, Florida 33010/305-887-8131



Patents issued/or pending for Coulter Electronics products throughout the world.

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Wilkins-Anderson's Waco air analyzer, to be on display in Houston, is an automatic colorimetric analyzer for continuously monitoring and recording the concentration of SO_2 or NO_2 in ambient air that utilizes the West-

Gaeke method for SO_2 . Conversion to NO_2 or NO_x is simple and rapid. A dual beam colorimeter, with automatic zero and calibration verification, is stable and accurate over extended runs. The unit uses a Gast pump, Brooks rotometer, and Swagelok fittings, and can convert from SO_2 to NO_2 or back again in 10 minutes, according to the company. The instrument has a variable range of from 0.5 to 4.0 p.p.m. full scale, and up to 10 p.p.m. with a change in rotometer. Conversion kits are available for NO and total oxides of nitrogen. Also to be displayed is the Waco calibrations of SO_2 or NO_2 monitoring instruments. It consists of a controlled water bath, refrigerated for operation down to -10°C ., and associated glassware and control valves. When used with cylinder nitrogen or air and a microdiffusion tube, calibrating gases of known concentration can be produced.

**Wilkins-Anderson Co.,
Booth 63**

WACO Calibration Bath—Model 311—A self contained unit for running dynamic calibrations of monitoring instruments for SO_2 or NO_2 . Consists of a closely controlled water bath, refrigerated for operation down to -10°C ., and associated glassware and control valves for regulating flow. Used with cylinder nitrogen or air, and an O'Keefe Micro Diffusion Tube, calibrating gases of constant known concentration can be produced.

**Wilkins-Anderson Co.,
Booth 63**

Howell Engineering Co., a Houston, Tex., firm that specializes in the design of steam generation and fuel combustion equipment, will have an exhibit centered on the company's design of a waste incinerator/boiler at Merichem's Houston plant. This boiler originally conceived for the conversion of waste pitch, but the final design included provision for combustion of all noxious fumes, waste products, and air pollutants of the plant and

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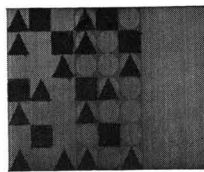
SPRAYING SYSTEMS CO.
3202 Randolph Street, Bellwood, Illinois 60104

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We rewrote the book-

Microbiological
Analysis of
Water



MILLIPORE

Describes improved procedures for the detection of fecal coliform, a new rapid screening method for algae, more complete data on total coliform analysis and a new section on pathogens, in addition to a detailed description of the Millipore method (an APHA standard) for the analysis of water and waste water. Millipore Corporation, Bedford, Mass. 01730.

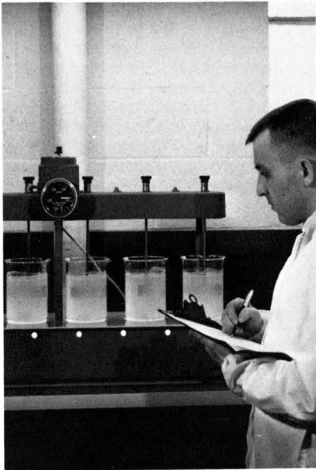
MILLIPORE

systems for analyzing and processing fluids

Circle No. 33 on Readers' Service Card

utilization of the waste heat for steam generation. Information will be available on the range of products and services that Howell handles, including packaged and portable water tube boilers, fire tube boilers, gas and oil combustion equipment, combustion control equipment, glass and ceramic coated pipe linings, and packless expansion joints.

**Howell Engineering Co.,
Booth 31**



Phipps and Bird, Inc., will display the Biomand 1, an automatic respirometer continuously recording, in a controlled environment, the oxygen demand related to the nature of biochemical materials in waste water. The applications of the instrument in water pollution control include: plant control of waste water treatment processes, by determining oxygen utilization at various stages of treatment; treatability studies; aeration efficiency studies; and correlation of oxygen demand with 5-day BOD results. Major features of the instrument are that it utilizes large sample size, compared with the dilution technique for BOD, and the sample is not destroyed in the analysis. It provides a rapid, complete oxygen demand record, and changes in demand rate are immediately recorded. The instrument accepts a variety of sample sizes, and is capable of continuous temperature control with variable monitoring. Also part of the Phipps Bird display will be a dipper type sampler for collecting samples of sewage, industrial waste or other liquids.

**Phipps and Bird, Inc.,
Booth 34**

WE CLEAN AIR

Dust Control?
Air Abatement?

Fume Control?
Air Pollution Control?

HANK FRIEDRICH — MARKETING
ROGER BROOKMAN — RESEARCH
CHUCK MAISCH — APPLICATION ENGINEERING

These men could care less what you call it.

Today it's called Environmental Science Technology. Hank Friedrich, Roger Brookman and Chuck Maisch know it's still one of the most serious problems facing industry. This team of experts has applied over 60 years of experience to its solution. They're all on one team. Exclusively at Dustex.

Here are three good reasons why your dust collection equipment needs should involve Dustex. There are many other reasons and they all center around experience.

So, the next time you become involved in a dust collection problem, call a Dustex representative; or call Dustex direct. A visit to our plant would enable you to see, firsthand, our manufacturing capabilities and our laboratory test facilities as well as meet our team of experts.

When dust collection or product recovery becomes your concern either through law, public pressure or your own corporate needs . . . turn to Dustex for the solution.

Inductaire Fabric Filter Installation: These high efficiency collectors effectively control airborne dust particles. Write for descriptive literature or ask for a Dustex air pollution control expert to stop in to see you soon.

DUSTEX

Division

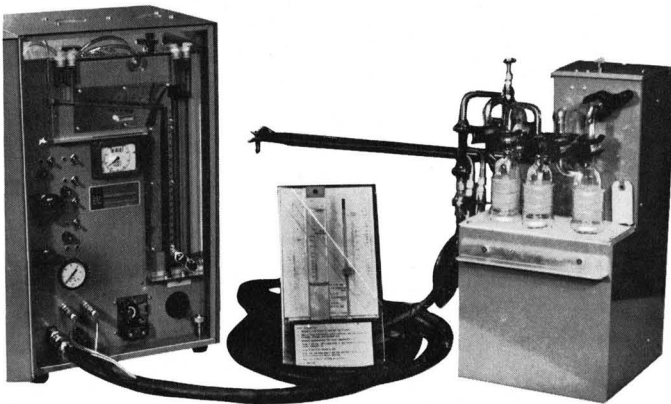
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Portable stack sampler measures stack gases and solids at low cost



Now you can easily—and at low cost—collect and measure solids, mists and gases directly from your stacks with Research Appliance's new portable Staksamplr.™ Developed and used successfully by the National Center for Air Pollution Control, this new sampler provides isokinetic collection of pollutants from most chemical and combustion processes. With a trained two-man crew, it can provide three samples per eight-hour day.

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National Pollution Control Conference and Exposition

AIR POLLUTION PANEL

Tuesday, April 22, 1969

9:00 AM

KEYNOTE ADDRESS

Dr. Walter Hibbard, Vice President, Research and Development, Owens-Corning Fiberglass, Granville, Ohio

10:00 AM to 12:00

PANEL

Chairman, Samuel Thomas, Director of Environmental Control, Owens-Corning Fiberglass, Granville, Ohio

Dr. John Middleton, Commissioner, Federal Air Pollution Control Administration, Arlington, Virginia

Robert G. Lunche, Air Pollution Control Officer, Los Angeles, California

W. K. Hunter, Vice President, Universal Oil Products, Darien, Connecticut

12:00

LUNCHEON

Mayor Samuel W. Yorty, Los Angeles, California

2:00 PM to 3:30 PM

TECHNICAL SESSION I

Chairman, W. K. Hunter

Petroleum—Dr. Charles E. Moser, Assistant to Vice President of Research, Texaco, Beacon, New York

Chemical—Al C. Faatz, Foster-Wheeler Corporation, Livingston, New Jersey

Transportation—Dr. Stanley M. Pier, The Pace Company, Houston, Texas

2:00 PM to 3:30 PM

TECHNICAL SESSION II

Chairman, Industry Representative

Power—J. F. McLaughlin, Union Electric Company, St. Louis, Missouri

Paper—James E. Roberson, J. E. Sirmine Company, Greenville, South Carolina

Heavy Industry—George H. Todd, Assistant to the Group Vice President, Armco Steel Corporation, Washington, D. C.

3:45 PM to 4:45 PM

PANEL DISCUSSION

"Accomplishments for the Past Year and Expectations for the Coming Year"

Chairman, R. L. Chass

Petroleum Power

Chemical Paper

Transportation Heavy Industry

WATER POLLUTION PANEL

Wednesday, April 23, 1969

9:00 AM

KEYNOTE ADDRESS

B. Q. Welder, Director of Marketing, Calgon Corporation, Pittsburgh, Pennsylvania

10:00 AM to 12:00

PANEL

Chairman, E. G. Paulson, Process and Waste Water Manager, Calgon

Corporation, Pittsburgh, Pennsylvania

Joe Moore, Commissioner, Federal Water Pollution Control Administration, Washington, D.C.

Samuel S. Baxter, Water Commissioner, Philadelphia, Pennsylvania

H. R. Sontag, Plant Manager, Good-year Tire and Rubber Company, Beaumont, Texas

Dr. H. Nugent Myrick, Assistant Professor, Cullen College of Engineering, University of Houston, Houston, Texas

2:00 PM to 3:30 PM

TECHNICAL SESSION I

Chairman, Joe Moore

Petroleum—Oliver J. Zandona, Ashland Oil & Refining Company, Ashland, Kentucky

Chemical—H. Clark Carbaugh, Manager of Consulting Services, Environmental Services Division, Hercules Incorporated, Houston, Texas

Transportation—James G. Moffitt, Manager of Operations, Marine Department, Humble Oil and Refining Company, Houston, Texas

2:00 to 3:30 PM

TECHNICAL SESSION II

Chairman, James Tucker, Brown & Root, Inc., Houston, Texas

Power—D. T. Hedden, Chief, Environmental Science Services, Northeast Utilities, Hartford, Connecticut

Paper—W. C. Kimbrough, Rust Engineering, Birmingham, Alabama

Heavy Industry—Earl W. Mallick, Vice President, South, U. S. Steel Corporation, Fairfield, Alabama

3:45 PM

PANEL DISCUSSION

"Accomplishments for the Past Year and Expectations for the Coming Year"

Chairman, Samuel Baxter

Petroleum	Power
Chemical	Paper
Transportation	Heavy Industry

7:00 PM

BANQUET

State Governor

SOLID WASTE PANEL

Thursday, April 24, 1969

9:00 AM

KEYNOTE ADDRESS

Richard L. Cheney, Executive Director and General Manager, Glass Container Manufacturers Institute, New York, New York

9:30 AM to 11:30 AM

PANEL

Chairman, Leo Weaver, Manager, Institute of Solid Waste, Washington, D.C.

Richard Vaughn, Director of Bureau of Solid Waste Management, Environmental Control Administration, Rockville, Maryland

Frank Bowerman, Duarte, California

John Vanderveld, President, National Disposal Service, Barrington, Illinois

12:00 AM

AWARDS LUNCHEON

U. S. Senator

1:30 PM to 3:00 PM

AN APPROACH TO ENVIRONMENTAL MANAGEMENT

Chairman, Frank Sebastian, President, BSP Corporation, San Francisco, California

Robert J. Sherwood, Manager, Environmental Marketing, BSP Corporation, San Francisco, California

L. Gene Suhr, Project Engineer, Cornell, Howland, Hayes & Merryfield

Dr. Robert B. Dean, Chief, Ultimate Disposal Research Activities, AWTB, FWPCA, Cincinnati, Ohio

Bertram C. Raynes, Vice President, Rand Corporation

3:15 PM to 4:45 PM

SUMMARY SESSION

Harry Henkel, Senior Engineer, E. I. DuPont, Victoria, Texas; Texas Director of Water Pollution Control Federation

John S. Lagarias, President, Resources Research, Inc., Reston, Virginia; President, Air Pollution Control Association

U.S. Representative—Policy Statement

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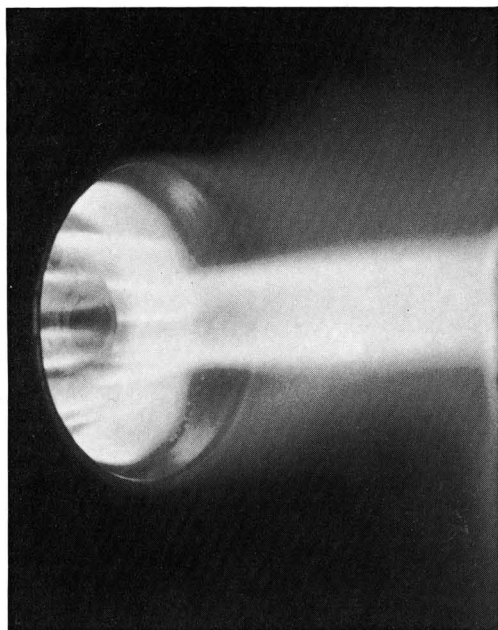


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Variation in the Composition of Brine from the Sylvania Formation near Midland, Michigan

G. C. Egleson¹ and C. W. Querio

The Dow Chemical Co., Midland, Mich. 48640

Brines from 51 wells in The Dow Chemical Co.'s brine field near Midland, Mich., were analyzed for major and minor components. The Ca, Mg, Na, Sr, Cl, and Br ions, which make up the bulk of the total dissolved solids in the brine, are fairly constant throughout the field, varying less than 10% above or below the mean. Another suite of ions—K, B, NH₃, Rb, Li, and I—varies from 25 to 50% above and below the mean. Analyses of trends and relationships among the ions indicate that dolomitization probably is the mechanism most important in determining the Ca, Mg, and Sr content of the brine; that the relative amounts of Li, I, and NH₃ are too high for them to have been derived directly from sea water evaporation; and that many interrelationships among the minor ions as yet are not well defined.

The Dow Chemical Co. operates a brine field near Midland, Mich., to obtain brine for the extraction of bromine and other chemicals. The area encompassed by imaginary lines connecting the outermost wells in the field is some 400 square miles, though brine is withdrawn from only a part of this area.

Brine samples from 51 wells in the field were analyzed for both major and minor components, and the results examined to see what trends and relationships could be discerned among the various ions.

Average Ion Relationships

The arithmetic average for the analytical data of the 51 wells was computed. The results are shown in Table I, and the concentration of the individual ions is compared to that in sea water. If appreciable bioconcentration has not occurred, bromine—since it does not form minerals—should be one of the better indicators of the degree of sea

water concentration, assuming that the brine is an altered sea water type. (Some bromine is lost to halite and other precipitated salts, but this is rarely more than 5% of the total.) In the case of the Sylvania brine, the concentration ratio for bromine as compared to sea water is about 43. The individual calcium and magnesium ratios are of little consequence, but the sum of these two calculated as equivalent or original magnesium gives a concentration ratio of 42, very close to that of bromine. This indicates that dolomitization has played an important part in the alteration of the brine.

The very close agreement of degree of concentration of sea water as calculated from bromine and total equivalent magnesium is fortuitous rather than necessary. In several instances in the geologic column in Michigan are found mixtures of dolomite and anhydrite which indicate that

Table I. Concentration Ratios of Brine Components

Component	Average Concentration, P.P.M.		Concn. Ratio ^a	Excess Factor ^b
	In Sea water	In Sylvania brine		
Ca	390	72,200	142	—
Mg	1300	9,200	7.1	—
Mg ^c	1300	53,100	41.9	0.98
Br	65	2,790	42.9	1.0
Sr	8	3,100	388	9.0
SO ₄	2580	44	0.02	—
K	370	8,000	21.6	0.5
B	4.5	333	74	1.7
Rb	0.12	15	125	2.9
Li	0.17	58	340	7.9
I	0.05	34	680	15.9
NH ₃	Low	398	High	High

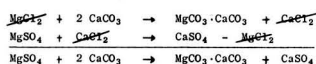
^a Amount in brine/amount in sea water.

^b Concentration ratio of given component/concentration ratio of bromine.

^c Magnesium equivalent of calcium plus magnesium in brine.

¹ Present address, Dow Chemical Co., P. O. Box 22468, Houston, Tex. 77027.

sulfate can be removed from brines during dolomitization as well as by bacterial reduction.

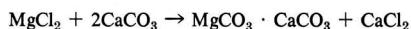


Theoretically, up to almost one third of the magnesium in sea water bitterns could be removed in this way. Other factors that may affect the total equivalent magnesium-bromine ratio are the influx of calcium and magnesium from continental drainage, the formation of magnesium-containing minerals, the addition of bromine by bioconcentrators, and the inclusion of bromine in precipitated salts and its re-solution therefrom.

The total equivalent magnesium, 53,100 p.p.m., divided by the bromine, 2790 p.p.m., equals 19. This is very close to the present-day sea water value of 1300 p.p.m. of magnesium divided by 65 p.p.m. of bromine or 20. Anderson *et al.* (1966) observed a linear relation in a log Ca^{+2} vs. log Br^- plot for subsurface Cl^- waters. They used as a reference point Ca^{+2} vs. Br^- in sea water. Since by far the greater part of the calcium in sea water precipitates during the early stages of evaporation as either calcium carbonate or calcium sulfate, a better reference would be the calcium equivalent of magnesium in sea water vs. bromine, and this point, $1300 \text{ Mg} \times (40 \text{ Ca}/24.3 \text{ Mg}) = 2140 \text{ Ca}$ vs. 65 Br falls very nearly on their plot, indicating that magnesium in the brines has exchanged for calcium in a 1 to 1 mole ratio.

Strontium, as shown later, is associated with the major ions. Its presence can also be explained by dolomitization. Kinsman (1965) says, "When carbonate sediments are dolomitized it (celestite) is abundant, being a by-product of the replacement of high strontium-bearing aragonite (up to 7000 p.p.m. strontium) by relatively low strontium-bearing dolomite (1000 p.p.m. Sr)."

This indicates that in the dolomitization reaction,



the strontium associated with both moles of CaCO_3 (or at least more than 6/7 of it) is released. Then in sulfate-free bitterns, SrCl_2 would be formed instead of celestite and would remain in the brine. The ratio of calcium to strontium in the Sylvania brine approximates that which would be expected from this mechanism.

Potassium in the Sylvania brine, as in most natural brines, is depleted relative to sea water. Most of that which is missing from the brines has undoubtedly been incorporated into clays and shales, and in some instances, perhaps, precipitated in potash salts.

The relationships and interrelationships among the minor ion concentrations are more complicated. It is highly unlikely that lithium, iodine, and ammonia at the ratios observed could accumulate by the simple evaporation of sea water. Collins and Egleson (1967) speculated that iodine in brines in excess of that from simple evaporation was derived by leaching of the remains of bioconcentrators. This is also the probable source of iodine in the Sylvania brine, as well as a small fraction of the bromine.

Ham *et al.* (1961) provide an inorganic mechanism by which boron from sea water might be redistributed to the extent observed in Sylvania brine. They state, "The average anhydrite contains 232 p.p.m. B_2O_3 Solution of

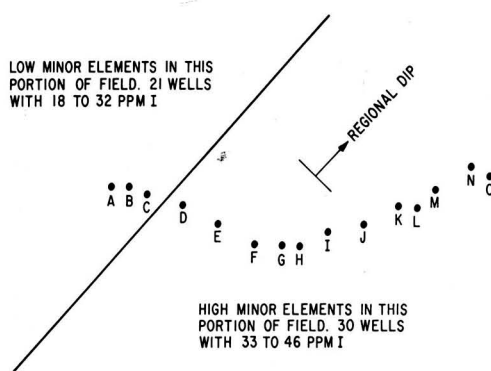


Figure 1. Spatial arrangement of selected wells
Cross section A-O, Figures 2 and 3

anhydrite during weathering results in the simultaneous formation of gypsum, but . . . the gypsum accepts only 40 p.p.m. B_2O_3 , leaving in solution nearly 200 p.p.m. B_2O_3 from the original anhydrite."

Speculations about the great excess of lithium indicate that it must have in some way been derived from the continent rather than from sea water.

Spatial Relationships

Geographic. Map plots of several of the minor ion concentrations noted that the minor ion concentrations tend to increase more or less regularly in a given direction. Figure 1 illustrates one such plot. The iodine contents at wells A, B, and C are 32, 30, and 31 p.p.m., respectively. As indicated in Table II, the concentration at the other 18 wells to the left of the line through Figure 1 is 32 p.p.m. or less, the lowest being 18 p.p.m. Brine from well D contains 35 p.p.m. of iodine and the iodine increases to a maximum of 46 p.p.m. at well L. Table II shows that all 30 of the wells to the right of the line through Figure 1 have 33 p.p.m. or more, the highest being 46 p.p.m. Thus, a single straight line can be drawn across the field in such a manner that all of the wells with iodine concentrations less than 33 p.p.m. are in one portion of the field, and all of the wells with iodine concentrations greater than 32 p.p.m. are in the other portion. In this way two sets of data were generated for comparison.

Table II shows the range of concentrations and the average concentration of the various brine components in each portion of the field. The ratio of the averages is also shown in the last column. Table II points out that the major components— CaCl_2 , MgCl_2 , NaCl , and SrCl_2 —have essentially the same range of concentrations and the same average concentration in both portions of the field. On the other hand, the range of concentrations of the minor components—B, NH_3 , Rb, LiCl, I, and KCl—do not overlap appreciably and their average concentration is significantly higher in one portion of the field than the other. This suggests that the observed major ion concentrations are the result of simple, widespread, consistent processes—i.e., sea water evaporation and dolomitization—while the minor ion concentrations are the result of more complicated, local, variable processes—e.g., re-solution of precipitated salts, leaching of organic debris, and interaction with drainage and sediments from the continent.

Table II. Minor Element Variation in Brine from the Sylvania Formation near Midland, Mich.

Item	Low Trace Elements (21 Wells)		High Trace Elements (30 Wells)		Ratio High/Low
	Variation	Average	Average	Variation	
Sp. gr.	1.2859-1.2942	1.2915	1.2913	1.2788-1.2959	1.00
CaCl ₂ , %	19.96-20.75	20.04	20.12	19.88-20.53	1.00
MgCl ₂ , %	3.49-3.83	3.61	3.61	3.40-3.78	1.00
CaCl ₂ /MgCl ₂	5.23-5.88	5.66	5.58	5.27-5.89	1.01
NaCl, %	4.82-5.53	5.32	5.34	5.03-5.65	1.00
SrCl ₂ , %	0.53-0.64	0.57	0.55	0.52-0.60	0.96
Br, %	0.2593-0.2776	0.2699	0.2852	0.2730-0.2925	1.06
SO ₄ , p.p.m.	36-51	42	45	36-54	1.07
KCl, %	1.08-1.54	1.33	1.66	1.51-1.80	1.25
B, p.p.m.	236-337	285	365	317-410	1.28
NH ₃ , p.p.m.	250-398	327	445	335-488	1.36
Rb, p.p.m.	10-15	12	17	14-19	1.42
LiCl, p.p.m.	220-340	280	400	320-440	1.43
I, p.p.m.	18-32	26	39	33-46	1.50

Depth. If all of the minor ions had been added to, and mixed with, the sea water prior to its concentration by evaporation, their degree of concentration relative to each other would be expected to be the same. The last column of Table II shows that this is not so. In an attempt to clarify the situation, a cross section of 15 wells was chosen as shown in Figure 1. The concentrations of several of the ions at the individual wells of this cross section were then plotted to determine their relation to each other, if any, and also their relation to other variables such as formation depth and thickness.

Figures 2 and 3 are examples of such plots. Figure 2 shows that the trends for iodine and ammonia are similar; and that for wells A through L these components tend to increase with depth. Figure 3 shows that potassium and rubidium have similar trends. These, however, reach their maximum value at a shallower depth than do iodine and ammonia. Braitsch (1965) has pointed out the relationship between rubidium in brine and rubidium in sylvite crystallizing from the brine and has concluded that syndimentary recycling occurs. This could be the effect observed in Sylvania brine.

Statistical Relationships

As a further aid to interpreting the data, the analyses were placed on punched cards and a computer was used to obtain correlation coefficients and factor matrices.

The correlation coefficient measures the degree of relationship between variables. When the correlation coefficient is close to -1 or +1, the variables are related. However, correlation is not evidence of causation. Table III shows the correlation coefficients obtained among the various ions. There are only two basic pairs in the table. (The "basic pair" has the reflexive property that each is more highly correlated with the other than to any of the remaining measurements in the matrix.) The basic pairs are Br and I with a coefficient of 0.963; and KCl and B with a coefficient of 0.958. The relationship between Br and I may be a reflection of a common organic source for the

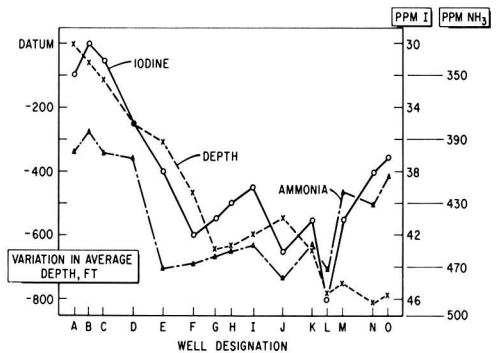


Figure 2. Plot of variation in iodine, ammonia, and depth
Cross section A-O

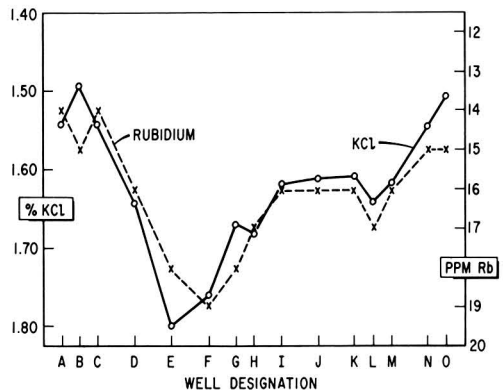


Figure 3. Plot of variation in rubidium and potassium chloride
Cross section A-O

Table III. Correlation Matrix of 51 Sylvania Brine Samples

Item	Br	I	B	KCl	LiCl	Rb	NH ₃	SrCl ₂	NaCl
Br	1.000	0.963	0.909	0.846	0.919	0.883	0.863	-0.594	0.312
I	0.963	1.000	0.945	0.921	0.955	0.929	0.910	-0.507	0.256
B	0.909	0.945	1.000	0.958	0.938	0.952	0.887	-0.477	0.233
KCl	0.846	0.921	0.958	1.000	0.897	0.944	0.859	-0.478	0.211
LiCl	0.919	0.955	0.938	0.897	1.000	0.925	0.917	-0.398	0.196
Rb	0.883	0.929	0.952	0.944	0.925	1.000	0.914	-0.395	0.168
NH ₃	0.863	0.910	0.887	0.859	0.917	0.914	1.000	-0.421	0.101
SrCl ₂	-0.594	-0.507	-0.477	-0.478	-0.398	-0.395	-0.421	1.000	-0.192
NaCl	0.312	0.256	0.233	0.211	0.196	0.168	0.101	-0.192	1.000

variable portion of these ions in the brine. The relationship between KCl and B is not known. There is no correlation between the minor ion suite and the ions such as Sr and Na.

By a combination of the representation of variables as vectors, and the use of matrix manipulation, "factors" are extracted which represent the independent coordinates of the space required to enclose a set of correlations, when these correlations are represented in space as vectors. Table IV shows the factor matrix for the present data. Factor 1 is indicative of some mechanism that is affecting all of the minor ions, since the loadings thereon are high. This might have something to do with paleotopography. For instance, both organic debris and sediments from the continent might be expected to collect in local low spots at which places interaction with the brine would be greatest. In factor 1 near equal loadings are found on B, KCl, and Rb (0.963 to 0.956) with lower, but significant, loadings on LiCl, I, Br, and NH₃ (0.903 to 0.841).

In the other factor columns, 2 through 9, high loadings are found only on a single component (or in the case of

columns 3 and 9, on two components related by calculation). In three columns there are, however, significant near equal loadings on minor ion components. These are:

Column	Loading High	Near-Equal Loadings
7	Depth (-0.885)	LiCl, Br, I (-0.204 to -0.233)
8	SrCl ₂ (-0.900)	KCl, B (0.122 and 0.126)
9	CaCl ₂ (0.777)	LiCl, NH ₃ , I (-0.223 to 0.229)
9	CaCl ₂ (0.777)	Br, Rb (-0.194 and -0.196)

Unfortunately, these only suggest, rather than define, relationships. Here again the KCl-B relationship shows up, as does that among the organically derived materials, Br, I, and NH₃. The association of LiCl with the latter is unexpected. The Br-Rb relationship could be a reflection of the syngedimentary recycling of potash salts which are high in both bromine and rubidium, as suggested by Braitsch (1965). Care should be taken not to read more into a study of this kind than is justified. At best it should be used as a first approximation and as a guide to further investigation.

Table IV. 51 Data Sets for Dow Monroe Brine Wells (Minerals Research, April 8, 1968)

Factor	Varimax matrix accounting for 100.0% of total problem variance									
	1	2	3	4	5	6	7	8	9	10
Sp. gr.	-0.036	-0.926 ^a	-0.125	-0.194	0.089	-0.010	0.097	0.063	0.259	0.003
CaCl ₂ , %	0.462	-0.237	-0.254	-0.084	0.056	0.011	0.224	0.036	0.777 ^a	0.012
MgCl ₂ , %	-0.014	0.019	0.985 ^a	0.059	-0.011	0.018	0.071	0.052	0.132	-0.007
Ratio, ^b %	0.237	-0.130	-0.915 ^a	-0.089	0.036	-0.009	0.046	-0.033	0.277	0.003
NaCl, %	-0.143	-0.007	-0.024	0.012	0.009	-0.985 ^a	-0.065	0.066	-0.013	0.003
KCl, %	-0.963 ^a	-0.089	0.054	0.006	-0.092	-0.066	-0.002	0.126	-0.075	0.065
LiCl, %	-0.903 ^a	0.061	0.066	0.159	-0.131	-0.049	-0.204	0.052	-0.228	-0.008
SrCl ₂ , %	0.365	0.070	-0.079	-0.184	0.016	0.082	-0.003	-0.900 ^a	-0.067	0.005
Br, %	-0.841 ^a	0.049	0.130	0.176	-0.068	-0.162	-0.216	0.274	-0.196	0.037
B, p.p.m.	-0.963 ^a	0.014	0.030	0.088	-0.012	-0.084	-0.055	0.122	-0.121	0.067
NH ₃ , p.p.m.	-0.879 ^a	0.044	0.146	0.190	-0.021	0.038	-0.106	0.081	-0.223	-0.313
I, p.p.m.	-0.903 ^a	0.016	0.036	0.124	-0.051	-0.099	-0.233	0.177	-0.229	-0.000
Fe, p.p.m.	-0.345	0.272	0.172	0.839 ^a	-0.021	-0.017	-0.086	0.235	-0.102	-0.011
SO ₄ , p.p.m.	-0.132	0.075	0.033	0.015	-0.983 ^a	0.009	-0.085	0.014	-0.052	-0.001
Rb, p.p.m.	-0.956 ^a	0.028	0.106	0.037	-0.037	-0.028	-0.027	0.047	-0.194	0.001
Depth	-0.292	0.111	-0.050	0.073	-0.114	-0.087	-0.885 ^a	0.001	-0.302	-0.007
Mg-PRI ^c	0.453	-0.228	0.086	-0.064	0.052	0.017	0.246	0.053	0.815 ^a	0.009

^a Significant loadings referred to in text.

^b Ratio of CaCl₂/MgCl₂.

^c Magnesium equivalent of calcium plus magnesium.

Conclusions

Trends and relationships among a number of ions in the Sylvania brine indicate that relatively simple, widespread mechanisms such as evaporation and dolomitization are responsible for its near-constant character with regard to Ca, Mg, Na, Sr, Cl, and Br. More complicated, local mechanisms are responsible for its variable character with regard to K, B, NH₃, Li, Rb, and I.

The relative amounts of NH₃, I, and Li are so high as to suggest that they were not derived directly from sea water. NH₃ and I may be a result of bioconcentration and subsequent leaching of organic debris; and lithium may have come from the continent.

The mechanisms affecting the variable components are not well defined. As is often the case, the data perhaps raise more questions than they answer. As similar data from other basins become available—particularly those where relative concentrations of minor ions are greatly dif-

ferent—comparisons and contrasts among data sets should prove helpful in understanding the geochemistry of brines.

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Received for review August 21, 1968. Accepted January 8, 1969.

Components of Wood Pulp Bleach Effluents

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■ Chlorination and alkaline extraction bleach effluents from a sulfite and a kraft wood pulp mill were concentrated by reverse osmosis and their dominating chemical properties investigated. The solids were high in ash and the organic residues were highly colored. Biological oxygen demand was found to be due to relatively high molecular weight species as well as to low molecular species. The ultraviolet spectra and ionization difference spectra of the effluents and fractions obtained by gel chromatography on two Sephadex gels in series are presented. Some of the ionization difference spectra were lower in intensity than expected for alkaline extraction products of chlorinated lignin. Other spectra suggested that much of the color in a kraft chlorination effluent was of carbohydrate origin. Catechol groups were found to be stable end-products of a sulfite pulp chlorination.

Two of the more undesirable properties of bleaching wastes have been their contributions to biochemical oxygen demand (B.O.D.) and color. This work describes the fractionation of B.O.D. and color contributing residues by gel chromatography. The colored residues are further characterized by ultraviolet spectral analysis and ionization difference spectra.

Four bleach effluents from two Wisconsin wood pulp mills are the subject of the study described here. The effluents were from chlorination and alkaline extraction stages of a sulfite and kraft pulp. Since chlorination of lignin is the principal reaction involved in generating the residues of these streams, the results of the ultraviolet analyses are discussed in terms of the current concepts of lignin chlorination. Two reviews on the subject summarize these concepts, Rydholm (1965) and Dence (1963). The finding of large quantities of catechol groups in the chlorination effluent of sulfite pulp is also discussed.

Experimental

Production conditions and source pulps for the effluents are outlined in Table I. The lignin values reported were calculated using conversion factors for Roe and Kappa numbers obtained from Rydholm (1965). The methoxyl content was assumed to be 15% of the lignin. Other information in Table I was obtained from mill authorities.

Reverse osmosis (R.O.) of the more dilute bleach wastes was effected with equipment manufactured by Havens Industries, San Diego, Calif., and similar to that described by Wiley, Ammerlaan, *et al.* (1967). Essentially the process involves forcing the aqueous solvent, under high pressure, through cellulose acetate membranes backed by a porous Fiberglas structure. To protect the R.O. membranes from acid or alkaline hydrolysis, all effluents were

With the recent interest in improving the quality of the water in our rivers and recent development of new and feasible techniques for concentrating dilute wastes, such as by reverse osmosis (Wiley, Ammerlaan, *et al.*, 1967), more information regarding the composition of wood pulp mill bleaching wastes seems desirable. The methods for disposal or utilization of these concentrates will depend on the nature of the components. There have been few reported studies of wood pulp bleach liquor components. Only studies on sulfite pulp bleach liquor (Lorås, 1965) and semichemical pulp bleach liquors (Björkqvist, Gustafsson, *et al.*, 1953) begin to describe the organic components likely to be found in bleach mill effluents.

Table I. Bleach Effluents Source and Production Conditions

	Sulfite Pulp	Kraft Pulp
Cook	Mitcherlich	22-28% sulfidity batch
Wood	Spruce	75% softwood (mixed pine) 25% hardwood (dense)
1st Stage		
Lbs. Cl ₂ /ton pulp	75-80	95-105
Final pH	2.2	2.2
2nd Stage (NaOH)		
Final pH	7.8-8.0	10.5-11.0
Lignin content before bleaching	5.9%	2.1%
Lignin content after 2nd stage	1.2%	0.6%
Molar ratio of Cl ₂ to methoxyl	0.9	3.4
Lbs. lignin lost/ton	94	32
Lbs. pulp lost/ton ^a	90	116

^a Includes fiber losses although the effluents as obtained from the mills contained little detectable fiber.

Table II. Properties of Sulfite Pulp Bleach Effluents before and after Concentration

	1st Stage		2nd Stage	
	Effluent as obtained from mill	Concentrate ^a	Effluent as obtained from mill	Concentrate ^a
Solids, g./l.	1.18	84	0.60	95
5-Day B.O.D., mg./g. solids	112	63	104	36
C.O.D., mg./g. solids	625	796	515	560
Ash, % of solids	—	34	—	41
Organic chloride, % of solids	—	5.7	—	7.8

^a Concentrated by reverse osmosis and vacuum evaporation.

Table III. Properties of Kraft Pulp Bleach Effluents before and after Reverse Osmosis

	1st Stage		2nd Stage	
	Effluent as obtained from mill	Concentrate ^{a, b}	Effluent as obtained from mill	Concentrate ^c
Solids, g./l.	1.65	119	1.82	108
5-Day B.O.D., mg./g. solids	114	20	25	65
C.O.D., mg./g. solids	143	190	530	643
Ash, % of solids	—	69	—	48
Organic chloride, % of solids	—	9.5	—	4.6

^a Obtained at different time from the same mill.

^b Concentrated by reverse osmosis followed by vacuum evaporation.

^c Concentrated by reverse osmosis only.

adjusted to pH 3 to 7 with sulfuric acid or sodium hydroxide. All except the second stage kraft effluent were further concentrated from 3 to 5% solids to 8 to 12% solids by vacuum evaporation.

Analytical data for the concentrates are given in Tables II and III. The solids there reported are so-called neutralized 24-hour solids⁷ (Salvesen and Hogan, 1948). Five-day biochemical oxygen demand values (B.O.D.₅), chemical oxygen demand (C.O.D.), and chlorides were determined by methods described in Standard Methods (American Public Health Association, 1965). Organic chloride was determined by the difference in chloride ion determinations before and after pyrolysis, using a pyrolysis procedure described in a Technical Bulletin (A. H. Thomas Co., 1961). Ash was determined by pyrolyzing samples at 550° C. for 24 hours. Both first stage bleach effluent samples were neutralized with sodium hydroxide to pH 7.0 before pyrolysis with the appropriate corrections made in the results to account for the added sodium ion.

The concentrates were fractionated on two 2.5 × 100 cm. columns of Sephadex gels connected in series. One column contained Sephadex G-50 and the second a mixture of about 50% LH-20 and a laboratory methylated coarse grade of G-25. These gels fractionate compounds primarily by their molecular weight differences (Flodin, 1963). G-50 reportedly excludes dextrans of molecular weights equal to and above 10,000.

A column of Sephadex gel has an external volume of solvent, *V_e*, and an internal volume of solvent occupying spaces with restricted diffusion, *V_i*. The term "Kd value" is used to describe the portion of inner volume available for diffusion for a given sample. For a sample which elutes from a column at a volume, *V_s*:

$$Kd = \frac{V_s - V_e}{V_i}$$

If all the gel is readily penetrated by the sample, the *Kd* will be 1. No penetration of the gel would result in a sample elution volume equal to the external volume of the gel and a *Kd* value of 0.0.

Using the combination of LH-20 and G-50 gels provided a wide range of fractionation with extra capacity in the overlapping regions of 500 to 5000 where many of the materials of interest were thought to be distributed. LH-20, an alkylated form of G-25, was used since it gave better fractionation and resolution of the ultraviolet absorbing components than does G-25. The internal volume for these columns was assumed to be the volume of the last high solids peak (small molecular weight inorganics) which corresponded to 470 ml. for most runs. The external volume was estimated to be 270 to 300 ml. since liginosulfonic acid preparations which are known to contain components greater than 10,000 in molecular weight consistently yielded a front running peak with this volume of eluate.

Ten-milliliter aliquots of the concentrates were used for the fractionations. The column eluates were monitored continuously with an LKB Uvicord II at 280 nm. using a 1-mm. quartz flow cell.

Ultraviolet spectra were determined on a Beckman DK-2A ratio recording spectrophotometer using 1-cm. quartz cuvettes. Samples for ionization difference spectra were prepared by adding two drops of concentrated sodium hydroxide for the alkaline samples and two drops of concentrated HCl for the acid samples in cuvettes containing

approximately 3 ml. of sample. The spectra were recorded with the alkaline sample in the sample beam and the acid sample in the reference beam. The amounts of acid and base were sufficient to provide the difference spectra between pH 2 and 11. Further addition of base or acid failed to increase the magnitude of difference. For difference spectra using intermediate pH values, the hydrogen ion concentration was monitored with a pH meter.

The adsorption spectra for the products of an alkaline degradation of glucose were prepared similarly. The alkaline degradation of glucose was carried out by heating a 2% glucose solution in a sealed tube at 110° C. for 2 hours in 1N NaOH.

Catechol groups were determined by a method described by Falkehag, Marton, *et al.* (1966). The method involved measuring the intensity of color of a complex with ferrous and tartrate ions at the peak of absorption between 550 and 590 nm. All samples were measured against blanks containing sample and all reagents except iron.

Results

Reverse osmosis of the bleach effluents resulted in some losses, especially of small inorganics and B.O.D. contributing components (especially low molecular weight volatile organics such as acetic and formic acids). Tables II and III summarize the results and compare the values for B.O.D.₅ and C.O.D. before and after concentration. All but second stage kraft lost B.O.D.₅. The loss of inorganics

is reflected by the increase in C.O.D. values. The B.O.D.₅ increase noted for second stage kraft was relatively large and could have been due to the loss of an inhibitor during the reverse osmosis. The uniform increase noted for C.O.D. indicated that the lignin residues and other nonbiodegradable residues were largely rejected by the membranes used. Absolute measurements of yields after reverse osmosis were not made since the volumes of effluents were difficult to measure accurately due to the large quantities (50 to 200 gallons) involved and to the formation of precipitates during the concentrating processes. Calcium sulfate dihydrate precipitated from the sulfite bleach concentrates and calcium carbonate from the second stage kraft effluent.

Despite disproportionate losses of low molecular weight inorganics, the ash values in Table II indicated solids in the concentrates to be from one-third to almost two-thirds inorganic. Since the bulk of the solids were inorganic, the solids peaks in the fractions obtained by gel chromatography (Figures 1 and 2) were interpreted as being primarily inorganic salts.

The B.O.D.₅ of fractions obtained by gel chromatography of the different effluents are recorded in Figures 1 and 2. The peaks in the large molecular weight ranges suggested that there were some polysaccharides with molecular weights between 2000 and 10,000. The peak of B.O.D. for second stage sulfite and first and second stage kraft effluents ran behind the front running ultraviolet absorbing peaks which suggest that the predominate molecular weight

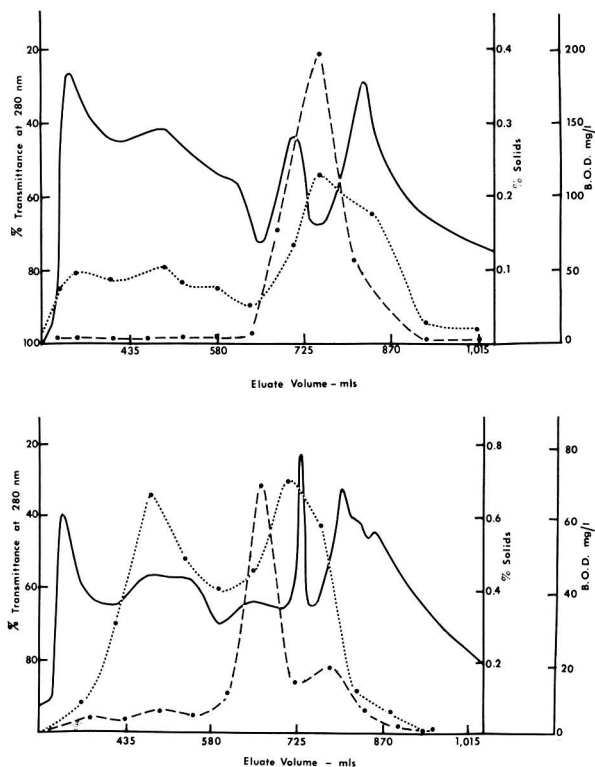


Figure 1. Gel chromatography of sulfite bleach effluent concentrate

— % Transmittance at 280 nm; - - - % Solids; B.O.D., mg./l.
Top, first stage; Bottom, second stage

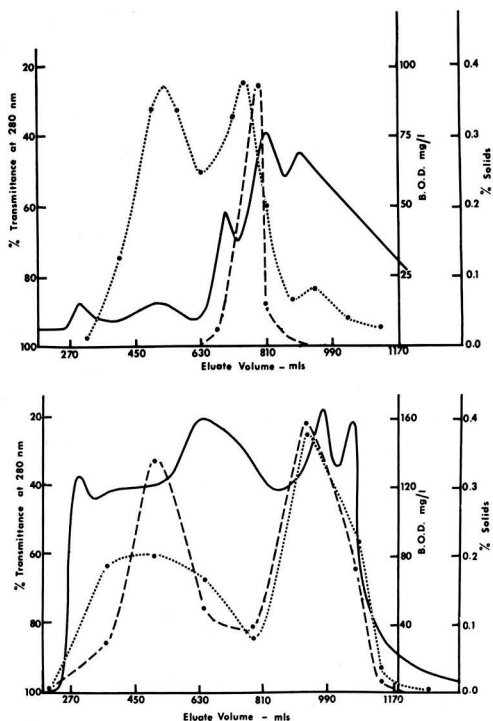


Figure 2. Gel chromatography of kraft bleach effluent concentrate
 — % Transmittance at 280 nm.; - - - % solids; ······
 B.O.D., mg./l. Top, first stage; Bottom, second stage

species was between 3000 and 7000. Such molecular weights are difficult to account for since the polysaccharides of wood are much higher in molecular weight, and when they are degraded they are generally thought to yield monosaccharides.

The small molecular weight B.O.D.₅ peak in Figure 2 (top) was not as symmetrical as the others, suggesting that some of the overlapping components may have inhibited the bacterial growth. Since the various dilutions used for the B.O.D. assays gave proportional oxygen depressions, the presence of an inhibitor was not further confirmed.

The lack of correlation of the B.O.D.₅ curves with any of the ultraviolet elution curves indicated that the lignin residues were not degraded and that the degradable residues were not involved in lignin carbohydrate bonds.

The high molecular weight solids peak in second stage kraft was not characterized although it appeared to elute simultaneously with the B.O.D.₅ contributing residues.

Ultraviolet Characterization

The ultraviolet absorption spectrum for the first stage sulfite bleach effluent was characteristic of lignosulfonic acids and chlorinated lignosulfonic acids as reported by Ivancic and Rydholm (1959) and by Dence and Sarkanen (1960). The ultraviolet absorption spectra fractions produced on columns similar to those used to produce the data shown in Figure 1 varied only in the degree of resolution of the 280-nm. peak and the intensity of the ionization difference peaks. The ultraviolet spectrum for the

fraction with a K_d value of 0.0 is recorded in Figure 3 along with spectra for the concentrate. The concentrate gave a much less intense ionization difference curve relative to the 280-nm. absorption which suggested that the high molecular weight fractions had proportionately more free phenolic groups (Goldschmid, 1954).

The first stage sulfite bleach effluent was the only one to give a positive test for catechol groups. Effluent taken directly from the bleach tower ahead of the washer gave 78 absorbance units per cm. at 560 nm. as the iron-tartrate complex and the same amount of uncomplexed bleach effluent gave 1180 units per cm. at 280 nm. The ratio of absorbance at 560 nm. as a complex, to absorbance at 280 nm. with no reagents, was 0.066. Similar calculations for pyrocatechol gave a ratio of 0.21 and for kraft lignin 0.016 (Falkehag, Marton, *et al.*, 1966). Apparently the first stage sulfite has about four times the number of catechol groups found in kraft lignin. Kraft lignin was estimated by Falkehag, Marton, *et al.* (1966) to contain about 6% of its aromatic rings as catechol structures. By analogy the bleached lignin here would have about 25% of its aromatic rings as catechol structures. The distribution of these groups in the various molecular weight fractions is presented in Figure 4. The lower the molecular weight the greater the ratio of 560 nm. to 280 nm., which suggested that the number of catechol groups per phenylpropane groups was larger in the smaller molecular weight fractions.

Second stage sulfite ultraviolet absorption characteristics were less indicative of aromatic structures and had less intense ionization difference spectra. Figures 5 and 6 record the spectra for characteristic fractions. Although the high molecular weight residues K_d 0.0 were typical of the usual lignin spectra, some of the low molecular weight residues, especially those with a K_d value of 0.7, were

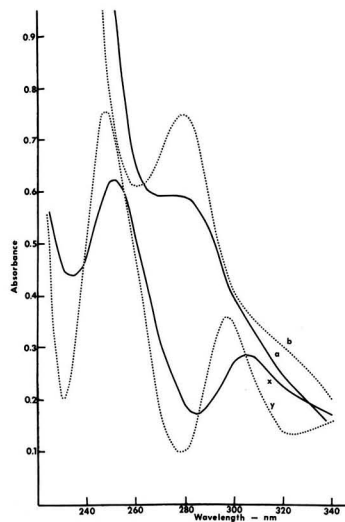


Figure 3. Ultraviolet spectra of first stage bleach effluent

- a. Diluted concentrate
- x. Ionization difference spectrum for diluted concentrate at twice the concentration for curve a
- b. Gel chromatography fraction from columns of G-50 and LH-20, $K_d = 0.0$
- y. Ionization difference spectrum for b

atypical. The ionization difference spectrum for this fraction was especially interesting in that it had only one peak at 285 nm. The residues with K_d values greater than 0.7 and less than 0.5 were similar to those with the high K_d values. Differences of 10 nm. for the wavelength of the maximum of the ionization difference spectra were noted but not given any significance at this time. The samples described in Figure 6, K_d 0.7 and 1.3, had peaks at 238 nm. which were not symmetrical. This suggests some sort of

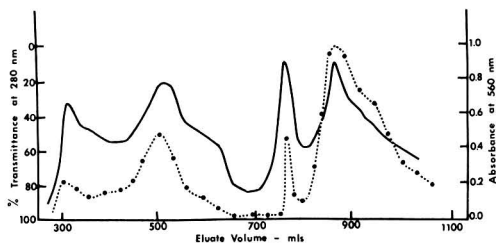


Figure 4. Gel chromatography of first stage sulfite bleach effluent concentrate

— % Transmittance at 280 nm.; ····· arbitrary absorbance units at 560 nm. as iron-tartrate complex

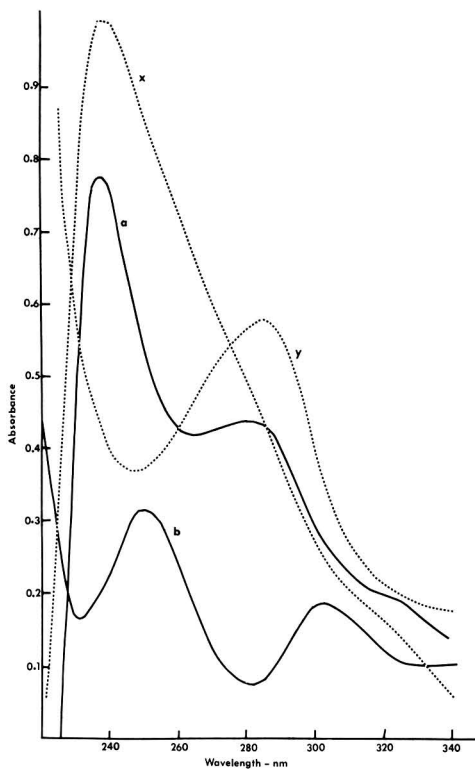


Figure 5. Ultraviolet absorption spectra for second stage sulfite bleach effluent

- a. Diluted concentrate
- x. Ionization difference spectrum for a
- b. Gel chromatography fraction from column of G-50 and LH-20, $K_d = 0.0$
- y. Ionization difference spectrum for b

mechanical or chemical interference during the measurements despite apparently satisfactory operation.

The first stage kraft effluent had considerable color and ultraviolet absorption. The curve for the concentrate presented in Figure 7 was not comparable to any curve published for lignin degradation products. For instance there are no similarities in the ultraviolet absorption curves to the chlorination degradation products of liginosulfonic acid preparations studied by Ivancic and Rydholm (1959). Their work included curves for degradation products using various ratios of chlorine to methoxyl up to 15. Most of the ultraviolet absorbing residues eluted in the lower molecular weight range, K_d 0.5 and above (Figure 2A). Fractions with K_d values of 0.6 and 0.8 were characteristic of the two types of ionization difference spectra found (Figure 7). No inflections at 280 nm. were found and the difference spectra had only one peak in this range, fraction with K_d 0.6, 300 nm. and K_d 0.8, 268 nm. The ionization difference spectrum underwent a large portion of its change between pH 6 and 2 and was accompanied by a deep color change around pH 4.0. These fractions apparently contained the predominating ultraviolet absorbing material since the curves for the diluted concentrate reflect both components. The fractions with K_d values 0.0 to 0.4, present in small quantities, had typical lignin spectra.

The lack of resemblance of these ultraviolet spectra to lignin degradation products prompted an investigation of the alkaline degradation products of sugars. Ultraviolet curves for dextrose treated to an alkaline cook are presented in Figure 8. The ionization difference curve resembled that for the fraction with K_d value of 0.8 of the first stage kraft. The broad peak with a 300 nm. maximum and the need to adjust the pH range from 2 to 11 to obtain the maximum ionization difference spectra were the most evident similarities.

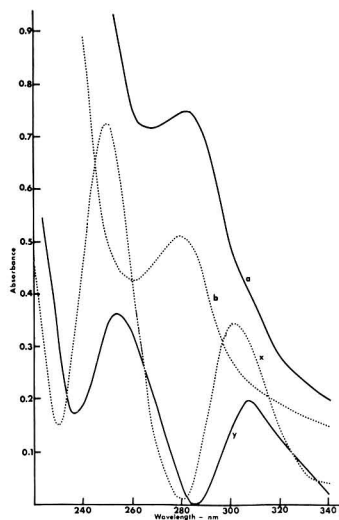


Figure 6. Ultraviolet absorption spectra of gel chromatography fractions from columns of G-50 and LH-20 of second stage sulfite bleach effluent

- a. Fraction K_d 0.7
- x. Ionization difference spectra for a
- b. Fraction with $K_d = 1.3$
- y. Ionization difference spectrum for b

The diluted concentrate of second stage kraft gave the ultraviolet curves presented in Figure 9. The ionization curves were independently prepared for the difference between pH 11 and 6 and pH 6 and 2. Most of the difference occurred between pH 6 and 2. The pK_a of this difference appeared to be 3.5 which might correspond to a carboxylic acid of perhaps hydroxy chloroquinones (Rydholm, 1965). This particular component was resolved on an LH-20 column at an elution volume of 230 ml. corresponding to K_d of 0.4. The magnitude of the ionization difference change between pH 11 and 2 was plotted for

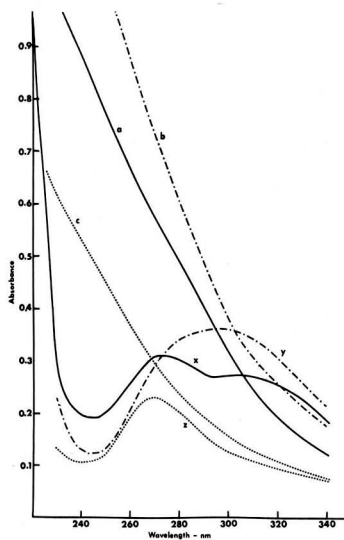


Figure 7. Ultraviolet absorption spectra for first stage kraft bleach effluent

- a. Diluted concentrate
- x. Ionization difference spectrum for a
- b. Fraction K_d = gel chromatography fraction from column of G-50 and LH-20 with a K_d = 0.6
- y. Ionization difference spectrum for b
- c. Gel chromatography fraction with K_d = 0.8
- z. Ionization difference spectrum for c

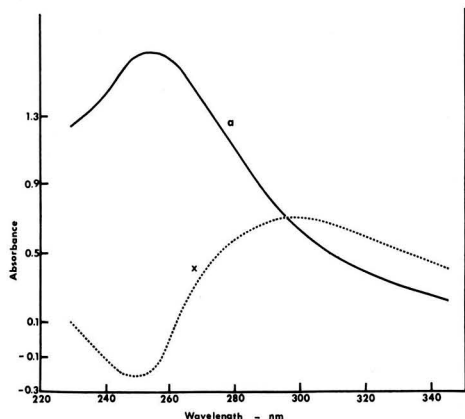


Figure 8. Ultraviolet absorption spectra of glucose alkaline degradation products

- a. Diluted media, pH 2.0
- x. Ionization difference spectrum for a

the various fractions along with the wavelength of the difference peak (Figure 10). The material with the unusual difference spectrum was not coincident with an ultraviolet absorption peak from the column. The lack of 280-nm. resolution for this component suggested that the residues responsible for the low pK_a ionization difference spectrum might be an aliphatic acid.

The higher molecular weight residues were more lignin-like but had low resolution at 280 nm. and very weak ionization difference spectra for these residues was not expected since it has been postulated that chlorinated lignin

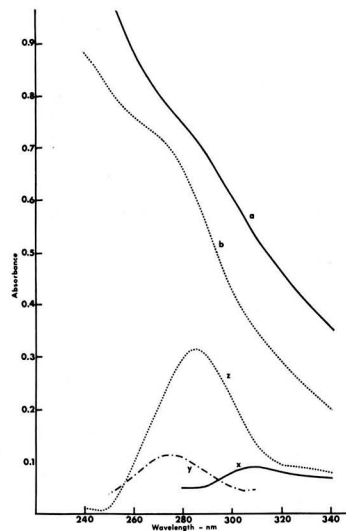


Figure 9. Ultraviolet absorption spectra for second stage kraft bleach effluent

- a. Diluted concentrate
- x. Ionization difference spectrum for a between pH 6 and 12
- y. Ionization difference spectrum for a between pH 2 and 6
- b. Gel chromatography fraction from single LH-20 column K_d = 0.4
- z. Ionization difference spectrum for b

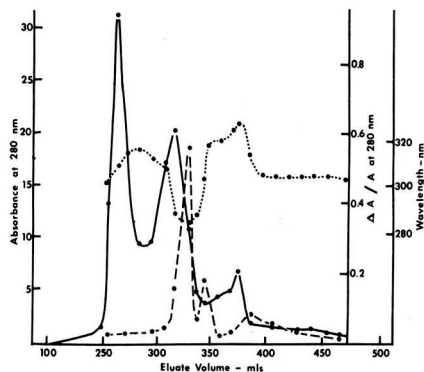


Figure 10. Gel chromatography of second stage kraft bleach effluent concentrate on 100×2.5 cm. Sephadex LH-20 column

- Arbitrary absorbance units at 280 nm.; - - - - . intensity of ionization difference spectra in arbitrary absorbance units; wavelength, nm., for maximum ionization difference absorption spectra

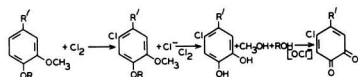
residues when subjected to alkali would lose the ring substituted chlorine to form phenolic hydroxyls (Newcombe and Marshall, 1955; White, Swartz, *et al.*, 1940).

Discussion

The low proportion of organic compounds in the bleach effluents studied will be a major consideration in searching for effective disposal methods or possible utilization in a salable product. The organic portion, although not completely accounted for in the concentrates, revealed several interesting chemical properties not entirely anticipated.

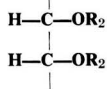
At this time it is not possible to account for the presence of biodegradable substances with molecular weight distributions between 2000 and 10,000. These substances probably represented an unusual degradation product of some polysaccharide or a low molecular weight natural polysaccharide. So far as it is known such substances have not been recognized previously.

The finding of catechol structures indicated that lignin chlorination can be terminated between demethylation and quinone formation. Quinones are no doubt produced by the chlorination since the pulp from which this effluent was taken was a bright orange. The insolubility of quinones would limit their extractability in the wash, thus favoring the catechol residues as the only detectable cyclic demethylation products. The low chlorine to methoxyl ratio may also have favored the accumulation of these catechol structures. The elemental chlorine which catalyzes the demethoxylation reaction (Sarkanen and Dence, 1960) would have been used up primarily by the substitution reactions which have been described as the initial and fastest reactions. Since only 0.9 chlorine molecule was present per methoxyl, ring substitution would have depleted the chlorine, leaving little left for oxidation reactions required to convert the catechol groups to quinones. The reaction sequence is outlined below describing those features of chlorination discussed here:



R = phenylpropane unit or H

R' = H₂C—OR₂ where R₂ = phenylpropane unit, SO₂, or H



Comparison of ultraviolet spectra for the effluent components and fractions obtained by gel chromatography with curves for laboratory chlorinations of lignosulfonic acids indicated that the original residues solubilized during first and second stage sulfite bleaching were lightly chlorinated lignin products with only one exception found in the second stage low molecular weight fractions. This low molecular weight component lacked aromatic character and gave a single peaked ionization difference curve. Other residues with unique ionization difference spectra dominated the first stage kraft fractions, one of which was directly comparable to alkaline degradation products of dextrose. The lack of residues with ultraviolet spectra characteristic of lignin or intermediate lignin chlorination products suggested that the ultraviolet-absorbing constituents

and therefore probably the chromophores in the first stage kraft were mostly derived from carbohydrates. Further studies by Webb (1969) show that the compounds from the alkaline degradation of glucose which give rise to these characteristic ionization difference spectra are not separated from the chromophores by Sephadex chromatography. Residues with ionization difference spectra more like alkaline degradation products of sugars than lignin also appeared in the second stage kraft effluent; however, such residues were not a major constituent of that effluent.

The strong color produced during the alkaline degradation of dextrose and other sugars suggests that during the "peeling reaction" of polysaccharides and cellulose many of the degradation products might give rise to color and yet not have been completely solubilized. Solubilization of such residues may be part of the reason why the greater ratios of chlorine to methoxyl are required in the kraft chlorination compared to the sulfite pulp chlorination.

The relatively low lignin content and larger losses of nonlignin pulp components during the kraft bleaching supports the conclusion that considerable carbohydrate degradation products require removal to obtain optimum pulp brightness.

Acknowledgment

The authors thank Ann Addie and Gerald Hovind for their technical assistance.

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Received for review April 12, 1968. Accepted January 21, 1969. Paper presented before the Division of Water, Air, & Waste Chemistry, 155th Meeting, ACS, San Francisco, Calif., March 31-April 5, 1968. This project has been authorized, supported, and financed, in part, by the Department of the Interior pursuant to the Federal Water Pollution Control Act.

Effects of Various Fluoride Sources on Citrus Growth and Fruit² Production

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■ The effects of fluoride accumulation by citrus trees were studied using several techniques of exposing the trees to soluble fluorine compounds. Weekly sprayings with dilute (0.00125 to 0.0025N) NaF or HF solutions resulted in gradual fluoride accumulation in citrus foliage and produced toxicity symptoms which were indistinguishable from those observed on similar trees exposed to low concentrations of HF gas. Results of intermittent exposure of young citrus trees to HF gas were very similar to those associated with comparable fluoride accumulation from weekly sprayings with NaF or HF solutions. Reduction in top growth of citrus exposed to soluble fluorides was closely correlated with reduced photosynthetic area resulting from smaller leaves and increased leaf fall. Continuous exposure to HF gas resulted in more severe growth retardation than intermittent exposure to higher concentrations or periodic sprayings with soluble fluorides even though approximately equivalent amounts of F were absorbed in all three treatments.

The effect of fluoride air pollution on citrus growth and fruit production has been of considerable concern both in California and in Florida since World War II because of the development and expansion of fluoride-emitting industries adjacent to large acreages devoted to citrus production. Attempts to assess the influence of elevated fluoride concentrations in citrus foliage on growth and crop production have involved several experimental techniques. Wander and McBride (1956) reproduced abnormal chlorosis patterns observed near phosphate factories in central Florida by spraying grapefruit foliage with 0.1N solutions of HF or H_2SiF_6 . Solution culture techniques were used by Brewer, Chapman, Sutherland, and McCulloch (1959) to introduce fluoride into Washington navel orange trees via their roots. Although tree growth and fruit yields were substantially reduced by a fluoride treatment which resulted in foliar fluoride concentrations of approximately 50 p.p.m. on a dry weight basis, abnormal root growth resulting from precipitation of insoluble fluoride compounds may have been the primary cause of poor growth.

Prolonged exposure of citrus trees to a few parts per billion of HF gas under greenhouse conditions with controlled humidity and temperature (Brewer *et al.*, 1960a, c) indicated the potential effects of fluoride air pollution on tree growth and toxicity symptom expression. Greenhouse fumigation chambers are of limited usefulness in studying effect of fluoride accumulation on fruit quality and yields, however, because of the large space required to accommodate

a sufficient number of mature, bearing trees. Gross influences on tree growth of the higher temperatures and humidity and lower light intensities associated with enclosure in a greenhouse are also serious complications when trying to determine the potential impact of a given environmental factor such as air pollution on tree performance in the field.

Unfortunately, practical interpretation of the results of field experiments wherein field trees are enclosed in glass or plastic chambers as recently reported by Leonard and Graves (1966) in Florida, or by Thompson, Taylor, Thomas, and Ivie in California (1967), is also complicated by atypical tree performance under greenhouse conditions. Repeated spraying at frequent intervals with very dilute solutions of fluoride solutions is an extremely practical means of slowly increasing the fluoride content of citrus foliage (Brewer *et al.*, 1960b) without causing foliar necrosis or abscission sometimes associated with short-term exposure to high fluoride concentrations in the atmosphere. Toxicity symptoms produced by this technique were indistinguishable from those produced on similar citrus foliage exposed to a few parts per billion of HF under greenhouse conditions. A single spraying with 0.001N HF or NaF solution raised the fluoride content of navel orange foliage approximately 5 p.p.m. on a dry weight basis.

Field Foliar Spray Experiments

A long-term fluoride spray experiment was established at the University of California Citrus Experiment Station in 1959 (Brewer *et al.*, 1967). Two predetermined levels of fluoride accumulation (75 and 150 p.p.m.) were induced yearly in bloom-cycle Washington navel orange foliage by spraying approximately 15 times at 10-day intervals with 0.00125 or 0.0025N NaF solutions, respectively. A third treatment, the control, involved a similar number of sprayings with 0.0025N NaCl to eliminate sodium as a factor in the experiment. A total of 48 trees (12 four-tree plots in a Latin square arrangement) received each of the three treatments for six consecutive years. Results of this experiment (Table I) indicated reductions in fruit production after the second year of treatment ranging from 7 to 40% at the 75-p.p.m. F level and 10 to 54% at the 150-p.p.m. F level. No significant effects on fruit quality were associated with the fluoride treatments. Measurement of approximately 1200 individual leaves from each of the three treatments indicated a 28% reduction in average leaf area associated with the accumulation of 75 p.p.m. of F and a 33% reduction associated with the 150-p.p.m. F level. Premature leaf drop, particularly at the high F level, was also associated with the fluoride treatments. The observed yield reductions

Table I. Average Fruit Production of Washington Navel Orange Trees Sprayed for 6 Years

Foliar Spray	F Content, P.P.M.	Fruit Yield, 6-Year Total, Boxes/Tree	Fruit Dia., Cm.	% Juice	Soluble Solids to Acid Ratio
0.0025N NaCl	10	22.9	6.6	47.5	13.0
0.00125N NaF	75	19.7	6.7	47.4	13.2
0.0025N NaF	150	18.5	6.7	47.9	12.9

were probably the result of reduced photosynthetic area caused by the combination of smaller individual leaves and accelerated leaf fall.

Results of a similar fluoride spray experiment under field conditions in Florida (Leonard and Graves, 1965, 1966) indicated that yields of Hamlin oranges and Marsh grapefruit were reduced 33 and 22%, respectively, by accumulations of 60 p.p.m. of fluoride in spring flush leaves and 42 and 46%, respectively, by the accumulation of approximately 150 p.p.m. of F from repeated spraying with 0.02N HF solutions. No significant effects of the fluoride treatments on fruit quality criteria were found.

Comparison of Soluble Fluoride Sprays with HF Gas

Although the visible fluoride toxicity symptoms associated with the absorption of F from NaF sprays were indistinguishable from those resulting from exposure to HF gas (Brewer *et al.*, 1960a, c), other responses such as growth retardation and reduced fruit set seemed to be affected to a lesser degree by 150 p.p.m. of F accumulated from NaF sprays than by the same concentration accumulated from HF gas. Part of this discrepancy might be ascribed to the fact that the NaF sprays were used on mature trees out-of-doors while the HF gas was used on young trees growing in greenhouses. To determine the effects of equivalent accumulations of F from NaF sprays and HF gas under comparable conditions, the following experiment was set up in 1962.

Experimental Procedure

Eighteen uniform budded Lisbon lemon trees on Macrophylla rootstocks were divided into three groups of six trees each. One group was placed in an air-conditioned greenhouse fumigation chamber to which HF gas was added in sufficient quantities to maintain a concentration of approximately 1 to 1.5 p.p.b. of F by weight. The other two groups of trees were housed in a duplicate chamber to which no HF was added. Approximately once a week, one of these latter groups of trees (the NaF group) was taken out of the greenhouse and sprayed with dilute NaF solution varying in strength from 0.001 to 0.0025N. Solution strength of the NaF sprays was dependent upon the rate of F uptake by the trees exposed to the HF gas. Fluoride contents of mature foliage on the three groups of trees were determined twice monthly using previously described sampling techniques (Brewer *et al.*, 1960a, b, c) and a modification of the Willard-Winter steam distillation procedure for determination of F content (Willard and Winter, 1933). Table II contains representative F analysis data and indicates the degree to which fluoride uptakes by the two groups were kept parallel during the experiment.

Table II. Fluorine Content of Mature Lemon Leaves on Trees Exposed to 1 to 1.5 P.P.B. HF Gas, Sprayed with 0.00125 to 0.0025N NaF, or Unsprayed and Grown in F-Free, Carbon Filtered Air
Concentrations expressed as part per million on a dry weight basis

Sampling Date	Treatment		Control
	HF gas	NaF sprays	
3/29	59	67	4
4/19	100	121	7
5/10	209	210	7
6/6*	9	10	7
6/27	45	59	8
7/17	79	73	8
8/17	128	107	12
9/17	146	137	11

* New flush of leaves sampled beginning June 6, 1962.

Table III. Growth Characteristics of Lisbon Lemon Trees Exposed to HF Gas, Sprayed with Dilute NaF Solutions or Grown in F-Free Carbon Filtered Air

Criteria Measured	HF Gas	NaF Sprays	Control
Trunk growth, mm.	14	18	20
Linear growth, cm.	501	821	772
Height of tree, cm.	54	62	79
Fresh weight of leaves, g.	209	644	766
Dry weight of leaves, g.	53	180	197
Fresh weight of twigs, g.	218	488	616
Dry weight of twigs, g.	91	194	252
Mean leaf area, sq. cm.	40	53	67

Results

The effects of the treatments on growth of the young Lisbon lemon trees are summarized in Table III. Approximately 140 p.p.m. of fluoride absorbed by lemon leaves from repeated sprayings with NaF was evidently much less damaging than a similar amount absorbed from continuous exposure to low concentrations of HF gas. The visible chlorosis patterns produced by the two fluoride sources were identical and initially appeared at approximately the same fluoride concentration range, between 50 and 75 p.p.m. Premature leaf drop was more prevalent with the HF gas than with the NaF sprays. This leaf drop was responsible for the very low leaf weights shown for the HF treatment in Table III.

This experiment was repeated with almost identical results in 1963, except that navel orange instead of lemon trees were used.

In 1964, a third experiment was carried out using navel oranges as the test plant. The same number of replicates and methods of treatment as in the first two experiments were used and a fourth treatment involving intermittent sprayings with dilute (0.0012N) HF solutions was added. It seemed possible that the acid characteristics of the HF might be more phytotoxic than a neutral salt such as NaF. Results of this experiment (Table IV) indicated that the difference in response was not due to the fluoride source, since NaF and HF sprays gave almost identical results. The only statistically significant difference between the NaF and HF sprays was slightly more chlorosis on foliage sprayed with dilute HF. These data also suggest that the primary detrimental effect of the fluoride on navel orange foliage is a reduction in the average leaf size. Since there was not a compensatory larger number of leaves, the reduced average leaf size meant reduced total leaf area and therefore photosynthetic potential. As expected, reductions in top weights correlate closely with reductions in total leaf area.

Intermittent vs. Continuous Exposure to HF Gas

In all previously described trials, fluoride accumulated from continuous exposure to low concentrations of HF gas was more toxic than similar amounts of fluoride accumulated from intermittent sprayings with NaF or HF solutions.

Table IV. Effect of Fluoride Spray

Effects of approximately 200 p.p.m. of fluoride absorbed by navel orange foliage from NaF and HF sprays and from continuous exposure to HF gas. All measurements made in November 1964, after 6 months of treatment

Criteria Measured	HF Gas	HF Spray	NaF Spray	Control
F content, p.p.m. dry wt.	211 _a	205 _a	205 _a	8 _i
Foliar chlorosis, %	83 _a	10.0 _b	1.3 _c	0 _c
Number of leaves	337 _{ns}	340 _{ns}	331 _{ns}	326 _{ns}
Weight of leaves, g.	253 _a	297 _a	287 _a	360 _b
Mean leaf area, sq. mm.	236 _a	352 _b	386 _b	478 _c
Total leaf area, sq. cm.	795 _a	1197 _a	1277 _b	1558 _c
Weight of wood, g.	86 _a	107 _b	114 _b	151 _c
Total linear growth, cm.	1047 _a	831 _{ab}	787 _{ab}	758 _b

^a All comparable values which do not share the same subscript are significantly different at 0.5 level of probability.

Figure 1. Diagram of citrus leaf showing sections analyzed separately for fluoride content.



A possible explanation of this discrepancy could be the difference in frequency of exposure. The sprays were applied at weekly intervals, so that between sprayings the fluoride which was absorbed may have been fixed as CaF or in some other way rendered less biologically active. Mechanical fractionation of citrus leaves following sprayings and exposure to HF gas indicated no significant differences in the physical distribution of fluoride within the leaf. The upper epidermis and palisade layer of representative leaves from both treatments scraped off with a razor blade were found to contain approximately 60% of the total F in the leaves. Analysis of similar leaves from both treatments divided into three equal sections (Figure 1) indicated the following distribution: basal portion (A) 25%, mid-section (B) 30%, and leaf tip and margins (C) 45%. NaF-sprayed leaves contained slightly more F in their mid-section and proportionally less in the leaf margins than leaves exposed to HF gas. The difference was not significant, however, amounting to less than 5% on a relative weight basis.

To test the possibility that the differences in response reported previously might be due to the difference in frequency of treatment, a fourth experiment, established in the spring of 1966, included all of the four treatments used in the previous experiment described above plus a fifth treatment which involved intermittent rather than continuous exposure to HF gas. Trees in this treatment were exposed for 30 to 36 hours weekly to 5 p.p.b. of HF, approximately the same TC (time × concentration) value as the continuous HF treatment. Fluoride content of the sprayed and fumigated citrus foliage was increased to approximately 175 p.p.m. over a 9-month period. The effects of these treatments are summarized in Table V.

Table V. Effects of Fluoride Accumulated by Washington Navel Orange Foliage Sprayed Weekly with Dilute Solutions of NaF or HF or Exposed Continuously or Intermittently to HF Gas

Criteria Measured	NaF Spray	HF Spray	Intermittent HF Gas	Continuous HF Gas	Control
Trunk diameter, mm.	14.3 _a	14.5 _a	14.9 _a	14.7 _a	15.5 _b
Tree height, cm.	182 _a	177 _a	163 _a	138 _b	190 _c
Linear growth, cm.	792 _{ns}	840 _{ns}	756 _{ns}	836 _{ns}	721 _{ns}
Mean leaf area, sq. cm.	31.3 _{ab}	33.4 _b	29.9 _a	29.1 _a	38.9 _c
Number of leaves	282 _{ns}	294 _{ns}	302 _{ns}	293 _{ns}	292 _{ns}
Total leaf area, sq. m.	8.83 _{ab}	9.82 _a	9.03 _a	8.53 _b	11.36 _c
Green wt. of leaves, g.	215 _a	213 _a	216 _a	185 _b	240 _c
Dry wt. of leaves, g.	69 _a	67 _a	68 _a	61 _b	81 _c
Weight of branches, g.	98 _a	94 _a	96 _a	96 _a	105 _b

These data indicate that the results of the intermittent HF gas treatment on the young orange trees more closely paralleled the NaF and HF spray treatment than the continuous HF gas treatment. In only one case, the mean leaf area, were the results of the intermittent gas treatment different from the spray treatments and similar to the continuous HF gas. A comparison of total leaf areas, probably of greater importance to the plant, indicates a significant difference, however, between the continuous and intermittent HF gas treatments and no significant difference between the intermittent HF gas and the NaF or HF spray treatments.

These data support the theory that the spray treatments are less toxic than continuous exposure to HF gas, because with intermittent exposure there is a chance for the absorbed fluoride to be chemically fixed or translocated between exposures, whereas there is no such "rest period" with continuous exposure. It is also evident that the F content alone is not always a valid indicator of plant damage. Widely differing degrees of plant injury may be associated with the same F concentration in the foliage, depending upon the frequency of exposure, the concentrations of HF or other soluble F source present, and the age of the foliage at time of exposure. Since weekly sprayings with a soluble F source such as NaF or HF produce results very similar to those produced by weekly exposures to HF gas, more frequent exposures to gas could be simulated by correspondingly more

frequent sprayings. Experiments designed to test this hypothesis are currently under way.

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Received for review June 13, 1968. Accepted December 9, 1968. Division of Water, Air, and Waste Chemistry, 153rd Meeting, ACS, Miami Beach, Fla., April 1967.

Comparative Size Measurements of Monodisperse Liquid Aerosols by Electrical and Optical Methods

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■ A new electrical method for sizing monodisperse aerosols of liquid or solid particles in the 0.03- to 10-micron diameter range involves charging an aerosol at atmospheric pressure and measuring the ratio of the electric mobility of the charged aerosol at two lower pressures. The particle size is then calculated by Millikin's equation for the slip correction to Stokes' law. Comparative measurements on monodisperse aerosols of dioctyl phthalate (DOP) by this method and the aerosol "owl" have given results agreeing within the limit of error of these methods. The somewhat smaller sizes of the same DOP aerosols indicated by a single particle optical counter (Royco PC 200) can be accounted for by the difference in the refractive indices of DOP (1.49) and the polystyrene latex particles (1.58) used in calibrating the optical counter.

Monodisperse aerosols of dioctyl phthalate (DOP), dibutyl phthalate (DBP), and other liquids of low vapor pressure are used for testing filters and in many studies involving aerosols. These aerosols can be produced readily by such generators as the well-known LaMer gen-

erator (Kitani, 1967; Muir, 1965), the thermal DOP generator (Knuth, 1967), and the atomization-condensation generator (Liu *et al.*, 1966). Monodisperse liquid aerosols have been produced by these generators over a size range from approximately 0.03- to 2-micron diameter.

Although liquid particles can be sized directly in a microscope, the microscopic technique is complicated by the fact that liquid drops lose their spherical shape when they are collected on the surface of the microscope slide. Thus the "spread factor" of the liquid drops—the ratio of the diameter of the flattened drop on the surface to the diameter of the spherical drop—must also be known. Some recent measurements on the spread factor are summarized in Table I. The values of Virin and Fuks (1967) and Schonauer (1967) given in Table I are obtained by a special electron microscopic technique involving freezing the collected drops at liquid nitrogen temperature and "shadowing" the frozen drops in a high vacuum evaporator.

Other techniques suitable for sizing liquid aerosols in the micron and submicron size range include the familiar drop settling technique, the aerosol "owl" (Sinclair and LaMer, 1949), the single particle optical counter (Whitby and Vomela, 1967), the impactor-photometer technique (Thompson, 1957) and the electrical particle counter (Whitby and Clark, 1966). The last three are secondary techniques in-

Table I. Spread Factor Measurements

Drop Material	Surface	Spread Factor	Drop Diameter, Microns	Reference
DBP	Glass	2.60-1.65	1.5-40	Goldschmidt (1965)
DOP	Oilphobic	1.45	50-150	Whitby (1965)
DOP and DBP	Formvar	1.72 ± 0.01	0.3-0.8 [‡]	Virin and Fuks (1967)
DOP	Tylose	2.7	Few microns	Schonauer (1967)

volving measuring instruments whose calibration must be established by aerosols of known particle size. The first two techniques are more fundamental, since the measured variables can be related directly to particle size by fundamental mechanical or optical principles, and sufficiently accurate results can usually be obtained without using calibrating aerosols of known particle size. All these techniques are limited to particles larger than approximately 0.2-micron diameter except the electrical particle counter, whose range extends from 0.01- to 1-micron diameter.

This paper describes a new fundamental electrical method for sizing monodisperse aerosols of solid or liquid particles in the 0.03- to 10-micron diameter range. Data presented give comparative measurements on several DOP aerosols by this electrical method and two independent optical methods.

Electrical Measurement

The electrical method consists of charging the monodisperse aerosol by unipolar ions at atmospheric pressure and measuring the ratio of the electric mobility of the charged aerosol at two lower pressures. The particle size is then calculated from the measured mobility ratio and pressures.

Since the electric mobility, *Z*, of an aerosol particle of diameter *D_p* carrying *n* elementary units of charge is

$$Z = \frac{neC}{3\pi\mu D_p} \tag{1}$$

the ratio, *R*, of the electric mobilities, *Z₂* and *Z₁*, of the particle at pressures *p₂* and *p₁* is

$$R = Z_2/Z_1 = C_2/C_1 \tag{2}$$

In Equations 1 and 2, *e* is the elementary unit of charge, *μ* is the gas viscosity, and *C*, *C₁*, and *C₂* are the slip corrections to Stokes' law at pressures *p*, *p₁*, and *p₂*. Equation 2 is valid irrespective of the level of charge, *n*, on the particle, provided it remains constant at the two pressures, *p₁* and *p₂*.

The slip correction, *C*, for oil drops is known with great precision from the very careful measurement of Millikan, whose results (Fuchs, 1964) can be expressed as follows to show the effect of pressure.

$$C = 1 + (0.163/D_p p) + (0.0546/D_p p) e^{-D_p p/0.151} \tag{3}$$

where *D_p* is the particle diameter in microns and *p* is the pressure in atmospheres. By means of Equations 2 and 3 the mobility ratio, *R*, can be computed for any combination of pressure and particle size. Figure 1 shows the result of such a computation for pressure ratio *p₁/p₂*, ranging from 2 to 10. More accurate values of *R* can be read from Table II.

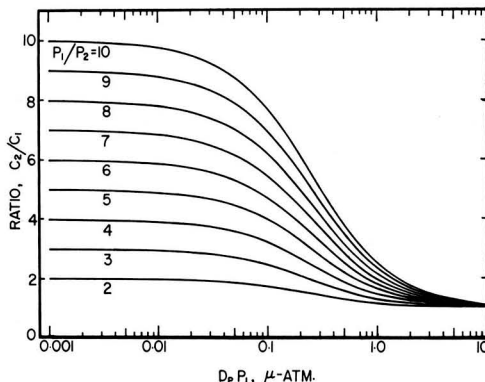


Figure 1. Ratio of slip corrections

To illustrate the use of Figure 1 for aerosol size measurement, consider the following example. The experimental mobility ratio, *R*, is 3.57 for *p₁* = 14 inches of Hg and *p₂* = 1.4 inches of Hg. Using the curve in Figure 1 for *p₁/p₂* = 10, we obtain the value *D_pp₁* = 0.550. Thus, the particle diameter is *D_p* = (0.550)/(14/29.921) = 1.175 microns.

According to Figure 1, the method is useful only over that portion of a curve where there is a "usable" slope. For example, under the conditions of our experiments, *p₁* = 14 inches of Hg and *p₁/p₂* = 10, a 3% error in the experimental value of *R* will result in a 70% error in *D_p* if *D_p* = 0.03 micron. Although the same error in *R* will result only in a 7% error in *D_p* if *D_p* = 10 microns, it is unlikely that the method can be used on particles much larger than 10 microns because of inertial and other limitations. Therefore, the useful range for this method is estimated to be from approximately 0.03 to 10 microns.

Figure 2 shows the experimental apparatus used in these measurements. It is similar to a system used in previous particle charging studies (Liu *et al.*, 1967), but includes apparatus of an improved mechanical design. In this system, the aerosol is first charged in the aerosol charger at atmospheric pressure and then expanded into the mobility analyzer at a lower pressure through a critical orifice. A second critical orifice expands the particle-free clean air from the atmospheric pressure level into the mobility analyzer. The same two critical orifices were used in all experiments. These were made by drawing out a fine glass capillary and calibrated by a wet-test meter. The flow rates were 9.4 and 19.8 cc. per second free air, respectively, for the aerosol and clean air. Pressure in the mobility analyzer

Table II. Ratio of Slip Corrections, C_2/C_1

$D_p p_1,$ $\mu\text{-Atm.}$	p_1/p_2								
	2	3	4	5	6	7	8	9	10
0.01	1.971	2.942	3.913	4.884	5.855	6.826	7.797	8.768	9.739
0.015	1.956	2.913	3.869	4.826	5.783	6.740	7.696	8.653	9.610
0.02	1.942	2.884	3.827	4.769	5.712	6.655	7.597	8.540	9.483
0.03	1.913	2.828	3.743	4.658	5.573	6.488	7.403	8.318	9.233
0.04	1.885	2.773	3.660	4.549	5.437	6.325	7.214	8.102	8.991
0.05	1.858	2.719	3.581	4.443	5.305	6.168	7.030	7.893	8.756
0.06	1.831	2.667	3.503	4.340	5.178	6.015	6.853	7.690	8.528
0.07	1.805	2.616	3.428	4.241	5.054	5.868	6.681	7.495	8.309
0.08	1.780	2.567	3.356	4.145	4.935	5.725	6.516	7.306	8.097
0.09	1.756	2.520	3.286	4.053	4.820	5.588	6.356	7.125	7.893
0.10	1.732	2.474	3.218	3.964	4.710	5.456	6.203	6.950	7.697
0.15	1.628	2.270	2.918	3.567	4.218	4.869	5.521	6.172	6.825
0.20	1.542	2.104	2.672	3.243	3.815	4.389	4.963	5.538	6.113
0.30	1.416	1.856	2.305	2.759	3.215	3.673	4.132	4.592	5.052
0.40	1.332	1.687	2.054	2.426	2.801	3.179	3.558	3.938	4.318
0.50	1.273	1.568	1.875	2.188	2.505	2.824	3.145	3.468	3.791
0.60	1.231	1.482	1.744	2.013	2.285	2.561	2.838	3.117	3.397
0.70	1.200	1.417	1.644	1.879	2.117	2.359	2.603	2.848	3.094
0.80	1.177	1.367	1.567	1.774	1.985	2.200	2.417	2.635	2.855
0.90	1.158	1.327	1.506	1.690	1.880	2.072	2.267	2.463	2.661
1.00	1.143	1.295	1.456	1.622	1.793	1.967	2.144	2.322	2.502
1.50	1.098	1.199	1.305	1.414	1.527	1.643	1.761	1.881	2.003
2.00	1.075	1.151	1.230	1.310	1.393	1.478	1.565	1.654	1.744
3.00	1.052	1.103	1.155	1.208	1.261	1.316	1.372	1.429	1.487
4.00	1.039	1.078	1.117	1.157	1.197	1.237	1.278	1.319	1.361
5.00	1.032	1.063	1.095	1.126	1.158	1.190	1.222	1.255	1.288

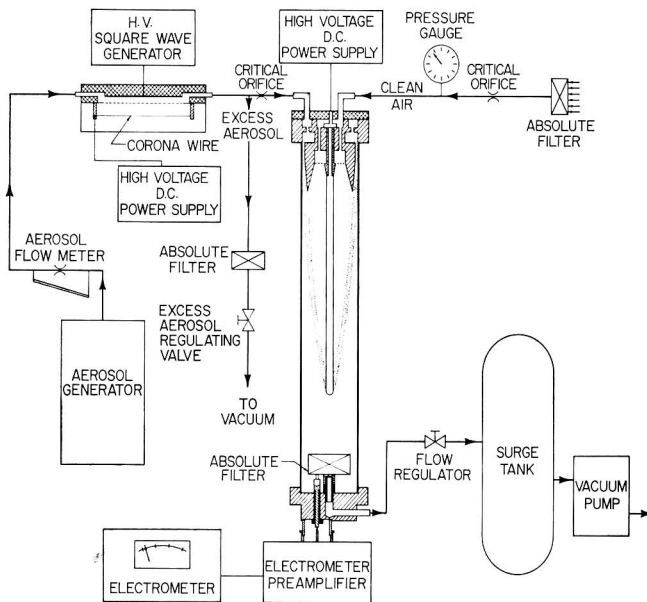


Figure 2. Experimental system for measuring the ratio of slip corrections

was maintained below approximately 15 inches of Hg to obtain critical flow in these orifices.

In the mobility analyzer the positively charged aerosol particles are attracted by the negative voltage applied to the center rod. For a specific center rod voltage, V , the trajectories of particles with mobility Z terminate at the lower end of the rod, where

$$Z = Kq/V = Kq_0/pV \quad (4)$$

In this equation q is the total rate of aerosol and clean air flow at pressure p , q_0 is the total flow rate reduced to a pressure of 1 atm., and K is an instrument constant for the mobility analyzer. K is difficult to determine exactly, since it depends on the patterns of the laminar air flow and the electric field, both of which are difficult to ascertain with precision. In an earlier publication (Liu *et al.*, 1967) expressions for K were derived by neglecting the "fringing" of the electric field near the upper and lower ends of the center rod and assuming the laminar flow to have uniform and fully developed velocity profiles. However, for a specific mobility analyzer operating with a fixed ratio of aerosol to clean air flow rates, K depends only on the operating Reynolds number of the mobility analyzer,

$$Re = vd\rho/\mu \quad (5)$$

where v is the average air velocity, d is the diameter of the outer tube, and ρ is the air density. This can be proved rigorously by dimensional analysis without any simplifying assumptions regarding the distributions of electric field and velocity, provided, of course, the air flow is laminar. Laminar air flow was assured in these experiments, since the Reynolds number was only 26. Further, since the same critical orifices were used, the total free-air flow rate, q_0 , and the product, vp , in Equation 5 were also constants. Thus, the Reynolds number and K in Equation 4 were both constants independent of the operating pressure level in the mobility analyzer. Under these conditions Equation 4 gives for the mobility ratio

$$R = p_1V_1/p_2V_2 \quad (6)$$

where V_1 and V_2 are the corresponding center-rod voltages at pressures p_1 and p_2 .

The experimental procedure for measuring the mobility ratio, R , was as follows. The proper operating condition was first established in the aerosol charger. The mobility analyzer was adjusted to pressure $p_1 = 14$ inches of Hg by the needle valve just ahead of the vacuum tank. The electrometer current was then measured as a function of the center rod voltage. A typical current-voltage curve is shown in Figure 3. The voltage needed to reduce the electrometer current to half of its maximum value was determined and taken as V_1 . Without changing the condition in the aerosol charger the mobility analyzer was adjusted to a lower pressure, $p_2 = 1.4$ inches of Hg and a voltage, V_2 , similarly determined. The mobility ratio was then computed by means of Equation 6.

In these experiments, a Cary Model 31 electrometer was used for current measurement, the mobility analyzer pressure was measured with a precision Wallace-Tiernan absolute pressure gage, and the center rod voltage was obtained directly from a Fluke Model 410B high voltage power supply, whose output voltage could be accurately set to within 0.25%. The probable error in the measured mobility ratio is estimated at approximately 3%.

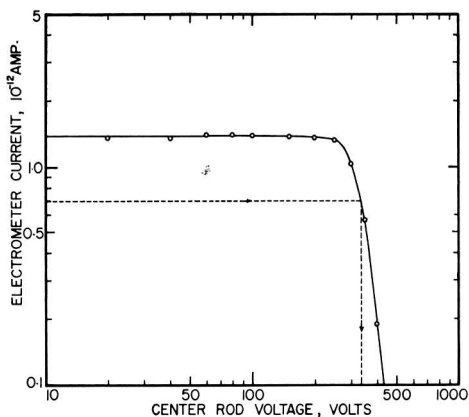


Figure 3. Typical current-voltage curve obtained by mobility analyzer

The operating condition of the aerosol charger affects the measurements in the following way. The electric charge on the aerosol particles should be as uniform as possible. This requires the use of a high charging electric field, E , and a high ion concentration, N , both of which tend to create turbulence in the aerosol flow due to the "electric wind" effect, thus making the aerosol output from the charger unstable. After some trial and error, the following charging conditions were found satisfactory: $E = 2400$ volts per cm.; $N = 8.35 \times 10^7$ ions per cc., t (aerosol charging time) = 0.07 second. These conditions were obtained for the specific charger by means of a square-wave charging voltage of 2400 volts peak-to-peak, a total corona current of $15 \mu\text{a.}$, and a total aerosol flow rate of 93 cc. per second, the charging region in the aerosol charger being a channel 2.54 cm. wide, 0.5 cm. high, and 10.2 cm. long, as shown in Figure 2.

Although the apparatus involved in the electrical method is considerably different from that involved in the familiar drop settling technique, the electrical method may be considered as the electrical analog of the drop settling technique. In the electrical method, measurements are made at two different pressures, primarily to eliminate the effects of the electric charge, n , and the instrument constant, K , since both of these quantities cannot be determined to a degree of accuracy needed for precise aerosol size measurements. This can be seen by referring to Equation 6, which shows that the mobility ratio, R , as determined by the procedure described above, is independent of n , K , and q_0 , being dependent only on the voltage and pressure ratios, both of which can be determined accurately.

Optical Measurements

Two independent optical methods were also used for sizing the monodisperse DOP aerosols. These included an "owl" and a single particle optical counter.

A schematic diagram of the "owl" is shown in Figure 4. The aerosol is illuminated by a beam of collimated light produced by the lamp (GE 1493) operated at 5 volts a.c. and the achromatic lens with a focal length of 4.4 cm. The illuminated aerosol is viewed through the microscope consisting of a $10\times$ microscope eyepiece, an achromatic objec-

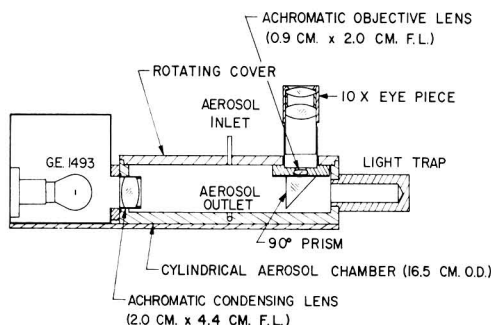


Figure 4. A new aerosol "owl"

tive lens with a focal length of 2.3 cm., and a 90° prism. The microscope is mounted on the top cover plate of the aerosol chamber. This top cover plate can be rotated and its angular position read from a graduated circle to 0.5°. There is also provision for inserting a polaroid in the microscope. In operation, the microscope is rotated from the forward direction until the aerosol appears red and the angular position is read from the graduated circle. The particle size is computed from this first angular red position, θ_1 , by means of the following equation derived from an equation in a somewhat different form given by Kitani (1960).

$$D_p = 10 \theta_1^{-0.7} \quad (7)$$

where D_p is in microns and θ_1 is in degrees. The above equation is based on theoretical calculations on light scattering by small particles and, according to Kitani, applies to particles with refractive indices in the 1.33 to 1.55 range. The refractive index of DOP is 1.49.

The aerosol owl described above is similar in operating principle to the instrument described by Sinclair and LaMer (1949). However, the mechanical design is considerably different. The 90° prism was used here, so that the entire optical path between the illuminated aerosol and the microscope can be enclosed within the darkened aerosol chamber. This reduces the stray light from the laboratory and aids in discerning the red in the Tyndall spectra. Also, the aerosol chamber is relatively large, permitting the microscope to be swung unobstructed over a large angle. Effective measurements can be made by this instrument over an angular range from 15° to 165°, as compared to the 30° to 150° range of the Sinclair-LaMer instrument.

The single particle optical counter used was a Royco PC 200 (Whitby and Vomela, 1967). The DOP aerosol of high particle concentration produced by the aerosol generator was first diluted by a capillary diluter (Whitby, 1967) before being fed to the optical counter. Care was taken to prevent loss of particle count by coincidence.

Results

Measurements were made on monodisperse DOP aerosols of four different sizes by the electrical method. Only the three largest aerosols could be measured by the owl and the two largest aerosols by the Royco, the smaller aerosols being below the range of these instruments. The

Table III. Results of Comparative Measurements on DOP Aerosols

Aerosol	Particle Diameter, Microns		
	Electrical Method	Owl	Royco (n.m.d.)
1	1.175	1.15 ($\theta_1 = 22^\circ$)	0.94
2	0.705	0.70 ($\theta_1 = 44^\circ$)	0.53
3	0.303	0.33 ($\theta_1 = 130^\circ$)	
4	0.060		

aerosols were produced by the generator described previously by Liu *et al.* (1966). The results are given in Table III.

The agreement between the electrical method and the owl for the two largest aerosols is very good, the difference being entirely within the limit of error of these methods. The 10% difference for the third aerosol is probably within the limit of error of the owl, since the aerosol size is very close to the lower limit of the instrument. The red color in the Tyndall spectra for this aerosol was not very visible and considerable judgment had to be exercised in determining its first angular red position. The fourth aerosol was below the limits of both the owl and the Royco. Therefore, no comparative measurements could be made for this aerosol.

The results in Table III show that the DOP particle sizes indicated by the Royco counter were, respectively, 20 and 25% smaller than the sizes measured by the other two techniques. The difference is probably due to the difference in the refractive indices of the DOP (1.49) and the polystyrene latex particles (1.58) used in calibrating the Royco counter. An examination of the theoretical calculations made by Hodkinson and Greenfield (1965) of the response characteristics of this counter shows that this difference can be accounted for entirely by this difference in the refractive index.

Conclusions

The very good agreement between the electrical method and the owl is particularly gratifying in view of the widely differing nature of these methods and the fact that in both methods the particle size is derived from the measured variables by fundamental mechanical or optical principles. The authors' experience with the electrical method shows that it has the following advantages.

The size range of the method, 0.03- to 10-micron diameter, is considerably wider than the other available techniques. The measured variables can be converted directly to particle size by means of fundamental principles in the mechanics of aerosols, permitting the size of liquid aerosols to be determined directly. The method is rapid and capable of high precision, since the measured variables, voltage and pressure, can both be determined readily and very precisely. The method can be applied to both solid and liquid aerosols, and the results are unaffected by such particle properties as density and refractive index. The aerosol being measured does not have to be very monodisperse, as is required when using the owl. According to Kitani (1960), the owl can be used only on aerosols with a standard deviation less than 0.12 micron.

However, because the mobility analyzer is operated at low pressure, one major limitation of this method is that the aerosol must not evaporate in the vacuum environment of the system. The transit time of the aerosol through the low pressure portion of the system is approximately 3 seconds at the pressure of 1.4 inches of Hg. Therefore, this method is applicable only to a nonvolatile aerosol whose size does not change during this interval of time.

Acknowledgment

We acknowledge the help of Jiri Tuma and Milos Tomaides, Research Institute for Air Engineering, Prague, Czechoslovakia, who suggested the optical design of the aerosol "owl" to us.

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Received for review July 5, 1968. Accepted January 10, 1969. Publication 123, Particle Technology Laboratory. Based on work performed under AEC Contract AT(11-1)-1248, publication No. COO 1248-16 under the AEC contract and USPHS Research Grant No. AP 00136-07.

Measurement of Mass Flow and Density of Aerosols in Transport

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■ Accurate methods for determination of the local mass flow and density of aerosol particles in a suspension include differential isokinetic sampling with a correction of depletion, and fiber optic measurement of the density of particles. These two probes can be combined into a single probe. Within the capability of the filters used, there is no lower limit for isokinetic sampling; the lower limit of fiber optics probe was 0.015 kg. per sq. meter. The average charge to mass ratio of a particle cloud can be determined using the same sampling probe.

Accurate measurement of local mass flow and local density of an aerosol suspension is basic to sampling in general and hydrodynamic evaluation of control apparatus in particular.

Primary methods for determining the particulate content of a gas include filtration of the solids in a gas, correlating certain physical characteristics of the particulate matter, such as radioactivity, dielectric constant, and ability to take on charge according to its size, and utilizing the attenuation of some energy source, such as light, sound, or atomic

radiation, passing through the particulate suspension (Mitchell and Engdahl, 1963).

General factors which complicate the probe are variable gas moisture content and temperature, variable particle-size distribution, variable gas velocity, extreme variation in physical properties of the particulate matter, and sensing probe cleanliness. Further, principles which appear promising at extremely high particle concentrations are not applicable to low density (Mitchell and Engdahl, 1963).

The earlier electrostatic probe (Soo, Trezek, *et al.*, 1964) performs on the basis of charge transfer and gives only the relative magnitude of particle flux. In the present investigation the filtration method was utilized for measuring the particle flux, while the attenuation of light passing through a suspension was used for monitoring the particulate cloud density. This optical system is an improved form of the earlier fiber optic probe (Soo, Trezek, *et al.*, 1964). Measurements were carried out in a 12 × 12 inch flow duct for various suspensions in air. Flow into a channel formed by parallel plates in this duct was studied.

Isokinetic Sampling Probe Theory

The basic requirement for measuring particle flux is that the sample extracted be totally representative of the particulate cloud at the sample point in the stream. The differ-

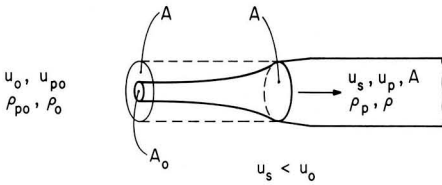


Figure 1. Sampling theory definition sketch, $u_s < u_o$

ences in mass flux, concentration, and particle size distribution between the particulate cloud and the sample must be as small as possible.

Mass Flux

Consider a particulate cloud having a density, ρ_{po} , and velocity, u_{po} , being carried by a carrier gas of density ρ_o and velocity u_o , approaching a sample tube (Figure 1), and let the sampling velocity, u_s , be less than u_o . The mass of particles which enter the sampling probe from the region $A_o = \pi R_o^2$, where R_o is the collision cross section radius for the air stream, is given by

$$\rho_{po} u_{po} A_o \Delta t$$

Under conditions for which $u_s < u_o$, a fraction α of the particles in the region $(A - A_o)$ also enter the probe. The mass contribution from the area $(A - A_o)$ entering the probe is $\alpha \rho_{po} u_{po} (A - A_o) \Delta t$. Hence, the total mass, M_p , entering the probe is

$$M_p = \rho_p u_p A \Delta t = \rho_{po} u_{po} A_o \Delta t + \alpha \rho_{po} u_{po} (A - A_o) \Delta t \quad (1)$$

Since

$$\rho_o A_o u_o = \rho A u_s \quad (2)$$

we get, after rearranging:

$$\frac{\rho_p u_p}{\rho_{po} u_{po}} = \frac{\rho}{\rho_o} \left[\frac{u_s}{u_o} \right] + \alpha \left[1 - \frac{\rho u_s}{\rho_o u_o} \right] \quad (3)$$

For $u_s > u_o$, the above is unchanged. If the fluid is incompressible, $\rho = \rho_o$, we have

$$\frac{\rho_p u_p}{\rho_{po} u_{po}} = \frac{u_s}{u_o} + \alpha \left[1 - \frac{u_s}{u_o} \right] \quad (4)$$

Hence, either under isokinetic conditions ($u_s = u_o$), or if the particle diameter is large—i.e., $\alpha \rightarrow 1$, ($u_s \neq u_o$)—we have

$$\frac{\rho_p u_p}{\rho_{po} u_{po}} = 1 \quad (5)$$

Therefore, a truly representative sample of particle mass flux is obtained either when the sample is extracted under isokinetic conditions, or when the particles are of sufficient size that, because of the particle inertia, the trajectory of the particle is unaffected by the carrier gas velocity. Further, mass flow sampling is unaffected by the relationship between u_{po} and u_o —that is, it is unaffected by slip between the phases.

Particle Density

From the definition of the particulate cloud density, one obtains

$$\rho_p = \frac{M_p}{V}$$

where V is the total volume containing M_p , and

$$V = V_p + V_g$$

where subscripts p and g denote portions of volume occupied by the particles and the fluid, respectively, and

$$M_p \equiv \bar{\rho}_p V = \frac{V_p}{v_p} m_p = V_p \bar{\rho}_p$$

for mass m_p and volume v_p of each particle. Elimination of V_p gives

$$\rho_p = \frac{M_p}{V_g} \left(1 - \frac{\rho_p}{\bar{\rho}_p} \right)$$

Solving for ρ_p gives

$$\rho_p = \frac{M_p}{V_g} \frac{1}{\left[1 + \frac{1}{\bar{\rho}_p} \frac{M_p}{V_g} \right]} \quad (6)$$

Further

$$V_g = A u_s \Delta t \quad (7)$$

Substituting Equations 1, 2, and 7 into Equation 6 gives

$$\frac{\rho_p}{\rho_{po}} = \frac{\frac{u_{po}}{u_o} \left(\frac{\rho}{\rho_o} \right) + \alpha \frac{u_{po}}{u_s} \left[1 - \frac{\rho u_s}{\rho_o u_o} \right]}{\left\{ 1 + \frac{\rho_{po}}{\bar{\rho}_p} \left[\frac{u_{po}}{u_o} \left(\frac{\rho}{\rho_o} \right) + \alpha \frac{u_{po}}{u_s} \left(1 - \frac{\rho u_s}{\rho_o u_o} \right) \right] \right\}}$$

Since the second term in the denominator is always less than 1, Equation 7 can be written as

$$\frac{\rho_p}{\rho_{po}} = \left\{ \frac{u_{po}}{u_o} \left[\frac{\rho}{\rho_o} \right] + \alpha \left[\frac{u_{po}}{u_s} \right] \left[1 - \frac{\rho u_s}{\rho_o u_o} \right] \right\} \left\{ 1 - \frac{\rho_{po}}{\bar{\rho}_p} \left[\frac{u_{po}}{u_o} \left(\frac{\rho}{\rho_o} \right) + \alpha \frac{u_{po}}{u_s} \left(1 - \frac{\rho u_s}{\rho_o u_o} \right) \right] + \dots \right\} \quad (8)$$

For $u_s > u_o$, the above is unchanged. Equation 8 takes into account slip between the gaseous and particle phase, nonisokinetic conditions, and any compressibility effects. Special cases are:

INCOMPRESSIBLE $\rho = \rho_o$ AND DILUTE SUSPENSIONS ($\rho_p / \bar{\rho}_p \ll 1$).

$$\frac{\rho_p}{\rho_{po}} = \left[\frac{u_{po}}{u_o} + \alpha \frac{u_{po}}{u_s} \left(1 - \frac{u_s}{u_o} \right) \right] \quad (9)$$

Under isokinetic conditions—namely, $u_s = u_o$ —

$$\frac{\rho_p}{\rho_{po}} = \frac{u_{po}}{u_o} \quad (10)$$

Hence, isokinetic conditions alone are not sufficient for density determination using a sampling probe.

INCOMPRESSIBLE FLUID $\rho = \rho_o$, with either dilute suspensions $\rho_p / \bar{\rho}_p \ll 1$ and no slip $u_{po} = u_o$, or as $\alpha \rightarrow 0$ —i.e., if the particle diameter is small, we have

$$\frac{\rho_p}{\rho_{po}} = 1 \quad (11)$$

Unlike the mass flux, isokinetic sampling conditions do not assure a sample density representative of the stream density. It is only when there is no slip motion between phases that a representative stream density can be obtained

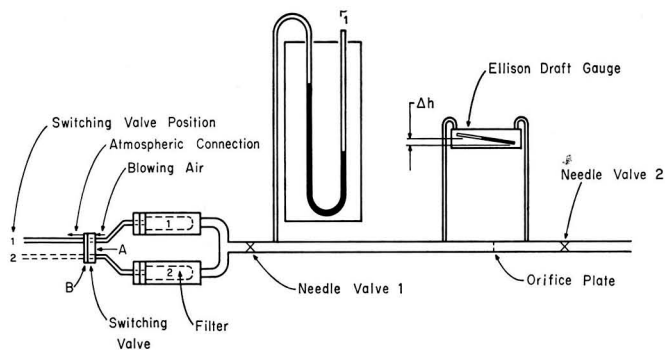


Figure 2. Schematic diagram of sampling apparatus

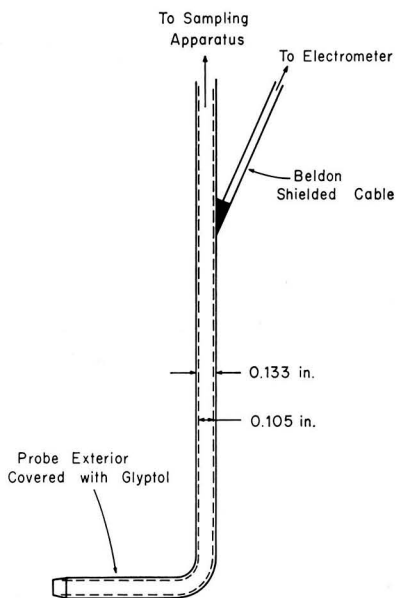


Figure 3. Sampling probe

through sampling procedures. Unless particle velocity is measured independently (Soo, Ihrig, *et al.*, 1960), sampling techniques cannot give cloud density in a carrier velocity gradient. However, independent measurement of velocity of a particle cloud is extremely difficult. An optical method for measuring the cloud density is described below.

Isokinetic Sampling System

An isokinetic sampling system consists of a sampling nozzle, a suitable filter for the extraction of the particle from the air stream, a means of weighing the filter accurately before and after each test run, a means for measuring the volume of the carrier gas extracted from the stream, a timing device, and a means for measuring the carrier gas velocity at the point where the sample is to be taken (Figure 2).

The fundamental purpose of the system is to extract an isokinetic sample from the stream over a given time period, Δt . To do this, isokinetic conditions must be set prior to

taking a sample. This necessitates having two filters and a switching valve.

Sampling Nozzle. The sample nozzle (Figure 3) is a hypodermic tubing, 0.105-inch i.d. and 0.133-inch o.d., coated with glyptol to provide insulation from the charged particles. Deposition of sampled particles occurred in the initial period. Once stabilized, further deposition became negligible because a layer of surface charge was built up by collected particles (Soo and Trezek, 1966). This initial deposition and adjustment from a previous condition of measurement were accounted for by the method of differential sampling described below.

Switching Valve. The switching valve was designed to take into account the fact that extraction from the system must be stopped effectively during the nonsampling period, and packing of particles into the sampling tube must be prevented during the nonsampling period.

The switching valve must effect the following (denote sampling filter thimble as thimble 1 and the standby filter thimble as thimble 2):

Mode A. Connect the sampling probe to thimble 1 for mass flow sampling over a time Δt .

Mode B. During the nonsampling period, connect thimble 2 to the atmosphere and connect the sampling probe to blowing air to prevent plugging.

Mode C. During the isokinetic matching period, connect thimble 2 to the sampling probe.

Referring to the diagrammatic setup in Figures 2 and 4, the sampling valve is denoted as two pieces, *A* and *B*. Figure 4 (upper) shows that *A* is fixed with holes connected to thimbles 1 and 2 blowing air, and *B* with center hole connected to the sampling probe and atmospheric connection. When *B* in Figure 4 (upper) is superimposed on *A* in the parallel sense we have Mode A.

Figure 4 (center) shows that *B* with quarter (90°) turn gives Mode B with thimble 1 cutoff, thimble 2 connected to atmosphere, and sampling probe connected to blowing air.

Figure 4 (lower) shows that *B* with a further $1/8$ turn (45° or 135° total) connects thimble 2 to the sampling probe only for isokinetic matching in the shortest possible time, Mode C.

The above sequence is reversed after isokinetic matching such that sampling probe is first cleared and then connected to thimble 1. Instant action of the valve was obtained by a notch and spring arrangement.

Particle Filter. An ideal filter should have high filter efficiency, low moisture absorptivity, low pressure drop

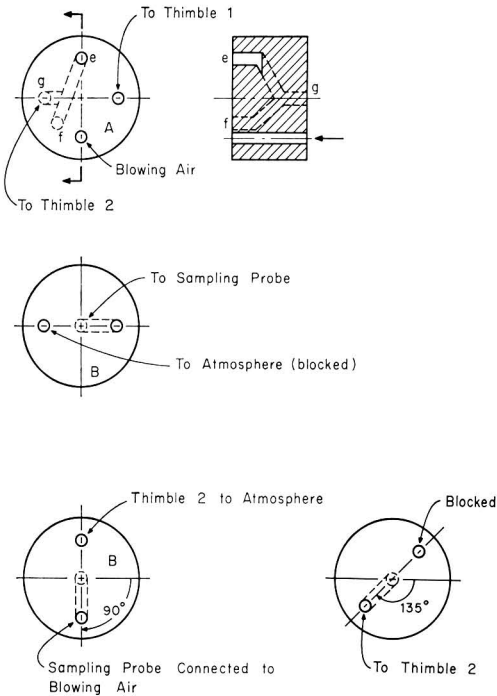


Figure 4. Switching valve for isokinetic sampling in a flow system

through the filter, and low particle retention in the filter pores. Low particle retention means that while particles are trapped in the filter, they do not become lodged in the interstices of the filter material. For the present study Whatman extraction filters were used. Whatman claims 100% filtering efficiency down to 2 microns. By using a "vacuum cleaner" technique, the filtering technique used consisted of placing a quantity of particles on a piece of paper and weighing the paper and particles. The sampling tube was then used to vacuum the particles off the paper into a preweighed thimble. The collection thimble and the paper with particles were then reweighed. By noting the difference between the weight loss of the paper with particles and weight gain by the thimble, the collection efficiency was estimated.

The moisture absorptivity of the Whatman filter is not minimal. The relative humidity of the room was kept fairly constant and, by utilizing a control filter with each set of filters, compensations were made for filter weight changes due to change in moisture content. The variation generally amounted to less than 1%.

Pressure drop through the filter was small and variations in the total pressure drop of the system due to different filters was entirely negligible. Pressure drop characteristics of the thimble change as the quantity of trapped particles increases. However, over the range of operation for the investigation, the pressure drop was virtually unaffected by particle buildup in the thimbles.

Particle retention in the pores was high for the Whatman filter. Since this investigation did not require chemical analysis or any similar processes, the filter shortcoming did not present any problem. A Sartorius analytical balance, Model 2743, was used for weighing the filters.

Carrier Gas Volumetric Control Unit. A calibrated orifice plate of $\pm 2\%$ accuracy, positioned as shown in Figure 2, was used to measure the volume of gas extracted. By proper manipulation of needle valves 1 and 2 (Figure 2), any desired gas velocity may be obtained at the probe entrance by adjusting the valves so that P_1 is 10 inches of Hg and Δh is the desired value as determined from the calibration curve.

Carrier Gas Velocity Measurement. The mean velocity in the flow system was measured by a commercial Pitot tube, No. 166-12 (Dwyer Instrument Co., Michigan City, Ind.). The physical dimensions are: outer tube, 0.120 inch; inner tube, 0.065 inch; length, 18 inches. An Ellison inclined manometer, reading in inches of water and using oil (S.G. 0.827) as the indicating fluid, was employed for velocity head measurement. Since the suspension was dilute $\rho_p/\bar{\rho}_p \ll 1$, the mean air velocity was known to be unaffected by the presence of particles (Peskin and Dwyer, 1964; Soo, 1962; Soo, Trezek *et al.*, 1964; Soo and Trezek, 1966; Trezek, 1965).

Differential Isokinetic Sampling

The sampling procedure includes collection of a sample of mass M_{p1} over time Δt_1 , for a total hold of W_p in the system

$$M_{p1} = \rho_p u_p A (\Delta t_1 - t_{\text{lag}}) \quad (12)$$

The time t_{lag} accounts for the consistent timing error in switching, the time lag due to the volume of the sampling time and filter volume itself. Correction for the t_{lag} is achieved by taking another sample M_{p2} from the restored holdup W_p over time Δt_2 . Let $\mu = \rho_p u_p$; Equation 12 and that for time Δt_2 are rewritten

$$c + M_{p1} = A \Delta t_1 \bar{\mu}_1 \quad (13)$$

$$c + M_{p2} = A \Delta t_2 \bar{\mu}_2 \quad (14)$$

and

$$\bar{\mu} = \frac{\mu_i + \mu_f}{2}$$

for each period, i for initial time, f for final time. For mass content W_p in the system, $\mu \alpha W_p$ or $\mu = \alpha W_p$, α being the proportionality constant.

$$\mu_f = \alpha W_{pf} = \alpha [W_{pi} - c - \bar{\mu} A (\Delta t)] \quad (15)$$

$$\text{or } \mu_f \left[1 + \frac{\alpha A}{2} \Delta t \right] = \mu_i \left[1 - \frac{\alpha A}{2} \Delta t \right] - \frac{\mu_i}{W_{pi}} c \quad (16)$$

when $\alpha = \mu_i / W_{pi}$, or

$$\begin{aligned} \bar{\mu} &= \frac{\mu_i}{2} + \frac{\mu_i \left[1 - \frac{\mu_i}{W_{pi}} \frac{A}{2} \Delta t - \frac{c}{W_{pi}} \right]}{1 + \frac{\mu_i}{W_{pi}} \frac{A}{2} \Delta t} \\ &= \mu_i \frac{2 - \frac{c}{W_{pi}}}{1 + \frac{\mu_i}{W_{pi}} \frac{A}{2} \Delta t} \quad (17) \end{aligned}$$

Substitutions of Equations 16 and 17 into Equations 13 and 14 give

$$\begin{aligned} \mu_i \left(1 - \frac{c}{W_{pi}} \right) &= \frac{M_{p1} - M_{p2}}{A (\Delta t_1 - \Delta t_2)} \left(1 + \frac{1}{2} \frac{\mu_i}{W_{pi}} A \Delta t_1 \right) \\ \left(1 + \frac{1}{2} \frac{\mu_i}{W_{pi}} A \Delta t_2 \right) &\sim \mu_i \quad (18) \end{aligned}$$

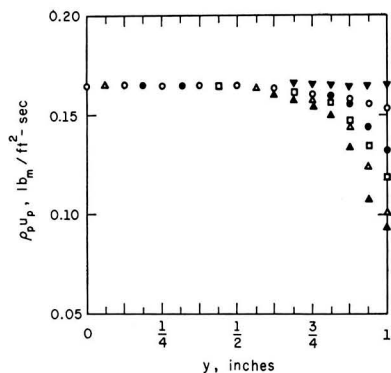


Figure 5. Typical mass flux distribution in duct formed by parallel plates

(14 microns MgO in air at mass flux ratio of 0.035, free stream velocity of 67 feet per second, 2 inches between plates, x measured from leading edge, y measured from center of pipe)

Symbol	x/b	$m_i^* = 0.035$
▽	0	
○	2	
●	4	$u_i = 67 \text{ ft./sec.}$
□	8	
△	12	$b = 1 \text{ inch}$
▲	20	

as a correction of the relation for finite holdup. c/W_{pi} is usually very small or $c/W_{pi} \sim 0$, although c/M_p is not negligible. This correction is not needed for a very large system, a steady-flow system, or a once-through system. Equation 18 is valid when W_p is restored to W_{pi} at the beginning of each sampling by replenishing the mass removed in the previous sampling. Equation 18 is valid only if W_{pi} is not completely depleted with Δt . When $(\mu_i/2W_{pi})A\Delta t$ is usually small, Equation 18 can be solved for μ_i to give:

$$\mu_i = \frac{(M_{p1} - M_{p2})}{A(\Delta t_1 - \Delta t_2)} \left[1 + \frac{(M_1 - M_2)}{2W_{pi}} - \frac{(\Delta t_1 + \Delta t_2)}{(\Delta t_1 - \Delta t_2)} \right] \quad (19)$$

as a correction for finite holdup. When depletion is negligible over the sampling times or when sampling is made for a steady supply of suspension, differential sampling is simply

$$\rho_p u_p A = \frac{M_{p2} - M_{p1}}{\Delta t_2 - \Delta t_1} \quad (20)$$

Results of measurement made on the mass flow distribution of 12-micron magnesia in air at 2, 4, 8, 12, and 20 inches downstream from the leading edge of a 4×12 inch flow channel are shown in Figure 5.

When the condition of no slip exists ($u_{p0} = u_0$), the local density, ρ_p , can be determined from the mass flux and the volumetric flow of air through the sampling probe. The volumetric air flow, V_g , can be determined from the orifice plate measurement over time Δt from the relation

$$V_{g1} = u_0 A (\Delta t_1 - t_{lag}) \quad (21)$$

with $(\Delta t_1 - t_{lag})$ being determined from Equation 12 and V_{g1} calculated for M_{p1} . For the present experiments $M_{p1}/V_g \ll \rho_p$, at $u_{p0} = u_0$, Equation 6 gives

$$\rho_p = \frac{M_{p1}}{V_{g1}} \quad (22)$$

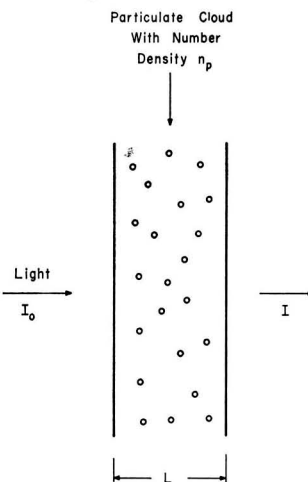


Figure 6. Definition sketch for extinction law

Fiber Optic Density Probe Theory

For improved sensitivity, an improved fiber optic probe was devised (Soo, Trezek, *et al.*, 1964). When particulate matter passes between a light source and a photosensitive device, the intensity of the light source as "seen" by the sensing device is altered because of light attenuation by the particles.

Since a photocell is a resistor whose resistance varies as the intensity of the light striking it, the change in the photocell resistance can be monitored by an appropriate circuit. To demonstrate the relationship among the change in light intensity, the photocell resistance, the density change, and the change in current of the monitoring circuit, consider first a monodisperse suspension of small particles.

Referring to Figure 6, the extinction law states that

$$\frac{I}{I_0} = \exp(-k\pi a^2 n_p L) = \exp(-k\pi a^2 \frac{m_p n_p L}{m_p}) \quad (23)$$

for number density n_p , radius a of particles of mass m_p ; k is a constant of proportionality. Since $n_p m_p = \rho_p$ we can express Equation 23 as

$$\ln \frac{I}{I_0} = -k \left(\frac{L}{a} \right) \left(\frac{\rho_p}{\rho_p} \right) \quad (24)$$

For L and a constant, the change in I for a change in ρ_p is given by

$$\frac{dI}{I} = -k' \left(\frac{L}{a} \right) \frac{1}{\rho_p} d\rho_p \quad (25)$$

From Equation 25 it is seen that for a fixed geometry, particle composition, and particle diameter, the per cent change in I is proportional to the change in the concentration.

If we now remove the restrictions of a monodisperse suspension and small particles, Equation 25 becomes

$$\frac{dI}{I} = -K' d\rho_p \quad (26)$$

with $K_1' = K_1'(L, \rho_p, a)$ where a represents a characteristic mean radius of the suspension, say, the average particle

diameter. If the photocell is operating in its "linear range," then

$$\frac{dI}{I} = K_p \frac{dR}{R}$$

where R is the photocell resistance.

Combining the above with Equation 26 gives

$$-K_1' d\rho_p = K_p \frac{dR}{R} \quad (27)$$

or
$$d\rho_p = K_p' \frac{dR}{R} \quad (28)$$

Over the range of operation used in the investigation, the circuit characteristics were such that

$$\frac{dR}{R} = K_i' di \quad (29)$$

Hence, substituting Equation 29 into Equation 28 gives

$$d\rho_p = K_p' K_i' di = K_L di$$

or
$$\rho_p = K_L i + \text{constant}$$

If the no particle condition is taken as reference—namely, $\rho_p = 0$, when $i = 0$ —then $\rho_p = K_L i$ (30)

The above equation holds only if the photocell is operating in its "linear" range, the relationship $K_1' d\rho_p$ holds where K_1' is assumed constant, and the circuit current response to a change in resistance is given by $dR/R = K_i' di$. The acceptance of Equation 30 also tacitly assumes that any particle buildup on the optical surfaces of the monitoring system is either negligible or remains constant over the range of operation. If the latter is the case, K_L becomes a function of the degree of buildup.

Density Probe Construction

The probe used for density measurements is shown in Figure 7. The probe is made up of four components—namely, two 1/8-inch AO flexible light guides made by American Optical Co., and a 1/8-inch glass tube through which the particulate matter flows.

Light from a G.E. No. 1488 bulb was transmitted by a light guide to the face of the glass tube (Figure 7). The light then made an initial pass through the suspension and was directed 180° back through the glass tube by a U-shaped light guide. Having made a second pass through the suspension, the light was transmitted by the second light guide to a Clairex 705HL photocell. By passing the light through the suspension more than once, say, by a series of U bends, the light extinction by the suspension can be further amplified. This amplification becomes important for dilute suspensions. If the suspension is dilute, the photocell resistance change due to the light extinction is minimal. Under these conditions circuit and probe noise can be significant. By increasing the light extinction by means of multiple passes through the suspension, however, a manageable output signal is realized from the photocell monitoring circuit because of the large resistance change of the photocell.

Two advantages are realized with this type of probe. First, the geometry of the probe combined with the fiber optic light guide allows the light source and photocell to be located at large distances from the point of measurement. This allows miniaturization of the instrument at the point of measurement. Second, the geometry of the

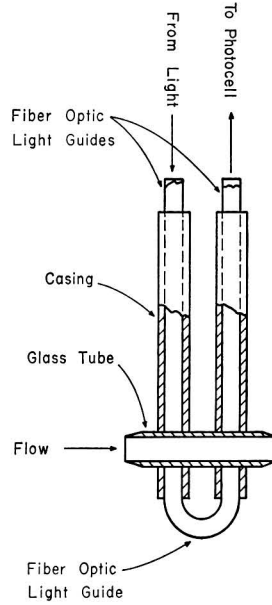


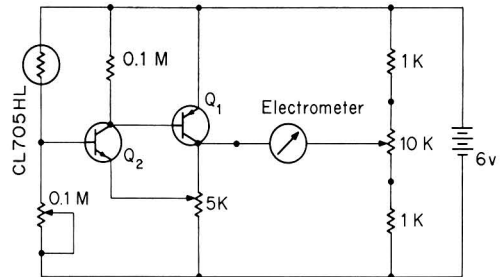
Figure 7. Fiber optic density probe

probe combined with the fiber optic system allows density measurements to be made at the point in question and examined at some far removed point.

When 12 volts were applied to the light, the light intensity output of the probe matched the sensitivity of the Clairex 705 HL photocell very well. The circuitry for the density probe is shown in Figure 8.

Concentration data were taken as follows: The monitoring circuit was adjusted to zero by means of the zero adjustment potentiometer of the circuit while the probe was out of the flow duct. The probe was then lowered into the duct core region ($u_{p0} = u_0$) upstream of the parallel plates where the particulate density is known from sampling measurement. The change in current due to the light attenuation was then recorded. From these measurements a calibration curve was generated (Figure 9).

Stream direction (x -direction) measurements were taken along the midpoint of the flow channel and referred to the plates entrance ($x = 0$). Next, traverse (y -direction) measurements were taken at each x position and referred to the midpoint of the plate gap ($y = 0$).



Q₁ - 2N1305 , Q₂ - 2N1304

Figure 8. Density probe circuitry

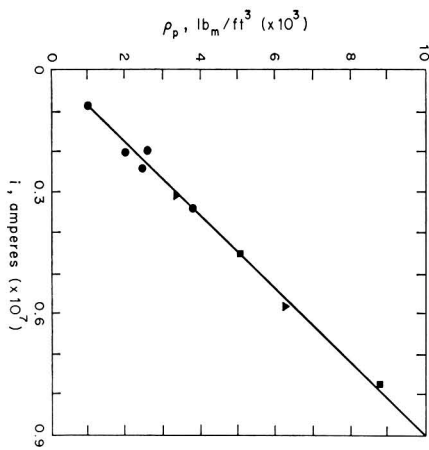


Figure 9. Density probe calibration curve

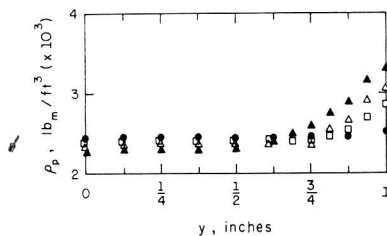


Figure 10. Typical density distribution in duct formed by parallel plates

14 microns MgO in air at mean flow ratio of 0.035, free stream velocity of 67 feet per second, 2 inches between plates, x measured from the leading edge and y measured from center of gap

Symbol	x/b	$m_i^* = 0.035$
●	4	
□	8	
△	12	$u_i = 67$ ft./sec.
▲	20	$b = 1$ inch

The output of the electrometer was recorded on a 20-mv. Leeds & Northrup Speed-O-Max strip chart recorder. A 500-ohm Heliplot shunted across the output of the electrometer provided a method for accurately setting the full scale sensitivity of the recorder without disturbing the input range switching on the electrometer.

Density Probe Calibration

The optical scale factor is evaluated by a normalizing procedure with respect to the parallel plate upstream conditions. Experiments by other investigators (Soo, Ihrig, *et al.*, 1960; Trezek, 1965) have shown that in the center region of a duct the particles are traveling at very nearly the fluid velocity. This fact is attributed to a small particle diffusivity in the duct center region so that a particle travels far enough downstream between successive contacts with the wall to be accelerated to nearly the fluid velocity. Since in the core region

$$u_{p1} = u_1$$

the sampling probe can be used to measure the density in the fully developed core of the duct. Therefore, from the sampling probe

$$\rho_{p1} u_{p1} A = \dot{m}_{p1}$$

or

$$\rho_{p1} u_1 A = \dot{m}_{p1}$$

Hence,

$$\rho_{p1} = \frac{\dot{m}_{p1}}{u_1 A}$$

If the no particle condition is taken as reference—i.e., $\rho_p = 0$, when $i = 0$ —then

$$\rho_p = K_L i$$

so

$$K_L = \frac{\rho_{p1}}{i_1} = \frac{\dot{m}_{p1}}{u_1 A i_1}$$

From Figure 11

$$K_L = 11.3 \times 10^4 \frac{\text{lb}_m}{\text{sq. ft.} \cdot \text{amp.}}$$

A typical mean density distribution for a magnesia suspension in air is shown in Figure 10. The data for Figures 6 and 11 were obtained in the same flow channel.

Combined Mass Flow and Density Probe

Figure 12 shows a density probe devised for concentration measurements which applied the same principle but a different configuration. In addition, this probe could be used to measure mass flow simultaneously with concentration. The fact that the suspension attenuated the light three times increased the measured sensitivity from that measured for a single attenuation. The sensitivity referred to here is the resistance change of the photocell from the

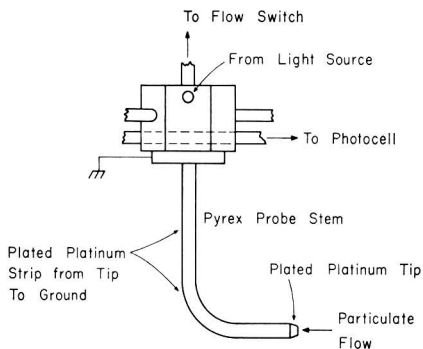
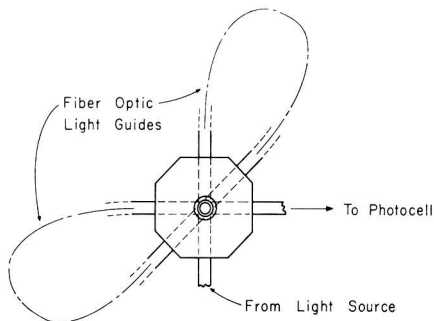


Figure 11. Fiber optic probe

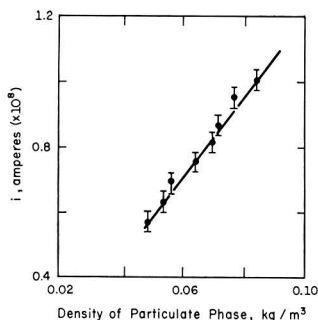


Figure 12. Calibration for fiber optic probe

case of clean air to that of dusty air divided by the photocell resistance for the case of clean air. A G.E. No. 1488 incandescent light source supplied by a 12-volt battery and a Clairex 705 HL photocell were employed. This combination provided the highest sensitivity found among the several tested. The calibration curve for the combination probe is shown in Figure 13.

Charge to Mass Measurement

Together with mass flow measurements, we can also determine charge to mass ratios of the particles. This is done with a shielded Belden cable soldered to the sampling probe (Figure 3). While maintaining the potential of the probe near ground potential, the sampling probe was allowed to discharge to ground through an electrometer. Since the mass flow rate is known, the average charge to mass ratio (\bar{q}/m_p) can be estimated by

$$\frac{i_p}{\dot{m}_p} \cong \frac{\bar{q}}{m_p}$$

Measurements were made where the probe potential was floated between ± 20 volts. The current under this

floated condition did not change appreciably. Charge to mass measurements obtained in this way were seen to agree favorably with those made by Min *et al.* (1963).

For the current ranges most often used, 10^{-7} to 10^{-9} ampere full scale, the input is 10^7 and 10^9 ohms, respectively. Therefore, for the probe to be acceptable, it must have at least a 10^{11} -ohm resistance, so as not to shunt the input to ground. The leakage resistance of the probe was greater than 10^{12} ohms. With this leakage resistance, 0.1% or less of the probe current was shunted to ground. For the same example of flow channel which gave Figures 5 and 11, charge to mass ratio of the order 10^{-3} coulomb per kg. was measured.

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Received for review June 20, 1968. Accepted December 19, 1968. Study supported under Grant USPH 1-R01 AP 00541-01, Division of Air Pollution, Bureau of State Services, U. S. Public Health Service, Department of Health, Education and Welfare. J. J. Stukel and J. M. Hughes sponsored by training grant 2 TI-AP-16-03,04 National Center of Air Pollution Control, U. S. Public Health Service, Department of Health, Education and Welfare.

COMMUNICATIONS

Concentration of Dilute Aqueous Phenol Solutions Utilizing Methylsulfinylmethane (DMSO)

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■ Vacuum distillation concentration with added DMSO (methylsulfinylmethane) gave better phenol recoveries than the same procedure without DMSO. Phenol recovery increased with the amount of DMSO employed. In the absence of DMSO, a 65- μ g-per-liter phenol solution showed 13% recovery upon vacuum concentration, while under identical conditions in the presence of 500 ml. per liter of DMSO, phenol recovery was 64%. *N*-methyl-2-pyrrolidone instead of DMSO gave a phenol recovery which was comparable to that obtained when the same volume of DMSO was used. The results obtained in this study suggest that vacuum distillation utilizing organic solvents will improve recovery of volatile compounds from aqueous solutions.

Evaporation at atmospheric or reduced pressures is by far the most frequently used method of solute concentration. It is usually the method of choice for non-volatile solutes. However, evaporation may not be used for volatile solutes because of loss. Previous studies in this laboratory (Gjessing and Lee, 1967) have shown that as much as 10% of the dissolved organic carbon present in natural waters is lost during evaporation under reduced pressure at 30° C. Johnson (1965) in this laboratory has shown that toxaphene may be recovered from natural waters by vacuum evaporation in the presence of paraffin oil.

This investigation was undertaken to explore other solvents for concentrating aqueous solutions with a minimum loss of volatile compounds. The compound used in this study was phenol. The method investigated consisted

of the addition of DMSO (methylsulfinylmethane) to an aqueous sample and concentration of the resultant solution by use of reduced pressure distillation at 40° C. A survey of the literature (Tranquillo, 1968) showed that no previous work had been done in this area.

Experimental

A Büchi rotary evaporator was utilized for concentration of samples. A stopcock was placed in the inlet feed line between the feed container and the Büchi evaporator. A second stopcock was inserted into the vacuum line to provide control over the pressure within the system. A cold ethylene glycol solution (ca. 5° C.) was pumped through the condenser coils for cooling.

A Lab Line Instruments' water bath was used to maintain an essentially constant evaporation temperature. Evaporation temperatures were controlled to within $\pm 1^\circ$ C. A water aspirator was used to maintain a reduced pressure within the evaporator. Reagent grade chemicals were used throughout this study.

The analytical method employed for the phenol determinations was the 4-aminoantipyrine-chloroform extraction method described in Standard Methods for the Examination of Water and Wastewater (American Public Health Association, 1965). A 100-ml. aliquot of the concentrate was added to 400 ml. of phenol-free distilled water and carried through the 4-aminoantipyrine-chloroform extraction procedure. It was found that 0.02 had to be added to the sample's absorbance to correct for the DMSO interference when analyzing concentrations obtained from runs where 500 ml. per liter of DMSO had been used. The correction factor decreased with decreasing initial amounts of DMSO. The nature of this interference is unknown.

Concentration Procedures

One-liter runs—X ml. of DMSO and Y ml. of phenol-free distilled water were mixed in a 3-liter, round-bottomed flask (such that X + Y = 1000 ml.) and cooled to room temperature. A known amount of the phenol working solution was then added to the flask. The flask was then placed on the Büchi rotary evaporator and 15 minutes allowed for the flask and its contents to attain equilibrium with the water bath. The pressure in the system was then reduced and the evaporation commenced. Occasionally the flask contents would boil. When this was observed, the pressure within the system was increased to stop the boiling. The pressure was then reduced and the evaporation would usually proceed without further boiling. After a given amount of distillate had been collected, the pressure within the system was brought up to atmospheric pressure and the flask removed. The concentrate volume was then measured and a 100-ml. aliquot removed for phenol analysis.

One and one-half liters Lake Mary (Vilas County, Wis.) concentration runs—five hundred milliliters of DMSO was mixed with 500 ml. of phenol-free distilled water in a 3-liter, round-bottomed flask and cooled to room temperature. One and one-half liters of filtered (Whatman No. 1) Lake Mary water (phenol-free as determined by the 4-aminoantipyrine-chloroform extraction procedure) was added continuously to the flask as the evaporation proceeded (attempting to maintain the rate of feed equal to the rate of distillation). The distillation rate was approximately 300 ml. per hour. After a given amount of distillate had been collected, the pressure within the system was

brought up to atmospheric pressure and the flask removed. The concentrate volume was measured and a 100-ml. aliquot removed for phenol analysis.

Five-liter concentration runs—X ml. of DMSO and Y ml. of phenol-free distilled water were mixed in a 3-liter, round-bottomed flask (such that X + Y = 1000 ml.) and cooled to room temperature. The flask was then placed on the Büchi evaporator without reducing the pressure to allow the flask and its contents to come to temperature equilibrium with the water bath. A known amount of the phenol-working solution was added to 5-liters of phenol-free distilled water. This solution was well mixed and then continuously fed into the evaporator, attempting to keep the rate of feed equal to the rate of distillation. At the termination of the run, the concentrate volume was measured and a 100-ml. aliquot taken for phenol analysis.

Results and Discussion

A three-factor, experimental design was employed for evaluating the relationships between the variables distillation temperature, initial DMSO content, and initial phenol content on the per cent recovery of phenol. Table I lists the experiments, conditions, and data obtained. All of the experiments utilized 1-liter samples and all were concentrated to 125 ± 10 ml. Table II lists the results obtained from an analysis of the design data. The design data were analyzed utilizing the procedure of Davies (1963).

Table I. Three-Factor Experimental Design

Experiment Number	Distillation Temperature, ° C.	Initial Concentration of DMSO, ml./L.	Initial Concentration of Phenol, µg./L.	% Phenol Recovery
1	40	100	111	38.1
2	40	100	333	37.8
3	40	25	111	14.6
4	40	25	333	15.2
5	60	100	111	39.6
6	60	100	333	36.6
7	60	25	333	11.0
8	60	25	111	14.8
9	50	62.5	222	27.6
10	50	62.5	222	26.7

Table II. Three-Factor Experimental Design Analysis for Recovery of Phenol by Vacuum Distillation in Presence of DMSO

Effect	Effect Value
Main effect of DMSO level	+12.0625
Main effect of phenol level	-0.8125
Main effect of temperature	-0.4625
Two-factor interaction of temperature and DMSO	+0.5375
Two-factor interaction of temperature and phenol	-0.8875
Two-factor interaction of DMSO and phenol	-0.0125
Three-factor interaction of DMSO, phenol, and temperature	+0.2125

Analysis of the design data showed the main effect of initial DMSO level was significant at the 95% confidence level while the other effects were not. Hence, it appeared that the per cent recovery of phenol was related to the initial DMSO content of the sample when all samples were concentrated to the same volume. An error estimate of approximately 1% was made by comparing the results of experiments 9 and 10 presented in Table I.

The relationship of DMSO level to per cent of phenol recovery was investigated at 40° C. by concentrating 1-liter samples containing 319.1 micrograms of phenol to 620 ± 20 ml. The data obtained are presented in Figure 1 which shows that the per cent of phenol recovery increases with increasing DMSO content in a linear fashion. A 100% recovery of phenol was obtained with a sample containing 500 ml. of DMSO per liter.

It was next decided to ascertain whether or in what manner phenol recovery varied with concentrate volume for three different initial DMSO levels. Twelve concentration runs were performed at 40° C. utilizing 1-liter sample volumes, each of which contained 319.1 micrograms of phenol. The data obtained are presented in Figure 2.

Figure 2 shows that, to a first approximation, per cent recovery of phenol decreases linearly with decreasing concentrate volume for the cases where 100 and 300 ml. of DMSO per liter were employed. In the case where 500 ml. of DMSO per liter was used, the per cent recovery of phenol did not fall off, but remained constant at 100% with decreasing concentrate volume. With increasing

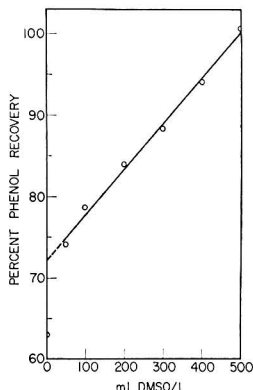


Figure 1. Phenol recovery as function of DMSO concentration, temperature 40° C., initial phenol 319.1 µg./l.

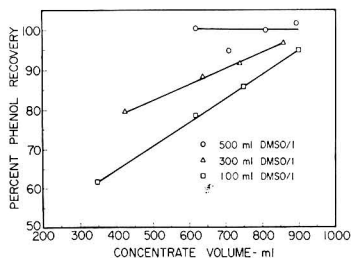


Figure 2. Phenol recovery at 40° C. as function of concentrate, volume initial phenol 319.1 µg./l.

DMSO levels, the slopes of the per cent of phenol recovery-concentrate volume lines decreased and became zero at an initial DMSO level of 500 ml. per liter. Hence, for optimum phenol recovery, an initial level of 500 ml. of DMSO per liter should be used.

Based on the previous results, it was decided to concentrate 5-liter samples of distilled water containing a known added amount of phenol. After mixing the DMSO and distilled water in a 3-liter, round-bottomed flask, the solution was cooled to room temperature because of the heat generated. The results obtained are presented in Table III. Some of the variability in the data is probably due to the difficulty of maintaining the rate of feed of sample equal to the rate of distillation.

Table III shows that an average phenol recovery of 66.6% was obtained when 500 ml. of DMSO was employed. The phenol recovery for the Lake Mendota sample (filtered through Whatman No. 1 paper prior to concentration) was 63.6%, which compares favorably with the distilled water runs. During the Lake Mendota concentration run, calcium carbonate precipitated and this might account for the smaller phenol recovery. An average phenol recovery of 78.0% was obtained when 700 ml. of DMSO was employed. In the one run where 800 ml. of DMSO was employed, a phenol recovery of 83.5% was obtained. Apparently, the more DMSO that is used the better the phenol recovery will be. These data tend to support the conclusion drawn from the experimental design data analysis.

Phenol-dosed, Lake Mary (Vilas County, Wis.) water was concentrated to see whether its high (compared to Lake Mendota water) organic content (dissolved organic carbon equal to about 30 mg. per liter) would adversely affect phenol recovery as compared with a distilled water system. The Lake Mary water samples were filtered through Whatman No. 1 filter paper prior to concentration. In the cases where phenol was added, the sample was filtered prior to the phenol addition. The data obtained are presented in Table IV.

Table IV shows that the phenol recovery for Lake Mary water is in good agreement with that of the distilled water sample. In the case where a phenol recovery of 76.9% was obtained, the rate of feed exceeded the rate of distillation. This points out the importance of maintaining the feed rate of sample equal to the distillation rate. Calcium carbonate precipitation was not observed while concentrating the Lake Mary water. The data tend to show that the high organic content of Lake Mary does not adversely affect phenol recovery when compared with a distilled water system.

Concentration of aqueous phenol solutions utilizing reduced pressure distillation results in a loss of 37% of the phenol present when a 1-liter sample is concentrated to 620 ml. while losses of 80 to 90% result when 5-liter sample sizes are concentrated to 730 to 780 ml. This work has shown that utilization of DMSO in the concentration procedure reduced these losses to a large extent.

One experiment was performed using M-pyrol (*N*-methyl-2-pyrrolidone) which was obtained through the courtesy of the General Aniline and Film Corp. One hundred milliliters of M-pyrol and 900 ml. of phenol-free distilled water were mixed in a 3-liter, round-bottomed flask and cooled to room temperature. Three hundred and twenty-five micrograms of phenol were then added to the

Table III. Recovery of Phenol with Vacuum Distillation in the Presence of DMSO

5-Liter Concentration Run Results				
Initial Ml. DMSO/L.	% Phenol Recovery	µg. Phenol in 5 Liters	Concentrate Volume, Ml.	Comments
0	13.3	325.5	730	Distilled HOH
0	17.3	325.5	780	Distilled HOH
500	63.3	325.5	730	Distilled HOH
500	72.6	325.5	725	Distilled HOH
500	64.0	325.5	640	Distilled HOH
500	0	0	835	Distilled HOH blank
500	0	0	745	Lake Mendota blank
500	63.6	319.1	910	Lake Mendota
700	72.9	325.5	890	Distilled HOH
700	80.0	325.5	930	Distilled HOH
700	84.3	325.5	1010	Distilled HOH
700	75.1	325.5	835	Distilled HOH
800	83.5	325.5	975	Distilled HOH

Table IV. Phenol Recovery by Vacuum Distillation in the Presence of DMSO

Lake Mary Water Concentration Run Data

% Phenol Recovery	Concentrate Volume, Ml.	µg. Phenol Added to 1.5-Liter Sample
0	715	0 (Lake Mary blank)
76.9	780	319.1 (Spiked Lake Mary)
95.3	845	319.1 (Spiked Lake Mary)
96.5	780	319.1 (Spiked distilled HOH)

flask. The flask then was placed on the concentration apparatus and allowed to reach temperature equilibrium with the water bath which was maintained at 40°C. The solution was concentrated to 660 ml. A 100-ml. aliquot of the concentrate was then analyzed for phenol as previously described for the DMSO concentrates. A phenol recovery of 81.1% was obtained. This compares favorably with the 78.7% phenol recovery obtained when a sample containing 100 ml. of DMSO per liter was concentrated to 620 ml. M-pyrol was used because it is an excellent solvent for waxes and hydrocarbons (General Aniline and Film Corp., 1965) whereas DMSO is a rather poor solvent for these compounds. However, more work will have to be

done with this solvent. The authors suggest that the use of M-pyrol, alone and in combination with DMSO, should be further investigated to determine its effects on the recovery of phenol and other volatile organic compounds.

Acknowledgment

The authors gratefully acknowledge the assistance of Linfield C. Brown in analyzing the statistical design data.

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Received for review April 26, 1968. Accepted January 16, 1969. This study was supported in part by Training Grant ST1-WP-22-05 and Research Grant WP-0037, both from the Federal Water Pollution Control Administration. Support for this investigation was also derived from the Engineering Experiment Station and the Department of Civil Engineering, University of Wisconsin, Madison.

Correction

DETERMINATION OF SULFATE AND PHOSPHATE IN WATER BY ION EXCHANGE-TITRIMETRIC METHOD

In this article by G. W. Dollman [ENVIRON. SCI. TECHNOL. 2, 1027 (1968)], on page 1028, column 1, under Calculation, the second sentence should read: Hence, 1 meq. of base equals 48.0 mg. of sulfate or 95.0 mg. of phosphate. In column 2, under Phosphate, the third sentence should read: While this method is not recommended for determining minute amounts of phosphate, a 1-ml. titration volume of 0.02N base is equivalent to 1.90 mg. of phosphate or about 0.62 mg. of phosphorus.

Colorimetric Determination of Carbonyl Compounds in Automotive Exhaust as 2,4-Dinitrophenylhydrazones

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Jackson Laboratory, Organic Chemicals Department, E. I. Du Pont de Nemours & Co., Wilmington, Del. 19898

■ A colorimetric technique was developed for determining the total molar concentration of carbonyls in a mixture of their 2,4-dinitrophenylhydrazones (DNPH). The method is based on the measurement of the colored species formed when alkali is added to a solution of the DNPH's in a 70% pyridine medium which stabilizes the colored product. The minimum detectable quantity is 0.5×10^{-8} mole and the reproducibility, determined on DNPH standard solutions, is $\pm 1\%$ relative. The method is applied to the analysis of carbonyls in vapor mixtures and automotive exhaust via collection of the DNPH derivatives in scrubbers. The recovery of the carbonyls by this technique is 98 to 106% and the reproducibility is $\pm 3\%$ relative.

Carbonyl compounds—i.e., aldehydes and ketones—are important constituents of automotive exhaust because several of these compounds are known to be toxic, odorous, and are believed to be a cause of eye irritation from photochemical smog. The 2,4-dinitrophenylhydrazine (DNPH) procedure reported by Iddles and Jackson (1934), and subsequently applied to flame combustion products (MalMBERG, 1954) and automotive exhaust (Oberdorfer, 1967), appears to offer a good procedure for separating the carbonyls from the bulk exhaust.

The gravimetric procedure reported by Oberdorfer (1967) determined the total carbonyl content on an "as formaldehyde" basis. This procedure is time-consuming and inherently inaccurate because the total can only be calculated using the molecular weight of a single carbonyl compound. The molecular weight of the derivatives varies significantly from formaldehyde (210) to tolualdehyde (302). Higher molecular weight species such as bis-dicarbonyl derivatives will, of course, contribute more serious errors. Alternatively an average molecular weight can be used to make the calculation but this depends on a prior knowledge of the composition. Thus, a better method for determining the total carbonyl content in the derivative mixture was desired.

Methods based on direct ultraviolet measurements of the DNPH's have been reported (Lawrence, 1965; Toren and Heinrich, 1955), but it was found that the benzaldehyde, tolualdehyde, and formaldehyde derivatives have substantially different λ_{\max} and ϵ values than the remaining carbonyl derivatives, and these are three of the most important carbonyl compounds in automotive exhaust. Thus, such a method would suffer the same type of limitation as does the gravimetric procedure.

Lappin and Clark (1951) reported a colorimetric method for carbonyls based on the addition of alkali to the DNPH derivatives to form a colored resonant ion. These authors reported that the colored product was stable and that a wide variety of carbonyl compounds had an absorp-

tion maximum (480 $m\mu$) and molar absorptivity, ϵ , which are very nearly independent of structure. Mendelowitz and Riley (1953) reported that the λ_{\max} is not 480 $m\mu$ and furthermore that it varies with the nature of the carbonyl compound. Pool and Klose (1951), Toren and Heinrich (1955), Lohman (1958), and Parsons (1966) reported that the color is not stable but fades rather rapidly.

The present study has substantiated the work reported by these latter authors—i.e., λ_{\max} is structure-dependent and the final color is unstable under the conditions reported by Lappin and Clark (1951). The formaldehyde derivative is the least stable and decomposes by first-order kinetics with a half-life of ~ 1 minute at room temperature. However, by changing the solvent medium to make it 70% in pyridine, the final color has been sufficiently stabilized to form the basis of a good method. Also, the ϵ values, at the selected wavelength, of all the carbonyls tested are almost the same, allowing a determination of total carbonyl. The reproducibility of this modified method was $\pm 1\%$ relative as determined with prepared standards. The minimum detectable quantity is 0.5×10^{-8} mole.

Experimental

Apparatus. A Beckman Model B spectrophotometer or equivalent is used to make absorbance measurements.

Reagents. The DNPH derivatives are prepared by the procedure of Shriner, Fuson, *et al.* (1956). The compounds are recrystallized to a constant melting point. The pyridine and methanol are reagent grade materials purchased from Mallinckrodt and Baker & Adamson, respectively. The methylene chloride (du Pont) is commercial grade. These solvents are used as purchased. The DNPH reagent is prepared according to Oberdorfer (1967). The *n*-hexane and DNPH reagent are "cleaned" by equilibrating equal volumes together for 2 minutes and passing the *n*-hexane through an activated alumina column to remove any DNPH derivatives. The alkaline solution is prepared by dissolving 10 grams of potassium hydroxide (Mallinckrodt analytical reagent) in 20 ml. of distilled water and diluting to 100 ml. with methanol.

Calibration Procedure. The DNPH derivative(s) is dissolved in a mixed solvent of methylene chloride-methanol (1 to 1). An appropriate aliquot of this solution is diluted with methanol to obtain a final concentration of DNPH derivatives between 0.05 and 3.0×10^{-7} mole per ml. Then 2.0 ml. of the diluted solution and 7.0 ml. of pyridine are pipeted into a 10-ml. volumetric flask. The solution is diluted to 10 ml. with the alkaline solution, the sample is thoroughly mixed, and the absorbance determined on the spectrophotometer at 440 $m\mu$ using 1-cm. cells. The sample should be read within 3 minutes.

Exhaust Sampling. The DNPH derivatives are obtained and isolated from vapor samples and exhaust via a procedure similar to Oberdorfer's (1967)—i.e., two scrubbers

in series. The precipitates are first transferred to filter funnels and the methanol (~10 ml.) used to start the dissolution from the filter funnel is first used to wash the scrubber units. Successive 10-ml. volumes of methylene chloride are used to complete the transfer and dissolution of the derivatives. The mother liquor (DNPH reagent) is extracted twice with 10-ml. volumes of *n*-hexane. The hexane washings and methylene chloride-methanol solution of the derivatives are combined in a 100-ml. volumetric flask and the mixture is diluted to the mark with methanol. This solution is appropriately aliquoted to obtain a concentration within the calibration range and run through the procedure described above (calibration procedure).

Results and Discussion

The modification of Lappin and Clark's (1951) original technique is the change in solvent medium. The presence of 70% pyridine stabilizes the final colored species (for at least 15 minutes) for all of the carbonyl derivatives tested except that of formaldehyde. This derivative still decomposes in this medium but at the reduced rate of ~0.3% relative per minute. Thus, no significant losses are incurred if the sample is read soon after the alkali is added. As the concentration of pyridine in the solvent mixture is

reduced, by replacement with methanol, the decomposition rate is accelerated.

This modified method circumvents the problems of the ultraviolet and gravimetric techniques—i.e., dissimilar ϵ values and molecular weights, respectively. The absorbance measurements are made at 440 $m\mu$, the λ_{max} for the formaldehyde derivative, which is the most prominent and thought to be the most important carbonyl present in exhaust. The ϵ values of the other carbonyl compounds tested are all similar to that of the formaldehyde derivative at the selected wavelength (Table I). In exhaust analysis the differences in ϵ values shown in Table I should cause only a small positive error due to the predominance of formaldehyde, benzaldehyde, and tolualdehyde. The bis-DNPH derivatives of 1,2-dicarbonyls (osazones) form blue colors ($\lambda_{max} \sim 600 m\mu$) and are significantly less responsive at the selected wavelength. However, these components are thought to be present at very minor concentrations in exhaust and thus would cause only a small negative error.

The analysis takes approximately 30 minutes' work-up time after complete reaction of derivatives (precipitation) has occurred. This represents a substantial savings in time over the gravimetric procedure which requires several hours (usually overnight) to evaporate the solvent and obtain a constant weight. The technique has been applied, with success, to the determination of total carbonyls in synthetic vapor samples and in exhaust. The values obtained on exhaust from standard vehicles have ranged between 40 and 150 p.p.m. The recoveries on synthesized vapor samples have ranged from 98 to 106% and typical examples are summarized in Table II. This table also shows the recoveries (as formaldehyde) obtained with and without the use of a back extraction with *n*-hexane to remove the dissolved derivatives. It is recommended that the back extraction be used routinely because this guards against the loss of the more soluble derivatives and accidental losses due to insufficient cooling of the reagent-precipitate mixture.

This method has been tested on many standards both as liquid solutions of the DNPH derivatives for calibration purposes and as vapor mixtures for checking the recovery and reproducibility through the entire procedure. The reproducibility of the calibration solutions is $\pm 1\%$ relative and the reproducibility of the vapor mixtures (through the entire procedure) is $\pm 3\%$ relative.

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Received for review July 11, 1968. Accepted January 24, 1969. Research & Development Division Publication No. 432.

Table I. Molar Absorptivities, ϵ , of DNPH Derivatives at 440 $m\mu$

Compound (as DNPH)	$\epsilon \times 10^{-4}$ (Liter Mole ⁻¹ Cm. ⁻¹)
Formaldehyde	2.12
Benzaldehyde	2.11
<i>p</i> -Tolualdehyde	2.07
Acetaldehyde	2.43
Propanal	2.32
Acetone	2.22
Acrolein	2.39
1-Butanal	2.20
2-Butanone	2.23
2-Butanal	2.25
Crotonaldehyde	2.64
2-Methylbutanal	2.36
3-Methylbutanal	2.36
1-Pentanal	2.24
1-Heptanal	2.45
2-Ethylhexanal	2.43
Glutaraldehyde	4.54

Table II. Carbonyl Recoveries from Vapor Mixtures

Sample ^a	Total Carbonyl Present, Moles $\times 10^4$	% Recovered	
		Without back extraction	With back extraction
A	2.918	92	99
B	3.227	97	105
C	3.550	96	103

^a Legend:

A = 90% formaldehyde, 2% 1-butanol, 2% 1-pentanol, 3% benzaldehyde, 3% tolualdehyde.

B = 80% formaldehyde, 3% 1-butanol, 3% 1-pentanol, 7% benzaldehyde, 7% tolualdehyde.

C = 70% formaldehyde, 4% 1-propanal, 3% 1-butanol, 3% 1-pentanol, 10% benzaldehyde, 10% tolualdehyde.

A Primer on Oil Spill Cleanup. 24 pages. American Petroleum Institute, 1271 Avenue of the Americas, New York, N.Y. 10020. 1969. Paper, 25 cents.

Prepared under the direction of the Task Force on Oil Spill Cleanup, Committee for Air and Water Conservation of the American Petroleum Institute, the publication presents basic facts about oil spills and methods of dealing with them. Intended for oil industry personnel who may one day have to cope with an oil spill, the book includes information on handling spills from tankers, barges, piers, and loading facilities, or other onshore installations. In addition, four basic steps in dealing with spills are described, as well as existing cooperative oil spill cleanup programs. Floating booms, bubble and chemical barriers, absorbents and adsorbents, sinking agents, and chemical dispersants are among the topics examined. ■

New Zoning Landmarks in Planned Urban Developments. Technical Bulletin 62. Lenard L. Wolffe. 32 pages. Urban Land Institute, Washington, D.C. 20036. 1968. \$6.00, paper.

The publication traces the legal aspects of three planned unit developments (PUD)—one in Pennsylvania, and two in New Jersey. The decision of the Supreme Court of Pennsylvania on the constitutionality and validity of the PUD concept, and the adoption by the State of New Jersey on a statute authorizing local governments to adopt PUD ordinances are discussed. Continued maintenance of open space—considered essential in the modern planned community—is covered in Part II, and a solution to the problem is offered. ■

The Nation's River. 128 pages. U.S. Government Printing Office, Washington, D.C. 20402. 1968. \$1.75, paper.

Prepared in answer to a presidential request for a program to assure that the Potomac River would serve as a model of scenic and recreational values for the entire country, the publication is a report from the U.S. Department

of the Interior. Included are recommendations for action by the Federal Interdepartmental Task Force on the Potomac which cover three broad aspects: those related to present and future water resources problems in the Tidal Basin; those related to protection and restoration of the Basin's scenic and natural resources; and those to ensure that future planning and action will proceed in a wise and coordinated manner. ■

Clinical Toxicology of Commercial Products—Acute Poisoning. Third Edition. Marion N. Gleason, Robert E. Gosselin, Harold C. Hodge, and Roger P. Smith. xi + 1539 pages. Williams & Wilkins Co., Baltimore, Md. 21202. 1969. \$24.50, hard cover.

Aimed at giving assistance to physician, pharmacist, health worker, or any individual who may be called upon in cases of acute or chronic poisoning, the book provides reference to more than 17,000 commercial products. These products include drugs, detergents, and cosmetics used in the home, on farms, and in industry. Highly specific as well as overall general procedures are described in the book, which is cross-indexed. Seven color-coded sections are divided as follows: Section I—First aid and general emergency treatment; Section II—Ingredients index, listing those chemicals commonly found in commercial products; Section III—Therapeutics index, summarizing experimental data on compounds and classes of compounds; Section IV—Techniques of supportive treatment; Section V—Trade name index, listing products which might be poisonous or harmful; Section VI—Basic formulas representative of types listed under trade names; and Section VII—Manufacturers' names and addresses. ■

Proceedings of the 1st Annual North Eastern Regional Anti-Pollution Conference. vi + 146 pages. University of Rhode Island, Kingston, R.I. 02881. \$15.00, paper.

The conference—sponsored by the Rhode Island Technical Services Program and the College of Engineering,

University of Rhode Island—was held July 22-24, 1968. Papers included in the publication deal with waste water treatment, air pollution, and solid waste disposal. ■

Water Treatment Plant Design. Prepared by American Society of Civil Engineers, American Water Works Association, and Conference of State Sanitary Engineers. ix + 353 pages. American Water Works Association, Inc., New York, N.Y. 10016. 1969. Members, \$7.50, nonmembers, \$15.00, hard cover. ■

Mineralogy in Soil Science and Engineering. SSSA Special Publication Series No. 3. Edited by G. W. Kunze, J. L. White, and R. H. Rust. ix + 106 pages. Soil Science Society of America, Madison, Wis. 53711. 1968. Members, \$2.00, nonmembers, \$3.00, paper. ■

Water Pollution Control and Solid Wastes Disposal. Chemical Process Review No. 32. Marshall Sittig. 244 pages. Noyes Development Corp., Park Ridge, N.J. 1969. \$35.00, paper. ■

Subsurface Disposal in Geologic Basins—A Study of Reservoir Strata. Memoir 10. Edited by John E. Galley. vi + 253 pages. American Association of Petroleum Geologists, Tulsa, Okla. 74119. 1968. Members, \$9.50, nonmembers, \$12.50, hard cover. ■

The Air We Live In—Air Pollution: What We Must Do About It. James Marshall. Coward-McCann, Inc., New York, N.Y. 10016. \$3.64, hard cover. ■

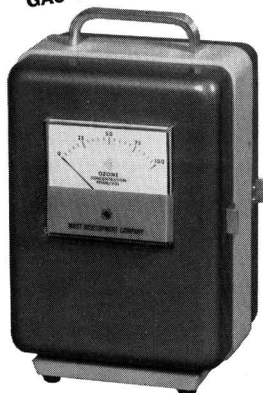
Atomic Absorption Volume II—Petroleum Chemistry. Methods Manual. 108 pages. Jarrell-Ash Division, Fisher Scientific Co., J-375 Fisher Bldg., Pittsburgh, Pa. 15219. \$15.00, binder. ■

The Treatment of Industrial Wastes. Edmund B. Besselievre. x + 403 pages. McGraw-Hill Book Co., New York, N.Y. 10036. 1969. \$16.50, hard cover. ■



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Environment, the University, and the Welfare of Man. Edited by Billy Ray Wilson. 184 pages. J. B. Lippincott Co., Philadelphia, Pa. 1969. \$5.25, hard cover.

The publication comprises nine essays which consider the interrelationships of environment, the university and man's welfare, presented at a 1966 conference at the State University at Rutgers. Topics discussed include the land, electric power, individual man in the technological society, excellence as the standard for scholar-teachers and students, and the city and the university. ■



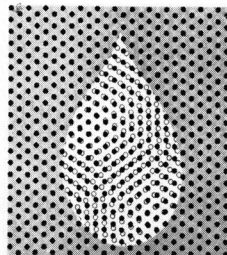
Bowen named managing editor of ES&T

Dr. D. H. Michael Bowen has been named managing editor of ENVIRONMENTAL SCIENCE & TECHNOLOGY. He succeeds Dr. Melvin J. Josephs, managing editor since ES&T's beginning. Dr. Bowen joined the staff of *Industrial & Engineering Chemistry* in 1967 as assistant editor.

Dr. Bowen received his B.Sc. (1960) and Ph.D. (1963) in chemical engineering from the University of Birmingham, England. After short stints with British Oxygen Co. (1957), British Petroleum Co. (1958), and Shell Chemical Co. (1959), he came to the U.S. in 1963. From 1963-1967, he was a research engineer working on polymer processing problems at the Experimental Station of the E. I. duPont de Nemours, Inc. Dr. Bowen is a member of ACS, AIChE, and the Institution of Chemical Engineers (London).

Dr. Josephs has been named managing editor of *Chemical and Engineering News*, sister ACS publication.

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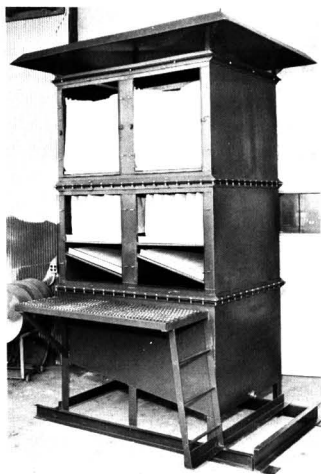
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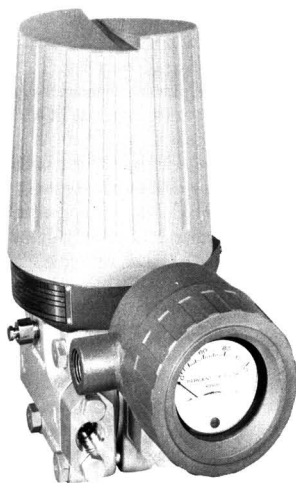
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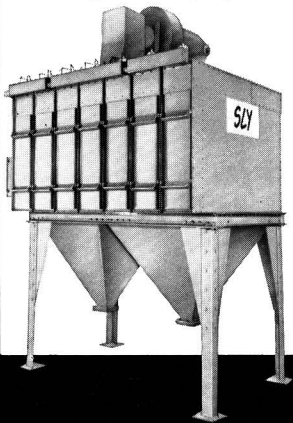
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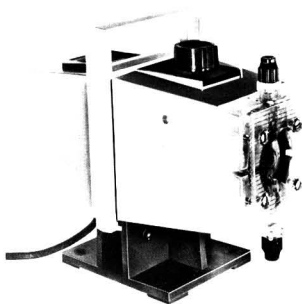


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Plastic Pipes

Polyethylene pipe in diameters up to 40 inches is available for use in potable water and waste disposal systems. The Aldyl D pipe is designed for municipal sewers, industrial waste disposal, gas gathering in oil fields, water distribution, and other pressure piping. The company claims that the pipe's light weight and flexibility provide advantages in a variety of applications. For example, the Aldyl D pipe can be laid in ditches which are not even or straight; it can be inserted into existing sewers; floated across lakes and rivers and sunk in place with metal collars; and made to conform to contours of lake and river bottoms. DuPont Co. **67**

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The Series 260-1 Analysis Systems for rapid and accurate testing of up to 48 different water and waste elements is available. Each system consists of an individually standardized photometer, procedure handbook, optional automatic-zeroing titration outfit, and custom drawn chart with required re-

agents for each test. Housed in a formica case, the photometer measures 9" x 8" x 5", and operates electrically or from an optional dry-cell battery for field use. Delta Scientific Corp. **68**

Air Sampling Unit

A device for collecting samples of particulate matter in large volumes of air features a quick-change filter holder. The Hi-Volume Air Sampler is compact, and contains a 24-hour flow recorder and 7-day timer for added convenience and efficiency, according to the manufacturer. W. H. Curtin & Co. **69**

Liquid Measurement

A device for use in measuring, metering, and monitoring fluid flow rates is available. The Flow Controlment is a combination of two basic elements—a flowmeter and a two-way valve—which can be supplied as a single unit or as individual units. The company says the device was designed for use in electronic cooling and ventilating systems, but has many applications, and is available in various sizes, pressure levels, fluid compatibility, interface connections, and mounting configurations. Mack Co. **70**



Measuring Thermal Decomposition

A thermal analysis system, developed for measuring thermal stability, volatility, patterns, and vapor pressure is available. The Pyrotector combines a high temperature flame ionization detector with a closely coupled temperature programmable furnace to determine thermal decomposition rates as low as 0.001% per minute, according to the company. Applications of the system include research in thermal decomposition of organic compounds, vapor pressure studies of high boiling materials, detection of trace organic contaminants, and as a tool for the direct determination of vapor pressure curves of organic compounds. Carle Instruments, Inc. **71**

Water treatment systems. An illustrated 4-page brochure includes specifications and design features of six Uni-Loc automated water treatment systems. Designed for continuous measurement and regulation of chemical balance of cooling tower water, the models are available for all size cooling operations, according to the manufacturer. The brochure also includes a reference chart summarizing features of each model. Universal Interloc, Inc.

91

Submersible electrodes. The Series Three pH Electrode Submersion Assembly is described in Bulletin 4085. Designed for continuous process pH applications in which pH electrodes must be submerged, the units are available in stainless steel or polyvinyl dichloride. The manufacturer says the assemblies are suitable for a variety of applications in a wide range of temperatures and pressures. Beckman Instruments, Inc.

92

Flocculant polymers. The Herculoc flocculant polymers are organic, water soluble polyelectrolytes for use in sludge conditioning. Bulletin ESD-102 describes the use of these polymers, listing case histories to demonstrate their advantages. Also included in the 12-page brochure are plant applications, methods of evaluation, and characteristic and properties of the polymers. Hercules, Inc.

93

Spectroscopy accessories. An illustrated 32-page catalog (1969-BE) lists the company's line of infrared spectrophotometer cells and accessories. Prices and parts numbers, performance characteristics, spectra, and application data are given for such analytical accessories as gas chromatograph fraction collector, high speed pyrolyzer, and mirror beam condenser. Barnes Engineering Co.

94

Gas detection equipment. A series of bulletins describes the company's line of gas detection instruments and equipment. Bulletin HA500 includes principles of operation, specifications, price

list, and other details of the 500 series of gas detectors—510 Duotector; 550 Chart-O-Gas, chart recording detector; and 520 Multitector, multiple channel detector. The company claims that the Hydrogen Sulfide Gas Analyzer (Bulletin HA 722 AEX) is useful for process stream monitoring, atmospheric sampling, air pollution measurement, and pipeline H₂S detection. The Model 750AEX total Sulfur Analyzer (Bulletin HAL 750) protects catalyst beds, monitors putiry of hydrocarbon feedstock, and automatically controls process streams, the company says. A Calibration Kit (Bulletin 722K) contains items for preparing accurate p.p.m. samples. Houston Atlas, Inc.

95

Air pollution detection. A 4-page bulletin describes the Mobile Air Pollution Monitoring Laboratory, which is designed to offer a complete battery of tests for monitoring ambient atmospheres. The laboratory features the CSM 6 AutoAnalyzer which utilizes continuous, automatic wet chemical techniques for analysis of air samples for up to six different parameters, according to the company. The bulletin also includes schematic drawings, photos, and specifications of the mobile unit. Technicon Corp.

96

Textile mill wastes. Charles D. Livengood, instructor, North Carolina State University, has compiled an annotated bibliography of literature references relative to textile wastes as stream pollutants. The work—Report No. 18 of the Water Resources Research Institute, University of North Carolina—is an updating and expansion of a previously compiled listing of chemical literature on sources of pollution from textile mills for the period 1954-64. "Textile Wastes—A Bibliography" includes abstracts published through June 1968. North Carolina State University, Raleigh, N.C. (Write direct)

Pollution abatement plan. "Water Pollution Problems and Improvement Needs: Lake Ontario and St. Lawrence River Basins" is the title of a 125-page report published by the Federal Water

Pollution Control Administration and the New York State Department of Health's Division of Pure Waters. Outlining a 31-point pollution control program for the area, the report describes the pollution problems, improvement needs, costs and benefits, and makes recommendations for immediate, long-range, and research needs. FWPCA, Room 805, 633 Indiana Ave., N.W., Washington, D.C. 20242. (Write direct)

Estuarine resources and conservation.

Two motion pictures, in color, and featuring original musical scores by the Charlie Byrd Quintet, are available from the U.S. Department of the Interior's Bureau of Commercial Fisheries. Both films were made in cooperation with the Gulf States Marine Fisheries Commission. "Estuarine Heritage" runs 28 minutes, and covers the role of estuaries as nurseries for various species of fish; as the habitat of waterfowl and furbearing animals; and as a recreational and esthetic resource. Major threats to these resources are examined. "The Boy and the Biologist," a 14-minute film narrated by Arthur Godfrey, tells of a boy interested in fishing and fun, and his meeting with an outdoorsman who teaches him a sense of responsibility. Bureau of Commercial Fisheries, Branch of Audio-Visual Services, 1815 N. Fort Meyer Dr., Arlington, Va. 22209. (Write direct)

Phosphate removal. "Tahoe Revisited," a 12-minute color film with sound track, examines the phosphate removal process in operation for the South Tahoe Public Utility District. The film covers all phases of the Lake Tahoe project, including solids removal and incineration, activated sludge aeration, and chemical clarification and phosphate removal with lime recalcination for reuse. Cities, consultants, and all officials concerned with environmental protection and water pollution abatement are eligible to borrow the film. BSP Corp., P.O. Box 8158, San Francisco, Calif. 94128. (Write direct)

April 7-11
Southwestern Radiological Health Laboratory, Public Health Service

Symposium on Public Health Aspects of Peaceful Uses of Nuclear Explosives
Frontier Hotel, Las Vegas, Nev.

The six sessions of the meeting will consist of more than 35 papers on such topics as environmental health and safety aspects in the event of large-scale use of nuclear explosives for peaceful purposes; roles of industry, Atomic Energy Commission, Public Health Service, and states.

April 9-11
North Carolina State University, Duke University, and University of North Carolina

Southern Water Resources and Pollution Control Conference

North Carolina State University,
Raleigh

The conference is designed to bring together representatives of industry, government, universities, and consultants to discuss water, utilization, and waste disposal in the southeastern U.S. Meetings will examine new treatment techniques, and designing and operation of treatment facilities for water utilization and waste disposal. For further information, contact: Maynard Shields, P.O. Box 5125, Raleigh, N.C. 27607.

April 9-12
Department of Geology, University of South Carolina

Meeting of Southeastern Section, Geological Society of America

University of South Carolina,
Columbia

Three symposia are scheduled for the 4-day meeting. A symposium on estuaries will consist of more than 50 papers applicable to estuary development; case histories from the U.S. and elsewhere are included. In addition, papers will be presented on such topics as chemical composition of various marine and estuarine invertebrates, plutonic rocks of the Southern Piedmonts, and southeastern phosphate mineralogy and technology.

April 13-16
Water Conditioning Association International, and Illinois Water Conditioning Association

Water Conditioning Management Institute

Hott Memorial Center, Monticello, Ill.

Aimed at dealers and management personnel, the institute will include marketing, organizational performance, sales management, finances, and communications. Limited enrollment. For information: Box 651, 325 Wesley St., Wheaton, Ill.

April 13-18
American Chemical Society

157th Meeting

Minneapolis, Minn.

The Division of Water, Air, and Waste Chemistry will jointly sponsor several symposia with other divisions, including a symposium on air conservation and lead, with Divisions of Industrial and Engineering Chemistry and Petroleum Chemistry, and a symposium on pollution control in fuel combustion, processing, and mining, with Division of Fuel Chemistry. In addition, there will be sessions devoted to such topics as chemistry of the Great Lakes, and chemical control in biological waste treatment, as well as papers on various aspects of water, air, and waste chemistry.

April 14-18
American Society of Civil Engineers

National Meeting

Kentucky Hotel, Louisville, Ky.

Theme of the meeting is *Structura/69*. More than 35 sessions are planned, including "A City Grows by the River," which will be devoted to urban planning and development. This one-day session is aimed toward civil engineers interested in developmental aspects of urban planning methods for river cities and the environmental impact of a river and its related civil engineering constructions.

April 17-18
University of Texas and National Pollution Control Federation

International Conference on Pollution Control

University of Texas, Austin

Title of the 2-day conference is "Environmental Countdown—Timetable for the 1970's." Panels will discuss such topics as shared responsibilities for environmental dangers; governmental science and administration; and realistic scientific goals, national and international.

April 20-23
Institute of Environmental Sciences

15th Annual Meeting

Disneyland Hotel, Anaheim, Calif.

"Man in His Environment" is the topic of the technical sessions of the meeting. In addition to presentation and discussion of papers, research development, application, and management advances in environmental stimulation will be covered. Topics for discussion include the general areas people, pollution, noise, transportation. For information: Frank Hallstein, Technical Program Chairman, TRW Systems, 1 Space Park, R-5/2063, Redondo Beach, Calif. 90278.

April 20-24
American Society of Mechanical Engineers

Diesel and Gas Engine Power Conference

Muehlebach Hotel and Towers,
Kansas City, Mo.

The technical program of the 5-day conference will emphasize engine research, development, and application, and will consist of eight sessions, including three panel discussions. These discussions will cover ambient rating of gas engine driven compressors, as well as other topics.

April 21-24
Industrial Medical Association, and American Association of Industrial Nurses

American Industrial Health Conference

Shamrock Hilton Hotel, Houston,
Tex.

The conference will encompass the 54th annual meeting of IMA and 27th annual meeting of AAIN. In addition to conferences and discussions of industrial and occupational health topics, the conference will include a number of field trips, a medical TV program, and a series of postgraduate seminars. Among topics for discussion are atmospheric contaminants and standards, underwater medicine, how to solve an environmental health problem in industry.

meeting guide

April 21-25 **International Association on Water Pollution Research**

4th International Conference on Water
Pollution Research
Prague, Czechoslovakia

The technical program of this meeting, rescheduled from September 2-6, 1968, features 48 papers in three sections: stream pollution; waste water treatment; and lakes, reservoirs, and the ocean. In addition, there will be a panel discussion on the reuse of water, and a technical film festival on water pollution subjects. Additional information can be obtained from: T. G. Shea, International Association on Water Pollution Research, Room 114 McLaughlin Hall, University of California, Berkeley, Calif. 94720.

April 22-24 **Houston Junior Chamber of Commerce**

National Pollution Control Conference
and Exposition

Astrosahl, Houston, Tex.

Environmental Equilibrium: Criteria, Cost, Cooperation is the theme of the 3-day conference, which aims to provide a forum for exchange of information on government regulations regarding pollution, technological advances, and subjects of general interest in pollution abatement. For additional information, contact: Aubrey LaFargue, c/o Pace Management Corp., 4710 Greeley St., Houston, Tex. 77006.

April 28-29 **American Medical Association**

6th Conference on Environmental
Health

Drake Hotel, Chicago, Ill.

The conference will examine the problem of noise as an environmental pollutant—its effects on man, its sources, and efforts for its control. Among topics to be discussed are: noise induced hearing loss; effects of noise on sleep; noise control on the local level; and sociometric aspects of noise. For information: Department of Environmental Health, AMA, 535 N. Dearborn, Chicago, Ill. 60610.

April 28-30 **Technical Association of the Pulp and Paper Industry**

6th Water and Air Conference

Robert Meyer Hotel, Jacksonville,
Fla.

Five technical sessions are planned for the conference, as well as tours of water and wastes facilities at area pulp and paper mills. Papers will be presented on water supply and treatment; re-use of water; waste water and sludge treatment; instruments; and air conservation. Inquiries should be directed to: H. O. Teeple, TAPPI, 360 Lexington Ave., New York, N.Y. 10017.

April 30 - May 2 **Association of Engineering Geologists, and American Institute of Engineering Geologists**

Governor's Conference on
Environmental Geology

Brown Palace Hotel, Denver, Colo.

Purpose of the conference is to provide a forum for public officials, planners and developers, engineers, architects, and others whose activities involve utilization and modification of environment, to meet with geologists. The 3-day session will include symposia covering such topics as urban growth and environmental geology, prevention of surface groundwater pollution and contamination, and legislation and our environment. In addition, a field trip is planned.

May 5-7 **Ann Arbor Biological Laboratory, Bureau of Commercial Fisheries, and Great Lakes Research Division, University of Michigan**

12th Conference on Great Lakes
Research

University of Michigan, Ann Arbor

The purpose of the meeting is to promote all aspects of Great Lakes research, and to disseminate research data on the lakes and their basins. This year's program will consist of 4 half-day sessions of contributed papers and 2 half-day sessions of invited papers. In addition to the technical sessions, a series of symposia will cover such topics as: quaternary history, economic geography, remote sensing, and pesticide problems.

May 8-9 **Maryland State Department of Health, and University of Maryland**

Conference on Air Pollution Control

Adult Education Center, University of
Maryland, College Park

Theme of the conference is Partners in Air Pollution Control—Government and Industry. Topics to be covered include air pollution control regulations in Maryland, legislative policy on air quality control, and federal air quality control regions and their impact in Maryland. A panel will examine the control of particulate emissions from industrial processes.

May 18-21 **American Institute of Mining, Metal- lurgical, and Petroleum Engineers, and others**

1st Annual Offshore Technology
Conference

Albert Thomas Convention and
Exhibit Center, Houston, Tex.

The 4-day session will cover such topics as economics of oil and gas operations offshore U.S.; the ocean environment; environmental effects of offshore installations; and disposal of oil produced during offshore well tests. For information: Offshore Technology Conference, 6200 N. Central Expwy. Dallas, Tex. 75206.

May 18-22 **Urban Land Institute First Land Use Symposium**

Doral Country Club and Hotel,
Miami Beach, Fla.

Major theme of the 5-day meeting is "Land: Recreation and Leisure." Emerging trends in land for resorts, hotels, second homes, ski lodges, golf courses, yacht harbors, parks, camp grounds, and shopping facilities will be discussed.

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May 18-23 American Water Works Association

89th Annual Conference

Convention Center, San Diego, Calif.

Theme of this year's conference, "New Horizons for Water Supply," will be carried out through a series of discussion groups and technical sessions. Among topics slated for investigation are: disposal of waste water from water filtration plants; conjunctive use of ground and surface water supplies; water reclamation by injection underground; and chlorination problems and how to solve them. For information: Conference Information, AWWA, 2 Park Ave., New York, N.Y. 10016.

June 4-6 Technicon Corp.

International Congress on Automated Analysis

Conrad Hilton Hotel, Chicago, Ill.

Environmental Science (air and water pollution and oceanography) is one of the topic areas for symposia. The subject will be discussed from the viewpoint of total management of the environment.

Courses

April 7-9 Department of Operations Research

Seminar and Lecture Course on Operations Research and Systems Engineering in Complex Water Resource System

Case Western Reserve University,
Cleveland, Ohio

The 3-day course is designed for professionals and educators in the water resource and hydraulic systems field, as well as operations researchers, engineers, and systems analysts interested in water resource systems.

June 2-7 Manhattan College and the Federal Water Pollution Control Administration

14th Summer Institute in Water Pollution

Manhattan College, Bronx, N.Y.

Two simultaneous one-week courses will be offered for advanced study in stream and estuarine analysis and biological waste treatment. Stipends and travel allowance are available for U.S. citizens associated with universities and state regulatory agencies. For information: Donald J. O'Connor, Civil Engineering Department, Manhattan College, Bronx, N.Y. 10471

Special Notices

Academic Year 1969-70 Cornell University

Graduate Programs in Agricultural Waste Management

Opportunities for graduate study and research are offered in an extensive multidisciplinary program in agricultural waste management. Areas of study include water resources engineering, agronomy, and animal science; research activities include liquid waste treatment, land disposal, and odor reduction and control. Research assistantships, associateships, and other financial support are available. For details write: Field Representative, Department of Agricultural Engineering, Riley-Robb Hall, Cornell University, Ithaca, N.Y. 14850.

1969-1970 Academic Year University of Colorado, Boulder

Federal Water Pollution Control Traineeships

Financial assistance is available for graduate study in water resources and sanitary engineering. Applicants with a background in engineering or science will be considered for the grants. Annual stipends for master's candidates are \$2400 per year plus \$500 per dependent. Those interested in graduate programs in water resources engineering or the chemical and microbiological aspects of water resources should contact: Director, Water Resources Program, Engineering Center OT 4-34, University of Colorado, Boulder, Colo. 80302.

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1969-1970 Academic Year University of Florida Department of Environmental Engineering

Environmental Research Program in
Terrestrial Ecology

Applications will be accepted for admission to a program of environmental research in tropical and subtropical terrestrial ecosystems. Emphasis of the project-oriented program is on the team approach, combining such specialists as agronomists, ecologists, entomologists, and the like, with environmental engineers, health physicists, and radiochemists. Research topics are available at the masters, doctoral, and postdoctoral level. Contact: Terrestrial Ecology Research Program, Department of Environmental Engineering, University of Florida, Gainesville, Fla. 32601.

1969-1970 Academic Year Harvard School of Public Health

The Kresge Center invites candidates to submit applications for enrollment and fellowships for study leading to the M.S. and D.Sc. in occupational medicine, environmental physiology, toxicology, aerospace health and safety, radiological health, air pollution control, industrial hygiene, and general environmental health. Fellowship stipends range from \$200-300 per month, with \$500 per year for each dependent, plus full tuition and fees. For details: Dade W. Moeller, Assoc. Dir., Kresge Center for Environmental Health, Harvard School of Public Health, 665 Huntington Ave., Boston, Mass. 02115.

1969-1970 Academic Year University of North Carolina, Institute for Environmental Health Studies

Environmental Health Fellowships
Applications may be filed for fellowships which provide tuition, fees, and a stipend, including a dependency allowance. Fellowships are available for masters or doctoral candidates, as well as for postdoctoral studies. Recipients participate in multidisciplinary programs designed to prepare students for careers in research, teaching, and practice in the various specialized fields in environmental health. For details: Institute of Environmental Health Studies, Box 630, Chapel Hill, N.C. 27514.

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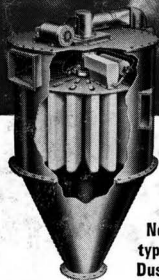
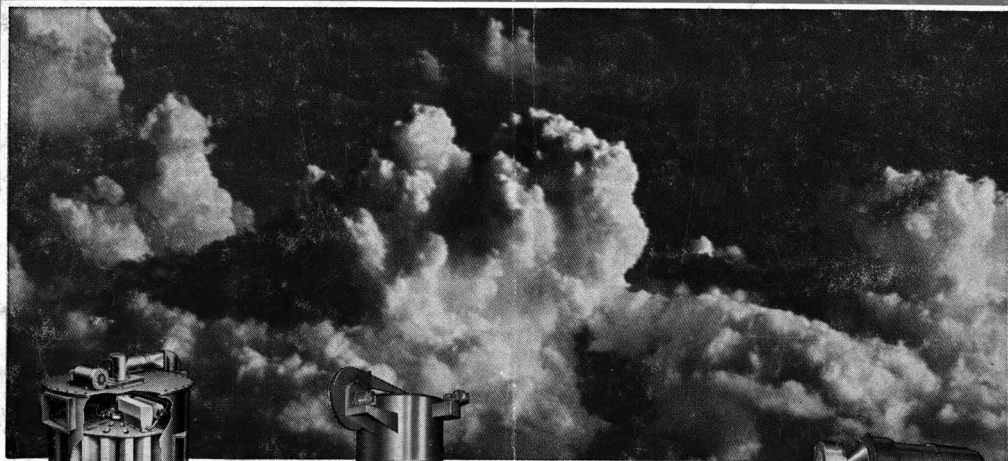
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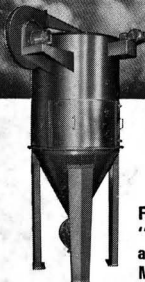
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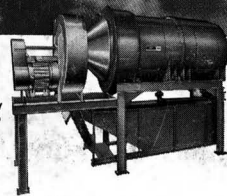
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