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Proceedings of the Symposium
on
ASSESSING THE INDUSTRIAL HYGIENE MONITORING NEEDS FOR THE COAL CONVERSION AND OIL SHALE INDUSTRIES

OTTO WHITE, JR., EDITOR

March 1979

BROOKHAVEN NATIONAL LABORATORY
ASSOCIATED UNIVERSITIES, INC.
UNDER CONTRACT NO. EY-76-C-02-0016 WITH THE
UNITED STATES DEPARTMENT OF ENERGY

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EDITOR'S NOTE

With the exception of a few minor alterations, most manuscripts were printed as submitted by authors. The conclusions drawn and the recommendations made in the manuscripts are the authors' alone. They do not necessarily reflect the views of the editor.

Transcriptions and printings of the Panel Discussion and Open Discussion were edited for clarity only and represent a sincere effort to convey the discourse of the participants. Any misrepresentation of a participant's statement is regretted and apologized for in advance.

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ACKNOWLEDGMENTS

The editor enthusiastically thanks the symposium participants (Appendix II) for their enlightening and persistent contributions. Their stamina in the face of a very trying agenda reflects their deep and sincere interest in protecting the work force in emerging energy industries.

Special thanks go to V. P. Bond, C. B. Meinhold, and L. D. Hamilton for their contributions and support. Hardy thanks go to Sandra Green and Jodi Earle for their skills and devotions beyond praise in this entire effort.

This work was supported by the United States Department of Energy, Division of Biomedical and Environmental Research, Analysis and Assessment Program, through the Safety and Environmental Protection Division at Brookhaven National Laboratory.

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FOREWORD

Under the auspices of the Department of Energy, Brookhaven National Laboratory undertook the task of assessing the industrial hygiene monitoring needs for the coal conversion and oil shale industries. To assist in accomplishing this task, the following authoritative working group was organized:

	Affiliation
Otto White, Jr., Co-chairman	Brookhaven National Laboratory
Samuel Morris, Co-chairman	Brookhaven National Laboratory
Thomas R. Cessario, Secretary	Brookhaven National Laboratory
Edward Baier*	National Institute of Occupational Safety and Health
Richard Brief	Exxon Corporation
Mort Corn	University of Pittsburgh
Harry Ettinger	Los Alamos Scientific Laboratory
David Fraser	University of North Carolina
Morton Lippmann	New York University
Andrew Sharkey	Pittsbrugh Energy Research Center

This group met for the first time during the annual American Industrial Hygiene Association Conference in Los Angeles, California on May 9, 1978. The second meeting took place during a two day visit to the Pittsburgh Energy Technology Center where the group sharpened its focus on industrial hygiene problems in coal conversion by inspecting specific processes and work practices.

The third meeting of the authoritative group was held at Brookhaven National Laboratory in conjunction with a two day symposium on Assessing the Industrial

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**Present affiliation is Diamond Shamrock Chemical Company.

Hygiene Monitoring Needs for the Coal Conversion and Oil Shale Industries. The symposium program (Appendix I) included presentations centering around the themes: "Recognition of Occupational Health Monitoring Requirements for the Coal Conversion and Oil Shale Industries" (November 6, 1978) and "Status of Dosimetry Technology for Occupational Health Monitoring for the Coal Conversion and Oil Shale Industries" (November 7, 1978). These proceedings represent the contributions of the symposium participants (Appendix II). This information proved to be invaluable when the working group met following the symposium for a third day (November 8, 1978) to draft its final report.

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OVERVIEW FROM FOSSIL ENERGY

John H. Abrahams

Environmental Activities Staff
Systems Engineering Division
Office of Fossil Energy Programs
Department of Energy

Presented at the
"Symposium on Assessing the Industrial
Hygiene Monitoring Needs for the
Coal Conversion and Oil Shale Industries"

Brookhaven National Laboratory
Upton, NY 11973

November 6-7, 1978

OVERVIEW FROM FOSSIL ENERGY

by John H. Abrahams
Environmental Activities Staff
Systems Engineering Division
Office of Fossil Energy Programs
Department of Energy

In undertaking an "Overview" of safety and health concerns in the Fossil Energy programs of the Department of Energy, three basic considerations are appropriate. These are:

1) The reasons why "Fossil Energy" is "in the limelight" as a major near- to mid-term energy source in the United States;

2) The relative place of Fossil Energy Technology, in relation to overall options for energy available to us;

3) The concerns of the Department of Energy's Office of Fossil Energy Programs (FE Programs) as to health and safety in developing Fossil Energy technology, and the potential problems affecting that development.

In this presentation, all three of these are addressed. The first two are discussed only briefly in order to put the latter in proper perspective and to set the stage for the theme of this Symposium.

An important reason why Fossil Energy technologies are receiving major attention is such that they offer possibilities to develop and utilize resources which are available without fear of possible influence on supply and/or price. Further, as generally known, many of the methodologies for Coal Conversion are not new. The opportunity thus exists for rapid improvement to known systems and possible extrapolation of basic knowledge to improved or new and more efficient processes.

Some understanding of the magnitude of the current Department of Energy effort in the Coal Conversion Program can be obtained by comparison of the funding levels for it, as compared with the total for the Office of Fossil Energy Programs (see Figure 1). From a very modest, but steadily increasing level of effort in the 1960 to 1970 time period (in the former Department of Interior Office of Coal Research), there have been and continue to be sharp increases in appropriated funds available. The FY 1979 planned level of expenditures for coal ($382.5 million) is forty-eight percent of the total ($801 million). Again, it should be noted that part of this increasing emphasis is a sharp focus of attention on our need to meet any future challenges to our energy supply, as typified by the oil embargo.

Today, our nation needs to work quickly in developing new technology and new processes so that fuel <u>resources</u> which are available in abundance can be turned to clean, safe, non-imported energy.

OFFICE OF COAL RESEARCH DEPARTMENT OF THE INTERIOR	
1964	$ 5,075,
1965	6,836,
1966	7,220,
1967	8,220,
1968	10,980,
1969	13,700,
1970	15,300,
1971	17,160,
1972	30,650,
1973	44,280,

ERDA (COAL ONLY)	
1974	$ 123,400,
1975	261,278,
1976	312,763,
1977	325,000,

DOE (COAL ONLY)	
1978	$ 385,400,
1979	382,500,

DOE (TOTAL FE BUDGET)	
1978	$ 743,000,
1979	801,800,

Figure 1. Appropriations for coal RD&D in thousand of dollars.

At the same time that we need to work with great haste, we need to work with great caution. For decades now it has been accepted knowledge that many of the substances of the petroleum industry, coal mining, coking, and other industries which use products from these processes, cause cancer or other illnesses. Recent tests and data lead us to SUSPECT that even greater numbers of substances and processes can cause cancer. So we are in the unhappy predicament of having to do the seemingly impossible--move quickly but with great caution. But haste and caution usually do not go hand-in-hand. To help understand "why" fossil fuels technologies are receiving major Federal commitments today, a review of pertinent well-known facts regarding reserves is essential. Coal and oil shales represent leading potential fuel sources for the nation's energy needs of the future. Coal reserves, as an example, according to the National Energy Plan are estimated at 436 billion tons. There could be as many as 600 billion barrels of recoverable petroleum reserve from oil shale. The importance of these reserves is emphasized by the fact that while the existing oil and gas supply accounts for only about 11 percent of known U.S. recoverable reserves, they are currently meeting about 75 percent of the nation's energy demands. On the other hand, these coal and solid fuel reserves make up over 77 percent of the nation's known reserves, yet contribute less than 20 percent to the nation's energy consumption.

How to make maximum use of these energy resources efficiently and safely is the principal concern of the Office of Fossil Energy Programs (FE Programs), under the Assistant Secretary for Energy Technology.

It is anticipated that a shift from current petroleum and natural gas sources to those associated with coal and oil shale is needed for near- to mid-term use through the middle of the twenty-first century, even if new petroleum reserves are discovered. Of course there is a need for research and development of other energy sources for the longer term; but we have the coal and oil shale resource now; we have the basic methodology, and with prudence can move ahead. Unfortunately, the few epidemiological studies we do have suggest that, in general, coal processing involves biological risk, but early and complete occupational safety and health plans and programs could minimize or eliminate these risks. FE Programs and the Assistant Secretary of Environment (EV) have identified that basic issues and requirements for such programs, and much of the needed research to fill the gaps. A comprehensive occupational safety and health plan for FE Programs is now being formulated for the guidance of FE Programs facilities, including those of our cost share partners. This "guidance" takes into account current safety, industrial hygiene, medical, and research programs and regulatory requirement. We are working closely with EV in this overt effort.

Figure 2 shows how FE Programs is organized to deal with these problems; how coal and oil shale conversion constitute a major segment of the FE Program; and that there are other processes under development by FE Programs.

FE Programs consists of four major technical elements, two staff components, and the Energy Technology Centers (ETCs). The technology elements are:

- The Division of Fossil Fuel Extraction
- The Division of Fossil Fuel Processing
- The Division of Fossil Fuel Utilization
- The Division of Magnetohydrodynamics

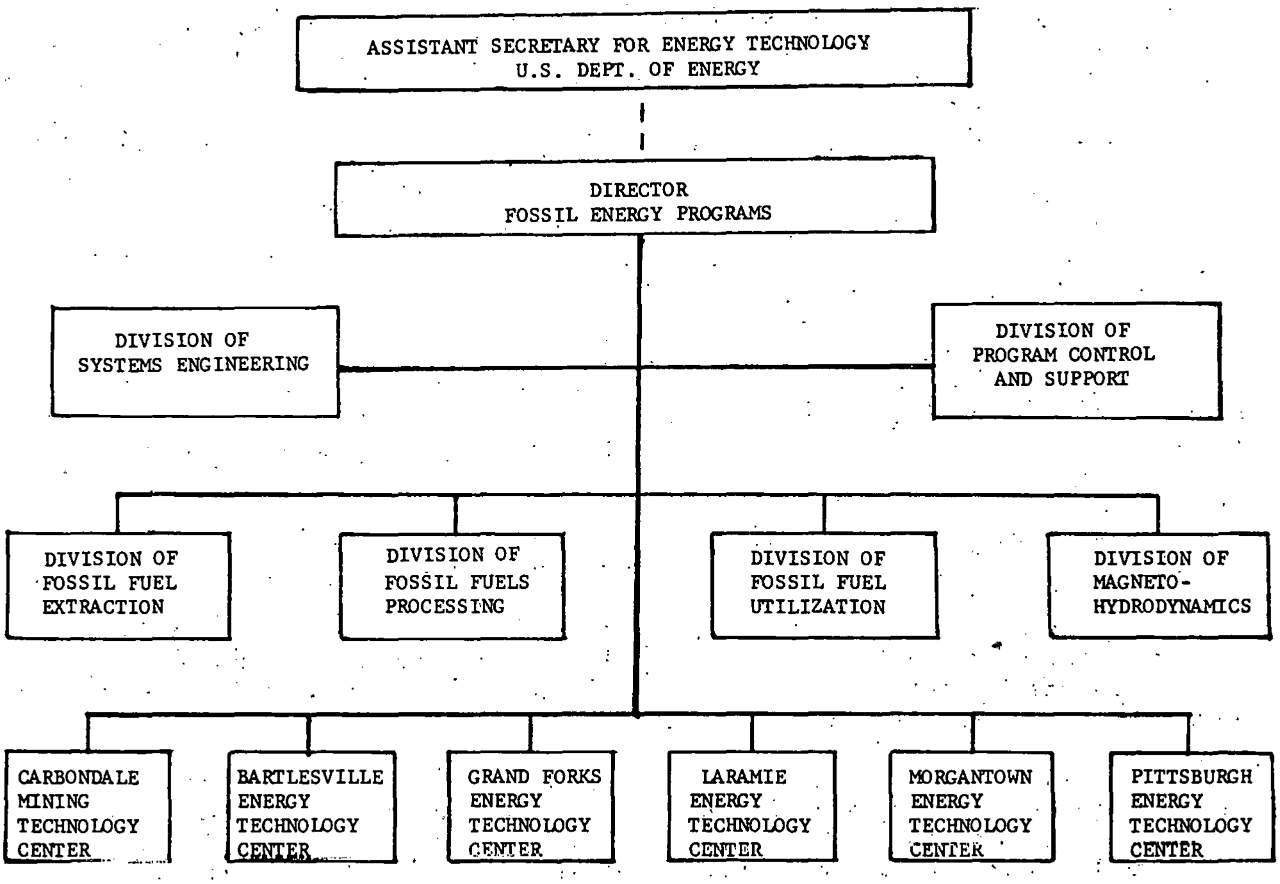

Figure 2. Organization of the Office of Fossil Energy Programs, Energy Technology, Dept. of Energy.

A brief description of the key elements of the FE Programs will help in directing attention to the areas of interest from a health and safety viewpoint. Within the Division of Fossil Fuel Processing, as an example, there are four major Coal Liquefaction processes under development. These are: Solvent Refining/Extraction, Direct Hydrogenation, Pyrolysis, and Third Generation Processes. A Solvent Refined Coal Demonstration Plant is currently in the design stage, resulting from operation of two pilot plants. The Coal Gasification Program includes both High Btu and Low Btu Pilot Plants, with at least one Demonstration Plant under design.

The realities of these developments is emphasized by the progress being made on a number of these technologies. Solid SRC I coal product, relatively sulphur-free, has been delivered to a commercial utility and used in commercial quantities for electricity generation; Liquid SRC II fuel has been delivered and burned in commercial boilers. Approximately 100,000 barrels of shale oil product are delivered to the U.S. Navy for use in vessels and aircraft. As the Demonstration Plants come on stream in the next several years, there will begin to exist a modest but increasing contribution to meeting our energy needs.

Numerous pilot projects also are underway for the underground gasification program. Other FE Programs include: Enhanced Oil Recovery, Enhanced Gas Recovery, Advanced Power Systems, Fuel Cells, and Direct Combustion. One point should be made clear, however, pilot plants are not miniature demonstration of commercial scale plants. Pilot plants are strictly for research and development of process technology, and frequently contain only components of complete systems. In addition, many units of pilot plants are not scalable to commercial applications.

The wide variety of FE Programs technology described covers a wide range of possible near- and mid-term developments, as well as those of longer-range potential. Some of the new developments in combustion systems, such as the fluidized bed process, are already being installed or will be in the near future in commercial plant applications. These latter technologies appear to present relatively small safety and health risks. Local environmental and site-specific safety requirements must be met, of course.

The principal FE programs for near- and mid-term utility should be viewed as assisting in filling needs for energy during the extended interim period when research goes forward on other alternative sources such as solar energy, geothermal applications, and biomass conversion. These latter, with nuclear energy, along with the coal conversion and oil shale technologies, constitute an integrated and coordinated DOE Energy Technology "system."

FE Programs, within that system concept, is presently concentrating its health and safety efforts on those technologies which are rapidly entering the Demonstration Plant stage - Coal liquefaction and gasification. There are similarities in the safety and health problems, and also differences; but it is hoped that the end products for commercial use, such as fuel oil, solids, or gases, will be reasonably free of "environmental pollutants." FE Programs has the sole responsibility for fossil fuels process development and the prime responsibilities for safety and health matters in its programs. The responsibilities of FE Programs and those of EV, regarding safety and health, are shown on Figure 3. This figure shows that technical line managers have the major,

ASSISTANT SECRETARY FOR ENERGY TECHNOLOGY
RESPONSIBLE FOR:

- ENVIRON. SAFETY AND HEALTH PROGRAMS AT FIELD ORGANIZATIONS AND WITH CONTRACTORS
- ASSURANCE OF COMPLIANCE THERIN OF DOE, FEDERAL, STATE, AND LOCAL EHOS REQUIREMENTS
- CLEAR ASSIGNMENT OF RESPONSIBILITY AND ISSUANCE OF APPROPRIATE GUIDANCE

ASSISTANT SECRETARY FOR ENVIRONMENT
RESPONSIBLE FOR:

- OVERVIEW OF LINE MANAGERS FUNCTIONS
- INDEPENDENT REVIEWS
- RESEARCH
- DEVELOPMENT OF DOE STANDARDS

*Interim Management Document No. 5001

Figure 3. Current DOE policy requirements.

direct responsibility for development and implementation of safety and health programs, while EV has overview. FE Programs is approaching these concerns for establishing a comprehensive Occupational Safety and Health Program as follows:

- Must extend from exploratory research to commercialization
- Provide for compliance with OSHA standards
- Be based on present knowledge, modified as new research results are available.

In every phase of the coal conversion technology development program, in both government-owned facilities and in industry, from exploratory research to commercialization, protection can be achieved by measures to:

1) Avoid inhalation of gaseous emissions;
2) Prevent physical contact with gases or liquids and high-temperature components;
3) Comply with existing OSHA Standards which apply to many of the potential exposures associated with coal conversion process.

The hazards to human health and safety associated with these technologies fall into two categories: physical and chemical. Risks from physical hazards generally can be mitigated through a comprehensive safety system analysis and program. The chemical hazards involve both the worker and the general population, since air and water pollutants are not necessarily confined to the site.

For example, there are many groups of workers other than those in coal conversion processes who are exposed to polynuclear aromatic hydrocarbons. A total of some 3,900,000 workers are estimated to be exposed, and this group includes printers, mechanics, roofers, electricians, as well as workers in the petroleum industry. It is estimated by the Department of Health, Education and Welfare, and its National Institute of Occupational Health and Safety (NIOSH) that about 9,100 excess lung cancer deaths each year might occur in this group. This is sufficient evidence to cause FE Programs to be intensely concerned about this potential health hazard.

Adequate data are available for only a small fraction of the substances and industrial processes which pose potential risks to exposed workers. Each year new processes and materials are introduced into the workplace and there are good reasons to believe these could be as hazardous as those used in the past.

It is inevitable that more and more substances are on their way and that more and more regulations are on the way which will affect both the private sector and governmental agencies such as DOE. The Occupational Safety and Health Administration (OSHA) and the Toxic Substances Control Act (TSCA) must be coordinated if they are going to be effective in their efforts to protect the American worker, the public at large, and keep a lid on economic feasibility at the same time. Interagency coordinating committees have been established to that end and are beginning to function.

We can't afford a time backlog between the development of a process or substance and the time that process or substance is allowed on the market. OSHA and TSCA must be in a position to act quickly once a carcinogenic or toxic substance or process is identified. We have an obligation under TSCA and OSHAct to develop adequate information which will move through the regulatory system without undue delay and contention.

The risks from chemical hazards are subtle and difficult to deal with since a large variety of potentially toxic carcinogenic or mutagenic substances may result from conversion processes. These substances will likely be present in complex mixtures, and include other compounds which are unknown and need to be identified and assessed for health impacts. In particular, the effects of chronic low-level exposure to potent by-product carcinogens, such as polycyclic aromatic hydrocarbons and aromatic amines, are poorly understood.

Current knowledge of the health effects of substances to which the work force may be exposed is, in general, limited and needs to be expanded. Moreover, there is a distinct possibility that there may be both synergistic and antagonistic effects of materials in the complex organic mixtures (especially polycyclic aromatics) produced during conversion processes. Little is known relative to the long-term effects of chronic exposure to such materials and mixtures. Biologic research should be employed to ascertain potential occupational risks and to assure that industrial personnel are not being exposed to unacceptable hazards.

However, few industries have been investigated adequately for evaluating the possible occurrence of occupationally related cancers and other occupational illnesses. It is generally agreed that the best basis for regulating a substance is epidemiological. But epidemiologic surveys are difficult to conduct and only agents and industrial processes which lead to rather large excess incidences have been identified to date. Although a number of toxicological investigation programs on coal conversion products are now underway, sponsored by the Department of Energy, FE Programs, and EV, we simply do not have a comprehensive and coordinated epidemiological program in progress. Although exposure to some of the more important occupational carcinogens and toxic chemicals has been reduced in recent years, there are still unregulated materials in the U.S. workplaces; a number of occupations are characterized by excess cancer risks which have not yet been attributed to specific agents.

Regardless of the current need for more information, we can, and indeed must, protect workers from illness or injury by applying what we now know. A suitable protection program, based on sound principles of occupational safety and health, must include:

- Clinical medical considerations, including preplacement, periodic and special physical examinations; measures for recognition, diagnosis and treatment of disease arising from occupational exposures; and the maintenance of adequate surveillance over medical records and participation in preventive health planning and programs.

- Environmental controls, including monitoring and surveillance over work room and process; industrial hygiene evaluations and controls, e.g., substitution, isolation, engineering design, etc.; personal monitoring and dosimetry.

- Provision of adequate personal protective equipment where engineering controls are not feasible.

- Education of supervisors and employees as to job hazards, results of exposures, and the means of protection.

- Research to amplify the current state of knowledge.

Each aspect of the development of coal conversion technologies is constrained by laws, standards, and regulations imposed to protect health, safety and the environment. In most cases, design and operation within these constraints involves higher capital and higher operating costs, which will necessarily be reflected in the price of the product. In addition, the refinement or imposition of new environmental regulations will alter the set of constraints under which facilities are designed, further affecting the price of product fuel.

The Environmental Protection Agency (EPA) has issued in the Federal Register its proposed approach to implementing the TSC Act. While EPA is developing testing protocols, they are not being made mandatory at this time. However, EPA has made it clear that the basic information required must be a thorough presentation as to projected uses and exposures, by-products, disposal methods, and as to toxicity and other tests performed. EPA will evaluate this information, not only on the basis of the data provided by the sponsor, but on all other information available to it. Thus, it is evident that great care is needed in developing and carrying out test programs, if needless delays are to be prevented in commercial utilization of fossil energy products.

In recent weeks, the Research News section of Science has been devoted to chemical carcinogens--"The Safety of Low Dosages, The Scientific Basis for Regulation," and "How Well the Laws Are Being Implemented." These articles have been excellent discussions of the confusion that exists within the scientific community itself over cancer research and testing procedures. Perhaps the best thing that could come from all this confusion over toxic substance regulation and OSHA regulation is a strengthening of the toxicology and epidemiology disciplines. Federal support is gradually increasing, and private industry is investing substantial sums in this area. But much remains to be done. The FE Programs is undertaking an Occupational Safety and Health Program effort which includes new emphasis in this area.

If the Fossil Energy Conversion Program is to succeed, there must be an intensive occupational safety and health program through every stage of the development. Obviously, the Occupational Safety and Health Programs must apply the current state of knowledge and the best professional practices, as currently recognized. There must be active and parallel programs which integrate the results of observations made as part of the Occupational Safety and Health Programs and the specialized research designed to improve the state of knowledge.

SIGNIFICANCE OF TRACE CONSTITUENTS IN COAL

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Presented at the

"Symposium on Assessing the Industrial
Hygiene Monitoring Needs for the
Coal Conversion and Oil Shale Industries"

Brookhaven National Laboratory
Upton, NY 11973

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Distribution of Trace Elements in US Coals

Increasing interest in the chemical composition of U.S. coals has prompted studies resulting in an extensive compilation of trace element data representing the major coal-producing areas. The U.S. Geological Survey (USGS) has a large ongoing program which will eventually characterize over 5000 coal samples for 30-40 elements. A report (1) convering the analyses of the first 799 samples is available. Table 1 summarizes the averages obtained for 36 elements in that initial study.

Less recent, but extremely comprehensive, work done by Zubovic and his co-workers at the USGS during the 1960s (2) characterizes the various coal basins. Their results indicate that the accumulation and distribution of inorganic elements in coal result from the interactions of various geological, physico-chemical, and biochemical factors. Geological factors include the rate of subsidence of a depositional basin, rate of uplift of the drainage area, the type of rocks being eroded and deposited, and the ratio of the size of drainage area to the area of organic accumulation.

The Illinois State Geological Survey (ISGS) has been involved with a smaller, but similar program, concentrating upon the Illinois basin (3). Table 2 lists the mean values for some 114 coals from the various Illinois coal seams. Some general observations from this study are that elemental concentrations tend to be highest in the eastern United States, lowest in coals from the western fields, and intermediate in the Illinois basin coals. It was observed that only a few elements were significantly enriched in coals relative to the earth's crust. Selenium is generally enriched whereas boron was found to be enriched in coals from the Illinois basin. Chlorine was found to be enriched in the Illinois and eastern coals. Many elements are depleted in coals, relative to the earth's crust. In the Illinois basin these include Mn, F, Ta, Tl, Cr, Na, Al, Ca, among others. Elements which have the largest relative ranges in concentrations include those associated with sulfate and sulfide minerals. Sometimes these high concentrations are related to mineral deposits. Elements which have the more narrow relative ranges are usually associated with silicate minerals or the organic (coaly) matrix. Some representative histograms of distribution are shown in Figure 1.

A comprehensive review of the literature pertaining to distribution and nature of trace elements in coal has been compiled by Gluskoter et al. (4). This review lists the many smaller regional studies that have been done for various elements.

Variations in the vertical distributions which in any coal seam are also quite pronounced. Figure 2 exemplifies the extreme ranges found in bench samples for Br, U, Mo, and V in typical Illinois coal seams. These data reflect the influence of the overlying and underlying shale and claystone as sources for some of these elements in coal.

Association of Trace Elements in Coal

Important as the range of concentration of an element in various coals the mode of occurrence or nature of association is equally desired. In most cases an element is associated with some discrete mineral phase--e.g. Zn as in the mineral sphalerite (ZnS). Elements such as Br, B and others are identified preferentially with the organic coal matrix. Still other elements such as Hg show both preferences. Table 3 from Gluskoter et al. (4) lists some minerals identified from various coals.

Washability (float-sink) data have been useful in determining the mode of occurrence of elements in coal. This is a process in which a ground whole coal sample is separated into various density fractions and analyzed for elements concerned. Elements which are preferentially concentrated in the lighter fractions are considered to be "organically" associated. Conversely those elements associated with the heavier mineral phases are considered to be inorganically bound. Figure 3 exemplifies some typical washability curves for Br, Cr, As, ash, and S.

By a normalization process the area under these curves are integrated and the relative magnitudes may be related to "organic" or "inorganic" association trend. Table 4 summarizes some observations for four Illinois coals (sets 1, 6, 8 and 9), an Alabama coal (set 2), two West Virginia coals (set 3 and 4), and an Arizona coal (set 4). It is apparent that an element does not generally exhibit the same float-sink (washability) behavior for coals in all geographical areas, however results from the four coals studied from the Illinois basin are quite similar reflecting the geological environment. Some generalizations from the Illinois basin are that Ge, Be, B, Sb were generally classified as organic whereas Zn, Cd, Mn, As, Mo, and Fe were generally classified in the "inorganic" group. The other areas studied generally indicate Ge, B, and Br to be organically associated.

Studies involved with demineralized coal (coal extracted with several acids) and analysis of coals extracted with ammonium acetate (5) generally confirm the trends observed from the washability studies. Although it is quite probable some of the oerganic materials are altered with the acid treatment (HCl, dilute HNO_3, HF, etc.) generally the organic sulfur content was unaltered and most elemental concentrations basically agreed with those values expected from washability curves. The ion exchange behavior of coals as exhibited from analysis of before and after ammonium acetate extracted coals confirmed, in cases such as Ca, the different associations for eastern and western coals, in that $\sim$55% Ca was extracted from the western versus less than 10% in the eastern coals studied.

These data can possibly emphasize the potential cleaning of coal for these elements concerned, however the particle size of the minerals also play a large role in the ease of cleaning. In an eastern Pittsburgh seam coal 95% of the pyrite occurs with an average size of 8 microns, finely divided within the coaly matrix. Hence organic affinity is only an indicator of cleaning potential.

Mobilities of Trace Elements During Coal Conversion

When heat, pressure, and chemical stimuli are imposed upon coal, as during combustion or conversion there will be a tendency for mobility and volatilization by many elements regardless of their association. The various processes of coal preheating, coking, combustion, gasification, and liquefaction each pose particular problems as far as evolution of potentially toxic materials is concerned.

During coal conversion trace elements may be "lost" or accounted for in various product and waste phases of the particular process. These "inventory" studies are best made by analyzing all phases of the process, if possible. This is a very difficult if not impossible procedure to carry out quantitatively. Material balances of from 50 to 150% are considered quite acceptable since sampling problems can be severe.

Several liquefaction processes have been studied for possible losses of trace elements. Some 34 elements were studied for their distribution and fate in the Solvent Refined Coal Process Pilot Plant in Fort Lewis, Washington (6). All elements were accounted for in one phase or another. Volatile elements including Se, As, Hg, and Br were found to a significant degree in the process water streams. The Synthoil process has been surveyed by Schultz et al. (7) and Lett et al. (8) with most elements studied being accounted for within the system. It was noted Cl was concentrated in the scrubbers. Analysis of effluent systems of the COED process (9) indicated the filtered aqueous effluent streams contained >1 ppm of B, Fe, Mg, Al, Cu, Mg, Mn, Ni, Pb, and Zn.

Several gasification processes have trace element data available. Gasior et al. (10) reported that most elements studied (including As, Be, Cd, Ni, Pb, Se, and V) in the SYNTHANE process were recovered in the char, however some Hg was unaccounted for. Attari (11) determined some 38 elements in feed coal and ash samples from the HYGAS process and predicted that Cl, Hg, Se, As, Pb, Cd, V, Sb, Be, Ni and possibly others would be significantly volatilized during the process however the quenching, acid-gas removal, and methanation styes would effectively trap them. Sather's et al. (12) work on feed coal and ash from the LURGI process indicated that significant amounts of As, Be, F, Pb, and V can possibly be subjected to the air or water streams during a day's run if not effectively trapped.

References

1. V. E. Swanson, J. H. Medlin, J. R. Hatch, S. L. Coleman, G. H. Wood, Jr., S. D. Woodruff, and R. T. Hildebrand, 1976, Collection, chemical analysis, and evaluation of coal samples in 1975: U.S. Geological Survey Open-File Report 76-468.

2. Peter Zubovic, 1976, Geochemistry of Trace Elements in Coal: Symposium Proceedings Environmental Aspects of Fuel Conversion Technology II, Hollywood, FL, December 1975. EPA-600/2-76-149, pp. 47.

3. H. J. Gluskoter, R. R. Ruch, W. G. Miller, R. A. Cahill, G. B. Dreher, and J. K. Kuhn, 1977, Trace elements in coal: occurrence and distribution: Illinois State Geological Survey Circular 499.

4. H. J. Gluskoter, N. F. Shimp, and R. R. Ruch, in press, Coal analysis, trace elements, and mineral matter: Chapter 7 of 2nd Supplementary Volume of "Chemistry of Coal Utilization", to be published by the National Research Council in 1979.

5. F. L. Fiene, J. K. Kuhn, and H. J. Gluskoter, 1978, Mineralogic affinities of trace elements in coal: Proceeding of US EPA Symposium "Coal Cleaning to Achieve Energy and Environmental Goals", Hollywood, FL, Septebmer 1978.

6. R. H. Filby and K. R. Shak, 1977, Trace Elements in the Solvent Refined Coal Process: Proceedings Symposium on Environmental Aspects of Fuel Conversion Technology, Hollywood, FL, September 1977.

7. H. Schultz, G. A. Gibbon, E. A. Hattman, H. B. Booker, and J. W. Adkins, 1977, The distribution of some trace elements in the ½ ton per day Synthoil process development unit, PERC/RI-77/2, 17 p.

8. R. G. Lett, C. E. Schmidt, R. R. DeSantis, and A. G. Sharkey, Jr., 1977, Screening for hazardous elements and compounds in process streams of the ½ ton per day Synthoil process development unit, PERC/RI-77/12, 33 p.

9. S. G. Hildebrand, R. M. Cushman, and J. A. Carter, 1976, The potential toxicity and bioaccumulation in aquatic systems of trace elements present in aqueous coal conversion effluents, Proceedings 10th Annual Conference on Trace Substances in Environmental Health, University of Missouri, Columbia, MO, June 1976.

10. S. J. Gasior, R. G. Lett, J. P. Strakey, and W. P. Haynes, 1978, Major, minor, and trace element balances for the Synthane PDU gasifier--Illinois #6 coal, Preprints Div. of Fuel Chemistry American Chemical Society Meeting, Volume 23 (2), March, 1978.

11. A. Attari, M. Mensinger, and J. C. Pau, 1975, Fate of trace constituents of coal during gasification (Part II), Preprints Div. of Fuel Chemistry, American Chemical Society Meeting, Volume 18(4), April, 1975.

12. N. F. Sather, W. M. Swift, J. R. Jones, J. L. Beckner, J. H. Addington, and R. L. Wilburn, 1975, Potential trace element emissions from the gasification of Illinois coals, Illinois Institute Environmental Quality Document 75-08, 18 p.

Table 1

Average Amounts of 36 Elements in All Coal Samples and in Different Ranks of Coal, Presented on Whole-Coal Basis
(from reference 1, p. 19)

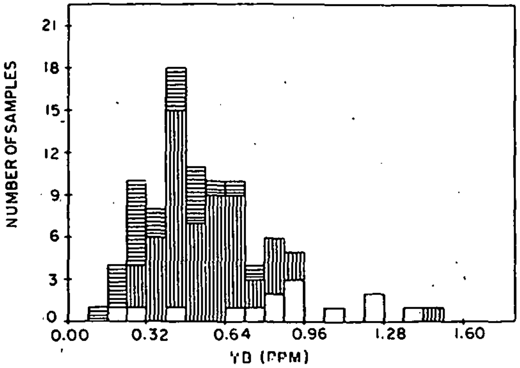
Percent	All coal (799 samples)	Anthracite (53 samples)	Bituminous (509 samples)	Subbituminous (183 samples)	Lignite (54 samples)	Average shale
Si	2.6	2.7	2.6	2.0	4.9	7.3
Al	1.4	2.0	1.4	1.0	1.6	8.0
Ca	.54	.07	.33	.78	1.2	2.21
Mg	.12	.06	.08	.18	.31	1.55
Na	.06	.05	.04	.10	.21	.96
K	.18	.24	.21	.06	.20	2.66
Fe	1.6	.44	2.2	.52	2.0	4.72
Mn	.01	.002	.01	.006	.015	.085
Ti	.08	.15	.08	.05	.12	.46
ppm						
As	15	6	25	3	6	13
Cd	1.3	.3	1.6	.2	1.0	.3
Cu	19	27	22	10	20	45
F	74	61	77	63	94	740
Hg	.18	.15	.20	.12	.16	.4
Li	20	33	23	7	19	66
Pb	16	10	22	5	14	20
Sb	1.1	.9	1.4	.7	.7	1.5
Se	4.1	3.5	4.6	1.3	5.3	.6
Tb	4.7	5.4	5.0	3.3	6.3	12
U	1.8	1.5	1.9	1.3	2.5	3.7
Zn	39	16	53	19	30	95
B	50	10	50	70	100	100
Ba	150	100	100	300	300	580
Be	2	1.5	2	.7	2	3.0
Co	7	7	7	2	5	19
Cr	15	20	15	7	20	90
Ga	7	7	7	3	7	19
Mo	3	2	3	1.5	2	2.6
Nb	3	3	3	5	5	11
Ni	15	20	20	5	15	68
Sc	3	5	3	2	5	13
Sr	100	100	100	100	300	300
V	20	20	20	15	30	130
Y	10	10	10	5	15	26
Yb	1	1	1	.5	1.5	2.6
Zr	30	50	30	20	50	160

Table 2

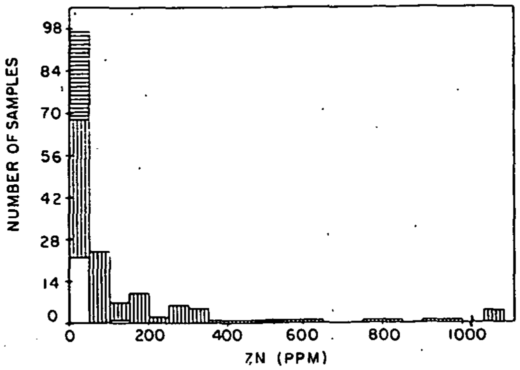
MEAN ANALYTICAL VALUES FOR 114 WHOLE COAL SAMPLES FROM THE ILLINOIS BASIN COAL FIELD

Element	Arithmetic Mean	Geometric Mean	Minimum	Maximum	Standard Deviation	Number Samples	Number Less Than Values
AG	0.03 ppm	0.03 ppm	0.02	0.08	0.02	37	
AS	14 ppm	7.4 ppm	1.0	120	20	113	
B	110 ppm	96 ppm	12	230	50	99	
BA	100 ppm	75 ppm	5.0	750	110	56	
BE	1.7 ppm	1.6 ppm	0.5	4.0	0.82	113	
BR	13 ppm	10 ppm	0.6	52	7.4	113	
CD	2.2 ppm	0.59 ppm	0.1	65	7.4	93	43
CE	14 ppm	12 ppm	4.4	46	7.5	56	
CO	7.3 ppm	6.0 ppm	2.0	34	5.3	113	
CR	18 ppm	16 ppm	4.0	60	9.7	113	
CS	1.4 ppm	1.2 ppm	0.5	3.6	0.73	56	
CU	14 ppm	13 ppm	5.0	44	6.6	113	
DY	1.1 ppm	1.0 ppm	0.5	3.3	0.42	56	
EU	0.26 ppm	0.25 ppm	0.1	0.87	0.12	56	
F	67 ppm	63 ppm	29	140	26	113	
GA	3.2 ppm	3.0 ppm	0.8	10	1.2	113	
GE	6.9 ppm	4.8 ppm	1.0	43	6.4	113	11
HF	0.54 ppm	0.49 ppm	0.13	1.5	0.25	56	
HG	0.2 ppm	0.16 ppm	0.03	1.6	0.19	113	
I	1.7 ppm	1.2 ppm	0.24	14	2.0	56	13
IN	0.16 ppm	0.13 ppm	0.01	0.63	0.11	56	6
LA	6.8 ppm	6.4 ppm	2.7	20	2.8	56	
LU	0.09 ppm	0.08 ppm	0.02	0.44	0.06	56	3
MN	53 ppm	40 ppm	6.0	210	41	113	
MO	8.1 ppm	6.2 ppm	0.3	29	5.4	111	6
NI	21 ppm	19 ppm	7.6	68	10	113	
P	64 ppm	45 ppm	10	340	60	113	7
PB	32 ppm	15 ppm	0.8	220	42	113	6
RB	19 ppm	17 ppm	2.0	46	9.9	56	1
SB	1.3 ppm	0.81 ppm	0.1	8.9	1.4	113	
SC	2.7 ppm	2.5 ppm	1.2	7.7	1.1	56	
SE	2.2 ppm	2.0 ppm	0.4	7.7	1.0	113	
SM	1.2 ppm	1.1 ppm	0.4	3.8	0.55	56	
SN	3.8 ppm	0.94 ppm	0.2	51	8.8	60	32
SR	35 ppm	30 ppm	10	130	23	56	2
TA	0.15 ppm	0.14 ppm	0.07	0.3	0.06	56	
TB	0.22 ppm	0.18 ppm	0.04	0.65	0.14	41	
TH	2.1 ppm	1.9 ppm	0.71	5.1	0.87	56	
TL	0.66 ppm	0.59 ppm	0.12	1.3	0.31	25	
U	1.5 ppm	1.3 ppm	0.31	4.6	0.93	56	
V	32 ppm	29 ppm	11	90	13	113	
W	0.82 ppm	0.63 ppm	0.04	4.2	0.69	56	
YB	0.56 ppm	0.53 ppm	0.27	1.5	0.21	56	
ZN	250 ppm	87 ppm	10	5300	650	113	
ZR	47 ppm	41 ppm	12	130	27	88	
AL	1.2 %	1.2 %	0.43	3.0	0.39	113	
CA	0.67 %	0.51 %	0.01	2.7	0.48	113	
CL	0.14 %	0.08 %	0.01	0.54	0.13	113	
FE	2.0 %	1.9 %	0.45	4.1	0.63	113	
K	0.17 %	0.16 %	0.04	0.56	0.07	113	
MG	0.05 %	0.05 %	0.01	0.17	0.02	113	
NA	0.05 %	0.03 %		0.2	0.04	113	
SI	2.4 %	2.3 %	0.58	4.7	0.7	113	
TI	0.06 %	0.06 %	0.02	0.15	0.02	113	
ADL	7.3 %	6.4 %	1.4	17	3.4	98	
MOIS	9.4 %	8.1 %	0.5	18	4.3	112	
VOL	40 %	40 %	27	46	3.1	111	
FIXC	49 %	49 %	41	61	3.6	111	
ASH	11 %	11 %	4.6	20	2.3	112	
BTU/LB	12712	12702	11562	14362	470	107	
C	70 %	70 %	62	80	3.0	110	
H	5.0 %	5.0 %	4.2	6.0	0.31	110	
N	1.3 %	1.3 %	0.93	1.8	0.19	110	
O	8.2 %	8.0 %	4.2	14	1.8	109	
HTA	11 %	11 %	3.3	20	2.5	112	
LTA	15 %	15 %	3.8	24	3.3	112	
ORS	1.6 %	1.4 %	0.37	3.2	0.6	112	
PYS	2.0 %	1.8 %	0.29	4.6	0.78	111	
SUS	0.1 %	0.05 %	0.01	1.1	0.16	109	
TOS	3.6 %	3.4 %	0.56	6.4	1.1	113	
SXRF	3.4 %	3.2 %	0.79	6.5	1.1	112	

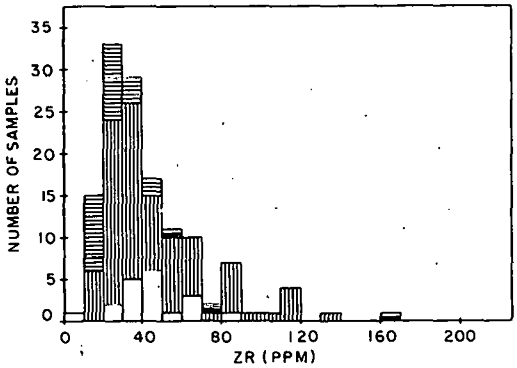
(from reference 3, p. 44)



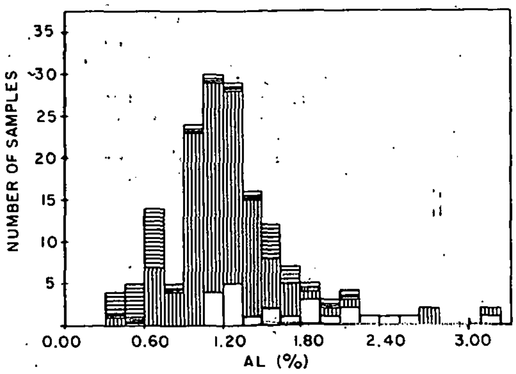
Distribution of ytterbium in coals analyzed.



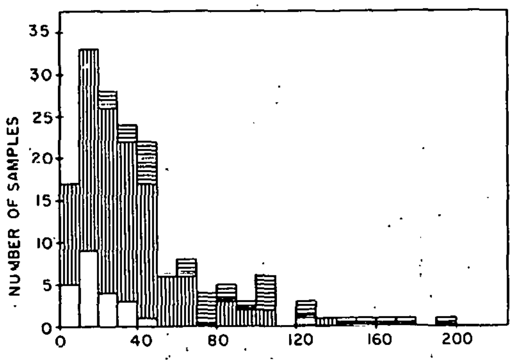
Distribution of zinc in coals analyzed.



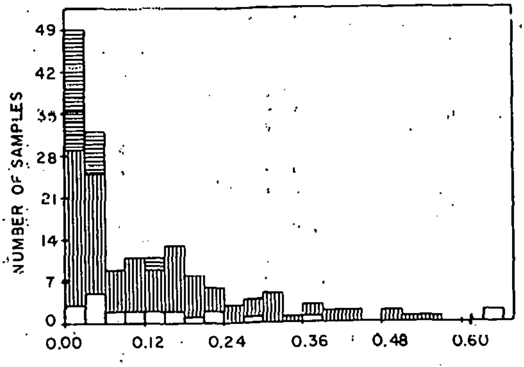
Distribution of zirconium in coals analyzed.



Distribution of aluminum in coals analyzed.

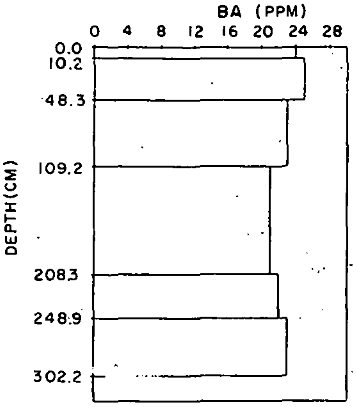


Distribution of calcium in coals analyzed.

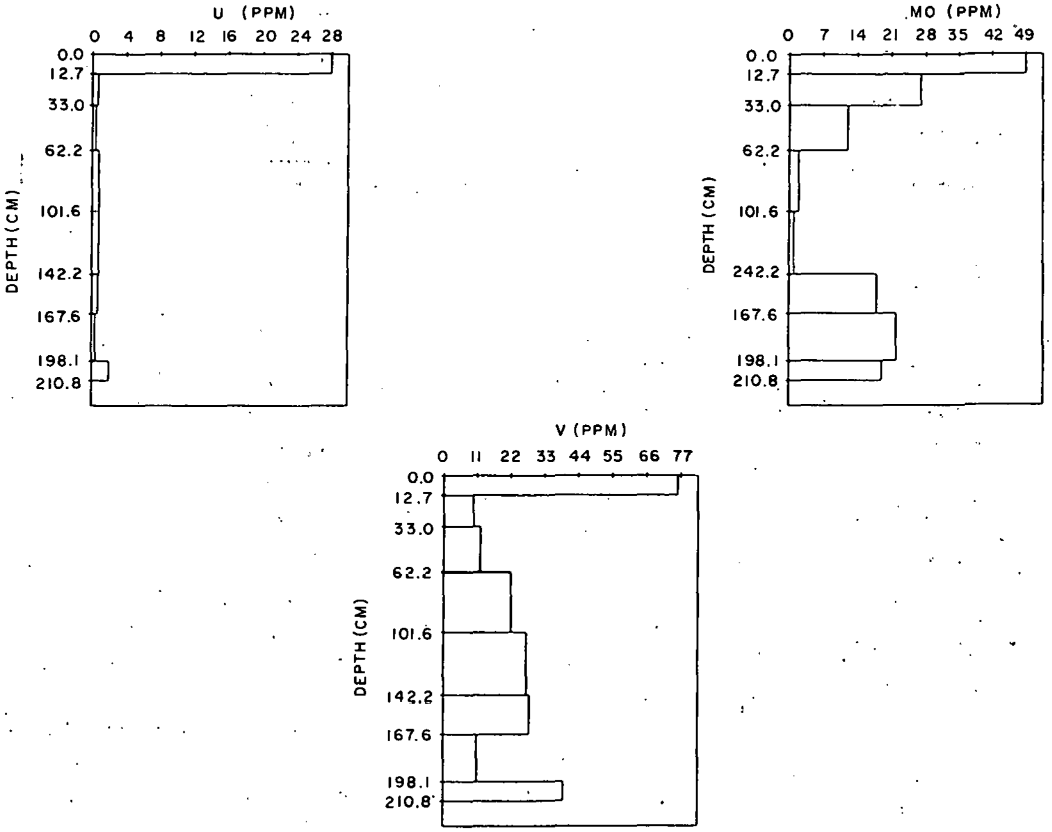


Distribution of chlorine in coals analyzed.

Figure 1. From reference 3, p. 68.



Distribution of bromine in coals of bench set 3.



Distribution of uranium, molybdenum, and vanadium in coals of bench set 1.

Figure 2. From reference 3, p. 85.

Table 3

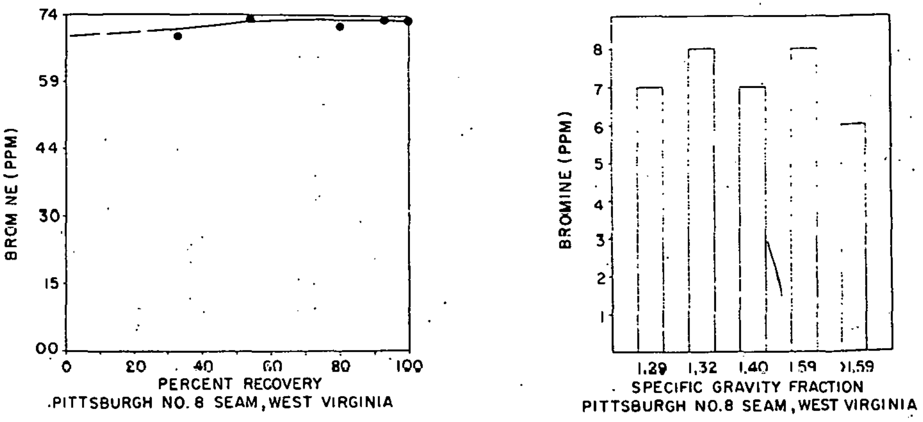
MINERALS IDENTIFIED WITH COALS

CLAY MINERALS	
Montmorillonite	$Al_2Si_4O_{10}(OH)_2 \cdot x\ H_2O$
Illite-sericite	$KAl_2(AlSi_3O_{10})(OH)_2$
Kaolinite	$Al_4Si_4O_{10}(OH)_8$
Halloysite	$Al_4Si_4O_{10}(OH)_8$
Chlorite	$Mg_5Al(AlSi_3O_{10})(OH)_8$
(Prochlorite, Penninite)	
Mixed-layer clay minerals	
SULFIDE MINERALS	
Pyrite	FeS_2
Marcasite	FeS_2
Sphalerite	ZnS
Galena	PbS
Chalcopyrite	$CuFeS_2$
Pyrrhotite	$Fe_{1-x}S$
Arsenopyrite	$FeAsS$
Millerite	NiS
CARBONATE MINERALS	
Calcite	$CaCO_3$
Dolomite	$(Ca,Mg)CO_3$
Siderite	$FeCO_3$
Ankerite (Ferroan dolomite)	$(Ca,Fe,Mg)CO_3$
Witherite	$BaCO_3$
SULFATE MINERALS	
Barite	$BaSO_4$
Gypsum	$CaSO_4 \cdot 2H_2O$
Anhydrite	$CaSO_4$
Bassanite	$CaSO_4 \cdot \frac{1}{2}H_2O$
Jarosite	$(Na,K)Fe_3(SO_4)_2(OH)_6$
Szomolnokite	$FeSO_4 \cdot H_2O$
Rozenite	$FeSO_4 \cdot 4H_2O$
Melanterite	$FeSO_4 \cdot 7H_2O$
Coquimbite	$Fe_2(SO)_3 \cdot 9H_2O$
Roemerite	$FeSO_4 \cdot Fe_2(SO_4)_3 \cdot 12H_2O$
Mirabilite	$Na_2SO_4 \cdot 10H_2O$
Kieserite	$MgSO_4 \cdot H_2O$
Sideronatrite	$2Na_2O \cdot Fe_2O_3 \cdot 4SO_3 \cdot 7H_2O$

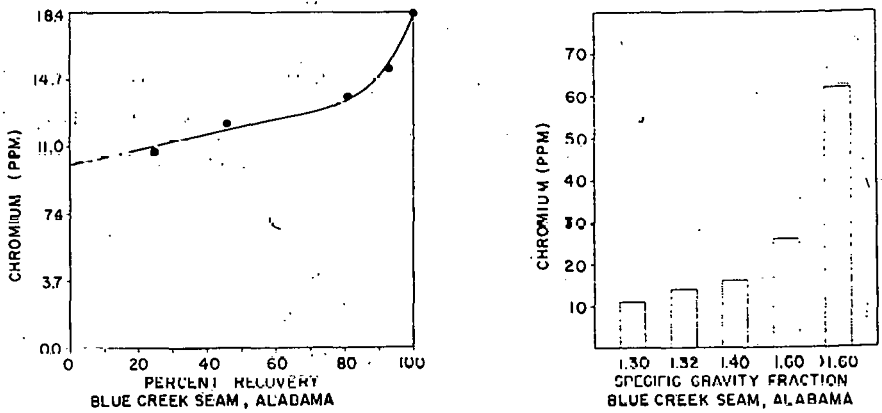
(from reference 4)

Table 3--Continued

CHLORIDE MINERALS	
Halite	$NaCl$
Sylvite	KCl
Bischofite	$MgCl_2 \cdot 6H_2O$
SILICATE MINERALS	
Quartz	SiO_2
Biotite	$K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$
Zircon	$ZrSiO_4$
Tourmaline	$Na(Mg,Fe)_3Al_6(BO_3)_3(Si_6O_{18})(OH)_4$
Garnet	$(Fe,Ca,Mg)_3(Al,Fe)_2(SiO_4)_3$
Kyanite	Al_2SiO_5
Staurolite	$Al_4FeSi_2O_{10}(OH)_2$
Epidote	$Ca_2(Al,Fe)_3Si_3O_{12}(OH)$
Albite	$NaAlSi_3O_8$
Sanidine	$KAlSi_3O_8$
Orthoclase	$KAlSi_3O_8$
Augite	$Ca(Mg,Fe,Al)(Al,Si)_2O_6$
Hornblende	$NaCa_2(Mg,Fe,Al)_5(SiAl)_8O_{22}(OH)_2$
Topaz	$Al_2SiO_4(OH,F)_2$
OXIDE AND HYDROXIDE MINERALS	
Hematite	Fe_2O_3
Magnetite	Fe_3O_4
Rutile	TiO_2
Limonite	$FeO \cdot OH \cdot nH_2O$
Goethite	$FeO \cdot OH$
Lepidocrocite	$FeO \cdot OH$
Diaspore	$AlO \cdot OH$
PHOSPHATE MINERALS	
Apatite (Fluor-apatite)	$Ca_5(PO_4)_3(F,Cl,OH)$

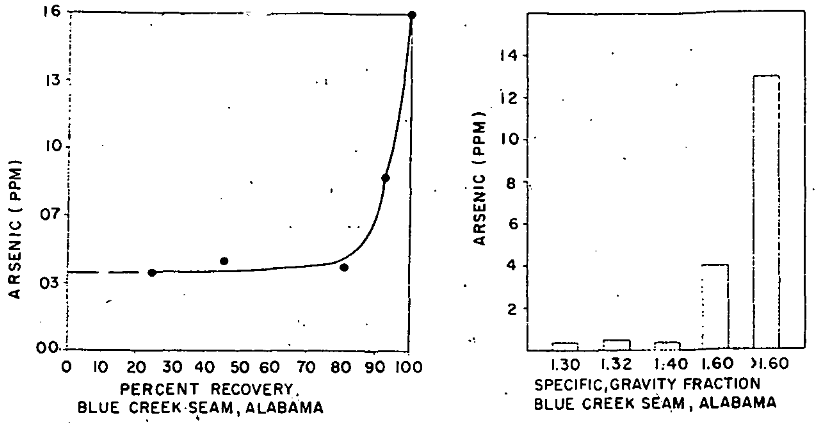


Bromine in specific gravity fractions of a sample from the Pittsburgh No. 8 coal from West Virginia. Left: washability curve. Right: distribution of bromine in individual fractions.

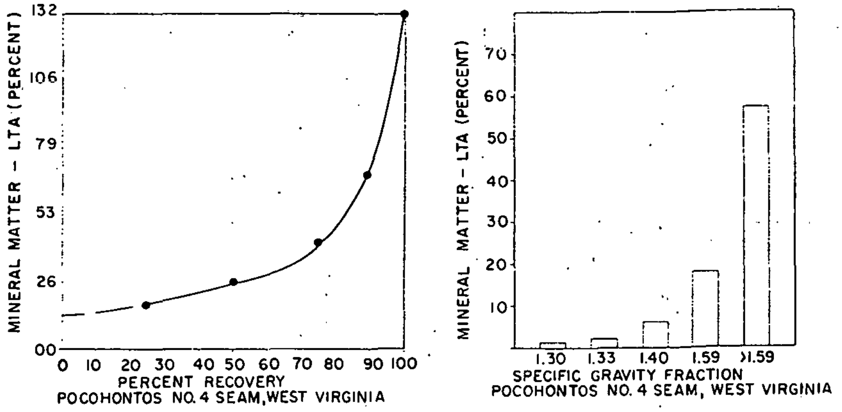


Chromium in specific gravity fractions of a sample from the Blue Creek coal from Alabama. Left: washability curve. Right: distribution of chromium in individual fractions.

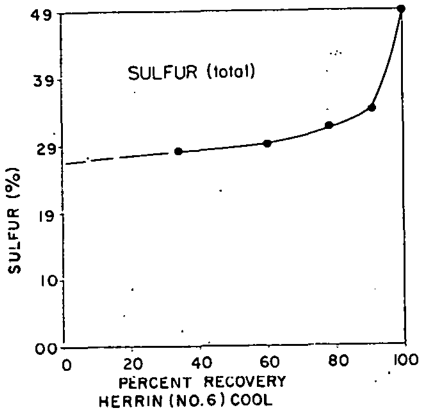
Figure 3. From reference 3, p. 107-108.



Arsenic in specific gravity fractions of a sample from the Blue Creek coal from Alabama. Left: washability curve. Right: distribution of arsenic in individual fractions.



Low-temperature ash in specific gravity fractions of a sample from the Pocahontas No. 4 coal from West Virginia. Left: washability curve. Right: distribution of low-temperature ash in individual fractions.



Washability curve of sulfur in specific gravity fractions of a sample from the Herrin (No. 6) Coal Member.

Figure 3. (Continued)

Table 4

ORGANIC AFFINITY OF ELEMENTS IN LABORATORY-PREPARED WASHED COAL SAMPLES

Float-Sink Set 1		Float-Sink Set 2		Float-Sink Set 3		Float-Sink Set 4		
Ge		Br		Co		Sr		
U		Ge		Br		Br		
Br		Co		Ni		B		
V		S		Sr		U		
Sb		Ni		Be		Ba		
Be		W		S		P		Organic
Dy		Cu		W		S		
		Dy		Du		Dy		
		Sr		Ge		Ge		
		Be		P				
		V		Fe				
		La						
	.85	U	.72		.66		.62	
Cr	.80	Pb	.67	Dy	.60	Pb	.61	
B		Sm		Yb		Eu		
Ni		Tb		Eu		Na		
Co		Eu		Cu		Be		
Cu		Sb		V		Co		
Na		Ce		Sb		Ga		Intermediate-Organic
Lu		Ba		Tb		Ca		
Eu		Ga		Ca		V		
K		P		Zn				
Sc				Lu				
	.55		.65	Ga	.50		.47	
Th	.49	Cr	.60	Ge	.49	Cu	.45	
Zr		Zr		Sc		Hg		
Hf		Se		Na		La		
Rb		Yb		B		Sm		
Ti		Ti		Sm		Ni		
Ta		Sc		Se		Zn		Intermediate-Inorganic
S		Lu		La		Sb		
Cs		Fe		Mn		Sn		
Yb		Hf		U		Mn		
Sm		Th		Cr		Cr		
		Al		Pb		Ce		
				Mg		Sc		
						Se		
	.34		.39		.37	Tb	.35	
Pb	.28	Ta	.33	Hg	.32	Yb	.33	
Se		B		Ti		Al		
Al		Ca		Ta		Fe		
Si		Zn		Th		Hf		
Mg		Na		Hf		Lu		
LTA		LTA		Al		Zr		Inorganic
Sn		Si		Zr		As		
Ba		K		LTA		Ta		
Ga		Mg		Cs		Th		
Cd		Cs		Rb		LTA		
Sr		Rb		Si		Rb		
Ce		Mn		K		K		
Fe		As		As		Si		
Mn						CS		
As						Ti		
La								
P								
Zn								
Ca								

(from reference 3, p. 118-119)

Table 4--Continued

Float-Sink Set 5		Float-Sink Set 6		Float-Sink Set 8		Float-Sink Set 9		
B		Ge		Ge		Ge		
Na		B		P		B		
P		Be		Be		Be		
Mg		P		B		Sb		
Ba		Se		Ga				
Fe		Sb						Organic
S		Cr						
Ni								
Co								
Br								
Sr								
Ca								
Be								
Dy								
Yb								
Cu								
V								
Lu								
Sb	.66		.68		.81		.69	
Sc	.63	Co	.66	Sb	.68	V	.56	
Ce		Ga		Co		S		
Se		Ca		Se		Ga		
La		Ni		Na		Mo		
Eu		K		V				Intermediate-Organic
Cr		V		K				
Tb				Ni				
U								
Mn								
W	.51		.60		.51		.49	
K	.49	Al	.58	Pb	.42	Na	.44	
Sm		Cu		Cu		Se		
Hf		Si		Si		Ni		
Zr		Mn		Al		Cr		Intermediate-Inorganic
Ta				Zr		Co		
Al				S		Hg		
Th				Hg		Cu		
Ga	.35		.36		.29		.24	
Rb	.34	Zr	.26	Fe	.22	P	.18	
Ti		LTA		LTA		Ti		
Sn		S		As		Fe		
Hg		As		Mo		Zr		
LTA		Cd		Cd		K		
As		Hg		Cr		LTA		Inorganic
Si		Mo		Mn		Al		
Pb		Pb		Zn		Si		
Cs		Zn		Ca		As		
Ge		Fe				Pb		
						Cd		
						Mn		
						Zn		
						Ca		

NOTE: Grouped in 4 catagories: organic, intermediate-organic, intermediate-inorganic, inorganic. Values for the indices of organic affinity separating classes are indicated.

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COAL GASIFICATION: PROCESS DESCRIPTION AND EFFLUENT CHARACTERIZATION*

J. C. Craun
Environmental Research & Technology, Inc.

Presented at the
"Symposium on Assessing the Industrial
Hygiene Monitoring Needs for the
Coal Conversion and Oil Shale Industries"
Brookhaven National Laboratory
Upton, NY 11973
November 6-7, 1978

*Paper not available for publication

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COAL LIQUEFACTION - PROCESS DESCRIPTION AND EFFLUENT CHARACTERIZATION

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Presented at the

"Symposium on Assessing the Industrial
Hygiene Monitoring Needs for the
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Coal Liquefaction - Process Description and Effluent Characterization

By

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The production of coal-derived liquids based on by-product coking began in both Germany and England in the 1840's. Such products were used for roofing, wood preservation and solvents. In the 1850's the coal tar dye industry was born and has lasted to this present day. Coal has provided the necessary feedstocks for most of the hydrocarbon liquids (aromatics) used by the emerging nations of the world. Examples of these products are solvent naphthas, benzene, toluene, xylenes, phenols, pyridine and most of the anilines. Such materials found their way into most all of our industrial growth products and provided the basis for the petro-chemical industry of the 1940-50's.

In the early 1920's there developed in Germany the direct coal liquefaction process. The Pott-Broche process was used by Germany during World War II to produce a host of oils and a solid. The recovered extract was similar to our present day Solvent Refined Coal, SRC-I, product. During the early 30's hydrogen was added into the process and the resulting Uhdepfirrmann process bears a close resemblance to the SRC-II process. Finally the Bergius process introduced a catalyst to aid in the rapid production of aviation fuel and diesel oils. At its height the Bergius process had 18 plants which produced 30 x 10^6 barrels of oil per year. Our modern H-Coal and SYNTHOIL processes were derived from the Bergius approach.

Again in Germany during the 1920's Fischer and Tropsch developed their process of gasifying coal to produce CO and H_2, which were then catalytically converted to a mixture of organic chemicals in a separate step under pressure. During World War II this process produced most of Germany's raw chemicals, including alcohols, oils and waxes. The Union of South Africa has a Fischer-Tropsch plant in operation today.

The United States began its interest in coal through the U. S. Bureau of Mines in the 1940's experimenting with both the Bergius process and Fischer-Tropsch synthesis. Research efforts were nearly terminated in the early 1950's with the discovery of large petroleum stores in the Middle East. It took another twenty years before our wants exceeded our needs and the petroleum supply was no longer under our control before coal conversion technology resurfaced.

Currently some twenty-odd liquefaction systems are in various stages of development by industry and federal agencies. Three major classifications of coal liquefaction technology can be identified;

1. Catalytic Hydrogenation
2. Noncatalytic Hydrogenation
3. Pyrolysis, Hydrocarbonization and others

1. Catalytic Hydrogenation

The Bergius, H-Coal and SYNTHOIL systems are examples of the reaction of coal in a slurry under high temperature (350-450°C), hydrogen pressure (2000-4000 psi), and in the presence of a catalyst to promote desulfurization and liquefaction. Of these three the H-Coal system developed by Hydrocarbon Research, Incorporated (HRI) is still in operation. The process is an extension of the H-Oil process ebullating bed technology originally employed to convert heavy petroleum oil residues into lighter fractions. The ebullating bed catalytic reactor converts about 90% of the carbon in coal to a liquid. Figure 1 gives a schematic representation of the H-Coal process.

2. Noncatalytic Hydrogenation

The solvent refined coal (SRC-1 and SRC-II) system was developed by Spencer Chemical Company for the U. S. Department of the Interior, and was subsequently purchased by Gulf Oil Corporation and run by Pittsburg and Midway Coal Mining Company, part of Gulf Oil. Coal is pulverized and mixed with a coal-derived vehicle solvent in a slurry tank. The coal slurry is combined with hydrogen, pumped through a fired preheater and passed into a dissolver. In the dissolver the coal and the solvent are hydrocracked into a wide range of hydrocarbon materials. The slurry of undissolved solids is then separated by filtration. Coal solution is then passed to the solvent recovery unit where the final SRC-1 product emerges as a liquid with a solidification point of 175°C. In the SRC-II process the product is partially recycled and distillation fractions represent the final liquid products. Figures 2 and 3 give schematic representations of SRC-I and SRC-II, respectively.

3. Pyrolysis and Hydrocarbonization

Pyrolysis of coal involves a mixture of combustion and recycled gases which fluidizes and heats the coal to about 175°C in the first stage. The coal is partially devolatilized and the gases evolved are scrubbed with recycle liquor and cooled. Most of the volatile matter contained in the coal is removed in stages II and III at 430° and 540°C, respectively. Pyrolysis gases and oil vapors pass through an external particulate separation system to remove solids. An absorption system removes oil vapors, and the product stream is treated for removal of H_2S and CO_2. Oil and water condensed from the pyrolysis stream are separated into lighter than water, heavier than water and aqueous fractions. The aqueous stream is ultimately discharged from a fluidized bed cooling step used to generate high pressure steam. The oil fractions are combined and sent for hydrotreating to remove residual sulfur, nitrogen and oxygen impurities. The resulting oil is the final product.

Typical output streams from the conversion of coal to liquid products summarized in table 1.

Table 1. Output streams of coal liquefaction.

Product oil
Sulfur
H_2SO_4
Ash
Carbonaceous residue
Water-coal drying
Water-waste
Spent catalyst
Tar
Fuel gas (Low BTU)
Sludge
Ammonia
Spent solvent
Coal dust
Filter cake
Char
Light distillates
Middle distillates
Vacuum distillates
Vacuum bottoms

Five major areas of concern involve: 1. sulfur-containing constituents; 2. concentrations of polynuclear aromatic hydrocarbons (PAH); 3. concentrations of weakly acidic components; 4. nitrogen heterocyclics; and 5. trace elements. These five major areas of concern can exist in four sample types, 1. gas/vapor; 2. liquids/slurry; 3. solids;and 4. particulates or aerosols.

Product Characterization

Following the prime output stream, the liquefaction product, through a general separation and characterization scheme may reveal clues to the chemical nature of the starting coal and the many effluents.

Let us consider a catalytic liquefaction process and view the product as the sum of ash, carbonaceous residue, and all distillate streams. A classical approach has been to solvent separate the product, figure 4. From the early 1930's total benzene solubility has been considered a measure of coal conversion to a liquid product. The more recent fractionation of benzene insolubles to preasphaltenes and ash/residue reflects the newer concepts of the structure of coal and its conversion to a liquid. Presently coal is considered a complex network of polyaromatic-heterocyclic hydrocarbons, held together with scissile bonds such as ether and ethylene linkages, that thermally disassociate into large active subunits containing free radicals. These free radicals can either accept hydrogen from other coal subunits or from the vehicle solvent. If vehicle solvent cannot donate hydrogen, the large coal-derived subunits may recombine to form an intractible solid. If hydrogen is available there is conversion of large units into smaller units with greater benzene solubility. Hence, the degree of conversion can be affected by the chemical nature of the vehicle solvent.

The oils and asphaltenes, from figure 4, comprise the total benzene solubles. Further separation of these fractions has been accomplished. The oils have been column chromatographed into saturate, aromatic, acid and base subfractions. The distribution of these subfractions will vary greatly with process conditions, an example is given in table 2. The asphaltenes

Table 2. Typical distribution of solvent separated fractions and functional groups in a coal liquefaction product.

	Weight percent			
	Oils	Asphaltenes	Preasphaltenes	Residue
	62	29	6	3
Hydrocarbons neutrals	64	33	25	--
Acids	20	45	50	--
Base	16	22	25	--

and preasphaltenes have been fractionated to give bases, acid and neutral hydrocarbon materials. Each of the various fractions can be subjected to an array of instrumental analyses, such as elemental (C, H, N, O and S), gas chromatography, mass spectrometry, nuclear magnetic resonance (^{1}H and ^{13}C), infrared and ultraviolet spectrophotometry, and molecular weight determination.

Analyses of coal liquefaction products as outlined above indicate that under 90% conversion conditions, as determined by benzene solubility, the major chemical features of the oils are: a number average molecular weight of 260 ± 15; a distribution of aromatic and hydroaromatic rings (2-4); usually one heteroatom per average structure, O > N > S; oxygen distributed as hydroxyl (60%) and ether linkages; nitrogen primarily as its basic form (80%) with some NH; and sulfur as thiophenic. Asphaltenes are much harder to define because of their low volatility. The number average molecular weight ranges from 400-700, with complex polynuclear aromatic clusters. A distribution can be made of acid, neutral and basic material, 35, 30 and 35, respectively. Preasphaltenes are larger yet, with number average molecular weights of 1500-2500. A similar distribution of compound types as in asphaltenes (acid, neutral and bases) is usually the case.

The residue/ash material has been extensively investigated by atomic absorption, spark source mass spectrometry and X-ray techniques to quantify the trace elements. Table 3 lists a typical analysis of trace elements. In summary the chemical nature of the effluents from coal liquefaction systems is tied very closely to the process conditions and, to an unknown extent, to the coal.

Table 3. Mass of some elements of possible environmental concern in major liquefaction process streams.

Process stream (Total Mass in Kg)	Mass of element present (mg)				
	Be	As	Se	Co	Zn
Feed Coal (15.9 Kg)	16	62	64	38	490
Recycle Oil (29.5 Kg)	4	50	30	50	500
Feed Paste (45.4 Kg)	21	145	130	100	540
Gross Liquid Product (40.2 Kg)	25	125	150	110	400
Centrifuged Liquid Product (34.6 Kg)	11	55	38	48	450
Centrifuge Residue (4.9 Kg)	12	49,	49	64	510

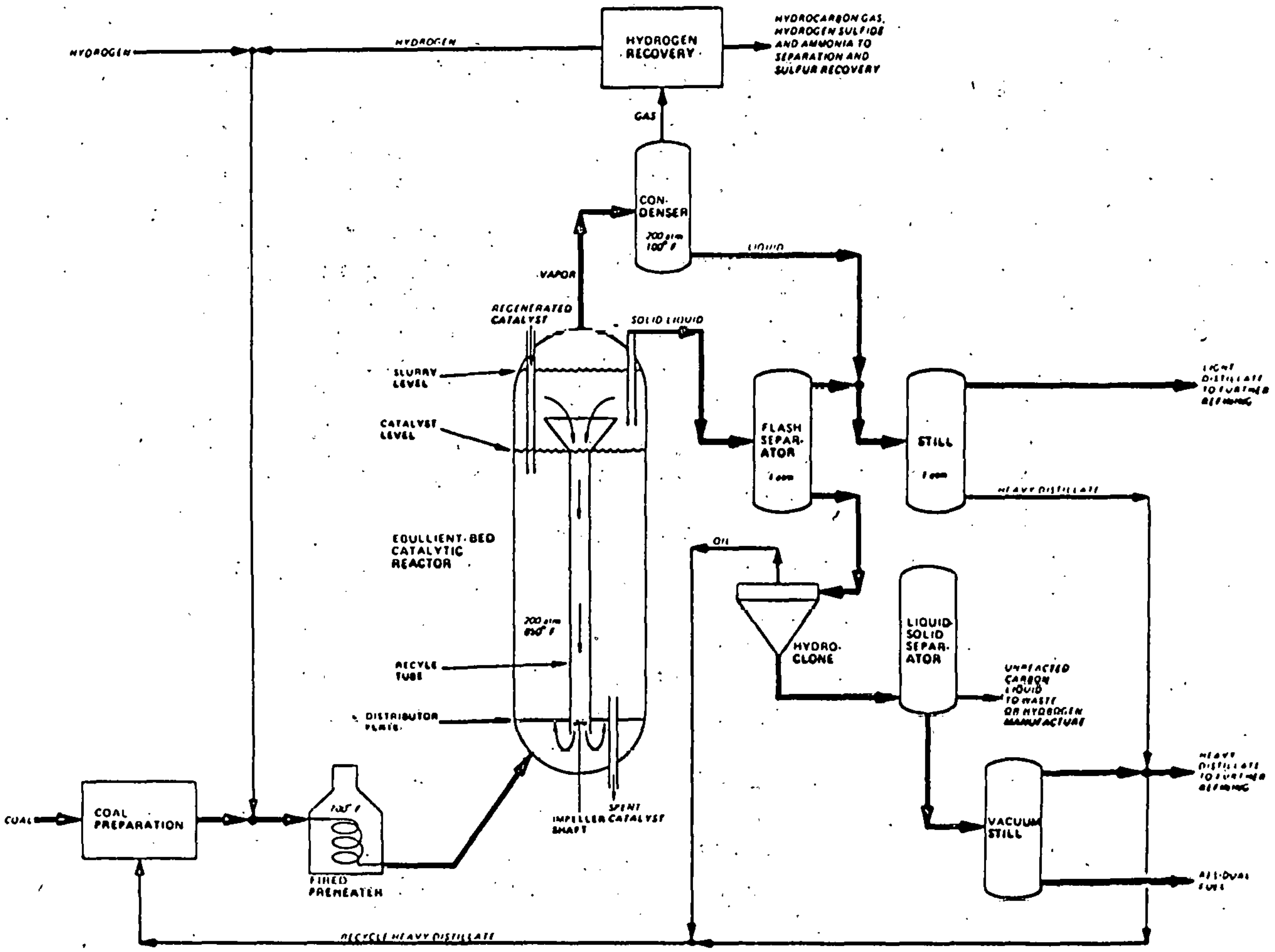


Figure 1. H-coal process schematic.

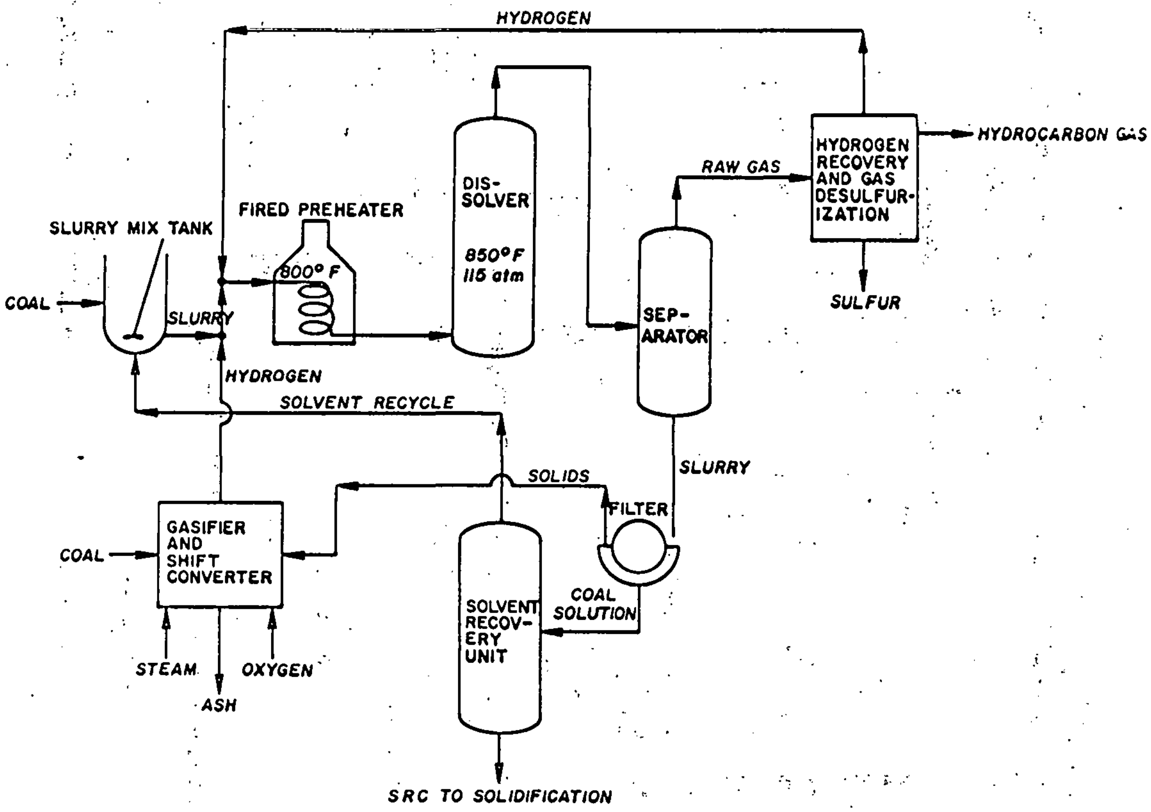


Figure 2. SRC process schematic.

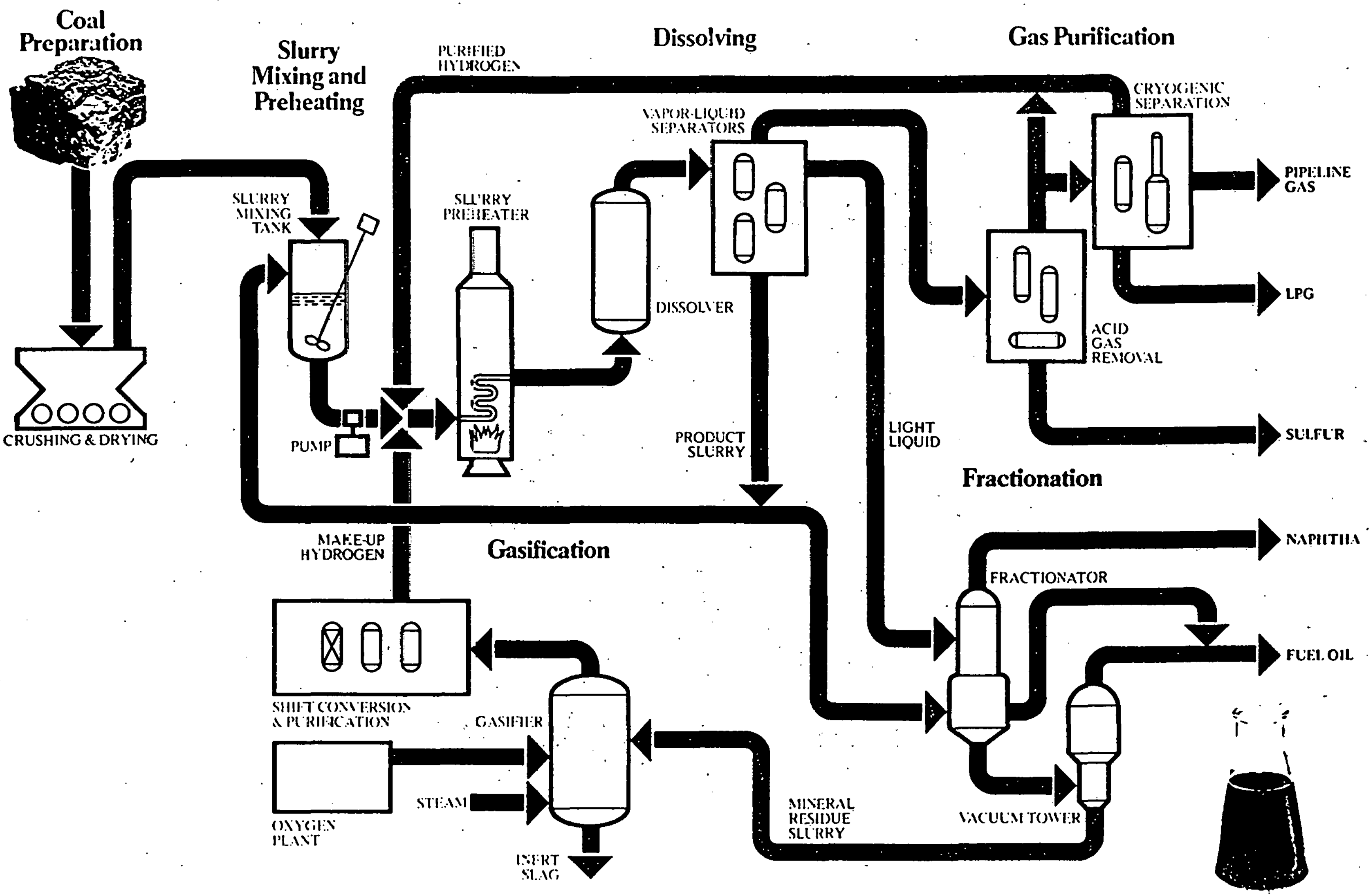
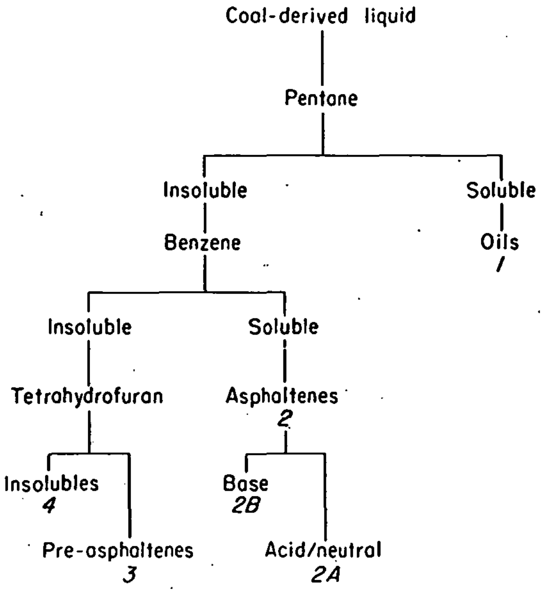


Figure 3. The SRC-II process.



Scheme I

Figure 4. Separation scheme for coal-derived products.

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OIL SHALE - PROCESS DESCRIPTION AND EFFLUENT CHARACTERIZATION

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Brookhaven National Laboratory
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OIL SHALE - PROCESS DESCRIPTION AND EFFLUENT CHARACTERIZATION

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Thank you Jack Sharkey for the introduction and Otto White for inviting me to speak to this group today. I am representing Colony Development Operation, which is a joint venture by Tosco Corporation and Atlantic Richfield Company. Colony was formed to design and build a full-scale 50,000 barrel a day oil shale plant on private land in Northwestern Colorado.[1] Colony began biological testing of oil shale materials as early as 1965, and is now completing an extensive test program which is managed by Tosco. Many of the chemical analyses to be presented today resulted from that program, which was jointly funded by Tosco, ARCO, Ashland, and partially by Shell.

My subject today will be limited to oil shale processing and the chemical characterization of products, byproducts, and process effluents. Figure 1 shows geographically the location and distribution of oil shale in the Green River Formation throughout Colorado, Utah, and Wyoming. The analytical results in this discussion will be limited to oil shale from the Piceance Basin where Colony owns land in Parachute Creek Canyon. The two Colorado Federal Lease Sites, Ca and Cb which are being developed by Gulf Oil and Standard Oil of Indiana, and by Ashland and Occidental respectively, are also located in the Piceance Basin.

Before discussing modern retorting, a quick look at the historical utilization of the Green River oil shale resource may be enlightening. One of the earliest "commercial" developments was the so-called Mormon Still. This crude batch retort was used during the late 1800s to obtain lubricating oils. A "modern" retort was constructed in the early 1900s by the Ute Oil Company. This retort produced oil in "commercial" quantities and also utilized a batch process.

RETORTING OIL SHALE

The objective of oil shale retorting is to convert the Kerogen in oil shale into oil and isolate the oil from the retorted solid. Kerogen is a three-dimensional, high molecular weight polymer that is insoluble in conventional organic solvents.[2] To convert Kerogen into oil, it must be heated to 800-900°F. This heating is called retorting, and can take place above ground or below ground (insitu).

There are two basic mechanisms of heating oil shale for retorting; indirect heating and direct heating. Indirect heating is heat supplied from outside the retort, while direct heating is heat supplied in the retort by combustion of some of the oil shale. This discussion will be limited to surface retorting with direct or indirect heating, and insitu retorting with direct heating.

The four major retort types are shown in Figure 2. In Type 1 retorts, heat passes through the retort walls to reach the oil shale. In Type 2 retorts, which would include insitu, a combustion zone created in the bed of oil shale, provides the required heat. Type 3 retorts receive their heat from contact with circulated externally heated gases. Type 4 retorts receive heat from contact with externally heated solids.

Figure 3 is a schematic of a Fischer Assay retort. This is a Type 1 retort, and is used as a standard laboratory method to determine the richness or oil yield of oil shale. In the Tosco variation of Fischer Assay, Tosco Material Balance Assay (TMBA), the product gases are captured and subsequently analyzed by gas chromatography. The gas analysis and volume measurement allow a complete material balance to be made around the retorting operation.

Figure 4 shows a schematic of an above ground direct heating retorting process (Type 2). Small oil shale particles or fines are generally incompatible with this type of retorting and must be removed from the crushed raw shale feed to the retort. Air for combustion is supplied to the retort, and spent or processed shale is the solid waste product from retorting.

A schematic of a modified insitu retorting process, which is also a Type 2 retort, is shown in Figure 5. One should realize that the modified insitu technique requires large amounts of raw oil shale to be removed, creating a rubblized retorting zone. This is significant since insitu workers would be exposed to raw shale dust in a similar fashion to miners in the mining operation for above ground retorting. Air is pumped into the insitu retort to create a combustion zone which supplies the heat for retorting. The retort products are a low Btu gas and oil.

A schematic of an indirect heating-recycle gas retort is shown in Figure 6. The raw shale fines must be removed from the feed to the retort using the Type 3 retorting process. Air and a heating fuel are used to supply hot gases to the retort. The spent or processed shale and hot oil mist and dust are removed from the retort. A separator removes the oil and a high Btu gas as products, and recirculates some gas to the recycle gas heater.

A schematic of the Type 4 retort, indirect heating with a solid heat carrier, is shown in Figure 7. This retorting method is typified by TOSCO II and Lurgi. A furnace is used to heat a solid heat carrier which is fed to the retort with the raw oil shale. This retorting method allows the oil shale fines to be retorted. The solid heat carrier is recovered from the retort and recirculated to the solid heater. The processed shale and oil mists are removed from the retort. A separator produces oil and a high Btu gas as products.

POTENTIAL WORKER EXPOSURE

The areas in which workers can be exposed to oil shale materials can be explained best by considering a complete oil shale processing complex as shown schematically in Figure 8. The exposures would be similar for modified insitu retorting, except for the processed shale disposal. Workers would be exposed to raw oil shale dust during mining and crushing operations. The equipment for oil shale mine use is huge, and has been demonstrated in prototype and demonstration mines. The proposed mines use the room and pillar mining technique. A mining horizon is 30 feet high and 50 feet wide. The pillars are about 50 by 50 feet, and are left in place to support the roof. A second stage in oil shale mining is the removal of an additional 30 foot horizon from the mine floor, which gives 60 feet between the roof and floor of the completed mine.

Workers in the retorting complex may be potentially exposed to oil mists and vapors, in addition to dusts from raw and processed oil shale. The control of oil vapors and mists should not present any situations that are not currently experienced in a modern oil refinery around a catalytic cracker or petroleum coking operation.

Exposure to processed shale dust will occur during processed shale disposal. In Colony's operation, the processed shale is moisturized to about 12 weight percent water in order to minimize dust levels, and to aid in compacting the processed shale in disposal embankments. After the processed shale is compacted, using normal earth moving and compaction equipment, the surface is prepared for revegetation. The surface is loosened and the salts are leached with water from the surface of the shale. Revegetation experiments at the Colony site since 1968 have demonstrated that revegetation is an acceptable method for surface stabilization of processed shale embankments. Even in the arid Colorado areas, revegetated processed shale does not require maintenance after 3 years.

CHEMICAL PROPERTIES

The intent of the previous discussion was to familiarize you with the areas of an oil shale processing complex where workers could potentially be exposed to oil shale materials. This section will provide chemical analyses of oil shale materials that would be present at such a complex.

Raw oil shale exposure is common to all retorting processes. Table 1 gives the mineral content of oil shale.[3] There is nothing unusual about the mineral composition, which is typical of many soils and rocks. The amount of alpha-quartz, which is usually about 10%, may significantly affect worker health and would require that dust levels during mining and crushing operations were controlled to acceptable concentrations. Raw oil shale slowly oxidizes at ambient conditions, changing the character of the retorted products.[4]

Table 2 gives an elemental analysis of Kerogen in oil shale.[3] Kerogen is the organic portion of oil shale which yields oil on thermal decomposition or retorting. This analysis demonstrates why oil shale may be converted to a liquid fuel without requiring hydrogenation, as coal liquifaction does. Hydrogen is present at 10%, an amount similar to fuel oils, while coal contains only about 4-5% hydrogen by weight.

The product and organic carbon balances around the retorting process are given in Table 3.[1] These data show that one ton of 33 gallon per ton oil shale yields 70 lbs. of high Btu gas, 23 lbs. water, and 1648 lbs. of processed shale while recovering 35 gallons of oil. The organic carbon balance is included to show carbon distribution in the products.

The product gas analysis in Table 4 was formed by retorting oil shale in an indirect heating/solid heat carrier retorting process (TOSCO II).[1] The product gas composition is dependent on retorting conditions and the type of retorting process. Higher temperatures will increase the amounts of olefins, produced by thermal cracking, and CO_2, resulting from thermal decomposition of the carbonate minerals present in oil shale.

Table 5 gives elemental balances for carbon, hydrogen, sulfur, and nitrogen around the TOSCO II retorting process.[1] These data show the distribution of these elements in all products.

The properties of raw, bottomless and hydrotreated shale oil are listed in Table 6. Raw or crude shale oil is the oil as it comes from the retort. Bottomless shale oil is the shale oil fraction that distills lower than 950°F, with the higher boiling or bottoms material removed. Removing the bottoms material is typical of the first refining step in a petroleum refinery. The heavy bottoms material can be coked, releasing light hydrocarbons by thermal decomposition, and forming solid coke. Hydrotreated shale oil is formed by catalytically hydrotreating the bottomless shale oil under pressure. These data show that each step in the refining process increases the amount of light material in the product oil.

The fate of trace metals during retorting is important when considering the potential health effects or an industrial hygiene program for an oil shale industry. Table 7 gives the elemental balances for trace metals around the Fischer Assay retorting of oil shale.[5] Analyses are given for trace metals that have reportedly adverse health effects, except for mercury. The TMBA equipment used for retorting, similar to Figure 3, uses a mercury relay switch to control the pressure of the product gas at one atmosphere. These experiments demonstrated that mercury contamination from the relay switch interfered with material balances. These data show that volatile elements were found in the oil, water and gas, while nonvolatile elements remained in the processed shale. No unusual concentrations of elements were found in the products.

Of equal concern for industrial hygiene programs is the potential worker exposure to organic compounds in oil shale materials. Of specific importance are polycyclic aromatic hydrocarbons (PAH), some of which have been shown to be carcinogenic to animals, and are suspected human carcinogens. PAH analyses always include the benzo(a)pyrene (BaP) content. The reasons for this are: there is substantial literature available concerning the BaP content of various materials, BaP is the most potent carcinogen of all environmentally occurring PAH, and BaP is a relatively easy PAH to detect analytically.

With this background, I would like to discuss some of the PAH analyses we have performed on oil shale and products from the TOSCO II retorting process. Tables 8 and 9 give the results of BaP analysis of raw shale, processed shale, crude shale oil, hydrotreated shale oil, TOSCO II atmospheric effluent, and shale oil coke. These data[6] show that mined raw oil shale contains half as much BaP as TOSCO II processed shale, and that hydrotreating shale oil reduces the BaP concentration.

It is difficult to draw meaningful conclusions from such BaP analyses without comparing these data with BaP contents of other common materials like those included in Tables 8 and 9. It may be concluded from these data that shale oil materials do not contain unusual or large amounts of BaP when compared to materials commonly utilized in present-day oil refineries. It can similarly be concluded that the solid byproducts from oil shale retorting do not contain unusual amounts of BaP when compared to many common materials, including soils.

Our extensive chemical analyses for PAH in oil shale materials has shown that they contain not only PAH, but also monomethyl and dimethyl PAH homologs. Table 10 gives the concentrations of all PAH and methyl substituted PAH compounds found.[7] The substituted PAH compounds were quantified by UV spectroscopy, using the extinction coefficients of the parent PAH. The UV spectra of methyl substituted PAH exhibited a small bathochromic shift, but otherwise were identical to the spectrum of the corresponding parent PAH. These analyses demonstrate how difficult it would be to identify 7,12-dimethylbenz(a)anthracene, a potent animal carcinogen, from the mixture of 60-plus dimethylbenz(a)anthracene isomers present. The similar properties of these isomers does not allow separation utilizing presently available techniques.

Exposure of workers to BaP contained in TOSCO II processed shale would be very low, as is shown in Table 11. The amount of processed shale allowed in the work environment would be 2.6 mg/M^3, based on current standards controlling worker exposure to alpha-quartz, and the 10 weight percent alpha-quartz found in processed shale. As shown in Table 11, this BaP level is considerably lower than BaP exposures experienced from everyday environments and common sources.[8]

INDUSTRIAL HYGIENE

While this paper was to address only the characterization of oil shale materials, I must briefly mention some aspects of industrial hygiene, which is the overall topic of this meeting. It is important to realize that the presence of chemically detectable amounts of carcinogenic compounds in a material do not mean that the whole material is carcinogenic. Animal experiments have shown that certain carcinogen-containing materials are not biologically active. The carcinogens can be held in the matrix of the material so tightly that they are not available to a biological system, and, therefore, cannot promote a carcinogenic response.

The concept of biological availability of carcinogens was effectively demonstrated in an extensive series of experiments[9,10,11,12] which are summarized in Table 12. These experiments determined the carcinogenicity of whole carbon black and the benzene extract of identical carbon black by skin painting, inhalation, feeding, and subcutaneous injection. The tests were done under identical conditions. In each test, the whole carbon black was found to be noncarcinogenic, while the benzene extract was carcinogenic by every route. Based on our biological tests, it appears that oil shale solids behave exactly like carbon black - they contain carcinogenic compounds, BaP, but do not cause cancer in animal tests.

Animal tests have proven the value of basic hygiene practices. The importance of removing potentially carcinogenic oils from a person's skin and clothing is dramatically shown by the data[6] given in Table 13. These data are from an animal experiment in which mice were painted with a cracked residual refinery stream. This material was a normal petroleum-derived substance, and not a synthetic fuel. The data show that the test material caused a 100% tumor incident in 26 weeks. However, if the animal's back was washed with a simple soap and water solution 10 minutes after the test material was applied, no tumors developed after 80 weeks of testing. The test material was applied each week. The remaining data show that the carcinogenic response was proportional to the length of time the carcinogenic material remained in contact with the skin.

Colony has been concerned with the potential health effects of oil shale processing, and contracted our first health-related studies to outside laboratories in 1965. Since that time, over $500,000 has been invested in chemical characterization and biological testing of oil shale materials. We have tested raw oil shale, TOSCO II processed shale, crude shale oil, hydrotreated shale oil, and TOSCO II atmospheric effluent for their toxicity and carcinogenicity. It is concluded from these experimental results that crude shale oil presents a carcinogenic hazard that is similar to or less than that of currently used petroleum products, that hydrotreating dramatically reduces this carcinogenicity, and that solid oil shale materials do not present a carcinogenic hazard.

References

1. "An Environmental Impact Analysis for a Shale Oil Complex at Parachute Creek, Colorado," Part I, Colony Development Operation, (1974).

2. Schmidt-Collerus, J. J., "Investigations on Colorado Oil Shale of the Green River Formation," Denver Research Institute, University of Denver, Final Report, (1971).

3. Smith, J. W., "Ultimate Composition of Organic Material and Green River Oil Shale." U.S. Bureau of Mines Rep. Invest., 5725, (1961).

4. Coomes, R. M. and Sommer, F. H., "Effects of Thermal History on Oil Shale Pyrolysis Products," Tenth Oil Shale Symposium Proceedings, Colorado School of Mines Press, 200, (1977).

5. Shendrikar, A. D. and Faudel, G. B., "Distribution of Trace Metals During Oil Shale Retorting," Environmental Science and Technology, 12, 332 (1978).

6. Coomes, R. M., "Health Effects of Oil Shale Processing," Quarterly of the Colorado School of Mines, 71, 101 (1976).

7. Coomes, R. M., "Carcinogenic Aspects of Oil Shale," Proceedings of Environmental Aspects of Non-Conventional Energy Resources II, American Nuclear Society, 26-I (1978).

8. Sawicki, E., "Analysis of Atmospheric Carcinogens and their Cofactors," Presented at the Symposium of Environmental Pollution and Carcinogenic Risks, Lyon, France, November 3-5, 1975.

9. Nau, C. A. et al, "A Study of the Physiological Effects of Carbon Black, Part I. Ingestion," Arch. Ind. Health, 17, 21 (1958).

10. Nau, C. A. et al, "A Study of the Physiological Effects of Carbon Black, Part II. Skin Contact," Arch. Ind. Health, 18, 511 (1958).

11. Nau, C. A. et al, "A Study of the Physiological Effects of Carbon Black, Part III. Adsorption and Elution Potentials; Subcutaneous Injections," Arch. Environ. Health, 1, 512 (1960).

12. Nau, C. A. et al, "Physiological Effects of Carbon Black, Part IV, Inhalation," Arch. Environ. Health, 4, 415 (1962).

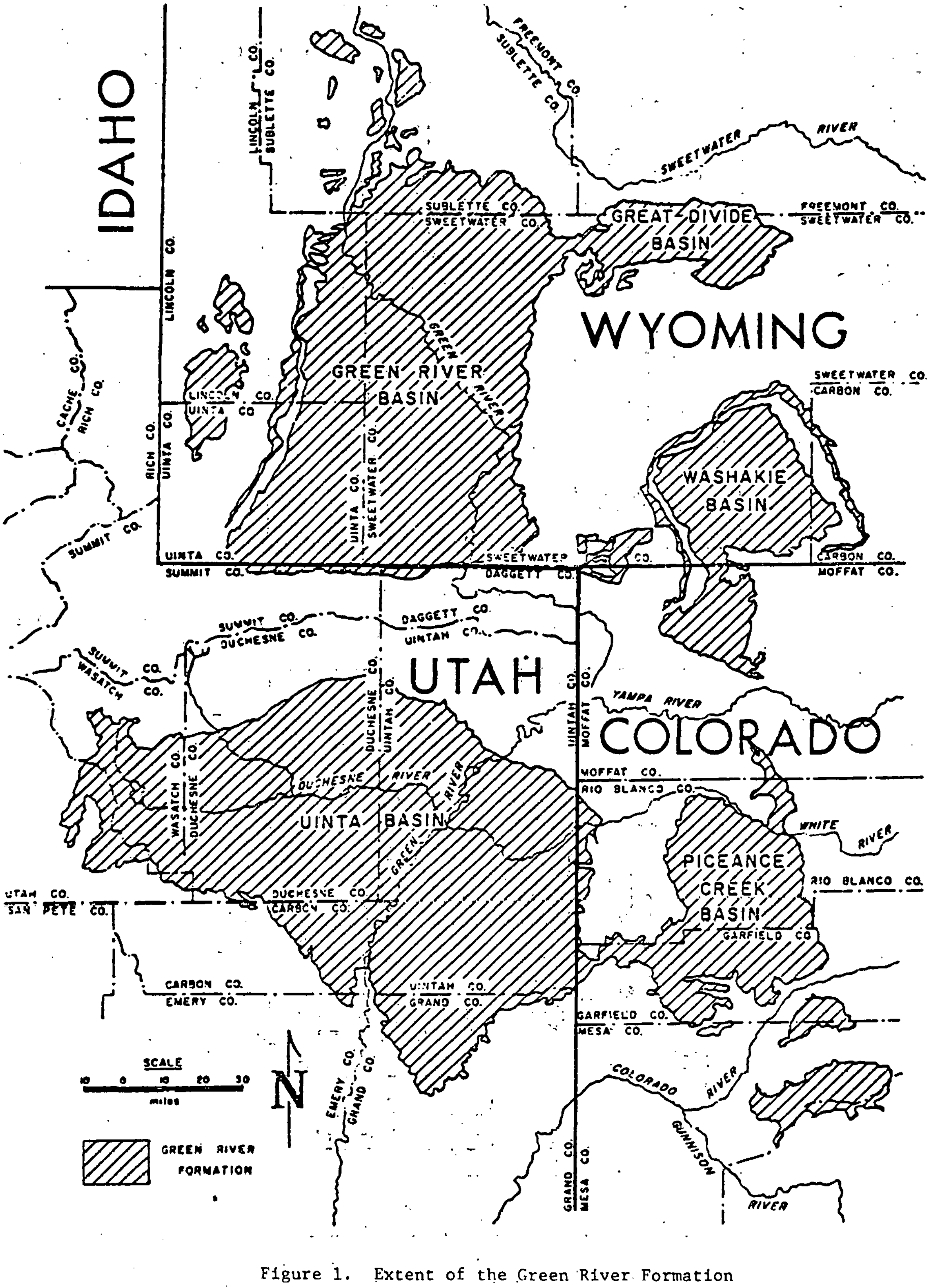

Figure 1. Extent of the Green River Formation in Colorado, Utah, and Wyoming.

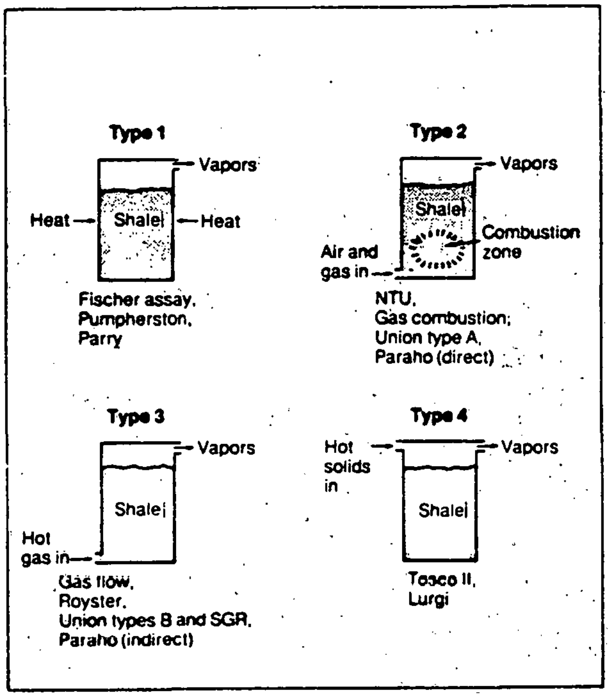

Figure 2. Retort types.

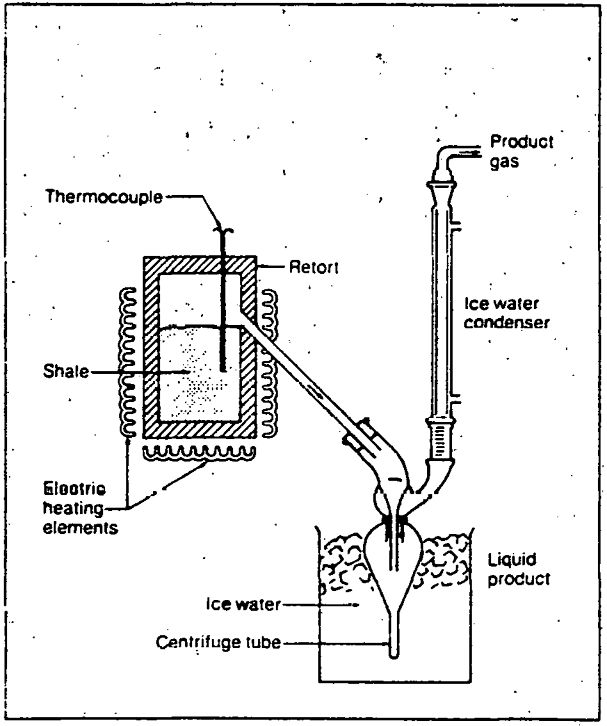

Figure 3. Fischer assay (type 1).

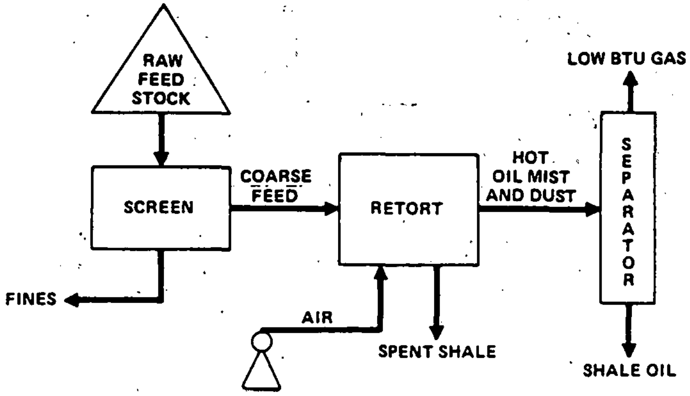

Figure 4. Schematic of direct heating retorting process.

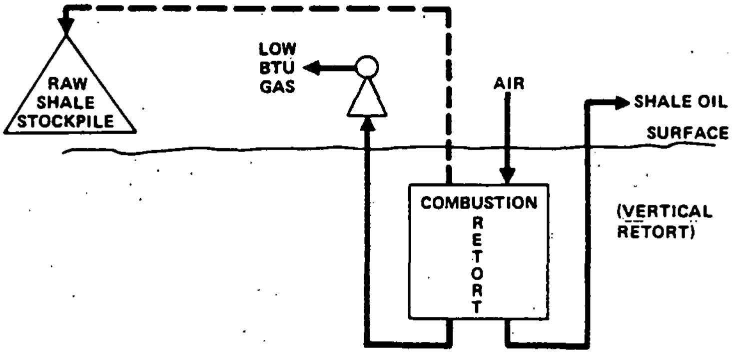

Figure 5. Schematic of modified in situ retorting process.

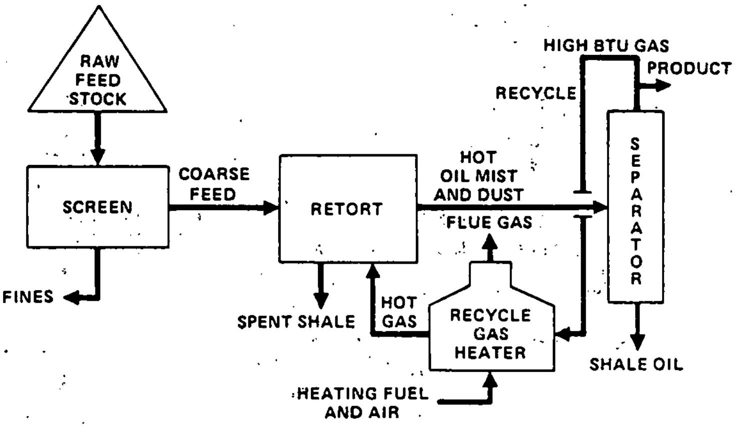

Figure 6. Schematic of indirect heating/recycle gas retorting process.

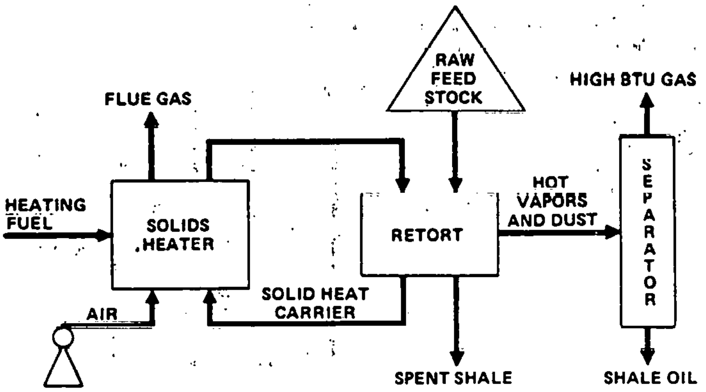

Figure 7. Schematic of indirect heating/solid heat carrier retorting process.

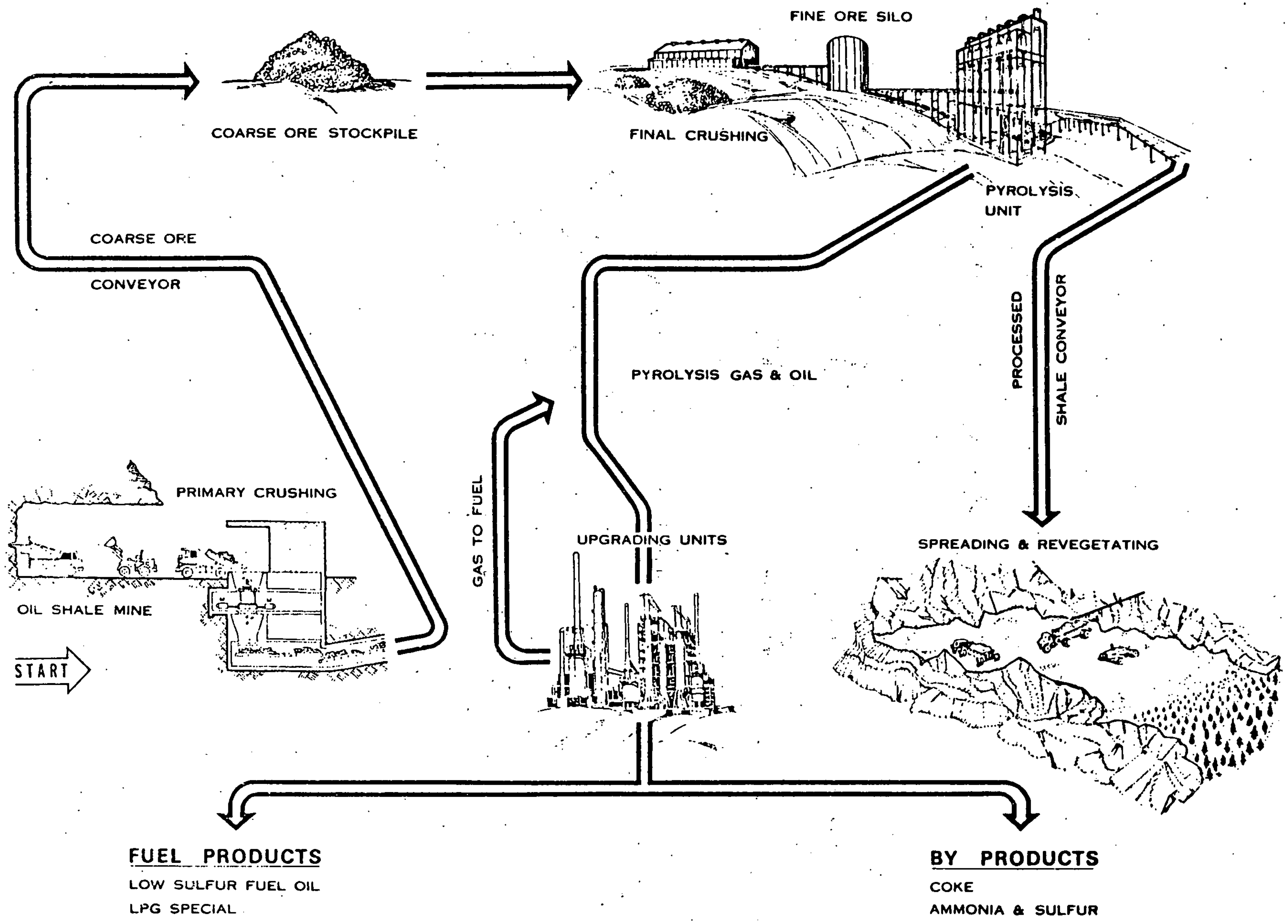

Figure 8. Schematic diagram of an oil-shale processing operation.

Table 1. MINERALS ANALYSIS OF RAW SHALE

Component	Weight Percent
Dolomite	32
Calcite	16
Quartz	15
Illite	19
Albite	10
Microcline	6
Pyrite	1
Analcite	1

Table 2. CHEMICAL ANALYSIS OF KEROGEN

Component	Organic Component, Weight Percent
Carbon	80.5
Hydrogen	10.3
Nitrogen	2.4
Sulfur	1.0
Oxygen	5.8

Table 3

Product and Elemental Balances
Tosco II Process*

Material	Weight of component (pounds)	Distribution of component (wt. %)	Weight of organic carbon (pounds)	Distribution of organic carbon (%)	Weight of sulfur (pounds)	Distribution of sulfur (%)	Weight of nitrogen (pounds)	Distribution of nitrogen (%)	Weight of hydrogen (pounds)	Distribution of hydrogen (%)
Feed										
Raw shale	2,000		330.6		15		9.2		43.0	
Product Slate										
Processed Shale	1,652	82.4	81.4	24.6	10.2	68.0	4.6	50.0	4.4	10.2
Oil	250	12.6	212.2	64.6	2.1	14.0	4.6	50.0	28.4	66.0
Gas	70	3.5	35.4	10.5	3.1	20.7	nil		7.0	16.3
Water	23	1.2	nil		0.1	0.7	0.3	3.3	2.6	6.0
Total	1,995	99.7	329.6	99.7	15.5	103.4	9.5	103.3	42.4	98.5
Recovery Percent	99.7		99.7		103.4		103.3		98.6	

*Basis: 2,000 pounds of raw shale (35 gallon per ton).

Table 4. PRODUCT GAS ANALYSES - TOSCO II PROCESS

Component	Weight percent
H_2	1.34
CO	3.14
CH_4	10.66
C_2H_6	7.53
C_2H_4	7.75
C_3H_8	4.87
C_3H_6	9.90
i-C_4H_{10}	0.37
n-C_4H_{10}	3.57
Butenes	6.07
C_5's	6.14
C_6's	3.60
C_7's +	0.89
CO_2	29.56
H_2S	4.61
	100.00

Table 5. Elemental Analyses of Oil Shale Materials around the TOSCO II retorting process (weight percent).

	Organic carbon	Sulfur	Nitrogen	Hydrogen
Feed				
Raw shale	16.5	0.8	0.5	2.12
Products				
Processed shale	3.3	0.6	0.3	0.3
Oil	84.7	0.8	1.8	11.3
Gas	48.9	4.4	nil	9.9
Water	nil	0.4	1.3	11.30

Table 6. SHALE OIL PROPERTIES

	Raw	Bottomless	Hydrotreated
Gravity, °API	21	25	40
Sulfur, Wt.%	0.7	0.7	0.01
Nitrogen, Wt.%	1.9	1.8	0.06
Composition, Wt.%			
IBP - 400°F	17	23	43
400°F - 650°F	25	30	34
650°F - 950°F	35	47	23
950°F - EP	23	--	--
Pour Point, °F	80	55	50
Viscosity, SUS at 100°F	96	48	35

Table 7
Oil Shale
Elemental Analysis (ppm)

Element	Raw Shale	Spent Shale	Oil	Water
Arsenic	61.7	62.3	21.2	0.0
Beryllium	0.87	1.05	0.0	0.0
Boron	74.0	78.6	0.60	0.55
Cadmium	1.35	1.67	0.0	0.0
Chromium	43.3	52.6	0.71	0.004
Cobalt	5.9	7.4	0.22	0.004
Copper	42.8	49.7	0.15	0.16
Fluoride	1018.	1282.	1.0	3.0
Lead	29.1	35.3	0.17	0.0
Magnanese	213.7	263.7	0.05	0.02
Molybdenum	33.3	40.7	0.63	0.006
Nickel	23.3	27.8	1.63	0.034
Selenium	12.2	13.8	0.0	0.1
Vanadium	49.8	62.1	0.38	0.0
Zinc	54.2	78.7	1.8	0.045

Table 8

BaP CONTENT OF OIL SHALE SOLIDS AND NATURAL MATERIALS

Material	BaP Content (ppb)
Raw Oil Shale	14
TOSCO II Processed Shale	28
TOSCO II Effluent	140
Shale Oil Coke	129
Farm Field Near Moscow	79
Oak Leaves	300
Rural-Mixed Forest Soil - Eastern U.S.	1,300
Garden Soil - Eastern U.S.	90
Plowed Field - Eastern U.S.	900
Sandy Soil - USSR	0.8 - 40
Soil Near Streets - USSR	1,000 - 1,500
Sediment	75 - 370

Table 9

BaP CONTENT OF PETROLEUM PRODUCTS

Petroleum Products	BaP (ppb)
Libyan crude oil	1,320
Cracked residuum (API 59)	50,000
Cracked sidestream (API 2)	2,000
West Texas paraffin distillate	3,000
Asphalt	10,000 to 100,000
Coal	4,000
Raw shale oil (Colorado)	3,200
Hydrotreated shale oil (0.25% N)	800
Hydrotreated shale oil (0.05% N)	690

Table 10

PAH Analyses of Oil Shale Materials
(concentrations in ppb)

Alkyl Groups	Raw Oil Shale			Tosco II Processed Shale			Effluent			Crude Shale Oil			Hydrotreated Shale Oil (0.05%N)			Shale Oil Coke		
	0	I	II	0	I	II	0	I	II	0	I	II	0	I	II	0	I	II
Pyrene	64	16	-	61	102	58	331	344	435	14,500	21,500	20,000	17,500	109,000	71,500	23	43	13
Fluoranthene	33	+	-	23	21	+	171	100	+	6,900	3,700	-	980	16,200	-	5	6	-
Benz(a)anthracene	13	13	10	27	43	45	83	89	145	2,700	4,550	2,050	-	1,800	1,435	53	54	34
Chrysene	36	25	26	30	52	55	105	105	447	5,600	6,850	5,350	915	5,600	3,450	21	50	50
Triphenylene	22	8	17	13	15	34	37	44	68	1,250	2,050	1,850	-	1,700	2,450	3	3	3
Benzo(a)pyrene	14	5	1	28	55	36	140	83	123	3,100	7,250	4,550	690	2,250	460	129	189	105
Benzo(e)pyrene	16	5	4	18	29	18	102	80	93	1,350	2,250	2,000	3,150	6,950	875	46	82	52
Perylene	3	-	-	6	9	3	35	+	-	980	720	-	-	-	-	6	20	-
Anthanthrene	3	-	-	5	5	3	77	47	-	525	-	-	310	-	-	16	29	-
Benzo(ghi)perylene	15	11	-	12	19	24	267	63	21	1,400	-	-	13,900	8,450	2,700	294	164	109
Coronene	4	-	-	5	-	-	78	-	-	-	-	-	515	-	-	20	-	-

+ trace, not quantified
- not detected

Table 11

ATMOSPHERIC CONCENTRATIONS OF BaP

Atmosphere or Effluent	BaP Concentration nanograms/M^3
Processed Shale (2.3 mg/M^3)(1)	0.06
Los Angeles (1971/72)	0.03 - 3.5
Auto Exhausts	4,000
Gas-Fired Heat Generators	20 - 350
Beer Hall in Prague	28 - 144
Truck Exhaust	1,500 - 36,000
Open Burning	2,800 - 173,000

(1) The amount of processed shale is based on the current nuisance dust standard: $\frac{30\ mg/M^3}{\%\ Quartz + 3}$

Table 12

BIOLOGICAL AVAILABILITY OF CARCINOGENS FROM CARBON BLACK

	Results	
Test Method	Whole Carbon Black	Benzene Extract of Carbon Black
Skin Painting	Negative	Positive
Inhalation	Negative	Positive
Feeding	Negative	Positive
Injection	Negative	Positive

Table 13

RETARDATION OF TUMOR FORMATION BY WASHING THE SKIN OF MICE WITH A SOAP SOLUTION

Period of Contact Before Washing Skin	Washing Agent	Maximum Incidence of Tumors (% weeks)
Control - no washing	None	100/26
10 minutes	Soap Solution	0/80
1 hour	Soap Solution	20/80
4 hours	Soap Solution	100/70

Relative Chemical Composition of Selected Synthetic Crudes*

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A knowledge of the composition of synthetic crudes can provide an important input into the assessment of occupational exposure monitoring requirements for the coal conversion and oil shale industries. This paper summarizes comparative compositional studies of coal- and shale-derived crude oils with petroleum crude oils as a reference point.

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Chemical Class Fractionation and Analysis

Many chemical class fractionation procedures exist. Several have been specifically applied to synthetic crudes derived from coal and oil shale versus natural petroleum as a point of reference. The results of each procedure can contribute to our understanding of the chemistry of synthetic crudes.

The most extensive comparison of coal-derived crudes with petroleum has been conducted by Dooley et al. (1) at the Bartlesville Energy Research Center. Six selected petroleum crude oils and five coal-derived crudes have been subjected to both routine crude oil physical property tests and an API separation procedure consisting of distillation, ion exchange, adsorption and gel permeation column chromatographies, followed by gravimetric and mass spectral analysis. Few differences were obtained in the physical property tests. The major differences between the coal liquids and the petroleum as distinguished by the simple compositional tests were the greater nitrogen content but lesser sulfur content of the former. Even greater nitrogen content (1.5 to 2 percent) has been reported for shale oil by Morandi and Poulson (2), suggesting a relative ranking by nitrogen content of shale oil > coal-derived crude > petroleum.

More revealing differences were found when the 370°-535°C distillates of the crudes were separated by chromatographic procedures into saturate, monoaromatic, diaromatic, and polyaromatic plus polar fractions. The data summarized in Table 1 indicate that the coal-derived crudes are characterized by a lesser saturate content than the petroleums, but a much greater aromatic content extending across the range of ring sizes from mono- to polyaromatic. In some of the extreme cases, the differences exceed an order of magnitude in percentage weight.

A more detailed characterization of the aromatic hydrocarbon content of the crudes was obtained by Dooley et al. (1), from a mass spectrometric analysis of the 370°-535°C distillate polyaromatic + polar fraction. The results indicated that the greater aromatic content of the coal-derived crudes is due in part to polycyclic aromatic hydrocarbons and their alkylated derivatives, ranging from at least acenaphthalene to benzo(ghi)perylene. The sum of the generically identified PAHs ranged 5-14 percent in the coal-derived crudes as compared to 1-2 percent in the petroleums. The smaller three and four ring PAHs were consistently more concentrated in the coal-derived crudes, but the greatest differences in concentrations were seen for some of the larger five and six ring PAHs. Most known carcinogenic PAHs fall in this range of ring sizes, such as benzo(a)pyrene and dibenz(a,h)-anthracene. However, the mass spectrometer cannot easily distinguish among isomers.

These results are in general agreement with data from the gravimetric analysis of polyaromatic isolates prepared in several laboratories from petroleum, shale oil, and coal-derived crudes, as shown in Table 2 (3). The data indicate the greater polyaromatic content of the coal-derived crudes, and suggest that the polyaromatic content of the shale oil may fall between that of coal-derived crudes and petroleum. However, this is hardly a statistically significant comparison, and thus only a suggestion of a trend is made. The data again emphasize the differences in polyaromatic content within the classifications themselves; in petroleum alone, the results range from 1.1 to 4.3 percent. Further, the data also emphasize the necessity of parallel studies. For some crudes, the percentage of polyaromatics will depend upon the fractionation procedure employed to define "polyaromatics", e.g. some may include nitrogen- or sulfur-heterocyclics.

Compositional studies at Oak Ridge National Laboratory of synthetic and natural crudes have concentrated on chemical class separation via Swain-Stedman-type acid-base-neutral fractionation (4). The procedure is diagrammed in Figure 1. Successive partitioning of the crudes with aqueous base/ether and aqueous acid/ether remove acidic and basic constituents, respectively, leaving the neutrals for further separation by adsorption column chromatography. Acids are sub-divided into weak and strong categories by acidification and extraction with ether. Results for the parallel application (5) of this method to two coal-derived and one shale-derived crude, one mixed petroleum crude (composed of a blend of six domestic and mid-east crudes), and a domestic crude (Louisiana Mississippi Sweet) are shown in Table 3. Again, the predominance of neutral constituents in all three types of crudes is emphasized. Except for Coal Synthoil C, the bulk of the neutrals appear to be hydrocarbons (hexane eluate of adsorption column). PAHs and other neutral, relatively non-polar polynuclear aromatics (hexane/benzene eluate) are a minor portion of the neutral constituents. No significant differences among the latter in the crudes were detected by this procedure. The remainder of the material in the crudes is spread among the other chemical classes, with a few percent appearing in each class. Coal Synthoil C seems to stand out with elevated amounts of sodium hydroxide-insolubles ($NaOH_I$). These constituents appear to correspond to the unidentified material which defys solution in most organic solvents. The coal- and shale-derived crudes are higher in ether-soluble weak acids (WA_E) and also water-soluble strong acids (SA_W) than are the petroleum crudes, with the Coal Synthoil C far exceeding the other in WA_E. The WA_E class most likely is composed of phenolic compounds, some of which - like phenol - may be toxic. In this regard, direct aqueous analysis methods have shown (6) considerable phenolic content in by-product waters from coal gasification and liquefaction, and enhanced carboxylic acid and amide concentrations in by-product waters from oil shale retorting.

Considering next the basic constituents in this fractionation procedure, the Shale Oil B is seen to contain by far the highest percentage of ether-soluble bases (B_E). This observation is supported by a separate analysis of another shale oil, where the B_E accounted for 6.7 percent of the crude oil. The coal liquids fall between the two extremes represented by shale oil and petroleum and the relative ranking thus parallels the nitrogen content of such crudes. These compositional differences may be important in light of recent research (7) demonstrating that polycyclic amines or basic azaarenes are among the most bioactive of the B_E constituents. The B_E contribute almost 40 percent of the mutagenicity of Shale Oil B and approximately 14 percent of Coal Synthoil C. In contrast, only a few percent of the mutagenicity of the other crudes is found in B_E. Interestingly, almost 70 percent of the mutagenicity of Coal Synthoil C resides in the precipitate B_{Ia}. The composition of the B_{Ia} of Coal Synthoil C is not known, but the mutagenicity result does emphasize the potential variability in coal-derived products. Overall recoveries are good, indicating little material was lost in the fractionation.

Swain-Stedman fractionation has been criticized because of the strong acids and bases contacting the sample. In recognition of this drawback, another approach to fractionation of crudes at ORNL has been through the "gentle" gel filtration on Sephadex LH-20 (8). Depending on the solvent, a remarkable range of separation mechanisms can be brought into effect. As shown in Figure 2, swelling the gel with methanol/water and passing the sample through in hexane affords a hydrophilic/lipophilic separation of constituents. The lipophilic compounds can be separated further into polymeric, hydrogen-bonding, and sieved classes by employing tetrahydrofuran as the solvent and gel swelling agent. A final "sorting" by molecular size and aromaticity into aliphatic and various aromatic classes is achieved with isopropanol. The results of the parallel application of this procedure to four of the five crudes examined also by the Swain-Stedman procedure are shown in Table 4. The predominantly aliphatic character of the crudes as determined by gel filtration is in good agreement with results from other procedures. No significant differences were detected among the aromatic fractions, with the possible exception of the elevated polyaromatics in the Mixed Petroleum A, which seems out of line with results from other methods. The insoluble material in Coal Synthoil C was again evident, but interestingly, the Coal Syncrude D was found to contain the greatest amount of polymeric constituents. Total recoveries are good, indicating a mass balance accounting of most of the materials.

Specific Class Isolation and Analysis

Because of their importance as known carcinogens (e.g. 9), PAHs have received particular attention in specific class isolation and analysis. PAH isolates have been generated from the same four crudes treated in the class fractionation studies, by a combination of solvent partitioning and adsorption column chromatography (10). Gas chromatographic profiles (3) of PAH isolates are shown in Figure 3 for (A) Petroleum Mix A, (B) Shale Oil B, (C) Coal Synthoil C, and (D) Coal Syncrude D. The major feature of these isolates is their complexity, particularly for the coal-derived crudes, but apparently less so for the shale oil. It may be important to note that recent studies (11) have indicated that multialkylated PAHs are responsible for the complex nature of the coal-derived PAH isolates and that the multialkylated PAHs can contribute twice the total mutagenicity of the parent plus simple alkylated PAHs by virtue of their greater quantity and only slightly lower specific activity. The parent plus simple alkylated PAHs would include most presently known carcinogenic PAHs.

Specific analyses were conducted in separate studies employing carbon-14 labeled PAH tracer for recovery corrections. Diaromatics were isolated and analyzed (3) using carbon-14 labeled naphthalene for recovery corrections. Results are shown in Table 5 for the four crude oils. Diaromatic concentrations are seen to be high, exceeding one percent by weight of the crude oil in the case of the coal-derived crudes. The shale oil and petroleum contain one-third to one-half the total diaromatics. The 2-methyl-naphthalene predominates in the coal-derived crudes, while 1,3- and/or 1,6-dimethylnaphthalene is the most concentrated diaromatic in shale oil and petroleum. Thus, the coal-derived crudes stand out in diaromatic content.

Polyaromatics also have been measured (12) by similar procedures, using carbon-14 labeled benzo(a)pyrene for recovery corrections. The data in Table 6 show concentrations of representative PAHs in the crude oils. Again, as with the diaromatics, the coal-derived crudes contain the greatest amounts of PAHs. The shale oil appears to contain higher PAH concentrations than do the petroleum crudes but less than the coal-derived crudes. The latter are more enriched in the larger, potentially bioactive PAH ring systems than the other crudes, in agreement with other studies (1).

One particularly interesting type of coal-derived liquid is the heavy oil derived from the rapid-flash hydropyrolysis or other similar processes. We have examined three such products and have found them to contain higher levels of PAHs than any other material we have examined thus far. Total PAH concentrations have ranged from 18 to 36 percent by weight, allowing the PAHs to be analyzed directly by gas chromatography and mass spectroscopy. The results of one such analysis are presented in Table 7. Diaromatics constitute one-half the PAHs and nearly one-quarter by weight of the oil. Above the diaromatics, the parent, unsubstituted PAHs predominate in marked contrast to other synthetic or natural crudes. Concentrations drop with increasing ring size, but even benzo(a)pyrene constitutes nearly 0.4 percent of the oil. Of particular interest here is the <u>tentative</u> identification by gas chromatographic retention time and mass spectrum of the very carcinogenic 3 - methylcholanthrene. It is to be emphasized that such critical identifications (both here and elsewhere) must be subject to confirmation by other, independent methods before acceptance. However, indications of its presence have been detected in only a few materials.

CONCLUSIONS

The overall conclusion of this review is that comparative compositional studies of the synthetic crudes are still on a preliminary level. Much further work needs to be conducted, particularly on the isomeric level so crucially determinant to bioactivity. However, the results of these studies suggest that the coal-derived crudes are characterized by their greater aromatic content, and the shale oils, by their greater nitrogen compound content. Potentially significant compositional differences may exist among these crudes, and occupational exposure monitoring requirements could differ for their respective industries.

References

1. J. E. Dooley, S. E. Scheppele, G. P. Strum, Jr., P. W. Woodward, and J. W. Vogh, "Comparative Compositions of Petroleum and Synthetic Crude Oils," Symposium on Potential Health and Environmental Effects of Synthetic Fossil Fuel Technologies, Oak Ridge National Laboratories, Gatlinburg, Tennessee, September 25-28, 1978. See also the cited references in the Symposium Proceedings.

2. J. R. Morandi and R. E. Poulson, "Nitrogen Types in Light Distillates from Aboveground and in-Situ Combustion Produced Shale Oils," ACS Preprints, Div. Petrol. Chem., 20(2), 162-174 (1975).

3. M. R. Guerin, J. L. Epler, W. H. Griest, B. R. Clark, and T. K. Rao, "Polycyclic Aromatic Hydrocarbons from Fossil Fuel Conversion Processes," in Carcinogenesis, Vol. 3: Polynuclear Aromatic Hydrocarbons, P. W. Jones and R. I. Freudenthal, Eds., Raven Press, New York (1978), p. 21-33.

4. A. P. Swain, J. E. Cooper, and R. L. Stedman, "Large Scale Fractionation of Cigarette Smoke Condensate for Chemical and Biologic Investigations," Cancer Res., 29, 579-583 (1969).

5. I. B. Rubin, M. R. Guerin, A. A. Hardigree, and J. L. Epler, "Fractionation of Synthetic Crude Oils from Coal for Biological Testing," Env. Res., 12, 358-365 (1976).

6. C. H. Ho, B. R. Clark, and M. R. Guerin, "Direct Analysis of Organic Compounds in Aqueous By-Products from Fossil Fuel Conversion Processes: Oil Shale Retorting, Synthane Coal Gasification, and COED Coal Liquefaction," J. Env. Sci. Health, A117, 481-489 (1976).

7. M. R. Guerin, C.-h. Ho, B. R. Clark, J. L. Epler, and T. K. Rao, "Separation of Mutagenic Components in Synthetic Crudes," 175th National Amer. Chem. Soc. Meeting, Divn. of Env. Chem., Anaheim, California, March 12-17 (1978).

8. A. R. Jones, M. R. Guerin, and B. R. Clark, "Preparative-Scale Liquid Chromatographic Fractionation of Crude Oils from Coal and Shale," Anal. Chem., 49, 1766-1771 (1977).

9. A. Dipple, "Polynuclear Aromatic Carcinogens," in Chemical Carcinogens, ACS Monograph 173, C. E. Searle, Ed., Amer. Chem. Soc., Washington, D.C., (1976), p. 245-314.

10. H. Kubota, W. H. Griest, and M. R. Guerin, "Determination of Carcinogens in Tobacco Smoke and Coal-Derived Samples - Trace Polynuclear Aromatic Hydrocarbons," in Trace Substances in Environmental Health - IX. D. D. Hemphill, Ed., Univ. of Missouri, Columbia, Missouri (1975), p. 281-289.

11. W. H. Griest, B. A. Tomkins, J. L. Epler, and T. K. Rao, "Characterization of Multialkylated Polycyclic Aromatic Hydrocarobns in Energy-Related Materials," Third International Symposium on Polynuclear Aromatic Hydrocarbons, Battelle Columbus Laboratories, Columbus, Ohio, October 25-27, 1978.

12. C.-h. Ho and B. R. Clark, "Determination of Polynuclear Aromatic Hydrocarbons in Fossil Fuel Materials," Twentieth Conference on Analytical Chemistry in Energy and Environmental Technology, Gatlinburg, Tennessee, October 12-14, 1976.

Table 1

Chemical Fractions from 370°-535°C Distillates of Coal-Derived and Petroleum Crudes[a]

Crude / Fraction	Wgt. Pct. of Crude Oil[b]	
	Coal-Derived	Petroleum
Saturate	3-10	9-16
Monoaromatic	2-20	2-5
Diaromatic	5-11	1-3
Polyaromatic + Polar	6-33	2-8
Total Aromatic + Polar	18-50	5-16

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[a] From Dooley et al. (1)

[b] Range of values reported

Table 2

Polyaromatic Content of Crudes (Weight Percent)[a]

	Method			Method		
Petroleum Crudes	I	II	Synthetic Crudes	I	II	III
Petroleum Mix	2.6		Shale Oil	2.0	5.0	
Gach Sach, Iran		3.5	Syncrude D	6.0	5.0	
Swan Hills, Canada		2.0	Syncrude K			7.7
Wilmington, California		4.3	Syncrude U			13.3
Recluse, Wyoming		1.1	Synthoil C	5.1		
Prudhoe Bay, Alaska		3.6	Synthoil W			14.6

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[a] From data collected in Guerin et al. (3)

Table 3

Fractionation of Coal- and Shale-Derived Crudes and Petroleum by Acid-Base-Neutral Extraction[a]

	Wgt. Pct. of Crude Oil				
Constituent Class	Shale Oil B	Coal Syncrude D	Coal Synthoil C	Mixed Petroleum A	LMS Petroleum
NaOH$_I$	1.0	0.9	14.1	1.3	2.9
WA$_I$	0.1	0.2	2.0	0.1	0.2
WA$_E$	1.3	1.9	6.5	0.3	0.8
SA$_I$	0.1	0.2	0.1	0.2	0.2
SA$_E$	0.4	1.1	1.9	0.4	0.5
SA$_W$	0.6	1.6	1.7	0.1	0.1
B$_{Ia}$	0.1	0.2	3.6	1.3	0.4
B$_{Ib}$	0.2	0.2	0.3	0.3	0.1
B$_E$	7.0	2.2	1.6	0.2	0.2
B$_W$	0.4	7.3	0.6	0.5	0.1
Neutral (Total)	(88.5)	(86.2)	(67.8)	(78.0)	(80.7)
Hexane	53.8	74.2	27.6	59.9	70.8
Hexane/Benzene	6.6	4.9	7.4	6.6	4.0
Benzene/Ether	13.8	4.7	21.7	7.5	3.4
Methanol	14.3	2.4	11.1	4.0	2.5
TOTAL	99.6	101.7	100.2	82.7	86.2

---

[a] Figure 1

Table 4

Gel Filtration of Coal- and Shale-Derived Crudes and Petroleum

Fraction	Wgt. Pct. of Crude Oil			
	Shale Oil B	Coal Syncrude D	Coal Synthoil C	Mixed Petroleum A
Volatile	1.1	7.0	-	10.7
Hexane Insoluble	1.3	0.2	51.2	2.5
Hydrophilic	7.0	3.4	11.0	0.8
Polymeric	2.3	7.4	0.4	3.4
H-Bonding	5.2	8.2	5.7	14.9
Aliphatic	59.8	55.0	21.8	39.2
Monoaromatic	4.9	6.8	3.3	2.5
Di- + Triaromatic	6.1	6.7	6.3	4.1
Polyaromatic	2.0	1.0	3.9	6.7
Residue	-	-	2.6	12.9
TOTAL	89.7	95.6	106.0	97.7

Table 5

Diaromatic Content of Crude Oils

PAH	Concentration[a], mg/g				
	Shale Oil B	Coal Syncrude D	Coal Synthoil C	Mixed Pet A	LMS Crude
Naphthalene	1.39	1.68	1.64	0.87	0.90
2-Methylnaphthalene	0.91	3.47	2.92	1.04	0.87
1-Methylnaphthalene	0.68	1.11	0.92	0.75	0.72
Biphenyl	0.06	0.44	0.22	T	T
2,6-Dimethylnaphthalene	0.10	0.81	0.44	0.08	0.08
1,3/1,6-Dimethylnaphthalene	1.63	3.01	1.80	1.48	1.31
2,3-Dimethylnaphthalene	0.28	1.53	1.01	0.51	0.24
1,5-Dimethylnaphthalene	0.03	0.67	0.20	0.08	0.09
1,2-Dimethylnaphthalene	0.19	0.23	0.26	0.31	0.35
Acenaphthalene	0.26	2.19	1.33	0.30	0.26
Acenaphthene	T	0.30	0.46	ND	T
TOTAL	5.23	15.4	11.2	5.42	4.82

---

[a] T = trace, ND = not detected

Table 6

Estimation of Polycyclic Aromatic Hydrocarbon Content of Crude Oils

PAH	Concentration[a], μg/g				
	Shale Oil B	Coal Syncrude D	Coal Synthoil C	Mixed Pet A	LMS Crude
Fluorene	940	485	345	108	220
9-Methylfluorene	410	IR	90	IR	IR
1-Methylfluorene	980	229	1,900	110	140
Phenanthrene + Anthracene	620	554	1,400	207	209
Fluoranthene	400	150	380	35	68
Pyrene	170	651	4,300	IR	IR
Benzo(a)fluorene	53	IR	IR	IR	22
Benzo(b)fluorene	140	IR	IR	IR	13
1-Methylpyrene	70	363	620	IR	36
Perylene	22	IR	ND	IR	31
Picene	ND	IR	380	ND	ND
Benzo(ghi)perylene	ND	263	1,500	ND	ND

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[a] ND = not detected, IR = incomplete chromatographic resolution

Table 7

Quantitative Analysis of PAHs Tentatively Identified in Heavy Oil from Rapid Flash Hydropyrolysis Process

PAH	Concentration, mg/g
Naphthalene	172.6
2-Methyl Naphthalene	20.2
1-Methyl Naphthalene	7.7
Biphenyl	18.0
2,6-Dimethyl Naphthalene	0.58
1,3 and/or 1,6-Dimethyl Naphthalene	1.51
1,5 and/or 2,3-Dimethyl Naphthalene	0.56
1,2-Dimethyl Naphthalene	0.51
Acenaphthene	3.98
Fluorene	30.4
9,10-Dihydroanthracene	0.6
9-Methyl Fluorene	2.70
1-Methyl Fluorene	1.83
Phenanthrene	46.7
Anthracene	3.53
2-Methyl Anthracene	0.50
1-Methyl Phenanthrene	1.34
Fluoranthene	7.16
Pyrene	16.0
Benzo(a)fluorene	3.28
Benzo(b)fluorene	3.69
1-Methyl Pyrene	0.29
Benz(a)anthracene	1.93
Chrysene	3.67
Benzo(b, j, or k)fluoranthene	3.37
Benzo(a)pyrene	3.56
Perylene	1.30
3-Methyl Cholanthrene	0.17
o-Phenylene pyrene	1.99
Picene	0.13
Benzo(ghi)perylene	2.83
Anthanthrene	0.99
Total Tentatively Identified	363.60 mg/g

CLASSIC ACID-BASE SOLVENT PARTITION SEPARATION METHOD

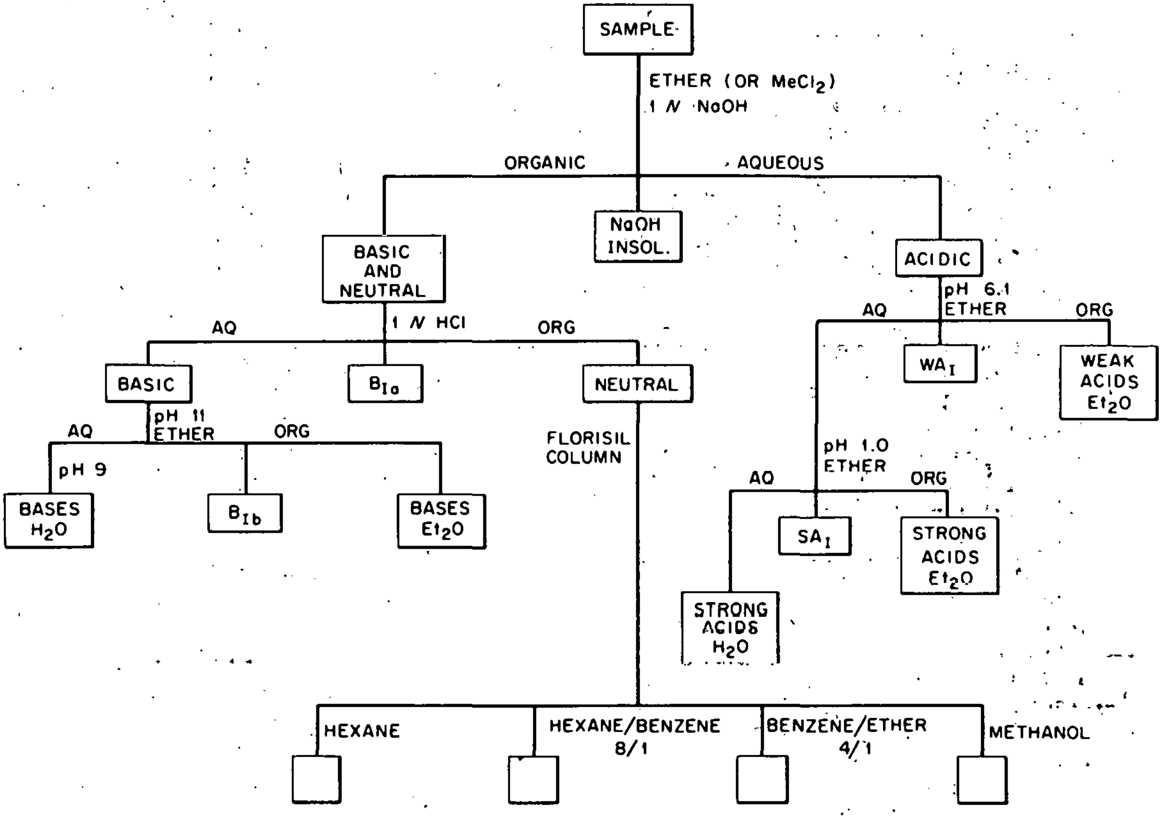

Figure 1. Swain-Stedman fractionation procedure.

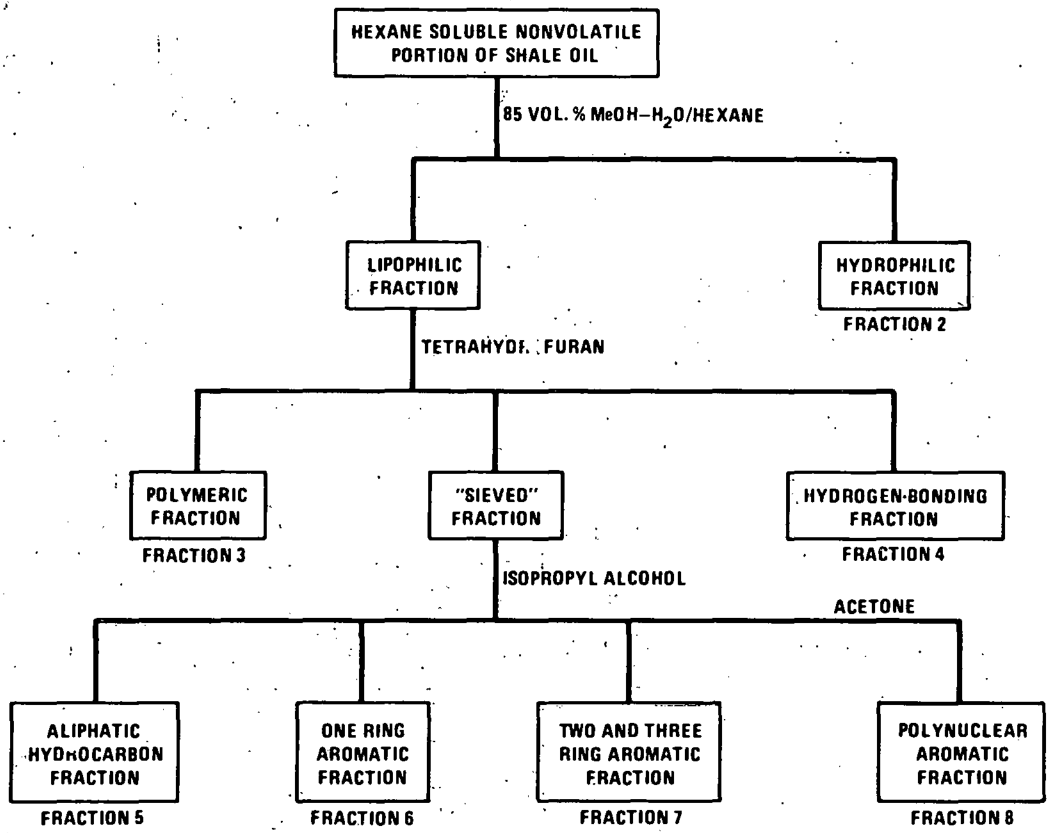

Figure 2. Sephadex LH-20 gel filtration procedure.

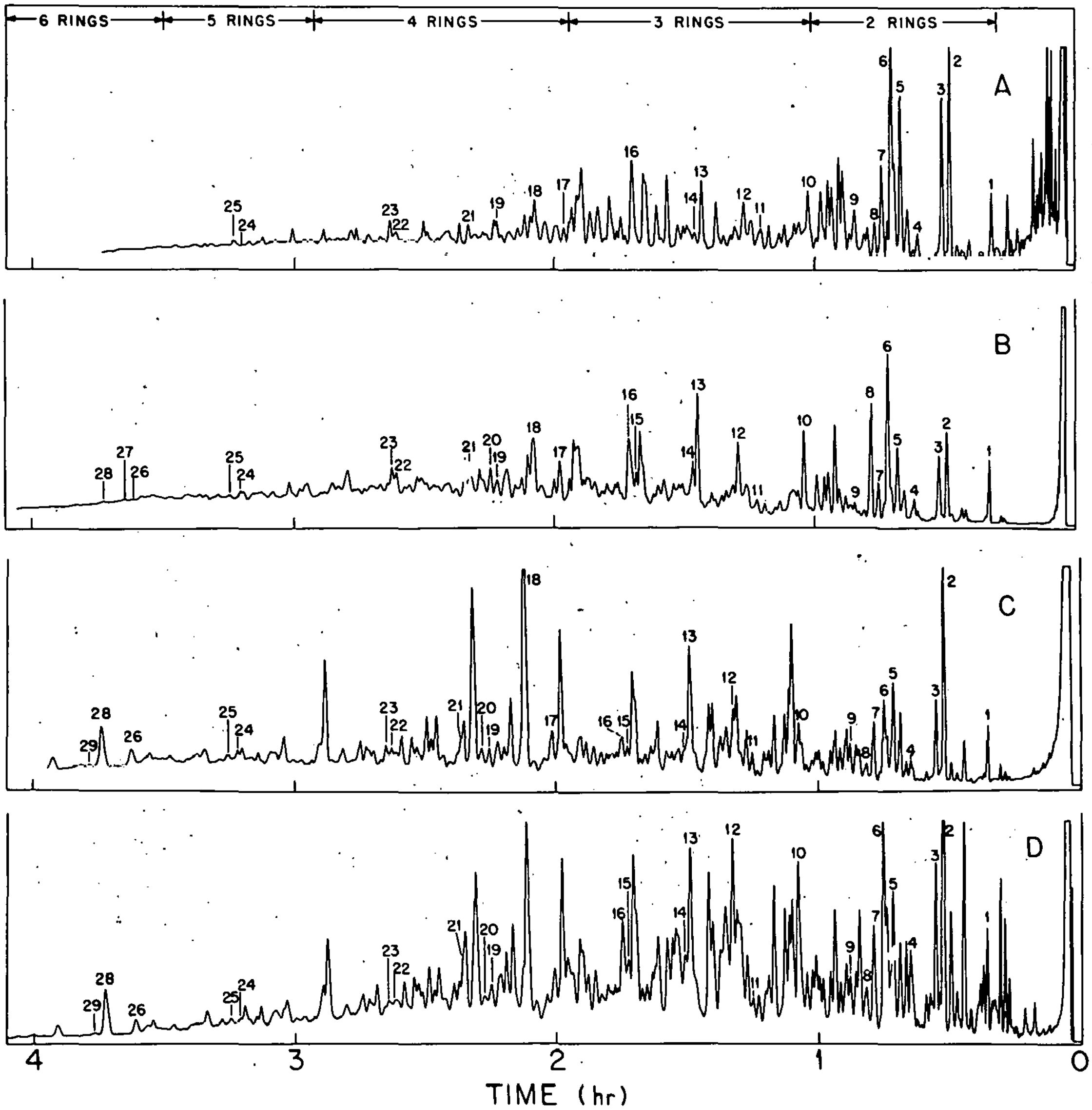

Figure 3. Gas chromatographic profiles of PAH isolates from (A) mixed petroleum A, (B) shale oil B, (C) coal synthoil C, and (D) coal syncrude D (3).

TOXICOLOGY AND CARCINOGENICITY OF OIL SHALE PRODUCTS

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Brookhaven National Laboratory
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TOXICOLOGY AND CARCINOGENICITY OF OIL SHALE PRODUCTS

INTRODUCTION

Studies of workers involved in the production and use of shale oil strongly suggest that the major health concern of this industry is the carcinogenicity of shale oil. It is well known from the reports of Bell[1] (1876) and Scott[2] (1923), that prolonged exposures to shale oil can produce skin cancer in humans. These reports, as well as reports of others, dictate that an assessment of the potential health effects of shale oil and shale oil products should be made as new technologies are developed for the expanding industry.

As great emphasis is being placed on developing domestic energy sources, it is most likely that oil shale will soon be commercially developed. The feasibility of extracting and processing oil shale has been known for some time and this industry would have developed sooner had it not been impeded by economic and political problems. The development of the oil shale industry in Estonia and Brazil gives added impetus that oil shale industry will soon be in full operation.

There are additional health and environmental concerns associated with oil shale extraction and processing. Workers may be exposed to dust, particulate organic matter (POM), CO, NO_x, SO_2, hydrocarbons, silica and metal salts from blasting, mining and crushing the ore. In addition to the above compounds, retort operations can produce polycyclic organic compounds, H_2S, NH_3, and volatiles. Some of these compounds, as well as metals, including arsenic, are produced in the upgrading process and disposing of the solid waste products, a major environmental concern. Many of these compounds may contaminate not only the atmosphere but water as well. Since water is a necessary commodity in the oil shale industry many of these compounds may be found in the waste and run off waters.

Although there may be many potentially hazardous chemicals present in the work area and the surrounding environment, the major health concern appears to be the carcinogenicity associated with shale oil use and production.

ACUTE AND CHRONIC TOXICITY

Weaver and Gibson[3] (1978) reported on the acute and chronic studies of four crude shale oils, three raw shales and four spent shales (Table 1). The results do not show that the materials are acutely toxic.

Table 1

Acute Studies of Shale Oil and Shale Oil Products*

Sample	Test	Results
Crude Shale Oils (4)	Oral LD50 (Rat)	8-10 g/kg
Crude Shale Oils (4)	Dermal LD50 (Rabbit)	5 ml/kg
Crude Shale Oils (4)	Eye Irritation (Rabbit)	minimal/reversible
Raw Shales (3)	Eye Irritation (Rabbit)	negative
Spent Shales (4)	Eye Irritation (Rabbit)	irritating/reversible
Crude Shale Oils (4)	Dermal Irritation (Rabbit)	0.5 g/72 hrs abraided/unabraided
Crude Shale Oils (4)	Sensitization (G. Pig)	negative
Raw Shales (3)	Sensitization (G. Pig)	negative
Spent Shales (4)	Sensitization (G. Pig)	negative

*Reported Weaver & Gibson (1978).

Weaver and Gibson[3] also reported on chronic inhalation studies of two raw shales and two spent shales. In the study rats and monkeys were subjected to the inhalation of the respirable dusts at concentrations of 10 and 30 mg/m^3. After more than one year of exposure no adverse effect was seen in the animals.

MUTAGENICITY

Two raw shale oils were tested for mutagenicity in two strains of Salmonella typhimurium, TA98 and TA100, using techniques developed by Ames[4] (1973). One drop of oil was used per plate as a spot test. When activated, both samples induced mutations in strain TA98 (Table 2) as indicated by the number of revertant colonies which were more than two times spontaneous revisions. The oils were not mutagenic to strain TA100 even when activated.

Raw or upgraded shale oil was injected intraperitoneally into hybird (101 x C3H) male mice to test the induction of dominant lethal mutations in gametes*. Mating intervals, related to administration of oils, served to separate the effects on spermatoza of the vas and epididymus (1st week), testicular sperm (2nd week) and spermatids (3rd week) (Oakberg, 1956)[5]. Following a single injection of 200 mg/kg body weight of a test oil (in mineral oil) or an equal volume of mineral oil, males were bred sequentially to virgin females for three weeks. After detection of a vaginal plug, females were replaced with new females. The bred animals were sacrificed on day 13 of gestation and scored for pregnancy and total implants, including live implants and early and late fetal deaths.

These preliminary experiments do not indicate that dominant lethal mutations were induced because the percent of dead implants per female bred to shale oil treated males was not greater than the percent observed in control females (Table 3). There was, however, a decrease in the total number of implants per female in each breeding period. This decrease was most pronounced in females bred the third week of injection of males with shale oil. These results suggest that both shale oils induce pre-implantation losses and the greatest effect was on spermatids. Future experiments, in which corpus lutea are scored and compared with the number of implantations, may indicate that pre-implantation losses do occur and are the result of dominant lethal mutations.

*Bingham, E., Murthy R. and Dressel, L., 1975, Unpublished data.

Table 2

Mutagenicity of Raw Shale Oil

Salmonella typhimurium

Raw Shale Oil	Number of Revertant Colonies			
	Strain TA98		Strain TA100	
	Activation[a]		Activation[a]	
	None	+	None	+
Sample 1	26	161	110	155
	(8)	(123)	(-4)	(0)
Sample 2	20	178	126	229
	(2)	(140)	(12)	(74)
Spontaneous Revisions	18	38	114	155

[a] Activated with 9000 x g supernatant from livers of Aroclor 1254 induced rats.

Table 3

Effects of Shale Oil on Gametes of Male Mice

Males-One Treatment (i.p.)	Time of Mating (days after treatment)	Number of Females	Fertile Mating (%)	Implants per Female (Mean + S.E.)	Live Embryos Per Female (Mean + S.E.)	Dead Implants	Decrease in Implants (%)
Mineral Oil	1-7	8	87.5	10.0±0.3	9.4±0.4	5.7	--
	8-14	6	66.7	10.0±1.1	8.8±1.4	12.5	--
	15-21	9	100.0	10.7±0.3	8.9±0.2	16.7	--
Upgraded Shale Oil (200 mg/kg)	1-7	16	68.8	9.6±0.4	8.9±0.4	9.4	4.0
	8-14	14	64.3	9.6±0.5	8.3±0.5	12.8	4.0
	15-21	15	80.0	8.4±0.3	8.1±0.4	11.9	21.5
Raw Shale Oil (200 mg/kg)	1-7	13	76.9	9.3±0.5	8.9±0.7	4.3	7.0
	8-14	14	57.1	9.4±0.6	8.9±0.4	5.3	6.0
	15-21	12	100.0	9.1±0.3	8.3±0.2	9.2	15.0

TERATOGENICITY

Disposal of solid wastes produced in oil shale processing presents an environmental problem. Because compounds leached from spent shale may create a teratogenic hazard, Bingham *et al.*[6] (1975) evaluate the embryotoxic and/or teratogenic effects of spent shale in rabbits.

Pregnant New Zealand white rabbits, 3-5 kg, were administered spent shale or carbon as a suspension in distilled water by oral intubation in doses of 250 or 500 mg/kg on the 8th and 12th days of gestation. Does were sacrificed on day 28 of gestation. Every third fetus was cleared and examined for skeletal defects; the remaining fetuses were placed in Bouin's for at least two weeks prior to evaluation of sections for soft tissue anomalies.

In comparison to the effects of carbon, spent shale induced a slight increase in malformations in skeletal and soft tissues (Table 4). Extra and rudimentary ribs are common in the offspring of rabbits and were included in calculations of malformations. Anomalies resulting from the administration of spent shale were severe: myelomeningocele, hydrocephaly, acephaly, folds in the retina, enlarged jagged foramen, overlapping frontals, and deformities in the supraoccipitals and occipitals. Anomalies resulting from the administration of carbon included: exencephaly, umbilical hernia, fused lumbars and overlapping parietals and interparietals. Results not reported here indicated that the embryos were most susceptible on the 8th day of gestation.

A dose response relationship was observed for both carbon and spent shale related to the number of live fetuses with one or more malformations. Dose response was not observed in relation to the total number of dead or resorbed embryos.

Dosages used in this study were in excess of amounts which might be injested by wild life, suggesting that spent shale would not present a teratogenic hazard. Considering the large volume of processed shale returned to the land, it would be prudent to investigate the leachates of spent shale in order to evaluate the impact on surface waters.

Table 4

Effects of Spent Shale on the Incidence of Fetal Anomalies in Rabbits

Agent Dose (mg/kg)	Distilled Water	Carbon[a] 250	Carbon[a] 500	Spent Shale[a] 250	Spent Shale[a] 500
Number of Litters Examined	4	8	4	10	15
Number of Implants	41	67	50	84	129
Number of Dead or Resorbed	4	10	6	9	9
Percent	9.8	14.9	12.0	10.7	6.9
Number of Survivors Malformed[b]	0	1	3	4	14
Percent	0	1.5	7.5	5.4	10.9
Gross Skeletal Anomalies[c]					
Ribs	4	8	3	7	17
Skull	0	1	1	2	13
Vertebra	0	0	4	8	7
Limbs	0	0	1	1	1
Other	0	2	1	3	1

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[a] Administered by gavage as a suspension in distilled water on days 8 and 12 of gestation.

[b] Rib anomalies not included. More than one skeletal or soft tissue anomaly per animal.

[c] One third of the fetuses examined. Frequently more than one defect per animal.

CARCINOGENIC STUDIES

In our carcinogenic animal studies we have reported the benzo(a)pyrene (BaP) content of test materials. This practice was predicated on the early belief that BaP was the carcinogen present in coal tar and therefore might be also present in shale oil. The isolation and identification of BaP from coal tar by Hieger[7] (1930) and Cook (1933)[8] led many investigators to study the carcinogenic constituents of shale oil. The search for the carcinogen in Scottish shale eluded many investigators until 1943 when Berenblum and Schoental[9] identified BaP in shale oil, but they also observed a fraction of shale oil to be carcinogenic that did not contain detectable quantities of BaP. Later Hueper and Cahnman[10] (1958) and Bogovsky[11] (1962) reported BaP free American and Estonian shale oil, respectively, to be carcinogenic in animal mouse skin painting studies.

Method

Young adult C3H/HeJ male mice were treated twice weekly with 50 mg of the test material. The material was applied to the interscapular area of the shaven backs with a microliter pipette or a calibrated dropper. In the case of solid materials, such as raw and spent shale, the materials were suspended in white mineral oil in 1:2 ratio (by weight). Mice were treated for 80 weeks or until the appearance of a papilloma. If a papilloma progressed and was diagnosed grossly as a carcinoma the mouse was killed and autopsied. However, if the papilloma regressed the treatments were resumed.

Results

In Table 5 you can see the results of skin painting with two crude shale oils from two different processes. The two oils produced very little difference in tumor incidences and average latent period.

Table 5
Carcinogenic Potency of Two Raw Shale Oils

Sample	Strain of Mice	Dosage	Number of Mice	Final* Effect Number	BaP %	Number of Mice Developing Tumors		Average Time of Appearance of Papillomas (Weeks)
						Malignant	Benign	
Shale Oil #1 Heat Transfer Process	C3H	50 mg 2x/wk	15	12	<0.00001	8	3	43
Shale Oil #2 Retort Combustion Process	C3H	50 mg 2x/wk	15	12	<0.00001	8	2	43

*Final Effective Number is the number of mice alive at the time of appearance of the median tumor plus those mice that may have died with tumors.

In another study we determined the BaP content found in a raw shale oil, upgraded shale oil, processed shale, processed water, native grass, leached water, raw shale and native soil. The results of these determinations can be seen in Table 6 BaP found in all samples was considered low. The results of topical applications of raw shale oil and upgraded oil to mouse skin is presented in Table 7. It may be seen that shale oil induced tumors in 86% of the effective number of mice with an average time for appearance of about 30 weeks, whereas the upgraded oil induced tumors in 13% of the effective number with an average latent period of 49 weeks. A solution of 0.05% BaP in toluene resulted in 91% of the effective number of mice developing tumors with an average latent period of 46 weeks. No tumors were observed in the mice treated with toluene alone after eighty weeks of topical application.

Four shale oils and raw and spent shales that Weaver and Gibson[3] studied are currently on test at Kettering Laboratory for their carcinogenic potential. After 67 weeks of topical applications of the materials to the backs of mice, all the animals treated with the shale oils have developed tumors or have died. The incomplete results of this study are presented in Table 8. No tumors have been observed in the mice receiving raw and spent shale suspended in white mineral oil.

Discussion

Animal studies using shale oil and shale oil products have shown that they are relatively low in acute toxicity. However, there is great concern about the long term effects of these products. One such concern is the carcinogenic properties of shale oil. It has been clearly demonstrated that raw shale oils, produced by a number of retort methods, are carcinogenic for the mouse's skin. The content of benzo(a)pyrene in these oils was quite low and could not account for the carcinogenic activity. It is likely that other carcinogens and perhaps cocarcinogens are

Table 6

Benzo(a)pyrene Content of Shale Oil Products

Sample	BaP
Raw Shale Oil	< 0.00005%
Upgraded Oil	0.0006%
Processed Shale	< 0.000005%
Processed Water	< 1 ppb
Native Grass	0.000065%
Leached Water	< 1 ppb
Raw Shale	< 0.000005%
Native Soil	< 0.000005%

Table 7

Carcinogenic Potency of Raw and Upgraded Shale Oil

Sample	Strain of Mice	Dosage	Number of Mice	Final* Effect Number	BaP %	Number of Mice Developing Tumors		Average Time of Appearance of Papillomas (Weeks)
						Malignant	Benign	
Raw Shale Oil	C3H	50 mg 2x/wk	50	45	<0.00005	21	18	30
Ungraded Shale Oil	C3H	50 mg 2x/wk	50	39	0.0006	3	2	49
Positive Control 0.05% BaP in Toluene	C3H	50 mg 2x/wk	100	92	0.05	75	9	46
Negative Control Toluene Only	C3H	50 mg 2x/wk	100	91	0	0	0	-

*Final Effective Number is the number of mice alive at the time of appearance of the median tumor plus those mice that may have died with tumors.

The number for the Solvent Control is the number of mice alive after one year.

Table 8

Carcinogenic Potency of Shale Oils and Shale Oil Products*

Sample	Strain of Mice	Dosage	Number of Mice	Final Effect Number	% BaP	Number of Mice Developing Tumors		Average Time of Appearance of Papillomas (Weeks)
						Malignant	Benign	
Raw Oil #1	C3H	50 mg 2x/wk	50	42	0.00018	15	19	31.9
Raw Oil #2	C3H	50 mg 2x/wk	50	43	0.00018	29	6	21.6
Raw Oil #3	C3H	50 mg 2x/wk	50	46	0.00023	30	10	28.5
Raw Oil #4	C3H	50 mg 2x/wk	50	48	0.00042	28	11	25.7
Raw Shale 101	C3H	50 mg 2x/wk	50		<0.00001	0	0	-
Raw Shale 102	C3H	50 mg 2x/wk	50		<0.00001	0	0	-
Raw Shale 103	C3H	50 mg 2x/wk	50		<0.00001	0	0	-
Spent Shale 201	C3H	50 mg 2x/wk	50		<0.00001	0	0	-
Spent Shale 202	C3H	50 mg 2x/wk	50		<0.00001	0	0	-
Spent Shale 203	C3H	50 mg 2x/wk	50		<0.00001	0	0	-
Spent Shale 204	C3H	50 mg 2x/wk	50		<0.00001	0	0	-
Control - No Treatment	C3H	50 mg 2x/wk	50		-	0	0	-
Control - Mineral Oil Only	C3H	50 mg 2x/wk	50		-	0	0	-
0.05% BaP in Mineral Oil	C3H	50 mg 2x/wk	50		.05	43	4	37.8
0.15% BaP in Mineral Oil	C3H	50 mg 2x/wk	30		.15	29	1	27.4

*Incomplete - 67 weeks duration.

Analytical*

The raw and spent shale samples contain only a few ppb of BaP (1 ppb to 24 ppb). The shale oil retort samples, on the other hand, contain 1000 to 5000 ppb of BaP and 3000 to 20,000 ppb of mono- and dimethylated BaP. The mono- and dimethylated BaP were analyzed together and reported as one value. The biological activities of the oil samples do not correlate with the amount of benzo(a)pyrene (Table 9) in the samples. As an example, the ratio of benz(a)anthracene to benzo(a)pyrene in samples RO-2 and RO-4 are 3.0 and 0.3 respectively while the ratio of methylated compounds are 0.6 to 1.4 in samples RO-2 and RP-4 respectively (Table 11).

In addition to benzo(a)pyrene and benz(a)anthracene, 10 other polycyclic aromatic hydrocarbons are identified (Table 10). One of these, acridine, is found only in sample RO-1. It should be noted that pyrene, fluoranthene, benzo(e)pyrene, and benzo(ghi)perylene have cocarcinogenic activities (Van Duuren, 1976)[13] in addition to aliphatic compounds (Bingham, 1969)[14] that are found in these complex mixtures. A number of heterocyclic aromatics are not found in these samples: carbazole, 11 H-benz-(a)carbazole, benz(c)acridine, 7 H-benzo(a)carbazole, dibenz(a,h)acridine and 7 H-dibenz(c,g)carbazole.

From these results it is important to look at the mixtures as a whole and to consider cocarcinogens and inhibitors that are present in the samples. Lastly, it has to be noted that BaP may not be a good indicator for carcinogenicity of shale oil.

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*These data were supplied by the API.

Table 9

Benzo(a)pyrene Content of Shale Retort Oils

(ug/kg ± S.D.)

Sample	Parent	Methyl Substituted
RO-1	1800 ± 141	4150 ± 1202
RO-2	1800 ± 00	21500 ± 707
RO-3	2300 ± 00	11500 ± 707
RO-4	4250 ± 71	8350 ± 212

Table 10

Relative Amounts of PAHs to BaP Standard

Shale Oil Samples

	RO-1		RO-2		RO-3		RO-4	
Compounds	Parent	Methylation*	Parent	Methylation*	Parent	Methylation*	Parent	Methylation*
Benz(a)anthracene	1.0	0.6	3.1	0.6	1.6	1.9	0.3	1.4
Chrysene	0.9	0.8	3.1	0.7	1.7	2.2	0.7	2.8
Benzo(a)pyrene	0.4	0.3	0.3	0.1	0.5	0.3	0.5	3.2
Fluoranthene	1.3	0.3	1.3	0.1	1.0	0.2	1.3	1.0
Pyrene	1.9	2.2	4.6	1.4	2.3	2.1	4.1	6.0

*Mono and di methyl substitution.

Table 11

Polycyclic Aromatics Present in Shale Oil

Carcinogen	Noncarcinogen
benzo(a)pyrene (strong)	pyrene*
benz(a)anthracene (weak)	fluoranthene*
	triphenylene
	benzo(e)pyrene*
Borderline Carcinogen	perylene
chrysene	anthanthrene
	benzo(ghi)perylene*
	coronene

*Cocarcinogenic Activity

References:

1. B. Bell. Paraffin epithelioma of the scrotum. Edin. Med. J. 22:135-137 (1876).

2. A. Scott. On the occupational cancer of the paraffin and oil workers of the Scottish shale industry. Br. Med. J. 2:1108-1109 (1922).

3. N.K. Weaver and R.L. Gibson. The U.S. oil shale industry: a health perspective. Presented at American Industrial Hygiene Conference, May 7-12, 1978. Los Angeles, California.

4. Ames, B.N. et al. Carcinogens are mutagens: a simple test system combining liver homogenates for activation and bacteria for detection. Proc. Natl. Acad. Sci. 8:2281 (1973).

5. Oakburg, E.F. Duration of spermatogenesis in the mouse and timing of stages of the cycle of the seminiferous epithelium. Am. J. Anat., 99:507-516 (1956).

6. E. Bingham, M. Zerwas, and W. Barkley. Unpublished data.

7. I. Hieger. Spectra of cancer-producing tars and oils and of related substances. Biochem. J. 24:505 (1930).

8. J.W. Cook, C.L. Hwett, and I. Hieger: The isolation of a cancer producing hydrocarbon from coal tar. J. Chem. Soc. I:395 (1933).

9. I. Berenklum and R. Schoental. Carcinogenic constituents of coal tar. Brit. J. Exper. Path. 24:232-239 (1943).

10. W.C. Hueper and H.J. Cahnmann. Carcinogenic bioassay of benzo(a)pyrene-free fractions of American shale oils. Arch. Path. 65:608-614 (1958).

11. P. Bogovsky. On the carcinogenic effect of some 3,4-benzopyrene-free and 3,4-benzopyrene-containing fractions of Estonia shale oil. Aceta Univ. Inter. Contra Cancrum. 18:37-39 (1962).

12. P. Bogovsky and H.J. Jons. Toxicological and carcinogenic studies of oil shale dust and shale oil. Presented at Workshop on Health Effects of Coal and Oil Shale Mining, Conversion and Utilization, Jan. 27-29, 1975. Department of Environmental Health, Kettering Laboratory, University of Cincinnati, Cincinnati, Ohio.

13. B.L. Van Duuren and B.M. Goldschmidt. Carcinogenic and tumor-promoting agents in tobacco carcinogenesis. J. Natl. Cancer Inst., 56:(6)1237-1242 (1976).

14. E. Bingham and H.L. Falk. Environmental carcinogenesis. Arch. Environ. Health, 19:779-783 (1969).

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LASL INDUSTRIAL HYGIENE
EXPERIENCES IN THE OIL SHALE INDUSTRY

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Presented at the
"Symposium on Assessing the Industrial
Hygiene Monitoring Needs for the
Coal Conversion and Oil Shale Industries"

Brookhaven National Laboratory
Upton, NY 11973

November 6-7, 1978

INTRODUCTION

Thank you, Mr. Otto White for inviting LASL to participate (or be a participant) in this symposium on Assessing the Industrial Hygiene Monitoring needs for coal conversion and oil shale industries.

Los Alamos Scientific Laboratory's (LASL) Health Division became interested in oil shale as part of a research program to study the long-term health effects of exposure to oil shale and its products.

LASL had the opportunity to study the PARAHO process of oil shale retorting, which is a surface retorting process using internal gas combustion, that is termed "ready for commercialization". It is the only process for which the complete technology - mining - retorting - Refining - and product utilization could be studied. Also, because, as some said it's "the only game in town."

At that time it was the only surface retort producing crude oil from oil shale. The facility is located at Anvil Points, Colorado, and is operated by Development Engineers, Inc. (DEI).

Two studies have been undertaken by LASL. The objective of the first study, which involved three trips to Anvil Points was to obtain samples and site-specific industrial hygiene data from the major points in the process stream.

Samples and data collected would serve as material for exposures to animals and to assess the results on the basis of exposure potential and threshhold limits.

The second study of the PARAHO process was to be more of an industrial hygiene survey of the entire PARAHO facility in conjunction with a joint LASL/API occupational health study of the present work force at Anvil Points. Only one trip was performed and because of eventual closure of the facility, the survey was cut drastically. Up to two weeks of work was initially scheduled so that all facets of operations could be sampled and so that sufficient samples could be taken to be statistically significant.

Although we have visited the Occidental Mining Company's modified in-situ process at Debeque, Colorado, only the PARAHO process will be covered in this talk.

Experiences in the Oil Shale Industry

I. TECHNOLOGY

The PARAHO oil shale process is a surface retorting process with the capability of using either direct gas combustion or externally heated recycled gas to achieve the retorting temperatures of 900 °F.

Coarseley crushed and sized oil shale is conveyed to and introduced at the top of a vertical kiln approximately 10-1/2' in diameter and 75' high. This retort is referred to as the semi-works and is capable of producing approximately 280 barrels per day of oil from the shale. The original and smaller 4' diameter pilot plant retort is still operating and is used to cool down the semi-works. It is also used to supplement the semi-works in oil shale processing.

II. RETORTING

The product shale is fed into the retort through a gas rotary seal then into a rotating apron "pant-leg" feeder. The shale then flows by gravity through a retorting zone to the bottom of the retort and through a discharge grate and bottom rotary seal. The "spent" or retorted shale is then conveyed to a disposal pile.

The combustion air and recycled gas is introduced into the retort by three distributers flowing counter current to the shale. Combustion of these gases with the residual carbon on the shale provides the temperature or heat needed for retorting.

Vapors of shale oil and residual gases are drawn off from the top of the retort and passed through an oil and gas separation consisting of an electrostatic precipitator and coalescer (demister). The remainder of the off-gas is recycled for combustion.

III. MINING

The oil shale is mined by underground room and pillar techniques using large diesel powered drilling, loading, and trucking equipment. The rooms are approximately 60' wide x 60' high and pillars 80' long x 60' high. Ammonium nitrate and fuel oil (NFO) are used as blasting agents. A 7-1/2 ft^3 front end loader is used to load the 50-ton capacity diesel ore trucks which transport the ore approximately five miles down to the crushing site. The runers are actually equipment operators. The mining is contracted out to the Cleveland Cliffs Mining Co.

IV. CRUSHING

From the stock pile of oil shale at the crusher site, oversize boulders are broken to a size which the crusher will accept. Then a front end loader is used to load the crusher.

The crushing operation consists of an apron feed, primary, secondary and tertiary crushers. Primary and secondary screening is used for sizing product shale for retorting. Fines from the screening process are conveyed to piles, some of which are used for road surfacing material (like gravel) for the mine road.

From the crusher, the product shale is again conveyed to storage bins. Some additional crushing occurs in bin storage. Dust generated in the storage bins is collected by a dust collector.

V. COMMERCIAL SCALE-UP OF THE PARAHO PROCESS

Development Engineers, Inc. propose a modular system of retorts. The modular retort will be 40' in diameter and 100' high. Each retort will produce 5,000 barrels of oil per day. A total of 20 such retorts will produce 100,000 barrels per day of oil.

VI. DISPOSAL OF RETORTED SHALE

The retorted shale is presently conveyed to a disposal pile at one side of the retort. Some trucking of retorted shale has been done for revegetation studies by Colorado State University. The retorted shale is moved occassionally to permit better disposal.

VII. INDUSTRIAL HYGIENE SURVEYS

In the Spring of 1977 LASL met with DEI on several occasions to arrange for the sampling trips to provide the information for the animal exposure studies. It was agreed that we would make at least two trips to Anvil Points to do a preliminary survey of the various operations to determine what we would need for a more accurate or refined sampling trip.

The complete survey was supposed to be conducted in a short span of time, but was extended into three trips. The second trip was to sample only the mine and crusher (winter weather becoming a factor) and the third trip to sample the retort.

No personal dust sampling was done at the request of DEI. Only area or operation sampling was done utilizing portable personal sampling equipment along with larger air sampling equipment.

The joint API/LASL industrial hygiene survey was scheduled to occur in two phases and was to be done over a two week period. Enough time was scheduled to sample all the desired operations and workers to obtain the necessary quality and quantity of material for analytical purposes.

Because DEI's contract with the Navy was completed and other funds could not be obtained, DEI had to close down its operations. Also, due to lack of maintenance during those last few days, equipment failures occurred which prevented us from doing the sampling we desired.

LASL was able to sample the crusher for only one day, the semi-works retort was shut down shortly after we started, and we were limited to sampling the mine without entering it.

VIII. SAMPLING NEEDS

Area samples were very important from the standpoint of characterization of the operations and the pollutants. Some of the equipment used to sample the operations were not compatible to field studies, for example, the Andersen Cascade Impactors. We frequently were unable to get the proper loading of dust on the filter media. Also the pumps used were shut out of commission.

One major recommendation regarding sampling facilities of this type is to perform as much of the analyses on site as possible, using the necessary lab and maintenance equipment to limit the transportation samples back to the laboratory. Transport of samples was very deleterious to our results.

Personal sampling equipment was useful in that no external power was required. In some cases, power available was so low we could not get the Andersen Impactor Pumps to turn over.

On our last survey, we provided our own diesel and gasoline power in ancitipation of low or lack of power at the facility.

More passive dosimeter samplers would be an asset to surveys where technologies are in development. This permits samlpling the man and separating out individual operations. These samplers should be for short term (15 minutes) and long term (8 hours) sampling.

All the sampling equipment we used addresses only the respiratory system as a route of entry.

Sample techniques are needed which can quantify skin exposures, from PNAH in oils and in water.

Biological sampling may be a technique useful for this type of evaluation. Also, we should arrive at a singular reference substance as an indicator of toxicity for polycyclic aromatic hydrocarbons.

IX. OTHER LASL RELATED STUDIES

LASL is currently acquiring a repository of oil shale materials for use in animal exposure and characterization studies. These materials are:

Oils

1. Paraho Crude Shale Oil - not upgraded.

2. Modified *in situ* shale oil - upgraded - limited supply.

3. Gulf coast crude oil - reference petroleum.

4. Middle eastern crude oil - reference petroleum.

Experiences in the Oil Shale Industry

Process Waters

1. Paraho - by separation from storage tank oil.

Raw Shale

1. Large Rock - Laramie Energy Technology Center (LETC).

2. Paraho crusher product.

3. Paraho bag house fines.

4. Estonian shale - limited supply.

Spent Shale

1. Paraho spent shale.

2. TOSCO II spent shale (restricted use).

3. Fischer assay spent shale.

4. Estonian spent shale (combustion ash?).

Also, LASL's Biology group is conducting animal toxicology exposure experiments on the PARAHO TOSCO II spent shales. Intratracheal exposures to the same materials plus silica; dermal toxicity and carcinogenicity studies to PARAHO crude oil, modified-in-situ crude oil, Gulf Coast crude oil and middle Eastern Crude oil are being conducted.

X. CONCLUSION

Industrial hygiene sampling studies and surveys of oil shale processes will require well formulated objectives and an appropriate allocation of personnel and materiel for both sampling and analysis. All data obtained should be referenced to present energy related industries experience to place this developing technology into perspective.

Table 1

Dust Sampling Summary

LOCATION	TOTAL DUST	% RESPIRABLE	MMAD
MINE	3.8 — 31.9	60%	2 μm
CRUSHER	2.3 — 47.2	50%	3 μm
BIN STORAGE	42 — 1179	45%	4 μm
RETORT	3.5 — 90.8	22 — 55%	6 7 μm
RETORTED SHALE PILE	5.3 — 84.6	30%	6 μm

Table 2

Gas and Vapor Sampling Summary

Retort Area (ppm)

	CO	THC	H_2S	HCN	HCHO	NH_3	NO_2
Top Seal	25	400	20	8	2	nd	nd
Bottom Seal	5	nd	trace	nd	nd	nd	nd
Recycle Gas Blower	600	<1000	10	15	15	35	nd
Mine Area							
Working Face	2-20	<10	nd	nd	trace	nd	<1
After Blasting	100	100	nd	nd	—	5	20

Table 3

Sampling Needs

- Use direct reading instrumentation whenever possible
- Do all sample analyses on site that is practical
- Use passive samplers for short and long term sampling
- Develop a personal PNAH sampler
- Develop an HCN specific sampler
- Need Diesel Fume criteria and sampler
- Need skin exposure evaluation techniques
- Need personal Total Hydrocarbon sampler
- Need for a field microbalance for large filters
- Need periodic samplers for dusts

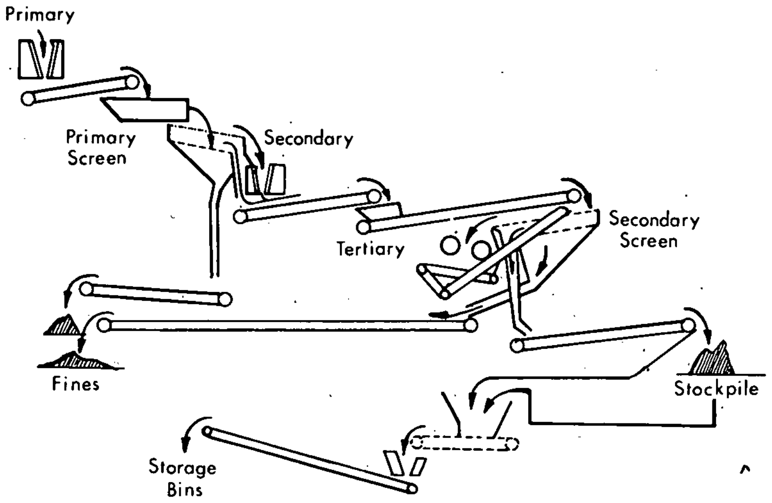

Figure 1. Navy crushing unit.

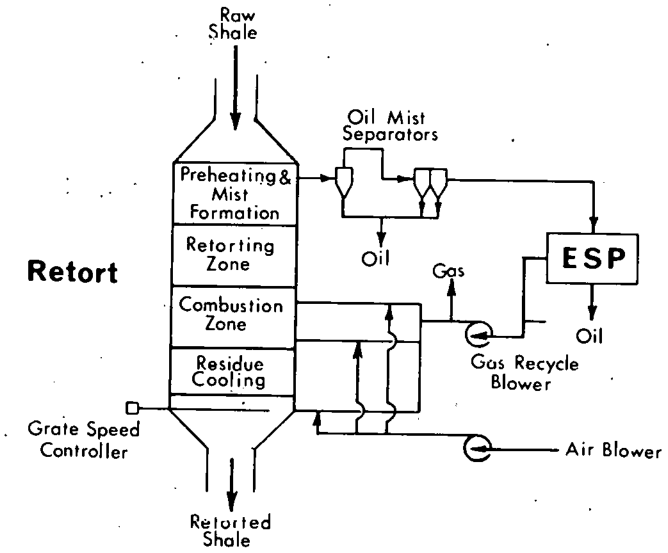

Figure 2. Paraho direct mode retort.

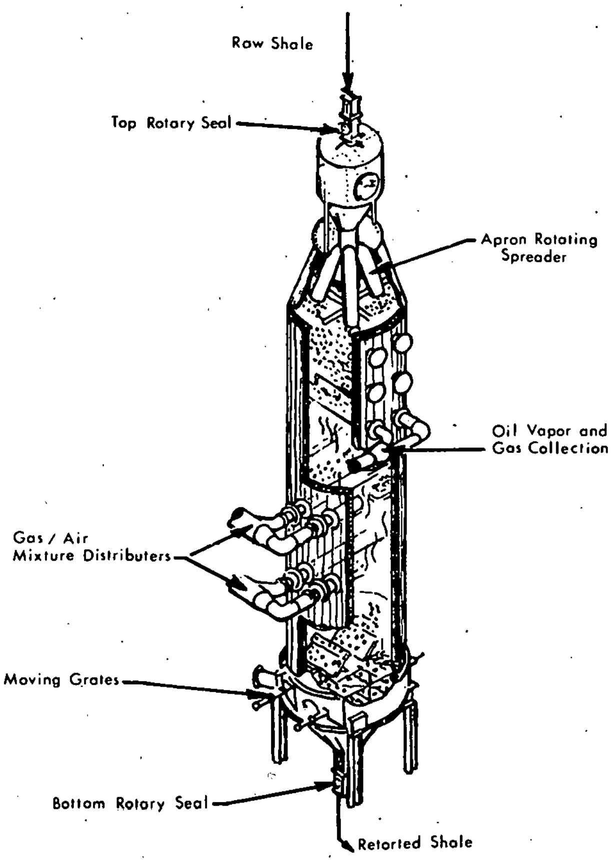

Figure 3. Paraho surface retort.

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INDUSTRIAL HYGIENE EXPERIENCE IN COAL LIQUIFICATION
(AN OVERVIEW)

H. E. Runion
Gulf Science & Technology Company

Presented at the
"Symposium on Assessing the Industrial
Hygiene Monitoring Needs for the
Coal Conversion and Oil Shale Industries"
Brookhaven National Laboratory
Upton, NY 11973
November 6-7, 1978

Brookhaven National Laboratory
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INDUSTRIAL HYGIENE EXPERIENCE IN COAL LIQUIFICATION (AN OVERVIEW)

H. E. Runion
Gulf Science & Technology Company

I. SOLVENT REFINED COAL (SRC) PLANT - FORT LEWIS, WASHINGTON

- o Department of Energy 50 ton per day research facility for deashing and desulfurization of raw coal.
- o End products include solid (SRC-I Process) and liquid fuels (SRC-II Process) and solvents.
- o Waste byproducts include sulfur compounds, mineral residual and phenols.

II. GULF INDUSTRIAL HYGIENE AND ENVIRONMENTAL MONITORING PROPOSAL - OBJECTIVES:

- o Eliminate or control health hazards to employees.
- o Prevent or minimize job related illnesses.
- o Assess health impact of all plant operations.
- o Apply findings and solutions to large second generation 6000 ton per day demonstration plant.

III. SCOPE OF STUDY

- o Define quantitative and qualitative character of contaminants in the work environment.
- o Assess points of fugitive emission and their control.
- o Characterize contamination levels and circumstances of exposure on an area and work or task basis.

III. SCOPE OF STUDY (cont.)

- o Principal contaminants of concern include:
  - o <u>Particulates</u>
    - . Total particulates
    - . Respirable fraction
    - . Benzene soluble fraction
    - . PNA composition
    - . Free silica and mineral residual dust
    - . Asbestos
    - . Welding fumes
  - o <u>Hydrocarbons</u>
    - . SRC light naphtha, SRC heavy naphtha, SRC recycle oil
    - . Phenols
  - o <u>Others</u>
    - . H_2S
    - . SO_2
    - . CO
    - . Noise
  - o <u>Skin contamination</u>
    - . Qualitative/quantitative analysis

IV. IMPLEMENTATION - FIELD STUDIES - DOE CONTRACT JANUARY 1976

- o Gulf Industrial Hygiene personnel - organize and manage study.
- o Gulf Physician - to organize and manage medical surveillance program.
- o Gulf Health Educator - designed an in-plant personnel training program.
- o Outside contractor - perform off-site air and water sampling functions.

V. IMPLEMENTATION - LABORATORY SUPPORT

- o Equipment and personnel assigned January 1976.
- o <u>Special analytical tools</u>
  - . HPLC - High Pressure Liquid Chromograph (HPLC)
  - . SPF - Spectrophotofluorometer (SPT)

V. IMPLEMENTATION - LABORATORY SUPPORT (cont.)

- Benzene soluble fraction analyses conducted in accordance with NIOSH procedures. PNA analyses to be performed by HPLC with UV and fluoresence detection.
- Develop improved method for PNA air sampling analysis.

VI. METHODS AND PROCEDURES

- Personnel air sampling
  - Pumps @ 0.2 and 2.0 lpm
  - Tubes
  - 37 mm silver membrane filters with Chromasorb backup - PNA's
  - Millipore filters - total and respirable fraction with 10 mm cyclone @ 1.7 lpm
  - Deployment on personnel and in strategic locations within work place.
- Area air sampling
  - High volume samplers - 40-60 cfm
  - 8 x 10 fiberglass filters
  - 37 mm glass fiber/silver membrane filters
  - Site selection considering nature of processes and meteorology
- Miscellaneous
  - SO_2
    - Detector tubes
    - Fritted bubbler with West-Gaeke analytical procedure
  - Phenols
    - Fritted bubbler with 0.1 N NaOH
    - Silica gel adsorbant tubes
  - CO
    - Direct reading Ecolyser
- Skin contaminants
  - Commercial alcohol prep skin wipe pads
  - Spiked samples and actual employee skin wipe experiments conducted
  - Prescribed sites on subject for wipe testing
  - UV lamp for periodic skin examination for evidence of lesions or other skin disorders

VII. SRC-I VS. SRC-II PROCESSES

- SRC-1 Process (Fig.1)

Coal preparation and slurry mix

Coal pulverized, sized and mixed with anthracene oil type solvent to form a 25-40% coal slurry.

Preheater and Dissolver

Slurry mixed with hydrogen and fed through preheater to dissolver for reaction. Ninety (90%) per cent of organic matter dissolves in 20 minutes @ about 800° F. and 1500 psig.

Sulfur Recovery, H_2 recycle and fuel gas

Sulfur compounds extracted by sulfur recovery unit producing elemental sulfur with remaining H_2 recycled and gases used as plant fuel.

Solvent Recovery

Vacuum flash distillation occurs producing light SRC-1 naphtha, heavy SRC-1 naphtha and processed solvent for recycle back to slurry mixing area.

Mineral Separation

The bottoms from flash distillation above is of heavy residual oil called Solvent Refined Coal containing less than .1% and less than .8% sulfur. Molten SRC product with undissolved solids are filtered. Following filtration, undissolved solid (mineral residual) is washed, then dried in a rotary kiln for waste disposal.

Product Solidification

Molten SRC material (300-400° F.) subsequently flows onto a stainless steel (Sandvick) belt for cooling where it solidifies and breaks up into chunks like peanut brittle.

- SRC-II Process (Fig. 2)

Primary difference with SRC-1 is the transfer of hydrogenated molten SRC liquid to the fractionation tower where the light and heavy naphthas, fuel oil and heavy SRC-II distillate are produced. The vacuum bottoms containing mineral residual are directed to the Sandvick belt for cooling and ultimate disposal. The SRC-II process eliminates mechanical filtration and produces only liquid products the prime fuel of which contains only ≈ 0.4% sulfur.

o SRC-I - Industrial Hygiene monitoring findings January 1974 - July 1977

Airborne organic vapors in plant. Concentrations of organic vapors and hydrocarbon gases were found to be generally less than 0.1 ppm.

Benzene survey - heavy and light SRC naphthas contained less than 1% by volume benzene. Occupational exposures were less than 1 ppm TWA.

Suspended particulates - plant air and personnel exposure

- Large mass of data now being processed
- Emphasis of moment - SRC-I vs. SRC-II processes, e.g.
  - Coal recovery and preparation areas
  - Solvent recovery
  - Product solidification
- Statistical findings to date

Welding fumes

Welding can be exposed to airborne concentrations of coal derived materials when working on contaminated metals.

Asbestos

Following initial experience in handling asbestos, installation of an exhaust ventillation system, exposure in the filter preparation area was less than 0.1 fiber per ml of air.

Mineral residual

Several types of calcined diatomaceous materials containing 50% by weight of free silica were used as a filter aid in the SRC process filter. Hence the mineral residual averaged 4.5% free silica as alpha quartz. Short term levels when loading on truck for disposal occasionally reached 10 mg/m^3.

Hydrogen Sulfide

H_2S levels found to be consistently low (>.1 ppm)

SO_2

Air samples collected from various fixed locations within the plant showed all levels to be .04 ppm or less.

Phenolic compounds

Phenolic compounds exist in many liquid streams; however, sampling indicated that airborne levelswere all below 0.5 ppm.

Noise

Noise levels in this particular plant were found to be consistently less than present day exposure criteria as evaluated with the use of sound level meters and dosimeters.

CO

CO exposures have occurred stemming from the plant inert gas (nitrogen) generation unit, which, due to incomplete combustion, can develop CO levels up to 1.5% CO in the inert gas stream. Corrective action: Repair and periodic replacement of rotary air lock in the coal pulverizer unit.

Settleable particulates - ambient air

Monthly dustfall samples collected in fixed sampling sites showed ambient dustfall concentrations considerably lower than those reported from a neighboring urban community.

Skin contamination

Preliminary efforts using "alcohol prep," gauze pads soaked in 70% isopropyl alcohol, showed demonstrable differences in terms of benzene soluble fractions between "contaminated" samples (taken before bathing or washing) and "clean" samples taken afterwards. Quantitative analysis was not successful due to need for more sensitive analytical methods not available at that time.

o SRC-II - Industrial Hygiene monitoring findings January 1974 - July 1978

Airborne organic vapors in plant. No increase in benzene exposure levels. The majority of samples taken were 0.01 ppm of n-hexane, benzene, toluene and xylenes.

Benzene

No increase in benzene exposure levels.

Suspended particulates - ambient air

Results indicated a significant lowering of contamination in conjunction with SRC-II processing.

Suspended particulates - personnel exposure

A significant reduction of exposure occurred in conjunction with SRC-II processing.

Welding fumes

Exposure to coal derived materials occurs during welding as a product of work practice or use of local existing control, not manufacturing methodology (i.e., SRC-II vs. SRC-I).

Asbestos

No asbestos sampling was conducted during SRC-II operation because neither asbestos nor asbestos containing filter aid materials are required with SRC-II processing.

Mineral residual

No sampling. The high alpha quartz containing substances used as part of the SRC-I mineral residual filter are not involved with SRC-II processing.

H_2S

It was determined that SRC naphtha(s) or other low boiling light distillates contained dissolved H_2S in the head space above liquids in tank cars on storage vessels. The equilibrated vapor space concentration of up to 10% have been observed. SRC-II middle and heavy distillate and fuel oil contained very little dissolved H_2S with less than 200 ppm in the vapor space.

SO_2

SRC-II results showed virtually zero occupational exposure to SO_2 in the various process areas.

Phenols

Sampling indicated that virtually no apparent phenols were present in the work place.

Noise

SRC-II processing did not result in increased exposure to noise.

CO

SRC-II processing did not increase CO exposure.

Skin contamination

Work continues toward the development of an effective and reproductive skin wipe procedure. Laboratory analysis employs high pressure liquid chromatography (HPLC) with special spectrophotofluorometric detection (SPF). Both "spiked" samples as well as actual wipes from employee's skin at various levels of contamination produced results which suggest that a reproducible skin wipe test procedure can be developed.

Settleable particulates - ambient air

Monthly dustfall samples during SRC-II processing were found to be less than levels associated with the SRC-I process.

VIII. HEALTH EDUCATION FOR EMPLOYEES

- All new employees regardless of assignment receive a health education indoctrination emphasizing:
  - Hazardous circumstances and recommendation for control
  - Measures for personnel protection
  - Use of protective apparel on equipment
  - Cause and prevention of occupational diseases including dermatitis and skin cancers
  - Personal cleanliness during work and at shift change
- Health Information Booklet for each employee

FACTORS FOR SRC DATA EVALUATION

- DISTRIBUTION OF DATA BEING TESTED
  - SKEWNESS (SYMMETRY)
  - KURTOSIS (SHAPE)

- PRELIMINARY FINDINGS SUGGEST DATA ARE LOG-NORMALLY DISTRIBUTED OR DATA APPROXIMATE LOG-NORMAL DISTRIBUTION

- AGREEMENT WITH LEIDEL AND BUSCH (NIOSH) AND COMMUNITY AIR POLLUTION ENVIRONMENTAL DATA

- CONDITIONS FOR LOG-NORMAL DISTRIBUTION (BUT NOT ALL NECESSARY)
  - THE CONCENTRATIONS COVER A WIDE RANGE OF VALUES, OFTEN SEVERAL ORDERS OF MAGNITUDE
  - THE CONCENTRATIONS LIE CLOSE TO A PHYSICAL LIMIT (ZERO CONCENTRATION)
  - THERE IS A FINITE PROBABILITY OF VERY LARGE VALUES (OR DATA "SPIKES") OCCURRING

TABLE I

HIGH VOLUME AREA SAMPLING IN VARIOUS PLANT LOCATIONS DURING SRC I AND SRC II

Plant Area	Operating Mode	Total Particulates mg/m^3			Benzene Solubles mg/m^3		
		GM	GSD	N	GM	GSD	N
Coal Receiving and Preparation	SRC I	0.67	5.3	71	0.06*	3.6	69
	SRC II	0.56	5.8	21	0.03	2.2	20
Solvent Recovery	SRC I	0.14*	2.6	34	0.06**	2.3	34
	SRC II	0.08	2.3	24	0.03	1.8	24
Product Solidification	SRC I	0.73**	3.2	81	0.32**	5.0	81
	SRC II	0.10	2.2	36	0.03	2.0	36

GM = Geometric Mean

GSD = Geometric Standard Deviation

---

* Significant difference at $p<0.05$ with 2 tailed t-Test

** Significant difference at $p<0.01$ with 2 tailed t-Test

TABLE II

PERSONAL SAMPLING IN VARIOUS PLANT LOCATIONS DURING SRC I AND SRC II

Plant Area	Operating Mode	Total Particulates mg/m^3 GM	GSD	N	Benzene Solubles mg/m^3 GM	GSD	N
Coal Receiving and Preparation	SRC I	0.86	7.0	8	0.04	4.6	8
	SRC II	1.3	3.7	30	0.03	4.1	30
Solvent Recovery	SRC I	0.56	2.3	9	0.06	6.5	9
	SRC II	0.20	5.0	7	0.04	5.1	7
Product Solidification	SRC I	2.3	3.0	8	0.96**	3.7	8
	SRC II	0.91	3.5	29	0.12	7.1	29

GM = Geometric Mean

GSD = Geometric Standard Deviation

** Significant difference at $p<0.01$ with 2 tailed t-Test

OCCUPATIONAL SAFETY AND HEALTH IN COAL GASIFICATION

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Presented at

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Upton, New York 11973

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OCCUPATIONAL SAFETY AND HEALTH IN COAL GASIFICATION

GASIFICATION PILOT PLANTS, 1976

Worker health and safety has always been a concern in the Department of Energy (DOE) Fossil Energy Pilot Plant program. However, in mid-1976, when NIOSH and Enviro Control, Inc. (ECI) first became involved in occupational health for coal gasification pilot plants, Fossil Energy was somewhat reluctant to pursue the subject. Yet, NIOSH and in turn ECI, received full cooperation both from the Fossil Energy project officers located in Washington and at the pilot plants.

During the Fall of 1976 and 1977 a NIOSH-ECI team visited all the major coal gasification pilot plants and several of the energy research facilities and national laboratories which were engaged in coal gasification. In general, we found a very positive emphasis on personnel safety. However, with a few exceptions there was little consideration given to the finer points of occupational health, particularly to the carcinogenic nature of the liquid products which many of the plants produced. In some cases management seemed unaware that this type of problem might exist. We seemed to be the first to bring detailed information and to ask questions on the subject.

As a result of the initial pilot plant survey, the information supplied by the national laboratories and energy centers, by the pilot plants, and material from epidemiological and toxicological literature was all compiled and published in 1977 as "Recommended Health and Safety Guidelines for Coal Gasification Pilot Plants". The guidelines took into consideration that no two coal gasification pilot plants are alike in process technology or hazards, and also recognized a variable and inconsistent nature of pilot plant operation. They were designed as down-to-earth guides emphasizing worker protection measures such as safe work practices, personnel protective equipment and clothing, industrial and personal hygiene, workplace medical monitoring, labelling and posting, hazard information and awareness, and record keeping. We had one major stumbling block. There was no real time, reliable method for monitoring PNA concentration. Consequently, we recommended CO or H_2S as proxy compounds.

DEVELOPMENT OF A CRITERIA DOCUMENT

NIOSH next turned to the development of a criteria document for commercial coal gasification plants. Toxicological and epidemiological evidence on which to base such a document was scarce. Information was available from gas works studies and from the coke oven work. However, these processes are totally unlike the modern coal gasification plant. The old gas works and most of today's coking plants leak like sieves, and many of the workers were, or are, constantly exposed. Modern coal gasification processes, particularly the high-pressure processes, are closed. Worker exposures should not follow the same patterns as those defined by the gas works and coke oven studies. But exactly what kinds of exposures do occur in modern plants? The only epidemiological data available was that of Sexton, which was obtained at the Union Carbide plant, Institute, West Virginia, for a five-year period in the late 1950s. This data pointed out the potential for a massive problem. Toxicological data based on rodents was available from the studies of Weil and Condra, which were made in conjunction with Sexton's work; studies by Hueper on materials obtained from the Louisiana, Missouri, pilot plant; and the study in 1970 by Bingham on materials obtained from the Synthetic Fuels Pilot Plant in Cresap, West Virginia.

These studies indicated that there was a carcinogenic problem, and that various streams from coal liquefaction plants exhibited a rather wide range of toxicities.

We next approached the companies which were seriously involved with coal gasification. The enthusiasm which met our requests for help and information was both startling and flattering. We visited all the commercial coal gasification plants operating in the United States today; Carey Lime and Stone Co., in Ohio, with three stirred, fixed bed Wellman-Galushas; Glen-Gery Co. operations - 6 Wellman-Galushas, firing anthracite, were used to produce a low-Btu gas for firing brick kilns, and the Holston plant in Kingsport, Tenn., which has 12 Willputte gasifiers. (It is hard to believe that in 1929 there were 12,000 gasifiers and gas works in small and large communities spread throughout this country; it was only in 1961 that the city of Reading, Pa., closed down its last gasifier. There is little information on their mode of operation and less on occupational health and safety.)

We next visited the offices of the firms who were actively engaged in the consideration of large high-Btu gasification plants. These included El Paso Panhandle Eastern Pipeline Co., American Natural Gas Coal Gasification Co., and Wesco at Fluor Engineers and Constructors. Here the engineering and control technology which was being designed to protect the worker was explained to us in detail. In my opinion concern for worker health went hand in hand with first class engineering design. However, they all, and without exception, urged that we visit the SASOL plant in South Africa.

SASOL

SASOL is a large operation, approximately one-half mile wide by over a mile long. The operation is based on gasification of coal. Synthesis gas from the 13 Lurgi gasifiers is purified in much the same fashion. Gas will be purified for high-Btu pipeline coal gasification plants. This purified gas is then reacted in a Fischer-Tropsch process to produce liquid paraffinic hydrocarbons. At SASOL, these hydrocarbons are then taken and used for the production of numerous petrochemicals. In 1977 there were 3400 whites and 2200 blacks employed there.

When we visited the gasification and gas purification sections of the plant, there was extensive construction in progress as the plant was being expanded from a capacity of 9000 tons of coal feed per day to 14,000 tons of coal feed per day. Despite the confusion and dirt caused by the construction, we found the housekeeping in the plant, with the exception of the tar gas-liquor separation area, was very good. The SASOL engineering staff includes a number of very dedicated environmentalists. The plant was and is making a large effort to insure that its effluents meet the rather strict environmental criteria of the South African government. SASOL has been largely successful in controlling their effluent composition with the exception of fluorine, which is present in high concentration in the Sigma coal used by the SASOL operation. Safety is a must and safety rules derived from experience are very carefully enforced in the plant. The Lurgi high-Btu coal gasification plants to be used in the United States will undoubtedly base their safety rules on SASOL experience.

At that time their industrial hygiene program was in the initial stages of implementation. Other medical problems seen at the clinic include gassings with carbon monoxide in the coal gasification plant and further downstream, ammonia. Burns are common, particularly steam burns. Other burns include those from catalysts in the gas purification plant, tar burns at the Kellogg reactors, and thermal burns during cleaning processes. Burns which occurred from hot wax which leaked out when blocked pipes were released were also reported.

Conversations with workers who had been at the plant more than 20 years showed that allergies were occasionally seen. These included allergies of the hands and other skin allergies associated with the use of indicators for dyes which seemed to clear up when the worker was removed from the site of the problem. The SASOL doctor stated that he had not seen any skin cancers among the workers. When the workers were questioned about skin cancer, they too stated that they had not seen any skin cancer among their fellow workmen. One foreman described three possible skin cancers, but these cases were not documented on any of the records that our team saw.

In the spring of 1978 one more piece of epidemiological information was developed. Under a NIOSH contract Dr. Alan Palmer of Stanford Research Institute looked at the medical records of and interviewed 50 workers identified by Sexton in the 1950s as having cancerous or pre-cancerous lesions. Of these workers, most of whom have been on the maintenance force at the Institute pilot plant, three had died of coronary problems. One of those dead had also had cancer. One of the living had prostate cancer. There were no other signs of cancer reported in 1977 by these 50 people.

Thus, what we see is a mixture of confusing data and information.

THE RECOMMENDED STANDARD

Employment in a coal gasification plant may entail exposure to a number of chemical compounds which may be toxic and/or carcinogenic. Exposure to these compounds can increase the risk of cancer to exposed employees. However, it was the consensus that there was insufficient evidence to develop new permissible levels of exposure to toxic substances. It was recommended that, where applicable, existing Federal occupational exposure limits or NIOSH recommendations be enforced.

An engineering approach separating coal gasification processes and unit operations was used to facilitate the orderly development of the criteria. Coal gasification was separated into three types of processes, distinguished not only by operating process and technology but also by the nature and extent of potential exposure:

1) High-Btu product coal gasification (which leaned heavily upon Lurgi technology),
2) Coal gasification (low or medium Btu product) utilizing bituminous coal or lower ranked feedstocks, and
3) Coal gasification (low or medium-Btu product) utilizing anthracite feedstock or very high temperatures.

Because of the large number of toxicants which may be present in a coal gasification plant, the guidelines were presented for an indicator monitoring method to allow real time detection of leakage in coal gasification plants (with the notation that before this indicator method is adopted as a procedure for compliance with standards, the method should be compared with other methods for the detection of specific hazardous compounds in terms of accuracy and sensitivity.) The document emphasizes both engineering controls and worker protection. In the area of cancer, it was recognized that skin cancer could be a common problem but that systemic cancer, where it occurred, would be a greater danger to the worker. It was also recognized that it was necessary to permit free and innovative design of engineering controls to protect the worker, and that any attempt at this point in time to specify the form that such controls would take would most likely result in more rather than less worker exposure over the long run. The document is specifically designed to encourage innovation in the design of equipment that will reduce potential exposure of gasification plant workers.

WHAT REMAINS TO BE DONE

In my opinion, insuring good occupational health within the coal gasification plant will be as important as community health outside the gasification plant or environmental integrity. My reasoning is that we are already developing the technology to insure that the environment will be protected, and the technology available for this should be even more sophisticated and effective when these plants go into operation. At the community level, if the worker inside the plant fence can be protected from fugitive emissions and other types of toxic hazards, then there should be few if any problems from these hazards in the community.

Frankly, we have a lot to do before we can achieve a comfortable position. There is a strong need to characterize and to identify the toxic hazards to which the worker may be exposed, especially at the commercial plant level. There is a far stronger need to develop engineering control technology which will reduce the potential for worker exposure to these toxic hazards as well as to safety hazards. It is obvious that better engineering control technology will mean greater available onstream time for the plant and less maintenance, and therefore less exposure. We need more effective, less expensive real-time monitoring equipment and we especially need to know what exactly are the synergistic effects of these toxic substances, especially the carcinogenic health hazards. However, even if an effective epidemiological program were initiated today, we would not have the answers we need for twenty years. In the meantime, we must protect the worker and therefore the community as best we can.

NIOSH has initiated several projects with EPA pass-through funds which will begin to answer the problem. These include the industrial hygiene characterization of coal gasification and liquefaction pilot plants and an occupational health engineering control assessment of coal gasification and liquefaction processes. At the same time the Department of Energy has initiated an extensive occupational health and environmental program in the "Gasifiers in Industry" program. The NIOSH program should begin to define the problem, particularly for the coal liquefaction or high-Btu coal gasification plants, while the better funded DOE program should prove to be exceptionally useful in defining the occupational health problems associated with low-Btu coal gasification and in defining controls required to prevent occupational exposure. For the larger plants, it would be exceptionally helpful if a multi-disciplinary program could be developed which would bring together experts from all over the country to work together.

GASIFICATION PILOT PLANTS, 1978

In 1978 I revisited one of the coal gasification pilot plants that I had visited late in 1976. The increase in awareness of the potential occupational health exposures within the plant was almost indescribable. Contract maintenance workers who had originally been considered unmanageable are being ordered to follow good work practices. Showers were being made mandatory for all workers within the plant. Air sampling techniques for areas frequented by the operators were being investigated and a professional industrial hygienist was to be added to the staff.

IN CONCLUSION

The awareness of the need for better occupational health procedures in coal gasification have come a long way since the summer of 1976. Now comes the hard part: to define the extent of the problem, to characterize it, and to develop equipment and procedures which will protect the worker. We don't have very much time to accomplish all this. If we work together, the private sector and government, environmentalists and hygienists, employer and worker, we can do it.

PANEL DISCUSSION

(Newell Bolton - Chairman)

Ettinger: This remark is directed to Mr. Jim Evans. I was interested in the information you brought back from SASOL and delighted, in fact, to hear that you can run such a facility safety, apparently from the data that you were able to gather from this.

Evans: Information, based on their data.

Ettinger: Based on their data? You have doubts that they were telling the truth?

Evans: No. There was not a systematic program to gather data. In effect, what they've got is information except for the death records. There just are no health records kept on the sort of thing that you and I would be interested in.

Ettinger: Well, we can accept, at least partially, that their information was reasonable although perhaps not complete in terms of the truth. The concerns are expressed in that NIOSH document about health effects from coal gasification processes, the document you alluded to in your presentation. How can we take such a positive position about the concerns for cancer? It seemed like an overkill from one point of view; in fact, with these data weighing it the other way.

Evans: Again, the only data we have are from Sexton. I'm confused. I'm completely confused. Because if you go to the centers where they have been doing coal work--consultants, coal libraries, PERC, IGT, etc.--you hear the same things said at SASOL. On the other hand, there is no systematic program to look at it (the data).

Hull: First of all, just a point of information, I remember when I was a kid or even a young man, there was a coal conversion gas works in the relatively small town where I lived. There must have been a number of such towns of many sizes all over the United States. I would think while some of the retrospective investigations that are now going on in regard to people exposed to radiation, it wouldn't be too hard for somebody to get the money to do it. There must be records of people who worked in such places; secondly, if you are going to go and look at their death certificates, you can track them down. You can say it was pre-Social Security, I'm not sure. People weren't as mobile as they are today, and it wouldn't be much of a project to do the retrospective (study) and take a look at this population which must be very considerable.

Evans: Two things: The gas works you are talking about aren't the same as the modern coal gasification facility. They really aren't. It's not to say that perhaps the materials coming out aren't similar in some cases, the pyrolysis process, for example, but a leakage is heck of a lot higher.

Hull: All to the better, isn't it, if we are giving off our limits?

Evans: Rather than looking here in the United States, we looked for German data. Nothing. Absolutely nothing. We felt that if anybody would have the data, the Germans would. They were very careful in their record keeping, but they did not keep industrial hygiene data as far as we could find.

Bolton: I still believe it is written down somewhere.

Evans: The people I've talked to, whose names I can't remember, knowledgeable people who are consulatnts today in the field, have tried to find it too through their friends. We went to Lurgas and tried to find it through those people.

Hull: I happened to see one of the few Xerox copies of a big study that APHA did under a $50,000 contract for the Ford Foundation to look at the health effects of different technologies; there was a very considerable section in there on the experience of coal workers. Isn't that useful or is it again so sloppy that it's just not appropriate for this use?

Evans: It's useful in pointing out the problem. The experience of Doll, etc. It's useful in pointing out the indidence of fatalities. That's exactly where the concern comes from in the NIOSH Criteria Document and the Recommended Health and Safety Guidelines...because of the experiences in other fields.

Beardsley: I have a question just in general to the panel. I agree with the comments that were made concerning the fact that you can't use benzo(a)pyrene as an index, but you have to take into consideration the cocarcinogenic factors and other compounds that may be present. In light of this, I was surprised that not much was presented or talked about in terms of using the benzene-soluble fractions that have been utilized by NIOSH in the coking industry. I just wondered what's the panel's consensus of using the benzene-soluble fractions as opposed to trying to get one index of some specific compound in either gasification, liquefaction, or oil shale (industries).

Evans: If I can express my opinion before I get swamped. People have the potential to be exposed to toxic gases and to tars. Tars are in everthing that condenses. People aren't exposed to single compounds.

Beardsley: Yes. That's the whole reason for my question. I mean I can understand the tars and the gases, but there are a lot of comments made about single compounds and very little comment made about the only thing that we've got to put a handle on right now, the benzene-soluble fraction.

Runion: Let me make a comment in this regard. We include in our battery of analyses the benzene-soluble fraction.

Beardsley: Yes, I saw your data.

Runion: We are doing one other thing that is not reflected in this report here. And that is because we've had problems in terms of equipment acquisition and manpower. But we are analyzing some of these samples. We've kept them all. We're going back and selecting a basis to analyze the samples using the high pressure liquid gas chromatography for a profile of the PNA's. We're looking for some common denominators. We realize that BAP is not the limit in terms of finding out whether you have problems. Maybe we can relate in time to such a profile with clinical observations. One of the things that has always been missing is that toxicologists, to whom we so often turn for clues as to how much is too much, are just now beginning to develop the kind of profile in this context in terms of characterization of atmospheric levels of exposure that are in their chambers, i.e., express the qualitative and quantitative character of the contaminant. So that later on when you start looking at the results of the biology and even later when you start looking at the epidemiological or early clinical findings, you begin to blend these things together. We need this kind of approach which today won't give us the answer but maybe five years or eight, ten years from now will begin to give us some kind of answer. Meanwhile, being programmatic and practical, maybe the benzene soluble fraction for lack of something better is better than nothing at all.

Beardsley: I'm concerned about the fact that benzo(a)pyrene is used so much.

Runion: I agree.

Beardsley: And used as an index by so many people.

Runion: Bob Scoler from Exxon who heads their toxicology group as well as Dr. Crown from Gulf repeated many times that experiment after experiment shows that you don't have to have any of this particular compound present to produce tumors. We all are looking for that tack. We are all searching for one, two, or three PNAs that we could identify with reasonable ease in the laboratory.

Beardsley: I realize that we are all seeking the utopia. Certainly in terms of doing the pathological studies and looking at the synergistic effects of a half dozen compounds simultaneously could price you out of the market. My concern is that I don't understand why a working group like this, for instance, doesn't come out and say, "Until something better is developed, we will not use the BAP index, but we will use such and such an index which is perhaps the benzene-soluble fraction." The problem is that there are a lot of people that really rely on the BAP rather than on the benzene-soluble fraction. And whenever you go to a symposium, you see the two camps arguing back and forth. Certainly, some sort of resolution needs to be made.

Bolton: In defense of using BAP, the whole process is historical when you think about it. But when we did the original work at Mellon Institute in the 50's, the one thing that was common, and I mean literally common to all the strains that they investigated, was BAP. Coupled with that was the fact that around 1974 NIOSH published a tentative or proposed TLV for BAP. It was really the only thing we had that had a tentative threshold limit value. So most of us for pragmatic reasons built that into our programs.

Beardsley: Well, that was the only index that you had at that point in time.

Baier: I think if you check the criteria document on coke ovens, which address that point, NIOSH did not recommend any kind of an environmental limit in that document. The BAP argument, I thought, got shot down at both the coke oven hearings and the carcinogen hearings. NIOSH did not do that either.

Bolton: You're right. It was ACGIH that published the tentative TLV. You're right.

Gammage: To continue with the question of indicator substances and the BAP problem, I can probably address this to any of the people who were talking about shale oil, Wayne Griest and Merrill Coomes in particular. BAP was obviously not a suitable indicator of the shale oil products. It was pointed out that shale oil products are different from coal conversion products in that a lot of mutagenic activity is contained in the basic nitrogen fraction. I wonder if one of the speakers would like to stick his neck out and suggest the substance equivalent of BAP that might be an abundant base nitrogen compound which would act as an indicator.

Griest: I'm not familiar with suggested indicators. I think the point should be that prior to the selection of an indicator compound, somewhere along the line we've got to establish a relationship between that compound and the rest of the family. This relationship may not hold for coal conversion and oil shale.

Beardsley: In the toxicological studies that I have done, it is much easier to use a pure compound for the study. Just using one compound you have a problem. When you start putting in more than two compounds, it becomes an impossible task. It has been shown so many times now in these types of processes that BAP does not follow the results you would expect from an indicator. It bothers me because it keeps coming up and people keep looking at BAP. Maybe someone has to come out and say, "Look, we're not going to use BAP anymore. Let's find another index."

Evans: When I was at Cresap, it was suggested that in coal liquefaction one should use sulfur-containing compounds without saying how they should be used as an indicator. At least you can smell them. But then you can smell most of the products in coal liquefaction processes.

Coomes: I showed some results from a rather extensive analysis and could perhaps relate a combined analysis to the carcinogenic potency. But those analyses are very expensive, very time consuming. Each one costs us $5,000 per sample. That's way too much time to be putting into something as an indicator. You point out the difficulties of testing two or three compounds. Here we have shale oil or a coal-divided liquid and it has thousands of individual polycyclic compounds. When you get up into the large fused ring systems with just a two methyl isomer compound, you've got hundreds of possibilities. So, this is one of the reasons that (inaudible) took an approach in animal testing to test the whole material. Disregard what's in there.

Audience: You get a whole mish mash and just look at the benzene solubles.

Coomes: Unfortunately, if you are testing oil shale, benzene solubles include the entire thing. Shale, as a crude material, is completely soluble in benzene; only a very small amount is insoluble. And so that, to me, does not seem to be a very good standard if you are applying it to liquids. I know you are thinking about solids. Let's look at solids, raw shale. Raw shale is approximately 2.8 percent soluble in benzene. The processed shale is about 0.2 percent soluble in benzene. But if you test most extracts by painting on mice, you find out that on the weight of the extract bases the processed shale is much more potent. You can analyze and spend $5,000 per analysis and will find out that each one contains the same polycyclic aromatic hydrocarbons.

Now to get back to the point of using BAP as an indicator compound. It was mentioned quite a while ago that BAP is always present. Well, almost always present when you test a carcinogenic fraction. The analytical capabilities at the present time are available to the same analysis for all other polycyclics, but it is just too expensive. Now, I believe it was the EPA that proposed a scheme to get a total polycyclic analysis of the materials. We went through the scheme and analysis of one scheme required about 3 man-weeks of the chemist's time. It is just a little bit difficult to have one thing substitute for a biological activity. You have to settle on something that's not perfect, something that's easy to do, something that's moderately good; and chemists can analyze for it if it shows up very nicely.

Gammage: What is the rationale for the biological testing, or the fractionations that identify the bad actors if we are going to give up on the industrial hygiene end and say it is impossible, it's not worth measuring these compounds. It seems lopsided considering the funding that is now available.

Griest: First of all, sometimes the crude materials are not amenable for animal testing. As a scientist aren't you interested in what materials are in these oils that are causing a lot of activity, how they differ among each other? This information perhaps could go back to the engineers. Here, you've got this compound. What can you do? Can you plead for controls?

Gammage: I might also as a scientist or industrial hygienist measure a small number of these materials that are representative of classes which were biologically active to give me a good handle on just what sort of hazard the worker is being exposed to.

Runion: I think that the work we are doing on the SRC project speaks to this mixed bag in an attempt to get some balance. We are all in a developmental R&D phase. The technology of converting coal and shale to some other form of energy is being developed. So, in the laboratory, in terms of toxicology, I contend that we will continue to characterize with some care the nature of that beast our animals are being exposed to for future reference. Go ahead and define the benzene-soluble fraction per se. Go ahead and define the partiuclate composition of the chamber atmosphere. Go ahead on this selective basis and characterize the PNA profile of this mateiral. And then, in the field as we are doing, take your air samples for the purpose of compliance with current standards which seems to be the most programmatic, most acceptable reasonable practice at the moment. But if you have the ability and the state of the art apparatus, go ahead and collect some samples in such a way that you can have a few analyzed in greater depth. Again, this is a sort of reservoir of knowledge of the future. Then as we go along on this path, we begin to see human experience. This is a new business. SRC has been going for four years now and the population of that plant is, from a health effect point of view, only four years old. You're not going to see tumors emerging at this point and we hope we don't. We need a certain amount of this kind of information. We don't need to blow all our bucks and do all of this at great depth.

White: It seems as if we may be a little premature in selecting proxy compounds. One of the points that I will be making tomorrow is the fact that we need these in-depth characterization studies to identify what sampling is required to monitor work place environmental conditions. It is possible that the combination of high volume samples and some of these in-depth analytical techniques and treatments will identify compounds which are more meaningful selections as proxy compounds. Until we get these kinds of samples analyzed, we could be barking up the wrong tree in terms of what causes adverse health effects.

Coomes: I just want to make one other comment on the standards already engaged. It seems to me that one has to consider and I agree that even more testing to get an idea of profiles is necessary; but I think that the temperature at which you're generating these compounds, and the BAP may reach a maximum at a certain point. You don't really have that kind of information available yet to say, "Well, because in some instances BAP may be a good indicator compound depending upon what temperature BAP is produced." We still need that type of information that is not available. I think that is very important to consider when you're looking at profiles.

Hull: Back to my previous question about epidemiology. I remember seeing in an ERDA-sponsored conference on Risk Assessment that somebody had looked at petroleum workers data assuming that there are a lot of analogous conditions in refineries and what not. The data generated were a sort of back and forth argument as I remember, questioning whether it was meaningful or not. On absolute standard mortality ratios, they didn't look convincing, but on proportional mortality ratios they did look somewhat convincing. Is that type of data source or experience useful in this business? Why not? I see you shaking your head.

Runion: I don't think so. And pursuant to this matter of running studies on a retrospective sense, we have such a small population here. Of course, you were raising a question about the fellows who used to work in your neighborhood. Even if you could find them again, you would be faced with this problem of having no way of finding out the levels of exposures or what they experienced. You're almost wasting your money. Retrospectively, yes. Indeed one of the things that we're talking about and beginning to develop is this type of retrospective study of...

Pallay: API has an epidemiological study under way in which they're beginning to collect data which may be somewhat relevant. NIOSH has an epidemiological study of TVA workers in TVA coal-fired facilities which may also be somewhat related.

Brief: The API has in their books a research project which hasn't started yet but is awaiting some samples. We're going to get a whole variety of components or products from petroleum sources and relate the PNA analytical experience to biologic activity and try with some correlation techniques to see if we can draw out two or three of those things and try to get some kind of a factor. Now, even if they draw this out, it will be related only to those products. If you have another set of products based on shale or on coal, I suspect that the same kind of thing would have to be done. But this would be an expensive project that would be taking place over several years. Just because the biologic activity information isn't complete, there are about fifteen or sixteen materials that you'd want to put into this package.

Pallay: There is also a NIOSH effort looking at shale workers as well, which I think I forgot to mention.

Sharkey: Several of us have alluded to the problem of instability of many of these coal-derived liquids at previous meetings. This is one of our main concerns. We're dealing with a very new coal-derived liquid and not something aged like petroleum. One of our major concerns is getting compositional data that are strictly irrelevant to the problems, and I think we have to keep this in mind. You can see major changes in viscosity with just minor heating above ambient temperature. Exposure to light, agitation, any of these factors can cause major changes. So I think it is very premature to attempt to extablish some one compound.

Runion: It is interesting you should bring this up. I was thinking about the fact that our people have warned me repeatedly that the character of samples obtained from certain phases of the process in SEC1 and SRC2 changes once the samples are removed and cooled. And, if you wish, the chemical half-life is very short. In the real world, it's there. The maintenance man or the operator may get that stuff on his body or may inhale it. But our people say, "We defy you to be able to capture this in a cylinder, get back to the laboratory, heat up the cylinder, and create that exposure experimentally.

Evans: At this point in the work that we're doing, I've got more questions than answers. One of the questions I have deals with the many lesions found in the Institute study. There was a tremendously large number found for such a small population. And yet, the work at SRC lasted about the same length of time but no lesions. Is it that we weren't looking for them? We are. And why don't we see them? Why is there a difference?

Runion: In terms of clinical experience with SRC, we've had two or three cases of transient photo dermalsensitization. No cases of cancer. One individual had cancer of the lip. This was associated with smoking and was so determined by a panel subsequently to the appearance of the problem. The only other thing, as I mentioned earlier that we've had some trouble with is this matter of phenol irritation of the eyes and to some extent transient cermal problems.

White: I would like to ask Jack Abrahams if he could provide a little more detail on Fossil Energy's industrial hygiene program. One of his slides showed the initiation of the industrial hygiene program in January 1978 and extending for several years. Can you give us a little more background on the plans or current activity?

Abrahams: The plans will depend somewhat on what will be called "Decentralization of Fossil Energy." The idea is to decentralize a lot of the responsibilities in the energy research centers. It would be looking at the energy research or pilot program which would be cost-shared with other functions. First of all, the energy centers would be operated the best we can. Then those programs would be developed along similar lines in the facilities. Now, we've got a rather unique situation of fossil energy, because almost all our facilities are cost shared, i.e., a lot of the facilities are completely funded by Fossil Energy but they're still operated completely by industry. So, in most cases, each of the industrial partners, whether it be Gulf or Exxon, has a plan or a system of its own. They are developing their own programs in the fossil energy program and not a program that Fossil Energy has imposed. At some time they will have to be merged into one program. We do want to keep the independent programs going but make sure that there is a minimum program that will be coming out of our association. So we will be developing something, I think, that is unique because we have such a very definite industrial input at this time. It should be emphasized that the pilot programs are just that. They are pilot programs. They're not necessarily representative of the demonstration problems. Many of the pilot programs are slowly phasing out. Some within the last several months. If there are no industrial hygiene programs there right now, we are trying to collect, particularly with NIOSH involvement in some of our facilities that are phasing out, as much information as we can. I would imagine that a whole industrial hygiene program may not develop in many of these cases. At what point do we develop a full-fledged industrial hygiene program when we have sizes all the way from process development studies to demonstration projects. We certainly hope that we have enough information to help demonstration programs that are underway and that we can have a comprehensive industrial hygiene program in demonstration plants.

White: I would suggest that the industrial hygiene involvement begins with the drawing of the ink into the pen used to layout the blueprint.

Bolton: No. It's before you start designing.

Evans: You have to realize that at one point the ink was made from coal. (laughter)

Abrahams: Some of the plants that we have right now were built quite a while back. The monies which were available all came out of the Office of Coal Research and there were virtually no funds set aside at that time for industrial hygiene studies except what may have developed subsequently. But, since that time, we have been looking as closely as we can at pilot plants. I think that in every case industrial hygiene information is being applied or designed in the demo plants. We're looking at two stages. Then again, I think we have some engineers who may argue about how much data obtained at a pilot plant you can use in the demo plant because it (pilot plant) is truly research. How much is scalable? If it is not scalable, you are not going to be using a particular process in the demo plant. It is interesting for the protection of the worker in that plant, but what does it do for workers in a demo plant? Why look at that plant as a demo plant if the demo plant is not going to have that particular process?

White: My reply to that comment is that in these plants you have a work force which is a group that should be kept under surveillance and they may provide answers long before commerical employees go through a latency period for some unsuspecting disease. In that way you may counteract or minimize the risk to those employees.

Abrahams: I think you miss what I'm trying to say. If the process in a pilot plant is only going to be used in the pilot plant, you should work for the protection of workers in that pilot plant, but you cannot scale that protection up to a demo plant because that process or that particular application may not be happening in a demo plant.

Runion: I think that one of the possible answers is that where there isn't direct conversion of knowledge from the pilot plant experience to the demo, those who need tha information are the industrial hygiene types. We are not just talking about PNA's and so forth, we're also talking about such rudimentary matters as noise so that when you start looking at big demo plants, you're wearing your industrial hygiene hat. You take the information you can from SRC1 and SRC2 with your other knowledge and other factors and put this into the design of the demonstration facilities. So one way or the other, there's going to be a large contribution from these small plants to the design of the commerical facilities.

Evans: An engineer, going from the bench scale to the pilot plant or from the bench scale to the 600 ton per day plant certainly has a mouthful of questions when he builds that pilot plant, but he uses as much of the data as he can, as carefully as he can, putting into the data what he knows or suspects will be the process configuration at the commercial plant. Obviously you are going to do some guessing. You're going to do a whole lot of guessing. It's better starting from zero.

Pallay: I want to reiterate that point. I'm Barry Pallay from NIOSH, and we strongly feel that way. We are going into coal liquefaction and gasification facilities, and we are going in with that attitude. If we understand the process, some of the parts of the unit, our scale calls for using that information but using it carefully.

Freeman: I have a comment and a question. My comment is derived from twenty years as a chemist working with coal and coal-derived products and has some bearing on what Howard Runion had to say. I am a little confused why apparently identical processes in the Pacific Northwest do not produce the same physiological results. We've had analyses of lignite seams where the chemical composition both inorganic and organic, from one side of a seam to the other, twenty yards wide, will vary significantly. I think this supports Dr. Beardsley's contention that we should be looking at organic contamination as a class rather than a distinct chemical material. Now, my question would be directed to Mr. Garcia. I notice in your slides, that you had drilling and blasting people running their trucks down unguarded mountain roadways, etc. Do you really expect that this population is going to survive (laughter) and see the industrial hygiene effects?

Garcia: The Paraho process is an experimental process. It is a shoestring operation and none of the things that you would expect in a normal control environment are found there. Ventilation in the mining area is never kept up to the face, etc. We're still in the initial stage of that study.

Audience: As far as I know, Paraho has been shut down, hasn't it?

Garcia: For some time.

Bolton: We're getting into an area that I like (laughter) obviously, and I would like to pursue it. In visiting industrial plants, I rarely find this situation not happening. I saw the same thing on the slides this morning. If there are not beards on those faces, they have the damnest contamination with polynuclear aromatic hydrocarbon that you ever saw. And yet, I see respirators required and so forth. Will the appropriate people comment on their respirator policy or respirator program? Do you permit respirators to be worn over beards?

Evans: Do you find respirators in lockers in the locker rooms?

Runion: We do not.

Bolton: This is a real problem because when you live within the DOE complex, you tend to think that everybody lives the way you do. All of the DOE facilities that I had the privilege of visiting have respirator programs, comprehensive respirator programs. It ain't so out there in the real world. It really isn't the same when you start talking about industry and using respirators, an adequate trained program and everything. It just don't get done out there. You know you're destroying some of my credibility as being in private industry at this point. I used to be DOE-inspired. Now I'm private industry. I'm faced with having to go into an industrial situation where the real important part is to make money at the end of the month. Not anything else, that's bottom line. And I've said: "Look, you need a comprehensive respirator program, and they see pictures in journals and magazines that show people with beards, you know, working in areas where respirators are required. Why, I have a lot of problems with credibility. You guys could help me.

Ettinger: Well, I think you as the industrial hygienist for industry have the choice of convincing the management of the plant that they can compare the cost of having an effective respirator program vs the cost of implementing engineering controls vs the cost of getting sued a few years in the future. They can make that sort of a management decision. Because if they are going to put respirators on people who have beards, they may as well not do it. It is all make believe. Twenty years ago that may have worked out fine--the make believe is there, the inspector goes away and it's done. But nowadays, when a guy dies, the first person a widow goes to see is probably the undertaker. The second one is a lawyer, and you know lawsuits are becoming a way of life. And if you've got an inadequate respirator program and management is well aware of the fact that it is inadequate, they run into trouble. They've got to balance those three things. Maybe they'll decide the lawsuit is the cheapest way to go. Or they've got their own ethical cares.

Bolton: I can convince my management. I don't have that problem. I'm just saying that I lose a certain credibility. Well, I'll give you a classic example. NIOSH sent a team of people to look at vinyl chloride, and they demand fresh air, and they have the longest, strangest beards, and the company, rather than take a positive stand allowed this. If I had been there, I would have said, "Okay boys, you can come in. You can wear this device, but you have to visit your barber first, you're going to have to shave off that adornment." But it's really put you in an adversary position. That's a real adversary position when you have to tell a government employee that he's got to do this before you let him in.

Hull: Well, of course a factor that wasn't referred to in this equation that I've seen way down the line is a sort of a national societal perception, particularly on the part of the small but vocal sector or subsector in our society that is not very happy about energy growth. If this business turns out to have a preceptible health cost, it is going to be in real trouble as is the nuclear business because the health cost can be alleged. And so in my perception, any management that is that callous is asking to be put out of business in the not very distant future.

Evans: On the respirator program, I know that SRC and Cresap both have a beard respirator program. You'd have a choice when you come into the plant, you can either not work there or you can shave off your beard. I got a lot of comments this past week when I was down there by the people. The only saving grace is that I was an engineer and I was not taking samples, not in the plant as much as my industrial hygienists who do not have beards.

Runion: In light of what you just said, I'd like to throw another question to the group. It has to do with the medical surveillance. Perhaps the panel would like to comment on their feelings in terms of the cost of a program and what DOE is proposing to do? I just wanted to get some sort of feeling because certainly it is a very large component of what we're talking about here. I just came from a conference of Occupational Health Society back West. The whole conference had to do with the legal aspects of medical surveillance in the areas that we are talking about, i.e., carcinogenic products and Workmen's Compensation. Certainly I think that this is something that we are well aware of. How are we going to solve the problem? What are your feelings about it?

Evans: I've got a personal comment. That is, before you start a medical program, the physician who is to operate the medical program must learn what he is dealing with. There are very few physicians who have any inkling of what they are up against in coal gasification, coal liquefaction, and oil shale program

Runion: I might add one thing too that has to do with medical directors. Many times when companies feel that they need a medical director; they also feel it has to be a physician. Would you like to comment on that too? Do you feel that a medical director has to be a physician?

Ettinger: To be totally consistent, the director of environmental health or whatever euphemism is used for that kind of department might not be a physician, but the medical director by definition is a physician.

Audience: I think the basic question is whether you think a medical director could work for an environmental scientist and direct the whole environmental safety program?

Audience: Yes, I guess you have to rephrase that because invariably you end up getting a physician to be a medical director and all he knows how to deal with are medical problems.

Runion: Again, back to good old SRC. Although my comments apply to our other enterprises, the coal and shale conversion business. All of these operations are under the direct surveillance and active participation of a Gulf physician. Dr. Peterson who was based in Los Angeles has spent many hours at SRC. He knows the plant very well and he has a firsthand working knowledge of the operation and has established a thorough medical surveillance program for all of the employees working there. And the same thing applies to our small pilot plant projects back in the Pittsburgh area and in Kansas. So, if this can be done and certainly I think this is true for Exxon; certainly firms of that size are paying attention to both sides of the equation, medical and environmental. You've got to work together.

Pallay: I'm almost afraid to participate. I am from NIOSH, and I have a beard, but I do want to comment that we are developing medical protocols for the coal conversion industry. That is a project. It is underway. I guess I would like to ask about any kind of record keeping that the companies are involved in now that are relevant to that.

Brief: I think that we are drifting so far away from our objective that we're missing the point.

Ettinger: I have a question as a member of the committee that has to sit here Wednesday and do something. I would like to ask the eleven or so people up front if they can make any specific comments relative to the monitoring requirements for coal conversion and oil shale industries. I know we've drifted on a lot of occupational and safety things, and they are kin of interesting to me. Since I've got to be here Wednesday and Otto is going to make me write something, I'd like to see if we can get some comments on this. I know Leroy had one viewgraph about some of the things that he perceived as needs in sampling on the basis of his experience on the Paraho facility. I would like to ask the panel whether there is anything they can toss out in terms of things that should be developed, whether it is sampling instrumentation, analytical procedures, techniques, etc.

Bolton: Would you like to take this in order or would you just like to volunteer?

Evans: I seem to stick my neck out further than most people. I think that the list that was presented was a good start. As a chemical engineer rather than an industrial hygienist, it is my feeling that in this field especially the multiplicity of potential problems we have in coal conversion are pretty permanent: monitoring techniques, availability of instruments, analytical techniques, etc.

Bolton: Anybody else on the panel want to comment?

Runion: This is no different from all the other things that we've been concerned with. The need for an instrument that is easy to wear, that gives you either long or intermittent readouts is something that we all want not only for coal conversion products which are particulates, gases, or vapors. We want the same thing in every oil refinery and in the steel mill. I think that what we need in terms of defining the nature of the beast and how hard it's going to bite is some better relationship between the substance there and what it means biologically. I think we're dealing with some fundamentals that are missing. I think that the gentleman who spoke of using benzene-soluble fractions as an index hit it on the head when he made the observation that we all want to (and we do) find some sort of tactic or group of tactics, if we can find them; then we can sharpen our sampling and analytical tools to zero in on the one, two, or three. But in the absence of more definitive information that pertains to these mixtures, I don't know that a lot of new tools peculiar to this particular industry, this particular problem, are called for. They are called for not only in this business. They are called for in oil refineries, steel mills, and so on.

Audience: I didn't have a question. I just wanted to point out that the system has the same problem as you do, those of you who are industrial hygienists. For instance, you refer to the vinyl chloride industry. A physician who was a medical director in that particular plant didn't know what he was looking for and even now it is difficult for the medical profession to survey these employees without perhaps performing a liver biopsy every year to find out if workers are getting cancer of the liver. I think the industrial hygienist has to have communication with the medical director to say, "in Building B we're experiencing a high level of respirable particulates." Perhaps he goes to the literature and sees that this particular partiuclate has a high percentage of asbestos, iron, and whatever. He needs to know what biological response to look for. You need to collect this information so that he can find out what he's looking for. For instance, I think that the most important thing in every industry is to perform base line studies when the worker comes in. Okay, it is hard to know what to look for. Right now you look at things like pulmonary functions, blood studies, urine. If you have these base line studies, then if the problem does arise, you have data to work with.

Bolton: I think the converse of what you are saying is just as important: for the physician to tell us he has seen something bizarre that he can't explain and for us then to go and look for it.

Vo-Dinh: Well, I have a comment. It's about the need to have proxy compounds and benzene-soluble fraction analyses. I think it is very useful to have these analyses as well as very thorough analyses of the sample to get detailed data. Let me for just a moment mention as Jim Evans has that there is a need for a real-time in situ monitor and we have the state of the art for the instrumentation, and in the next five to ten years we can expect to have a monitor which can measure 20 to 40 compounds at the same time. So we have to stick out our necks and apply our knowledge to define the types of compounds, maybe not one or two, but a half dozen so that the analytical chemists can develop analyses along those lines for the next five or ten years. Because after five or ten years, we will get epidemiological data to correlate to the real-time results.

Campbell: I have one comment relating to Harry's question about need. I hope to make this conclusion tomorrow in my paper. I think we have the technology available to develop sampling techniques and analytical techniques. The need right now is to develop a united front and work together. Howard Runion and his people have developed good sampling and analytical techniques for some of their work, and I think maybe the committee can use its position to start designating directions and areas which require more effort.

Lippmann: I share Harry's apprehensions about Wednesday since I have to be there with him. After listening quietly today to a lot of information and some things that weren't information, I suggest that everybody here look at the interim summary that Otto has passed out with the registration materials. Recognizing a lot of ignorance, those of us on this committee put our heads together and came up with this. I'm really frustrated because I don't know any more today than I knew when we wrote this a few months ago and I wonder if anybody else in the committee feels as I do that we're spinning our wheels and that this day has not been very productive. I'm not sure that it is anybody's fault. I think that we are all confronted with the same large body of ignorance. We have no concept in the world of an indicator chemical that is better than BAP, but we know that BAP isn't any good. If we measure soluble, we measure everything. We may as well not bother with the benzene and just weigh everything. I'm not sure that's any good. And so, we have no idea and we certainly won't be any better off in five or ten years from now. We probably won't have any disease because we are all so frightened of cancer that we're going to have processes that are pretty tight. So, I think it's very difficult to define the monitoring needs except for indicative things like carbon monoxide which can be measured and used to tell us if the processes are leaking. If the process is leaking, we'll just tighten it up. I'm not sure that we need any instrumentation at all in this field, and I'm not going to vote for recommending millions on instrument development when I don't see that it will be productive at all.

Bolton: Carbon monoxide is the one indicator that we recommended, by the way, at the University of Minnesota. It seemed to be a reasonable approach. It's common to all the streams. If you've got CO out, it's an indication that you've got a leak.

Hull: Well, I'm listening to this with fascination as a health physicist. You always sought background with good engineering practices as a qualitative thing to help monitoring practices and good sampling practices, as a certain state of the art. And if you are pursuing that with a reasonable amount of diligence, you are stuck on what the trade offs are. You know in radiation you can make a wild guess at what the value of eliminating a person-rem is, but in this business you can't engage in things of that sort. But aren't you stuck with being pretty qualitative and again I guess as I already heard that there is a parallel in the close range of radioactivity. You know for most real-time monitoring purposes you can't get much beyond that unless you want to spend a lot of money is some particular process and you are focusing right on one particular nuclide. But short of that you tend to go to rather close methods because these are the only things you can do with reasonable cost. Then you can do some sampling back in the laboratory as a backup. That's one comment. If no one wants to respond to that now, I have one more comment. Does anyone want to say anything about this now on the panel?

If you want to know if you can do any more, I sort of hear somebody saying, "Well, you ought to develop some instruments rapidly." I haven't the foggiest idea from listening to this discussion today what you should do, but I've been trying to pay attention to it.

Bolton: If I could take the chairman's perogative and make one comment quickly, I read preliminary reports of the committee. Frankly I didn't think it was all that bad. Now, in my opinion, if this meeting only reinforces that fact that that wasn't too bad a protocol, the meeting will have been worthwhile if you think about it.

Evans: On the carbon dioxide-H_2S indicator, there is one problem. We really don't know how closely we could use it as an indicator. We've been thinking about this for a couple of years. It really needs some work. I hope that is what's going to be done.

Audience: We've been talking about a CO monitor for coal gasification. You're not going to follow a coal liquefaction facility with a CO monitor and feel comfortable. Let's be sure we understand that.

Runion: That's what I was going to say. I wouldn't buy that for a minute in terms of SRC. We've got carbon monoxide here and we also have hydrogen sulfide, but that's no way of handling the problem.

Ettinger: I guess I should come back, reword my question, and direct it to anyone on the panel. I think Howard Basically said he thought that coal conversion is no different from other industrial hygiene sampling problems, and that might very well be true.

Runion: It isn't even different when we talk about the steel industry.

Ettinger: Yes, I'll accept that as a possible answer. My question now concerns sample needs in general. In which areas do you feel there are great needs: real-time monitors, high technology, low technology? People get carried away with high-technology sampling. Maybe we need low technology. I hope Ed Palmes doesn't take any offense, but I would consider a passive sampler as low technology but very very useful. It is cheap. You can place it on a person and you don't have to do anything with it. Yet it is not a high-technology real kind of readout system. What do we need? Looking at it from your point, what are the biggest needs in air sampling requirements, whether for oil shale, coal liquefaction, coal gasification, or the steel industry?

Craun: I'm not on the committee. I am an industrial hygienist who has been asked to come in and talk about coal gasification. Certainly, I heard people talk about indicator compounds like CO and BAP. Perhaps I could, as an outsider, try to tell you some things I have heard come out today that partly reflect my own concerns. As far as indicator compounds, it's always been spoken of here in the singular--indicator compound one, two, or three. If you're going to spend the money to develop that kind of technology, perhaps it ought to be stated that it might be useful to develop it for indicator classes, that is benzene solubles, only perhaps more refined classes such as nitrogen heterocyclics, etc. The second is that given a lot of uncertainty about sample stability, the uncertainty of about the use of indicator compounds, the uncertainty about how tight your controls are, etc. I would offe the fact that in many ways, pilot and demonstration plants are, even if not scalable, they are very nice places to start to address some of those questions, develop methods on samples which are perhaps not exactly indicative of what you'd see commercially but are probably better samples than you can create in a laboratory trying to figure out whether or not the box is really going to work. These plants give us an opportunity to try to figure out whether or not you can really sample a high pressure process gas or characterize tars that by the time you get to the laboratory will have cooled and condensed. It's a place to look at possibly the performance of existing kinds of equipment for sampling fugitive emissions versus what can be developed.

Fraser: As one of the committee members who unfortunately had to miss the second meeting of the committee in Pittsburgh, I would like to comment that today's program has been most enlightening to me and most valuable. I am grateful for it. I'm wondering if any of the panel can give us any idea as to how much of our problem is related to, say, the primary process, as compared to general housekeeping, secondary processes, disposal of effluents, and this sort of thing. Is our major problem really going to be the primary process scaled up to a demonstration level? I'm wondering just what our problem is going to be.

Runion: There is a little bit of mental telepathy. One of the things that struck me at least with respect to our operations is that although we spend a lot of time concerning ourselves with our airborne PNAs, when you get right down to it, the people who find themselves most deeply immersed, if you wish, in these materials, are the maintenance people; and you find this is skin contact and this is conjecture on my part, but maybe some of the problem is dirty hands and what have you. You can't discount inhalation, but you know, and I'm guilty just like everybody else, we spend an awful lot of time in air sampling. I think to some extent it's because we have something there we can measure and we we have some criteria. Whether we like it or not, we can go back and look at it and say, "Ha! We are or we're not in trouble." Skin contamination is yet to be quantified. It seems to me that this is one area that we all have got to focus on. How we are going to handle it? How much is too much in terms of skin contamination? It's easy to say, "Howard, you can wash it off," but you could have said that 50 years ago about inhalable contaminants. But we did come around to finding ways and means of measuring inhalable contaminants, controlling them, and getting some quantitative handle on how much is too much for inhalation. Is it not possible to do something of the same nature in terms of skin contamination?

Bolton: I think we had better think about quitting. I will close this session by saying, "Don't get so wrapped up in the science that you forget the objective. The objective is to protect the people by whatever means you choose, but protect the people." You are adjourned.

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ADEQUACY OF CURRENT DOSIMETRY TOOLS FOR THE COAL CONVERSION AND OIL SHALE INDUSTRIES

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ADEQUACY OF CURRENT DOSIMETRY TOOLS FOR THE COAL CONVERSION AND OIL SHALE INDUSTRIES

The chemical hazards that employees are potentially exposed to in the coal conversion and oil shale industries are many and varied. They range from gaseous compounds, H_2S and CO, to heavier polynuclear aromatic hydrocarbons (PNA) and intermediate or lighter weight organics such as pyridine, benzene and naphthalene. The sampling techniques and instrumentation for measuring these chemical stresses are also of a wide variety. This presentation will be limited to a discussion of the current state-of-the-art techniques available for personnel monitoring of coal tar pitch volatiles.

The PNA exposure to workers in coal conversion and oil shale industries must be evaluated. Not only must personal exposure potential be quantified, it is also necessary to properly evaluate the effectiveness of engineering and other control measures. A third reason for evaluating the individual workers exposure is to comply with regulations.

Since the individual's personal exposure is of primary concern in the evaluation of the PNA hazard, it is pertinent that any sampling technique used for this purpose be capable of determining time-weighted average concentrations at the worker's breathing zone. The sampling device must be light and compact. One of the main hazards of the polynuclear material found in coal tars is skin cancer from contact of the material with the intact skin. The air sampling capabilities necessary for determining breathing zone exposures do not reflect the extent of exposure to the individual's skin. Because of this, a method for monitoring PNA contamination of exposed skin areas is necessary to totally evaluate the worker's exposure. This paper will discuss the NIOSH-approved method for determining breathing zone exposures to coal tars and reflect on some ideas related to longwave ultraviolet light surveillance of exposed skin.

NIOSH has recommended the use of the cyclohexane soluble fraction total particulate matter (CSFTPM) method for evaluating the breathing zone atmosphere of workers exposed to coal tar products.(1) Previous recommendations suggested the benzene soluble fraction, but because of the inherent hazards related to benzene, the less toxic cyclohexane is now being recommended. The standard has been reduced from 0.2 mg/m^3 for the benzene soluble to 0.1 mg/m^3 for the cyclohexane soluble. The following is the recommended procedure for determination of worker exposure to PNA-containing particulate matter.

Full-shift (8-hour) samples should be collected with a personal sampling pump at a flow rate of 2 liters per minute. Samples should be collected on 0.8 micron pore size silver membrane filers (37 mm diameter) preceded by Gelman glass fiber A-E filters encased in three-piece plastic (polystyrene) field monitor cassettes. The cassette face cap should be on and the plug removed. The rotometer should be checked every hour to ensure that proper flow rates are maintained.(2)

Cyclohexane extraction of collected material using ultrasonic techniques is recommended. After the extract has been evaporated down to 1 ml, 0.5 ml of it is pipetted into a pre-weighed teflon weighing cap and evaporated to dryness in a vacuum oven at 40^{0}C for 3 hours. The extract is then weighed on an electrobalance to the nearest microgram.(2)

The CSFTPM method discussed has some disadvantages. The sensitivity of the analytical method is low, resulting in the need to make eight-hour samples. Peak exposures for short periods of time are difficult to determine using this method. At the TLV an eight-hour sample just reaches the lower level of detectability. There have been many questions raised about whether the silver membrane filter is a functional part of the system. One investigation determined that there was no breakthrough of particulate matter through the glass fiber to the silver membrane. This was determined by separate analysis of the two filter media.(3) Another question has been raised about using the silver membrane in areas where H_2S is present. The silver may react with H_2S forming A_gS and clog the pores, making the filter ineffective.(4) H. J. Seim et al(5) believe that the plastic cassette adsorbs some of the low molecular weight volatiles. For their studies they used machined aluminum cassettes to eliminate this potential error.

Another area of great concern is the breakthrough of low molecular weight volatiles. Significant amounts of low molecular PNA's have been found in the backup cellulose support pads.(5) Other evidence of breakthrough problems have been found by Jackson and Cupps.(6) Solid sorbent materials such as Tenex GC, Chromosorb 102 and XAD-2 have been suggested as a third stage in the sampling train to collect any breakthrough material from the filters. The significance of the breakthrough problems needs to be defined and, if necessary, a standard sampling technique developed.

Another significant problem associated with the NIOSH recommended method is the variability of the sampling efficiency. The sampling efficiency is dependent on the amount of particulate present in the air. At high particulate loadings, most of the PNA's are retained on the filter because they adsorb to the particulate. At low loadings it has been found that the backup pad will contain more PNA's than the filter. What this means is that the filters have a continuously variable collection efficiency that is dependent on the nature and the quantity of the particulate.(5)

Despite these disadvantages, the CSFTPM method is the only method available for breathing zone sampling of coal tars. Before this technique can be considered a reliable method for the evaluation of individual worker exposures, many of its problems must be investigated. The inherent errors, such as those relating to sampling efficiency, must be defined and standardized. The effectiveness of the silver membrane must be investigated. If the silver membrane does not increase the sampling efficiency of the system, perhaps it should not be included as part of the system. The use of solid sorbents should be further investigated and made part of the standard system. A combined effort between government and industry is necessary to develop a standardized sampling technique, otherwise, it will be difficult to correlate data obtained from different processes.

The potential for exposure via the respiratory route is a very real problem but surveying exposed skin areas for contamination by coal tars is another important area of personnel monitoring that must be discussed. Longwave UV light monitoring of skin is a technique that has been used to determine the extent of contamination. This practice has come under considerable criticism by some in the field of industrial hygiene. NIOSH does not endorse this technique because of the potential co-carcinogenic effects between UV and PNA's. Although this technique may have some risks involved, it also has some benefits. Primarily, it is a quick and easy technique and is reassuring to the worker to go home every day knowing he has not been contaminated by PNA's. Others say that the deleterious effects of the PNA's occur so rapidly that any screening mechanism, including UV light, is of little benefit at the end of an 8-hour shift. Research in this area is necessary to determine the risk vs. benefit of U.V. skin surveillance. Research should also be conducted to develop similar monitoring techniques that do not pose the potential hazards UV surveillance does.

The determination of personnel exposure to PNA's in the breathing zone is essential. At present, the NIOSH-recommended method may not be completely acceptable, but it is the best method available. Much work is presently being conducted on developing more sensitive analytical techniques for determination of PNA's. With the large errors that seem to be inherent in the sampling technique discussed, these more sensitive analytical methods may be of little value. The primary area of concern is the standardization and development of a good sampling technique to determine breathing zone, time-weighted average concentrations of potentially exposed workers in the coal conversion and shale oil industries.

REFERENCES

1. Federal Register, 1976 c.

2. National Institute for Occupational Safety and Health: Criteria for a Recommended Standard.... Occupational Exposure to Coal Tar Products. Cincinnati, U. S. Dept. of Health, Education and Welfare, Public Health Service, Center for Disease Control, NIOSH, 1977, p. 165.

3. Ealy, J. A.: Personal communications, Oak Ridge National Laboratory, 1978.

4. Evans, James: Personal communications, Enviro Control, Inc., Rockville, MD 1978.

5. Seim, H. J., Hanneman, W. W., Barsottli, L. R. and Walker, T. J. (1975): An Initial Study of Factors Affecting the Collection of Coal Tar Pitch Volatiles (CTPV) in Air. Presented at the 1975 American Industrial Hygiene Conference, Minneapolis.

6. Jackson, J. O. and Cupps, J. A.: Field Evaluation and Comparison of Sampling Matrices for Polynuclear Aromatic Hydrocarbons in Occupational Atmospheres, Carcinogenesis, Vol. 3: Polynuclear Aromatic Hydrocarbons, edited by P. W. Jones and R. I. Freudenthal. Raven Press, New York, 1978.

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Criteria for Occupational Health Monitoring in the Fossil Fuel Conversion Industries*

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Presented at the
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Coal Conversion and Oil Shale Industries"
Brookhaven National Laboratory
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*Work performed at Brookhaven National Laboratory under contract with U.S. Department of Energy

Criteria for Occupational Health Monitoring in the Fossil Fuel Conversion Industries*

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The occupational health professional is being confronted with the monumental problem of identifying and evaluating the potential health hazards associated with the emerging fossil fuel conversion industries. The problem is enhanced by the complex composition of the base materials. Wiser's (1) proposed structure of coal (Fig. 1) contains many analogs of known hazardous organic compounds (Fig. 2). Coal also contains many metals with known health consequences (Table 1). Kerogen, the base material for the oil shale industry, also represents a structurally complex material as illustrated by the reduced chlorophyllin model proposed by Jackson and Decora (2) (Fig. 3). Kerogen's pyrolysis products are comparable with their toxic counterparts derived from coal.

Treatment of these base materials, which vary widely in carbon to hydrogen ratios as well as distribution of trace elements, with heat, pressure and various gas and solvent streams results in the generation of a host of chemicals which produce health effects ranging from simple asphxiation to cancers and death. Characterization studies of process and effluent streams have identified a host of chemicals which are known or suspected to be hazardous to man (Fig. 4).

Although the works of Potts (3), Volkmann (4), Butlin (5), Lueke (6), Henry (7,8), Kurado (9), Telekey (10), the Kenneways (11,12), Doll (13,14) and Lloyd (15,16) when studied chronologically, represent a very strong case in demonstrating a positive relationship between increased cancer incidence and exposure to certain fossil-derived materials, the absence of a strong epidemiological base does not permit the traditional assignment of priorities for occupational health protection.

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*Work performed at Brookhaven National Laboratory under contract with U.S. Department of Energy.

The mandate to provide workers in the coal conversion and oil shale industries a safe and healthy work environment is clear. Protection of this workforce will require monitoring for the following purposes:

1. Health hazard evaluation
2. Performance trends in engineering controls
3. Development of design requirement for new engineering controls
4. Documentation of exposure levels
5. Compliance determination
6. Measurement of process losses
7. Selection of suitable respiratory protection devices
8. Identification of contamination sources
9. Assessment of emergency conditions
10. Establishment of baseline data

The focus of this paper is to provide the occupational health professional with a criteria that will assist in establishing priorities in occupational health monitoring programs for the synthetic fuel industries. Elements which must be considered in establishing monitoring criteria are as follows:

1. Identification of hazardous operations and processes
2. Hazard classification of contaminants
3. Identification of workforce members at high risk
4. Total risk assessment involving all occupational safety and health hazards
5. Monitoring strategy

Identification of Hazardous Operations & Processes

Characterization studies of process and effluents streams can provide much information relating to the prioritization of those operations and processes which pose predictable levels of risk. Not only must the chemistry and the physics be known but also the engineering. Failure rate of pumps, valves, pressure relief devices, components fatigue and failure histories are required to accurately identify the system's hazards.

Job safety analyses deploying a system's approach will identify hazards often overlooked. Not only must attention be focussed on process feed material, product and waste streams, but also additive streams, catalyst beds and scrubbing solutions. Maintenance procedures as suggested in the "Recommended Health and Safety Guildlines for Coal Gasification Pilot Plants" (17) should be reviewed in detail to determine the degree of hazard associated with all stages of the operation. Exposure of workers to O_2 deficient or contaminated vessels may undermine all the efforts put into a monitoring program capable of quantification of all isomers of dimethylbenz(a)anthracene.

A Fossil Energy Report—FE-2213-1 (18) entitled, "Carcinogens Related to Coal Conversion Processes" summaries two documents which addressed hazards associated with coal conversion processes:

1. Battelle Energy Program Report on Carcinogenic Potential of Coal and Coal Conversion Products concludes:
    a. Elimination of spills and leaks should minimize carcinogenic exposures in coal gasification systems. Crude gas containing tar, oil, sulfur compounds, etc., may create carcinogenic hazards which may be reduced by appropriate health and engineering measures.
    b. Proper engineering in coal liquefaction systems should attenuate the carcinogenic risk associated with some high molecular weight aromatics in distillates, centrifuged oils and centrifuged cake residues.

   c. Precautions should be exercised in solvent-refining operations and in avoiding contact with process streams, filter cakes, recycled solvents and liquid coal.

2. Battelle/Radian Document on Potentially Hazardous Emissions from the Extraction and Processing of Coal and Oil Conversion Products describes the results of an examination of the two coal conversion systems in which 25 process steps were reviewed. It's conclusions were:

   a. Coal gasification is likely to produce dangerous substances which can be contained, thereby minimizing emissions.
   b. Quenching and cooling of gasifer off-gases and tar separation are important potential sources of toxic emissions.
   c. Liquefaction products may be dangerous but more containable than gasification products.
   d. Potentially significant emission sources in liquefaction are the slurry preparation and fugitive losses from leaks and equipment failures.
   e. Liquefaction products are potentially more hazardous than crude oil products. Refining and utilization are likely to be worse offenders than the corresponding petroleum operations.

Similarly, FE 2213-1 suggests that hazards associated with coal conversion process relate (a) to possible exposure of worker and the general public to process and waste streams, (b) to occupational exposure during handling and utilization of products, and (c) to environmental exposures to combustion emissions and coal derived products. It concludes that adequate protection against exposure can be obtained by proper design and operation of coal conversion plants with emphasis on material handling, industrial hygiene practices and control methods to minimize spills, leaks and emissions.

Identification of Workforce Members at High Risk

Once the processes and operations which pose potentially significant risk have been identified, the next logical step is to review the duties of all members of the workforce which interact with the system. From supervisory through maintenance personnel, exposures to the processes and operations must be reviewed to identify their specific duties, exposure time, associated equipment/material utilized to accomplish required tasks and specific work environments. Sampling and testing procedures may result in the release of significant quantities of toxic materials into the work environments of an ordinarily enclosed system. Certain maintenance operations may require a different workplace to accomplish the required task such as degreasing tanks and sand blasting booths. Improper emphasis to these situations may expose workers to unnecessary concurrent hazards.

Identification of the employees at highest risk takes on another connotation other than the employee who received the highest exposure, who is in contact with the system for the longest period and who is least knowledgable of the potential hazard. Employees who are predisposed to increased risks due to physical conditions, medication requirements, cosmetic and grooming preferences, poor hygienic practices and heriditary factors must be identified, informed and educated to the enhanced risk. To complement this task, a positive medical surveillance program which includes pre-employment physicals as well as periodic followups is required.

Hazard Classification of Contaminants

Hazard classification of contaminants in the work environment is essential to the establishment of occupational health monitoring programs. Knowledge of the pollutant species, acute and chronic toxicological properties, potential quantities, mode of dispersion, mode of exposure, physical and chemical properties, metabolic fates, threshold levels, environmental fate, synergistic and antagonistic properties are all ideal parameters that would assist in the development of a hazard classification scheme. Obviously, with such formidable lists of potential pollutants as have been demonstrated through the various process and effluent characterization studies, much of this preferred information is not available and may even hamper the decision process if relative weights are not assigned to each parameter.

A simple scheme such as the workplace selection standard utilized at Brookhaven Laboratory could be used with an acceptible degree of confidence (19). A typical approach would be the following four category scheme:

A. Immediately Hazardous to Life and Health

This category would include those materials which are present in sufficient quantities that acute exposure could occur and that the health and/or safety effects associated with this exposure could result in immediate and/or serious impairment to life and health. Examples of this category include the following materials:

1. H_2S - acute poison >400 ppm, affects central nervous system and induces respiratory failure
2. CO - acute chemical asphyxiant
3. NO_x-NO_2 - delayed pulmonary edema
4. O_2 deficiency
5. Coal and shale dust - explosion hazard
6. H_2 - explosion hazard

Phenols, hydrogen cyanide, metal carbonyls and carbon disulfide would also be placed in this category if present in significant quanties.

B. High Risk, But Not Immediately Hazardous to Life

This category is reserved for substances which cause delayed irreversible effects and which are not present in sufficient quantities to produce acute toxicological effects. Examples in this category include the following:

1. Aromatic Amines - aniline, β-naphthylamine, benzidine, etc.
2. Aromatic Hydrocarbons - benzene, xylene, toluene, etc.
3. Heterocyclic Aromatics - pyridine, acridine, dibenzofuran and dibenzothiophene
4. Nitrosamines - dimethylnitrosamine, diethylnitrosamine, etc.
5. Polycyclic Aromatic Hydrocarbons - 3-methylcholoanthrene, benzo(a)pyrene, etc.
6. Certain Metals - arsenic, beryllium, cadmium, chromium, nickel, etc.
7. Certain Fibers and Dust - asbestos and silica

C. Moderate Risk and Not Immediately Hazardous

This category could include, in addition to some of the above substances/classes which are not present in the work environment in significant quantities, those compounds which cause reversible toxicological effects. Examples in this category would include the following:

1. Sulfur Oxides
2. Ammonia
3. Paraffins

D. Low Risk

This category is reserved for those chemicals which poses low or nuisance type health hazards. Examples would include the following:

1. Carbon Dioxide
2. Nitrogen
3. Steam

Risk Assessment Involving All Occupational Health Hazards

Very little discussion has been focussed toward the fact that the processes and operations in the fossil conversion industries will represent sources of high noise generation and of high temperature emitters, that maintenance activities will require entry into confine spaces, that fire and explosive hazards will co-exist with carcinogenic hazards, and that exposure via contact is likely to be as significant as inhalation. Using the methodology of risk evaluation as proposed by Herbert Inhaber (20) of the Canadian Atomic Energy Control Board, all components which contribute to the risks of accidents, disease and death incurred in producing a gallon or cubic foot of converted fossil fuel must be taken into account. The forest versus the trees syndrome is a real potential in this instance where an overwhelming accumulation of data from process and effluents characterization studies have identified the presence of carcinogenic chemicals and biological test results support these analytical findings. Prior to the establishment of occupational health monitoring efforts, experience dictates that emphasis be placed on the major contributors to the overall workplace risk and that stripping this risk of its components should identify areas for implementing engineering controls. Those areas which engineering control cannot adequately reduce risk warrants monitoring. When the risks are associated with health effects, key areas for occupational health monitoring have been identified.

Monitoring Strategy

If one starts with the premise that the major purposes for occupational health monitoring for these emerging industries are (1) to ensure that the employees are provided a safe and healthful work environment, (2) to identify and evaluate health hazard, (3) to document exposure levels, and (4) to determine compliance status, immediate considerations must be given to the following factors when establishing the monitoring strategy:

A. Selection of Parameters

B. Monitoring Frequency

C. Types and Numbers of Samples

D. Analytical Treatment

E. Value and Use of Analytical Results

Selection of the parameters which warrants monitoring should be determined from the risk evaluation discussed previously. Decisions to use proxy or indicative parameters should reflect their ability to accurately quantify the risk component at issue. Monitoring tools which measure several parameters may provide a more accurate description of the workplace conditions than single index devices. Minimal programs must monitor those substances in the work environment for which safe level, compliance limits and human health effects are known. For those parameters for which no limits exist nor safe level identified, the use of a tiered program as suggested by Bora (21) and Dean (22) could assist in the decision process.

Monitoring frequency should be a factor of the hazard classification, the variability of the environmental conditions, the economy (time and dollars) associated in obtaining a result, and the potential for workplace conditions degrading into serious adverse levels/situations. The availability of real time, continuous monitoring devices as opposed to time consuming grab samples with subsequent lengthy analytical procedures will often assist in the decision process.

Determination of the types and the numbers of samples to collect will be dictated by many of the above factors in addition to the mobility of the workforce and the constraints of the workplace. Area sampling could be used advantageously in areas where the variability of the contaminant is low but could be impractical for most outside areas which are susceptible to broad meterological variants. Personal sampling may solve some of these problems, but will greatly increase the number of samples because a representative number of the workforce must be sampled and the collection limitation of the sampling tool may inhibit the application of several analytical techniques to a given sample. Often overlooked in monitoring strategy is the usefulness of bioassays and surface contamination monitors.

Hi-volume area sampling should be an initial choice in characterization of the workplace atmosphere followed by detailed and specialized analytical procedures. This initial effort should cover not only normal conditions, but also maintenance and downtime situations. A relatively few of these samples will permit the health professional a greater insight into potential problem areas. Consequently, the analytical treatment will depend upon the value and use of the results. Characterization studies requiring sophisticated treatment cannot be equated to real time, continuous and/or direct reading devices.

Occupational health monitoring for the coal conversion and oil shale industries will represent the greatest challenge to date for the occupational health professional. The requirement to use all the tools, knowledge and experiences obtained in the past and apply them to this frontier dictates that initial broad criteria be used to minimize the chance that some unturned leaf does not conceal future compensation liabilities equal in magnitude to the black lung and the asbestos problems.

References

1. Wiser, W. H., "Some Chemical Aspects of Coal Liquefaction. In paper--Short Course on Coal Characteristics and Coal Conversion Processes, 1973, Pennsylvania State University, University Park, Pennsylvania.

2. Jackson, L. P. and Decora, A. W., "Thermal Reactions of Shale Oil Components: Plant Pigments as Probable Precursors of Nitrogenous Compounds in Shale Oil", BM-RI 8018, 1975, U.S. Department of Interior, Washington, D. C.

3. Pott, P., 1775, "Cancer Scroti" in Chirurgical Observations, Hawes, Clarke and Collings, London, pp. 63-68.

4. Volkmann, R., 1875, "Beitrage Zur Chirurgie", Druck and Verlag von Breitkepf and Hartel.

5. Butlin, H. T., 1892, "Cancers of the Scrotum in Chimney Sweeps and Others", Brit. Med. Jour. 1, pp. 1341-1346 and 2, pp. 1-6, 66-71.

6. Lueke, A. W., 1907, "Epithelioma in Carbon Workers", Cleveland Med. Jour. 6, pp. 199-202.

7. Henry, S. A., Kenneway, N. M., Kenneway, E. L., 1931, "The Incidence of Cancer of the Bladder and Prostate in Certain Occupations", Jourittyg (Camb.), 31, pp. 125-137.

8. Henry, S. A., 1946, "Cancer of the Scrotum in Relation to Occupation", London, Oxford University Press.

9. Kuroda, S. and Kawahata, K., 1936, "Uber die gewerbliche Entstehung des Lungen Krebses bei Generatorgasarbeitern", Z. Krebsforsch 45, pp. 36-39.

10. Telekey, L., 1937, "Occupational Cancer of the Lung", Jour. Ind. Hyg. Toxicol., 19, pp. 73-85.

11. Kenneway, N. M. and Kenneway, E. L., 1936, "A Study of the Incidence of Cancer of the Lung and Larynx", Jour. Hyg. (Camb.), 36, pp. 236-267.

12. Kenneway, N. M. and Kenneway, E. L., 1947, "A Further Study of the Incidence of Cancer of the Lung and Larynx", Brit. Jour. Cancer 1, pp. 260-298.

13. Doll, R., 1952, Jour. Ind. Med., 9, p. 180.

14. Doll, R., Fisher, R. E., Gammon, E. J., et al., 1965, "Mortality of Gasworkers with Special Reference to Cancers of the Lung and Bladder, Chronic Bronchitis and Pneumocomiosis", Brit. Jour. Ind. Med., 22, pp. 1-12.

15. Lloyd, J. W. and Clocco, A., 1969, "Long Term Mortality Study of Steelworkers: I. Methodology", Jour. Occup. Med., 11, p. 229.

16. Lloyd, J. W., 1971, "Long Term Mortality Study of Steelworkers: V Respiratory Cancer in Coak Plant Workers", Jour. Occup. Med. 13, p. 53.

Ref. continuation

17. National Institute of Occupational Safety and Health, 1978, Recommended Health and Safety Guidelines for Coal Gasification Pilot Plants, DHEW (NIOSH) Publ. No. 78-120, NIOSH, Rockville, Maryland.

18. Energy Research and Development Administration, 1976, Carcinogens Relating to Coal Conversion Processes, FE-2213-1, ERDA, Washington, D. C.

19. Laboratory Workplace Standard for Nonradioactive Toxic Substances, 1977, Brookhaven National Laboratory Safety Manual, Occupational Health and Safety Guide #2.2.1, BNL, Upton, New York.

20. Inhaber, H., "Risk of Energy Production", Atomic Energy Control Broad, Ottawa, May 1978, Report AECB-1119/Rev. 1.

21. Bora, K. C., "A Heirarchical Approach to Mutagenicity Testing and Regulatory Control of Environmental Chemicals", Mutation Research, (1976), 41, pp. 73-82.

22. Dean, B. J., "A Predictive Testing Scheme for Carcinogenicity and Mutagenicity of Industrial Chemicals", Mutation Research, (1976), 41, pp. 83-88.

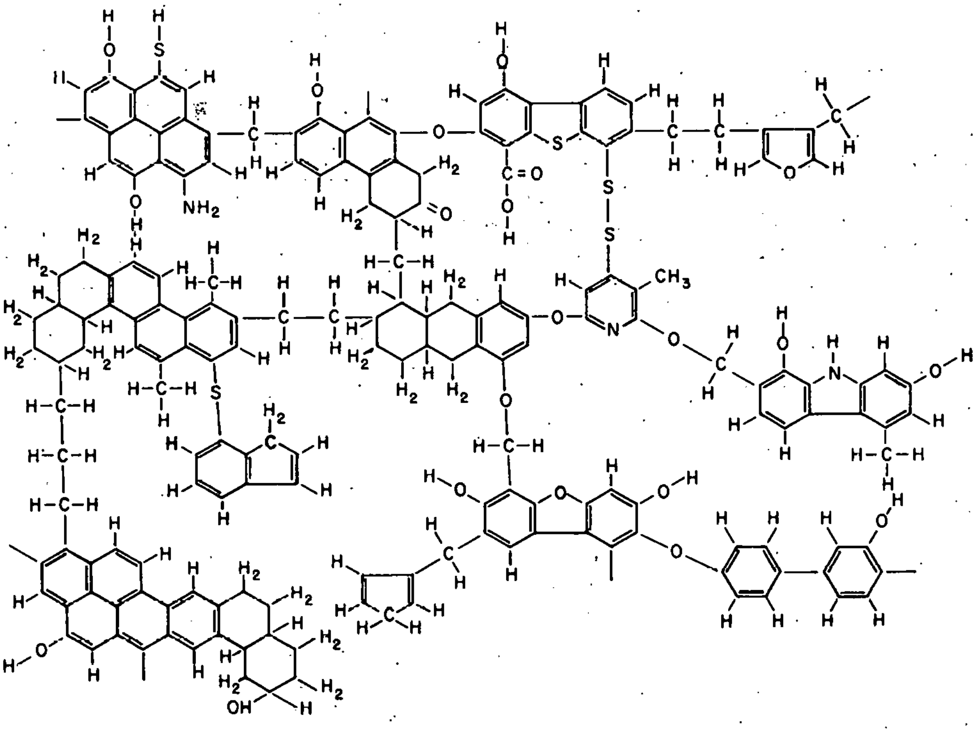
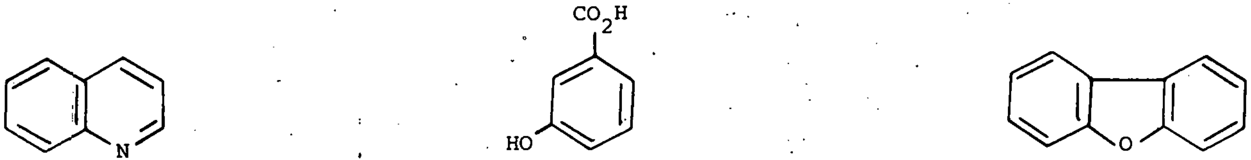


Figure 1. Functional group model of bituminous coal (Wiser).

PHENOLS AROMATIC HYDROCARBONS ALICYCLIC HYDROCARBONS POLYCYCLIC HYDROCARBONS



NITROGEN HETEROCYCLICS ACIDS OXYGEN HETEROCYCLICS

Figure 2. Potential organic contaminants from coal.

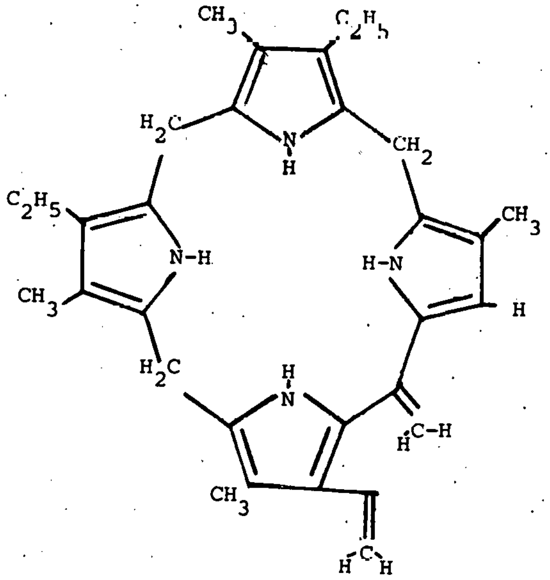


Figure 3. Decarboxylated hexahydrochlorophyllin.

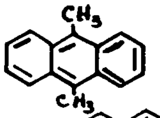
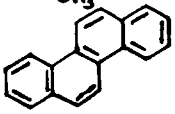
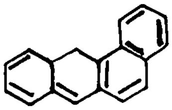
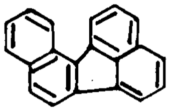
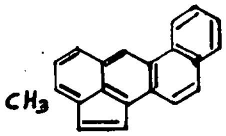
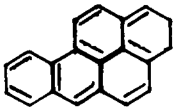
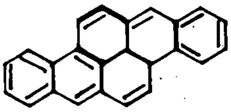
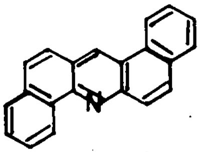
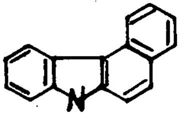
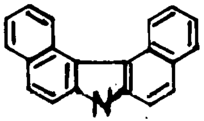
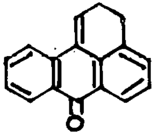
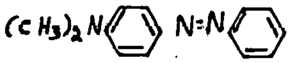
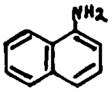
Compound Class	Representative Compound	Structure
Polynuclear Aromatic Hydrocarbons		
Anthracenes	9-,10-dimethylanthracene	
Chrysenes	chrysene	
Benzathracenes	benzo(a)anthracene	
Fluoranthenes	benzo(j)fluoranthene	
Cholanthrenes	20-methylcholanthrene	
Benzopyrenes	benzo(a)pyrene	
Debenzpyrenes	dibenzo(a,h)pyrene	
Nitrogen-,Sulfur-, and Oxygen-Containing Polycyclic Compounds		
mono- and dibenzacridines	dibenz(a,h)acridine	
benzocarbazoles	7H-benzo(c)carbazole	
dibenzocarbazoles	7H-benz(c,g)carbazole	
benzathrones	7H-benz(d,e)anthracen-7-one	
Aromatic Amines		
Aminoazobenzenes	4-dimethylaminoazobenzene	
Naphthylamines	α-naphthylamine	

Figure 4. Classes of known or suspected carcinogenic or cocarcinogenic compounds associated with processing and utilization of coal.

TABLE 1

Trace Metals

Mean Analytical Values for 101 Bituminous Coals

Constituents	Mean	Standard Deviation	Minimum	Maximum
Antimony	1.26 PPM	1.32	0.20	8.90
Arsenic	14.02 PPM	17.70	0.50	93.00
Beryllium	1.61 PPM	0.82	0.20	4.00
Cadmium	2.52 PPM	7.60	0.10	65.00
Cobalt	9.57 PPM	7.26	1.00	43.00
Chromium	13.75 PPM	7.26	4.00	54.00
Lead	34.78 PPM	43.69	4.00	218.00
Mercury	0.20 PPM	0.20	0.02	1.60
Nickel	21.07 PPM	12.35	3.00	80.00
Selenium	2.08 PPM	1.10	0.45	7.70
Vanadium	32.71 PPM	12.03	11.00	78.00

Adapted from Ruck et al. (1974)

TABLE 2

High Resolution Analysis (Intensity %) of the Aromatic Portion of a Hydrotreated and an Untreated Tosco Shale Oil Boiling in the Range 320 to 430°C

		Tosco Shale Oil	
C_nH_{2n+x}		Untreated	Hydrotreated
x =	Mono aromatics	36.9	61.8
-6	Alkyl benzenes	10.4	18.3
-8	Naphthene benzenes	9.6	20.4
-10	Dinaphthene benzenes	16.9	23.1
	Di aromatics	27.3	24.1
-12	Naphthalenes	9.4	12.4
-14	Acenaphthenes, biphenyls	10.4	5.4
-16	Fluorenes	7.5	6.3
	Poly aromatics	3.3	3.4
-18	Phenenthrenes	2.0	2.2
-20	Naphthenephenanthrenes	1.3	0.9
-22	Pyrenes	--	0.3
C_nH_{2n}- $_{+x}$NH			
x =	N-Containing aromatics	26.7	10.2
-6	Pyridines	9.4	2.4
-8	Naphthenopyridines	4.4	2.3
-10	Indoles	6.3	3.5
-12	Quinolines	2.8	1.4
-14	Naphthenoquinolines	2.1	0.2
-16	Carbazoles	1.7	0.4
	Other N, O, S types	8.3	0.4
	%N (from the analysis)	1.7	0.6
	%N (elemental analysis)	2.2	0.9
	Est. mol. wt	250	250

Adapted from Peters and Bendoraitus (1976)

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PRELIMINARY THOUGHTS ON PROXY PNA COMPOUNDS IN THE VAPOR AND SOLID PHASE*

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Coal Conversion and Oil Shale Industries"

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PRELIMINARY THOUGHTS ON PROXY PNA COMPOUNDS IN THE VAPOR AND SOLID PHASE*

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INTRODUCTION

In recent years there has been increasing awareness of the possible adverse health and environmental impacts of polynuclear aromatic (PNA) compounds. Many of these compounds have been shown to be carcinogenic and/or cocarcinogenic. A new, potentially large source of PNA exposure is the coal conversion (gasification and liquefaction) and oil shale technologies.

Given the potential long term health effects of PNA compounds and the potential for exposure to tars, respirable particles, and vapors, a good industrial hygiene program must be committed to protecting workers from these PNA compounds. Economic considerations, inadequacies of analytical techniques, and incomplete understanding of the complex synergistic effects prohibit the routine monitoring of all PNA compounds suspected of being carcinogenic. On the other hand, a fairly simple, rapid indication is required to provide near real-time warnings of sudden increases in exposure levels. Also needed is a limited

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*Research sponsored by the Office of Health and Environmental Research, U.S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corporation.

number of indicator compounds that can characterize the worker's chronic exposure to PNA compounds. This paper attempts to stimulate some thinking about this problem, recognizing fully that much initial research and development work will be required to establish reliable correlations, if possible, between suggested proxy or indicator compounds and the more complete PNA exposure distribution.

PROXY COMPOUND CONCEPT

The indicator substance concept suggested for coal gasification pilot plants is in response to the need for a simple, easily measured index for real-time detection of leaks. A single substance, usually carbon monoxide (CO), acts as a proxy for all the components of a given process stream (1). The concept of using a gas compound (CO) for indicating concentrations of fugitive airborne particulate matter is not wholly satisfactory because their rates of dispersion will differ. The indicator compound is a proxy for substances that cannot be analyzed in real time, or that are difficult or impossible to analyze at prevailing concentrations. The need to estimate the toxicity of tars in an industrial hygiene setting offers possibilities for expansion of the indicator substance concept to nonroutine operating situations, where simple gases are not related directly to the amounts of PNA-containing tars that are present.

One should first address the critical question: is there sufficient merit to measuring one or more specific PNA compounds in coal derived samples as opposed to measuring only the cyclohexane soluble fraction of particulate matter (CSFTPM)? There is no regulation regarding exposure limits for specific PNA compounds, except for some of the lightest, more volatile members, such as naphthalene with a time weighted average (TWA) concentration of 10 ppm. This is not surprising since the capability of easily measuring individual compounds in complex PNA mixtures is quite poor at present. The hazard of an individual component is also difficult to evaluate, especially when taking into account the promotional and synergistic effects of coexisting species. For these reasons, Occupational Safety and Health Administration (OSHA) concentration limits have not been set. The time for regulatory standards concerning the majority of single PNA compounds has not yet arrived.

There is still, however, a need for characterization work that will involve the selection and monitoring of a handful of indicator PNA substances. A need exists to find out what is occurring in contaminated occupational zones. Information needed includes determination of parent PNA profiles of fugitive emission, how these profiles change with time and exposure to light, what are the products of photochemical oxidation, and what is the nature of contaminants that build up on surfaces. Coal tar products from various conversion technologies, or from different parts of a single plant, can differ appreciably in mutagenic and carcinogenic activity. Measurement of CSFTPM does not by itself reveal differences in biological activity. A measurement of the small number of proxy PNA compounds, each an indicator for a particular chemical group exhibiting biological activity, would be an improvement. This group would be even more useful if their measurement could be made in real or near real time.

PROXY COMPOUND SELECTION

If vapor phase detection of PNA compounds is the aim, the compounds present with highest volatility will produce the largest concentractions under equilibrium conditions. Since work areas are normally ventilated or open, one will not in general be monitoring vapors at saturation vapor pressure. The abundance of the PNA compounds in the liquid or solid contaminant from which the vapors are emanating will then have a bearing on the measured vapor phase concentration. Naphthalene and its methyl derivatives are attractive compounds in both respects (Fig. 1). They are quite volatile, and they are ubiquitous and abundant in coal conversion oils and tars. Naphthalenes can comprise as much as 10% by weight of coal tar products (2). Preliminary investigations of PNA vapors in air that has passed over naphtha or light oils from the Solvent Refined Coal I and II processes show that naphthalene and both of its mono-methyl derivatives are dominant species. These are vapors that can be measured quantitatively in real time.

Quinoline vapor should also be considered for some special reasons. It can be a fairly abundant nitrogen base component of coal liquefaction products, 1.1% by weight in one particular instance (3). Being a liquid at ambient temperatures, it is certainly volatile, and in addition it is a carcinogen and a mutagen (4). For each of these reasons its presence should be sought, either in its own right or as a proxy compound for nitrogen containing PNA vapors. Human exposure to quinoline should be carefully monitored and reduced wherever possible.

Tar compounds in the solid phase present a more complex and analytically taxing situation. Quick response can be obtained only by observation of gross fluorescence with the naked eye. The information obtained simply tells one whether or not a surface is contaminated. The CSFTPM method, on the other hand, is quantitative but only with respect to cyclohexane soluble matter, and no information is obtained with regard to any specific PNA compound or groups of compounds. Furthermore, the recommended National Institute of Occupational Safety and Health (NIOSH) procedure for conducting the analysis consumes about 4 hours (5). This stretches one's conception of a near real-time analysis.

If there is a proxy having widespread acceptance among the high boiling, nonvolatile PNA compounds, it is benzo[a]pyrene (BaP). This is because it is the most intensively studied PNA in the environment and its metabolites, especially 7,8-diol-9,10 epoxides (6), are being investigated intensively because of their mutagenic and carcinogenic potency. The rather common practice of measuring the BaP content of a complex PNA mixture has come about more for reasons of familiarity than sound reasoning. It is inappropriate to use BaP as the proxy, or to use any single proxy, for all situations. Some reasons are: (1) it may be a minor constituent compared to other PNA compounds, (2) the biological activity of a particular sample may be associated primarily with other types of PNA compounds, (3) as a fugitive emission it might be chemically less stable than other PNA compounds and therefore less suitable as an indicator.

The parent PNA profiles (7) shown in Fig. 2 serve to illustrate two important points. In one environment (the aluminum plant), benzopyrenes are abundant, while in another (the Soderberg paste plant) they are reduced by nearly two orders of magnitude compared to other PNA compounds and are a minor PNA constituent. Only in the former case is BaP a suitable indicator compound. The second point to make is that parent PNA profiles differ considerably from one type of sample to another.

Generalized statements cannot be made about which PNA compound or compounds are the best indicators.

Within both parent PNA profiles shown in Fig. 2, fluoranthene and pyrene are abundant constituents and for this reason might be considered as candidates for proxy. Phenanthrene and anthracene, although abundant, are probably too volatile to be good proxy compounds for liquid and solid samples.

Another important factor to consider is the constancy of the parent PNA profile for a particular type of fugitive emission. Bjorseth has stated recently (7) that "once the parent PNA profile is established it does not change significantly." This might be so in the workplace, close to the source of the emission, and before the escaped PNA material has had a chance to evolve photochemically. A need is seen, therefore, for examination of PNA parent profiles in plant fugitive emissions to establish their degree of variability. Small variability would enhance the value of monitoring PNA proxy compounds.

Fugitive emissions are, however, not always caught soon after their escape. One will be exposed in such an instance to an evolved photochemical system. Selection of indicator compounds in a "aged" PNA sample should take into consideration susceptibility to photochemical oxidation or other degradation processes. One may even choose to monitor one or more of the degradation products to assess the state of evolution. For example, the halflife of BaP deposited on a surface and exposed to sunlight is orders of magnitude greater than that of the PNA as an aerosol exposed to sunlight in the presence of ozone (8).

With the exception of quinoline, the discussion of proxy PNA compounds has so far excluded heterocyclics. Chemical fractionation and testing for biological activity of synthetic crudes from coal and shale oil, however, revealed the active mutagenic character of basic nitrogen constituents such as the aza-arenes (9). Since crude synfuels are composed of from 1 to 10% by weight alkaline constituents and this fraction carried 50-80% of the mutagenic activity, one should seek a nitrogen heterocyclic PNA proxy compound. At this time little guidance can be given in suggesting suitable heterocyclic PNA proxy compounds. Few coal conversion products have been analyzed quantitatively for their nitrogen base components. One recent analysis of a coal liquefaction product (3) showed it to contain about 10% by weight of such material with azafluorenes, acridines, benzoazafluorenes, and azapyrenes each constituting of the order 1% by weight. One might suggest acridine as a surrogate; methylated benzacridines and dibenzacridines have long been recognized as tumor initiators.

MEASUREMENT OF PROXY COMPOUNDS

Measuring proxy PNA compounds in the workplace should ideally be conducted in real time. For vapors of the low boiling PNA compounds there is good hope that this can be achieved with instruments such as the second-derivative UV-absorption spectrometer (10) described at this meeting.

Solid and liquid samples are not seen as yielding to real-time analysis in the near future. Still one can hope to avoid extensive and time consuming chemical fractionation procedures such that results are forthcoming in near real time. The room temperature phosphorescence (RTP) technique, also described in a paper at this meeting, offers multicomponent analytical capabilities (11), provided the definition of near real time can be extended to about one hour. In this technique a sample of Synthoil is subjected to a separation into acid, base, and neutral fractions and much of the coloration removed by passage through a Florisil column. The RTP analysis is conducted on 3 µl of solution spotted onto a substrate of filter paper. The RTP spectrum of pyrene in the neutral fraction of Synthoil is shown in Fig. 3.

Pyrene is the most abundant PNA compound in this coal liquefaction product (4300 ppm by gas liquid chromatography (GLC) profiling). The still complex neutral fraction can be selectively excited to produce an RTP spectrum very similar to that of pure pyrene together with the quantitative result of 5800 ppm ± 30%. The high abundance of pyrene in this type of product and the means for fairly rapid and accurate analysis allow one to recommend pyrene as the best PNA indicator compound for this particular coal liquefaction product.

In this same neutral fraction, BaP is a minor constituent (41 ppm by GLC profiling). This concentration of BaP is about at the lower limit of detectability by RTP. By resorting to standard additions of BaP (Fig. 4), the concentration of BaP was estimated to be 50 ppm. Because BaP is a relatively minor constituent in this sample and is difficult to analyze using a rapid screening technique such as RTP, it is not the ideal PNA proxy compound for this particular sample.

It is worth mentioning that heterocyclic PNA compounds are suitable for analysis by RTP. Compounds such as acridine (Fig. 5) can be detected with nanogram sensitivity.

Other techniques for the rapid determination of workplace and environmental samples--select compounds and especially BaP--are being actively developed. A rapid thin layer chromatographic separation and in situ fluorescent analysis is being integrated with an automatic isolation procedure (12). Because application of up to 18 samples on a thin layer chromatography plate is accomplished semiautomatically by a multispotter, and the fluorescence analysis is carried out directly on the plate with a motorized scanner, the method has good potential for a high degree of automation. There also seems a good possibility for replacing the fluorescent analysis step with a RTP step to enhance the multicomponent analytical capability through added compound selectivity. So the outlook for reasonably rapid analysis of select compounds is not bleak and the next year or two should see some significant advances, which is all the more reason for early consideration of proxy PNA compounds.

SUMMARY

Better monitoring data for PNA compounds are needed to establish the level of worker exposure. This need, together with the inaccuracy of the method for CSFTPM, and because the latter does not always correlate well with the PNA content, are the best reasons one can advance for measuring PNA proxy compounds. Proxy PNA compounds would be used, for the time being at least, to characterize rather than regulate the PNA compounds in fugitive emissions.

The concept proposed by Bjorseth (7) is recommended as the first step in the selection of proxy compounds. A PNA parent profile is determined, and one or two of the more abundant PNA compounds are chosen. Pyrene and fluoranthene are generally prominent and thus are attractive candidates for proxy. Benzo[a]pyrene, when it is abundant, is likewise a suitable indicator compound. The common practice, however, of measuring BaP as the single proxy without foreknowledge of the parent PNA profile should be discouraged. Attempts to gauge the mutagenic and carcinogenic potential of each sample via its BaP content can be misleading. In certain cases, a basic nitrogen-containing PNA would be a more valuable proxy than BaP. It is recognized, however, that because the concentration of heterocyclic nitrogen compounds is one or two orders of magnitude lower than the homocyclic PNA compounds, their detection will be difficult. Nevertheless, species such as quinoline and acridine may be suitable proxy compounds. In vapor phase monitoring, naphthalene and its methyl derivatives are the most attractive indicator compounds due to their high volatility and high concentration in most synthetic fuel products.

While it may be a bit premature to identify specific compounds to serve as indicators for the presence of complex, multicomponent mixtures, the need for such proxy compounds has clearly been established. These proxy compounds not only must be readily measured and indicative of their parent sample in the work environment, but should themselves be of biological interest. Considerable research and development is required in each of these areas to understand more fully the behavior, both chemical and biological, of these complex PNA mixtures. Also required is continued development of improved measuring techniques and instrumentation that can provide more economic and efficient monitoring of selected proxy compounds.

REFERENCES

1. *Recommended Health and Safety Guidelines for Coal Gasification Pilot Plants,* DHEW (NIOSH) Pub. No. 78-120, p. 111 (1978).

2. *Environmental Health and Safety Aspects of Coal Conversion: An Information Overview,* ORNL/EIS-94, Vol. 1, p. 4-106 (1976).

3. *Characterization of the Heterocyclic Compounds in Coal Liquefaction Products. Part 1: Nitrogen Compounds.* PERC/RI-77/7, p. 11 (1977).

4. Dong, M., Schmeltz, I1, LaVoie, E., and Hoffmann, D., *Carcinogenesis, Vol. 3: Polynuclear Aromatic Hydrocarbons,* Ed. Jones P. W. and Freudenthal R. I., Raven Press, p. 97 (1978).

5. *Criteria for a Recommended Standard - Occupational Exposure to Coal Tar Products,* DHEW (NIOSH) Pub. No. 78-107 (1977).

6. Yang, S. K., Roller, P.-P., and Gelboin, H. V., *Carcinogenesis, Vol 3: Polynuclear Aromatic Hydrocarbons,* Ed. Jones P. W. and Freudenthal R. I., Raven Press, p. 285 (1978).

7. Bjorseth, A., "Determination of Polynuclear Hydrocarbons in the Working Environment", presented at the 3rd International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, Ohio, October 1978.

8. Compiled from presentations at the 3rd International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, Ohio, October, 1978.

9. Guerin, M. R., Epler, J. L., Griest, W. H., Clark, B. R., and Rao, T. K., *Carcinogenesis, Vol 3: Polynuclear Aromatic Hydrocarbons,* Ed. Jones P. W. and Freudenthal R. I., Raven Press, p. 21 (1978).

10. Hawthorne, A. R., and Thorngate, J. H., *Appl. Opt.* 17, 724 (1978).

11. Vo-Dinh, T., and Winefordner, J. D., *Appl. Spectrosc. Rev.,* 13(2), 261-294 (1977).

12. *Analytical Chemistry Division Annual Progress Report,* ORNL/5360, p. 53 (1977).

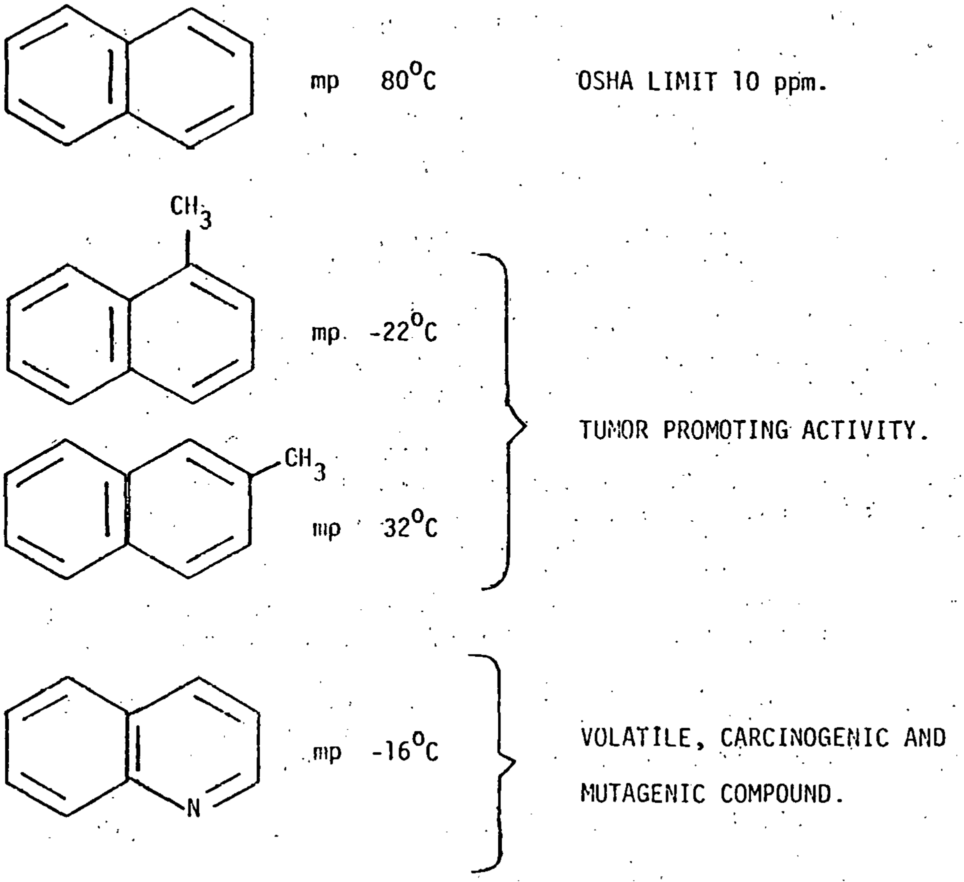

Figure 1. Possible proxy PNA compounds for monitoring in the vapor phase.

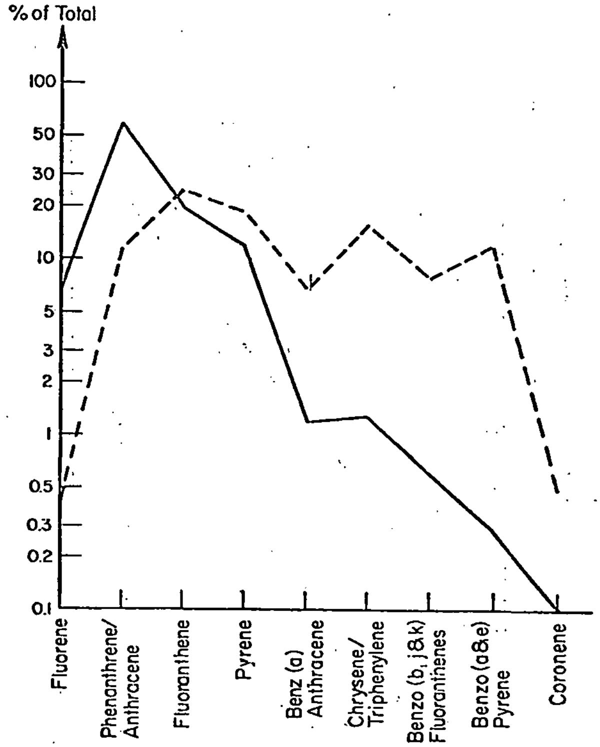

Figure 2. Parent PNA profile of PNA compounds in particulate matter from an aluminum plant (---) and a Soderberg paste plant (——).

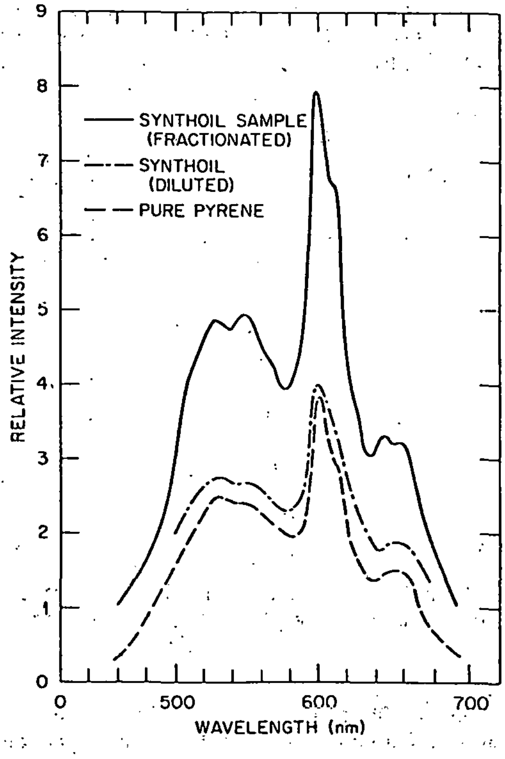

Figure 3. RTP spectra of the coarsely separated neutral fraction of Synthoil compared to that of pure pyrene.

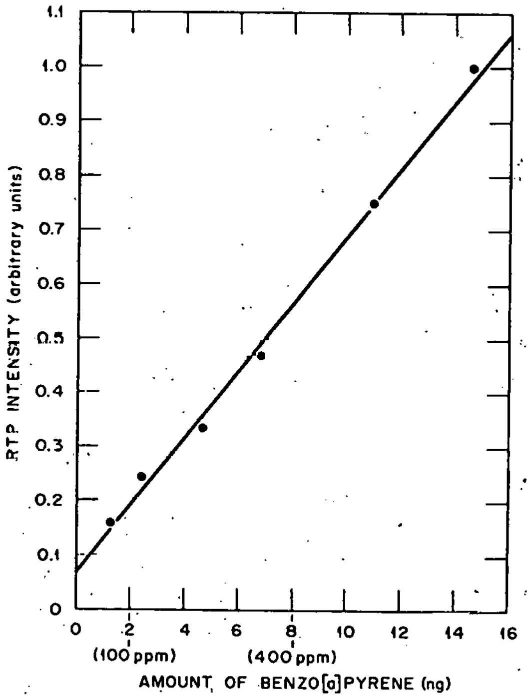

Figure 4. RTP analysis of BaP in a crude fractionated 20 µg sample of Synthoil using standard additions of BaP; phosphorescence occurs at 690 nm. Intercept is equivalent to 50 ppm of BaP in the original sample.

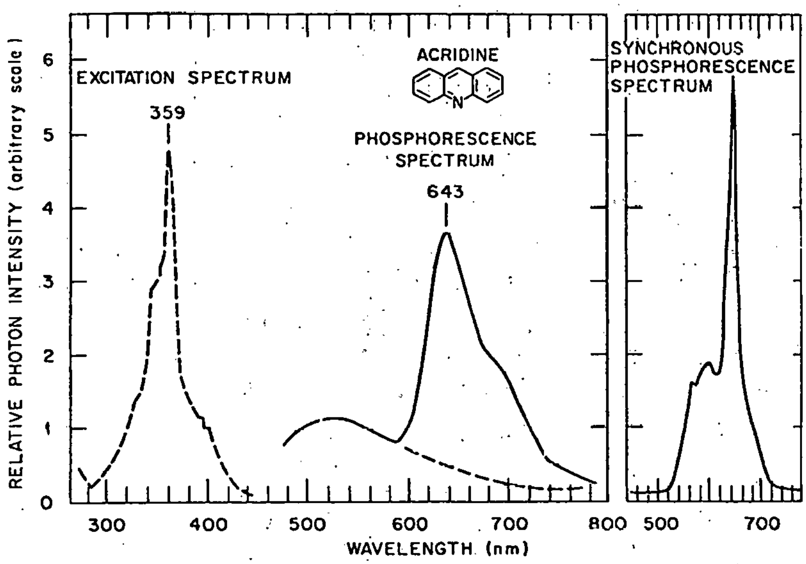

Figure 5. Normal and synchronized excitation-emission room temperature phosphorescence from acridine adsorbed onto filter paper.

DUVAS: A FIELD PORTABLE SECOND-DERIVATIVE UV-ABSORPTION SPECTROMETER FOR MONITORING PNA VAPORS

Dup

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INTRODUCTION

The potentially hazardous environment at coal conversion facilities places significant responsibility on the industrial hygienist in that many of the process chemicals either are acutely toxic or are carcinogenic, thus requiring exposures to be kept to a minimum. Exposure to potential carcinogens requires a special commitment to worker protection, since there are often no detectable warning signs of exposures that may result decades later in cancers.

Given this potential for worker exposure to compounds that give no immediate warning signs and yet may cause cancer years later, a real-time, continuous, portable monitor is needed to warn of elevated concentrations in work areas. This monitor is needed in addition to measurements of integrated exposures obtained by personnel monitors requiring subsequent laboratory analysis. Portable, real-time monitors will also prove valuable in detecting small leaks in process streams and in pinpointing important sources of exposure.

This paper discusses the development of a portable monitor that can be used to measure volatile polynuclear aromatic (PNA) compounds as part of an industrial hygiene area monitoring and leak detection program.

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Results are somewhat preliminary, as the prototype instrument has only recently been completed and further optimization will be required before field testing.

PROTOTYPE INSTRUMENT

Ultraviolet(UV)-absorption spectrometry provides good sensitivity for the detection of most PNA compounds. However, selectivity between various PNA compounds in a mixture poses a problem since these compounds often exhibit considerable spectral overlap. Derivative UV-absorption spectrometry is a technique that permits improved selectivity between overlapping spectral bands (1-3). In particular, this procedure tends to enhance the signals from compounds that exhibit narrow-band absorption while diminishing the signals from compounds with broad band absorption.

Work is in progress at Oak Ridge National Laboratory (ORNL) to develop a prototype second-derivative UV-absorption spectrometer (DUVAS) for analyzing parts-per-billion levels of many trace gases in air. Figure 1 shows the prototype spectrometer with the 1-m multipass air sampling cell attached. A particular emphasis is being placed on the detection of volatile PNA compounds. This instrument is designed to be considerably reduced in size and substantially faster in spectrum scanning speed relative to a commercially available spectrometer, the Lear-Seigler, Inc., Model SM-400 second-derivative spectrometer (4). It is also microcomputer-controlled whereas the SM-400 is not.

Theory

Detailed treatment of the theory of wavelength-modulated derivative absorption spectrometry may be found elsewhere (1,3,5,6). Briefly, the technique consists of modulating the incident wavelength by a few nanometers and detecting the second harmonic of the modulation frequency.

This signal gives a response that is proportional to the concentration of the compound being measured. Since a second-derivative spectrum is a measure of the curvature of the absorption spectrum and not of the transmitted light, the technique of second-derivative absorption has the important advantage of being independent of sample opacity, light intensity fluctuations, and source-energy variations. This advantage is particularly useful when no sample preparation to remove particulate matter is performed prior to analysis.

Optics

The optical system of the prototype DUVAS consists of a deuterium lamp light source, monochromator, sample compartment, and photomultiplier tube (PMT). The small monochromator is a 10-cm holographic grating monochromator having a resolution of 8 nm/mm. Wavelength modulation is achieved by replacing one of the mirrors in the monochromator with a commercially available taut band vibrator that oscillates with a frequency of 400 Hz. The second harmonic signal at 800 Hz is sufficiently removed from the 120-Hz line voltage noise to allow good filtering, thus improving the moise level.

Another distinct advantage of the higher modulation frequency relative to the commercial SM-400 second-derivative spectrometer is that, when coupled with an integrating technique (discussed in the next section), much faster scanning speeds can be obtained. Whereas the SM-400 has scanning speeds of 2.5 or 10.0 nm/min, the DUVAS scanning speed can be varied between 30 and 240 nm/min, thus allowing a sample scan to be completed in considerably less time.

Monochromator positioning and scanning are accomplished with a four phase bidirectional stepping motor. When used with a 2:1 gear reduction, this motor gives a stepping resolution of 0.25 nm/step.

Electronics

Figure 2 is a block diagram of the DUVAS showing the relationships of the major electronic components of the prototype instrument. In addition to the previously mentioned deuterium lamp, PMT and preamp, stepping motor, and mirror coils, the electronic components consist of three printed circuit (PC) boards.

One PC board contains an F8 microcomputer that provides the control logic for scanning a spectrum. It positions the stepping motor to a beginning wavelength, scans to the stopping wavelength at a selected speed from 30 nm/min to 240 nm/min, and stores data in its memory at resolutions of 0.25, 0.50, 0.75, or 1.00 nm/data point. The data points are obtained by counting the pulses from a voltage-to-frequency (V/F) converter for a time interval determined by the scanning speed (e.g., a scanning speed of 120 nm/min gives an integration time of 0.125 seconds/point). This integration of the second-derivative signal helps to improve signal-to-noise (S/N) ratios without requiring the much slower scanning speeds that would be required by a low-pass electronic filter having the same S/N ratio. The F8 microcomputer also provides a parallel interface to external computers that can transfer scanning parameters to the F8 and receive a spectrum scan from the F8. A teletype interface is also provided, permitting the use of a teletype as an input/output device when desired.

The second PC board is a commercially available voltage programmable high voltage (HV) supply for the photomultiplier tube. A control voltage input of 0 to -5 V gives a 0 to -1200 V output. The programmable feature allows an automatic-gain-control (AGC) signal to the HV board to control the gain of the PMT by varying the applied voltage. The second-derivative signal is not affected if the time constant of the AGC is slow relative to the 400-Hz modulation frequency because varying the gain is equivalent to changing the light intensity, and the second-derivative signal is insensitive to light intensity changes. The AGC feature acts as an automatic iris to ensure that dc signals from the PMT are neither too small nor too large, thus ensuring that signals fall within the optimum range for the signal processing electronics.

The final PC board contains signal processing and control circuits. Figure 3 is the block diagram of this PC board. The AGC circuit can be adjusted for the desired dc signal from the PMT. This AGC circuit then acts as a servo control to adjust the PMT voltage to give the desired output. Also, on this PC board is the mirror-driving and sensing circuit. This circuit oscillates the mirror and provides a 400-Hz reference signal to a frequency-doubling circuit, which gives an 800-Hz reference signal for use in the synchronous detector circuit. A stepping motor control circuit takes a direction signal and step pulse from the F8 microcomputer and provides the proper sequence of pulses to the four-phase stepping motor.

The signal from the PMT, which has an 800-Hz ac component containing the second-derivative information, is input to a logarithmic amplifier circuit. This circuit eliminates the need for a divider circuit that the SM-400 requires and also eliminates a nonlinearity in the second-derivative signal (1). Following the log circuit is a bandpass filter/amplifier with a central frequency of 800 Hz. This circuit filters out both high and low frequencies, including 120-Hz noise from line voltage and some of the 400-Hz signal due to the first-derivative signal. A synchronous detector circuit then selects only signals with an 800-Hz frequency and, with a subsequent filter/amplifier circuit, converts this ac signal into a dc signal proportional to the second derivative of the absorption curve of the measured compound at the measured wavelength. This analog signal is available at the rear panel of the instrument for use with a chart recorder. The final circuit on the board is a V/F converter, which provides a frequency signal proportional to the second-derivative signal for the F8 microcomputer to record as digital data.

Computer Interface

As stated, the F8 microcomputer has a parallel interface for communication with an external computer. The DUVAS has been operated with a Digital Equipment Corporation (DEC) DECLAB 11/03 minicomputer and a Commodore PET 2001 microcomputer. Figure 4 shows a spectrum as displayed on the 11/03 system. For laboratory use the PDP 11/03 provides much flexibility, with dual floppy discs for mass data storage and program storage plus a video display for plotting spectra and displaying analyses.

For field use the PET 2001 is an inexpensive microcomputer, which provides a 9-in. video display, a communication keyboard, a magnetic tape cassette data recorder, and a microcomputer programmable in BASIC for data analysis (Fig. 5). Using the PET keyboard, the user may define the spectral region he wishes to scan, as well as the speed and resolution. The spectrum is displayed on the screen and may be permanently saved on magnetic tape. The PET microcomputer can be located remotely from the DUVAS, with only an interface cable connecting the two. Software development is currently in progress on a series of programs for controlling the spectrometer, plotting spectra in a variety of modes, and analyzing the data by comparison with a cassette of library spectra.

Modes of Operation

The DUVAS can be used to analyze both liquid and gaseous samples. As a trace gas analyzer, a 1-m multipass sampling cell is attached to the spectrometer. The total pathlength of light through the sample is adjustable, with a 12-m pathlength typically used. An air-sampling pump pulls air through the cell with a flow rate of approximately 4 ℓ/min. A heating blanket surrounds the sample cell and can be used to prevent condensation of low vapor pressure compounds within the cell that would otherwise produce anomalies or background signals.

The DUVAS can also be operated in a liquid analysis mode. A 1-cm quartz cuvette is used to hold a 1-ml sample. Water, cyclohexane, and ethanol are suitable UV-transparent solvents for use in second-derivative spectrometry. Since DUVAS is insensitive to sample turbidity (7), it may be operated as an on-line analyzer for monitoring wastewater streams. A small sampling pump is used to pull the water through a flowthrough cell.

CONCLUSIONS

Although further evaluation and optimization are needed to assess the full potential of the DUVAS, the instrument should prove to be a useful tool for industrial hygiene monitoring and location of point source exposures. Analytical data are somewhat limited from the prototype DUVAS as optical and electronic component optimizations are still in progress. Some data are available, however, on an earlier second-derivative spectrometer (8). Figure 6 illustrates both the sensitivity and selectivity for vapor phase PNA compounds. Naphthalene and 2-methylnaphthalene are each measured separately at parts-per-billion concentrations and in a mixture of the two compounds. Separation of these two similar compounds is clear even without the aid of a computer program. Figure 7 shows a typical calibration curve for a PNA vapor.

The ability to measure naphthalene and its methyl derivatives in real time should prove useful for indicating potential exposures to other PNA compounds. Naphthalene and its methyl derivatives are often a major component within the synthetic crude product. In addition, these volatile PNA compounds should prove suitable indicators even for spills and contaminated equipment encountered in maintainence operations where other indicators such as carbon monoxide would not be present.

Field evaluation of a prototype version of a DUVAS is scheduled at the University of Minnesota-Duluth low-Btu gasifier during the following year. The instrument will be used to characterize vapor emissions from the gasifier and to evaluate its usefulness as part of an industrial hygiene program. The results of this evaluation should prove this instrument to be a useful addition to the monitoring tools available to the industrial hygienist.

REFERENCES

1. Hawthorne, A. R., and Thorngate, J. H. (1978): Improving analysis from second-derivative UV-absorption spectrometry. *Appl. Opt.*, 17: 724-729.

2. O'Haver, T. C., and Green, G. L. (1975): Numerical error analysis of derivative spectrometry for the quantitative analysis of mixtures. *Anal. Chem.*, 48: 312-318.

3. Williams, D. T., and Hager, R. N. (1970): The derivative spectrometer. *Appl. Opt.*, 9: 1597-1605.

4. Hager, R. N. (1973): Derivative spectroscopy with emphasis on trace gas analysis. *Anal. Chem.*, 45: 1131A-1138A.

5. Bonfiglioli, G., and Brovetto, P. (1964): Principles of self-modulating derivative optical spectroscopy. *Appl. Opt.*, 3: 1417-1424.

6. Hager, R. N., and Anderson, R. C. (1970): Theory of the derivative spectrometer. *J. Opt. Soc. Am.*, 60: 1444-1449.

7. Hawthorne, A. R., Thorngate, J. H., Gammage, R. B., and Vo-Dinh, T. (1978): Trace organic analysis using second-derivative UV-absoprtion spectroscopy. *Proceedings of NBS Conference on Trace Organic Analysis, 1978.* (in press).

8. Hawthorne, A. R., and Thorngate, J. H. (1978): Application of second-derivative UV-absorption spectrometry to PNA analysis. *Appl. Spectrosc.*, 32: (in press).

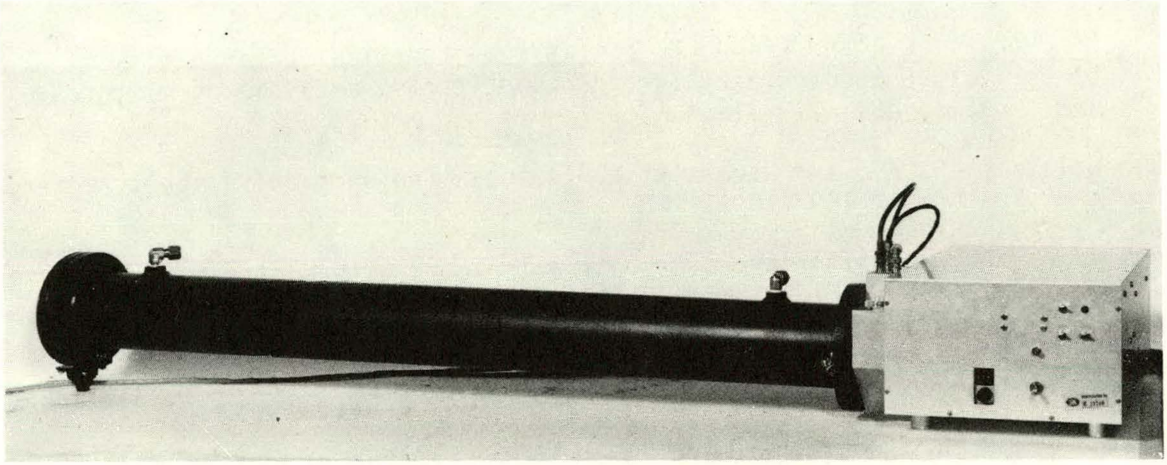

Figure 1. Photograph of DUVAS with 1-m multipass air-sampling cell attached.

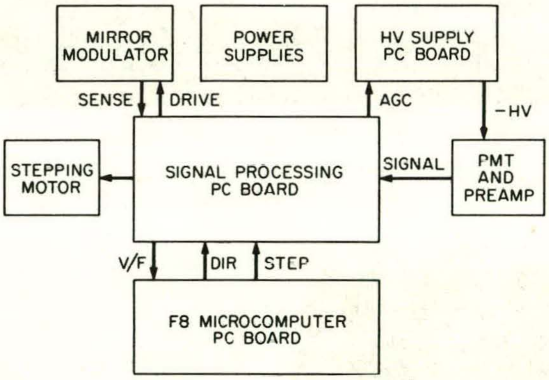

Figure 2. Block diagram of DUVAS major electronic components.

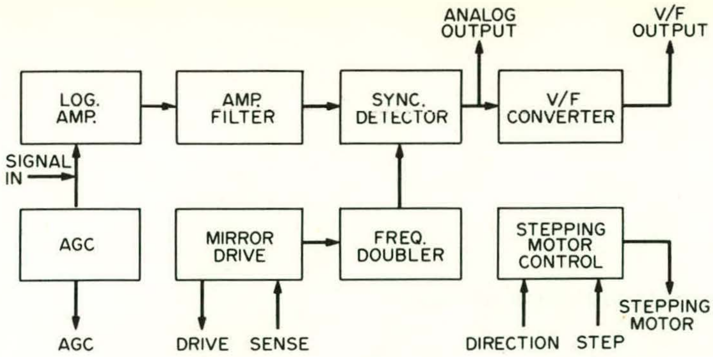

Figure 3. Block diagram of DUVAS signal processing and control circuits.

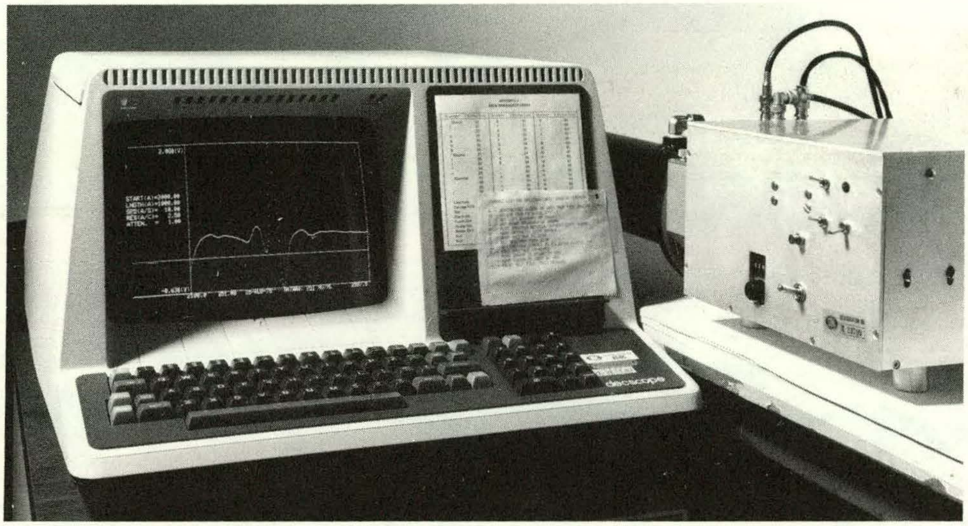

Figure 4. DUVAS spectrum displayed on a DECLAB 11/03 system.

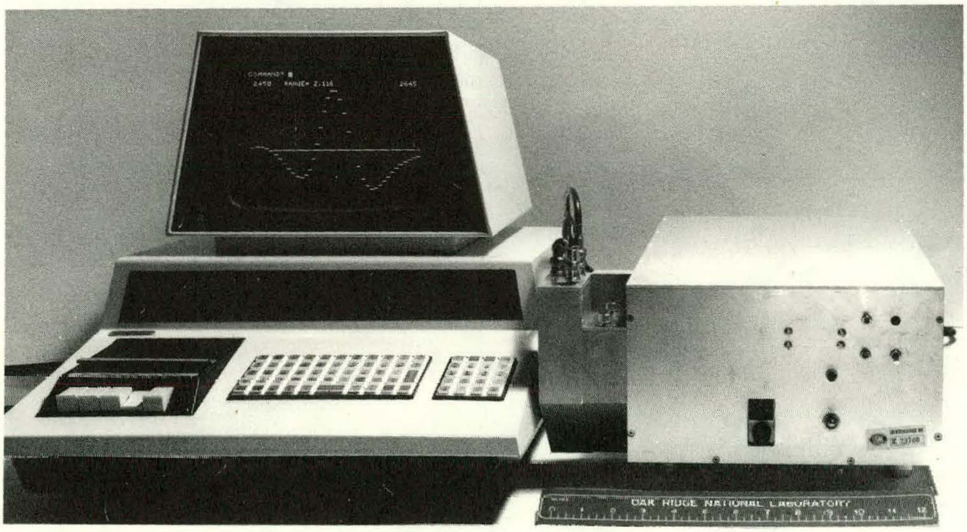

Figure 5. DUVAS with liquid sampling compartment attached and PET-2001 microcomputer used for data analysis.

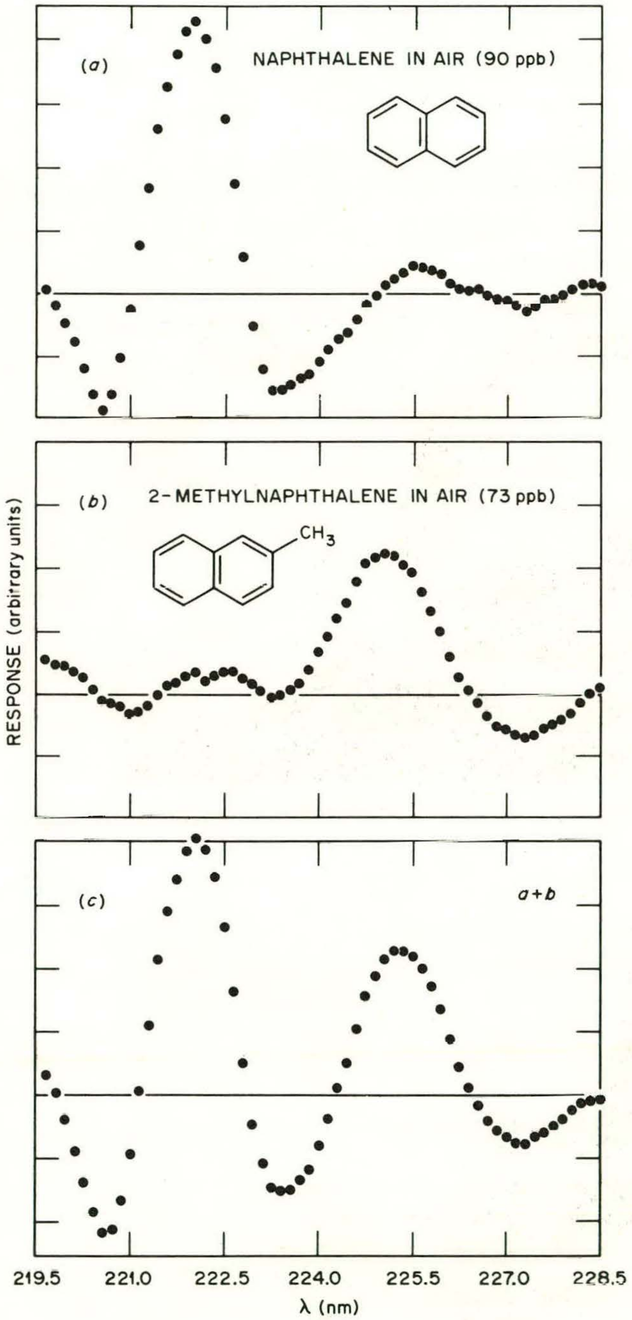

Figure 6. Second-derivative spectra of naphthalene and 2-methylnaphthalene and a mixture of the two illustrating the selectivity of the technique.

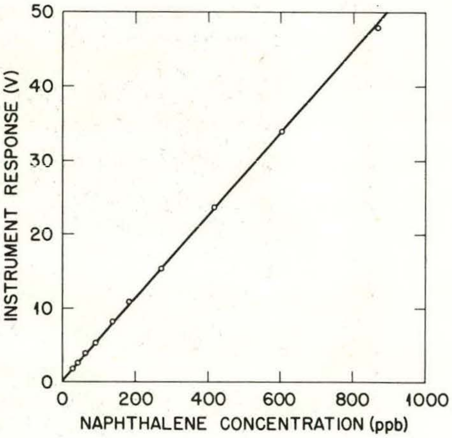

Figure 7. Calibration curve for naphthalene in air.

PASSIVE DOSIMETERS FOR GASES

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PASSIVE DOSIMETERS FOR GASES

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I would like to begin by distinguishing between an active and a passive sampler. The active sampler requires external power to move air through the absorbent or detector and, because of this, it has considerable weight and cost and requires maintenance. The passive sampler has little or any of the above. The active sampler, on the other hand, can be used to collect both particles and gases, but the passive sampler will not collect particles because of their extremely low coefficients of diffusion. The active sampler is capable of measuring peak concentrations over extended periods. The passive sampler, on the other hand, is designed primarily to measure time weighted average exposures to gases for relatively long periods.

For explaining the principles of the diffusion sampler (the simplest type of passive dosimeter), I would like to use as an example the NO_2 sampler reported by Palmes, et.al. (1976). This sampler is small, light-weight and can be conveniently worn on the worker's person for a full shift. It consists of a short acrylic tube capped on both ends during storage and with one cap removed when sampling so that the open end is exposed to the environment to be measured. At the closed end of the tube the other cap contains three screens coated with tricthanolamine (TEA), a very efficient absorbent for NO_2. A steady state condition is established in a very short time and during this steady state there is a transfer from the open to the closed end of the tube by molecular diffusion. I would point out again that all the energy for this transfer is furnished by the motion of the gas molecules themselves. The triethanolamine keeps the concentration at the closed end very nearly at zero while the open end is at the ambient concentration. This sets up a concentration gradient down the tube and the transfer of NO_2 by diffusion can be predicted from Fick's First Law. In its simplest form this can be stated as follows:

$$J = -D \frac{dc}{dx}$$

where:

J = diffusion flux (moles/cm^2/sec)

D = coefficient of diffusion (cm^2/sec)

c = NO_2 concentration (moles/cm^3)

and x = length of diffusion path (cm)

We then multiply both sides of the equation by cross sectional area (A) of the tube in cm^2. The equation then takes the form:

$$JA = D \frac{A}{L} c$$

You will note that there are three constants, the coefficient of diffusion of NO_2 in air, cross-sectional area of the tube, and the length of the tube. These along with the one variable, concentration, determine the sampling rate in moles per second. To estimate the quantity of NO_2 collected in moles, one multiplies both sides by the time in seconds, to give the equation:

$$Q = JAt$$

where

t = time (seconds)
Q = quantity of NO_2 trapped during exposure (moles)

For the NO_2 sampler described, the constants are as follows:

$D = .154\ cm^2/sec$
$A = 0.71\ cm^2$
$L = 7.1\ cm$

Changing the units to more conventional ones for industrial hygiene, the equation becomes:

$$Q \text{ (nanomoles } NO_2) = 2.3 \text{ (ppm } NO_2 \times \text{hrs)}$$

Samplers were calibrated by exposing them for definite times to NO_2 atmospheres created by diluting the NO_2 from a permeation tube with a known volume of room air. The results were routinely in excellent agreement with theory and demonstrated that Fick's Law could be used to predict the rate of sampling using tube dimensions as measured and a coefficient of diffusion obtained from values in the literature.

I would next like to discuss a slightly different type of sampler which depends on permeation rather than diffusion. In this sampler the atmosphere to be sampled is separated from a collecting medium by a thin membrane. There are two types of collection media used here: liquids and solids. In the first, reported by Reiszner and West (1973), the sampler was designed to collect SO_2 from the ambient air by having it permeate through a thin silicone membrane on the other side of which, contained in a tube, was West-Gaeke SO_2 collecting reagent. This group showed that individual samplers of this type gave very reproducible results but that the thickness of the membrane was not sufficiently constant so that a single value could be used for individual samplers and each had to be individually calibrated. Nelms, et.al., 1977, reported a similar sampler for vinyl chloride; charcoal was used as the solid adsorbent. In this case, also, the constant for the permeation rate of each sampler was determined individually. A very similar sampler was reported by Bailey and Hollingdale-Smith, 1977, who used membranes of the order of 0.001 inch thick as the diffusion barrier for organic gases. For the SO_2 sampler a colorimetric procedure was used for the final determination; all the organic gas samplers used gas chromatography to determine the material after elution from the charcoal.

It should be pointed out that the coefficients of diffusion for gases in air can be estimated by a number of techniques and it is possible for the coefficients to be determined independently so that all of the constants for the solution of the diffusion equation can be obtained without resorting to empirical measurements. In the samplers which depend on permeation through membranes, it appears that the coefficients of diffusion are not nearly as well defined. In the three examples of permeation samplers cited, only approximations were given and it appears that all have grouped the three constants of the equation, D, A and L, into a single permeation constant. From the examples given in these publications, the coefficient of diffusion of the gas through the membrane would appear to be on the order of 10^{-6} to 10^{-7} cm^2/sec as opposed to the approximately 10^{-1} cm^2/sec for similar gases in air. We believe that there are and will be many applications and needs for both types of samplers in the measurement of airborne gases.

I would now like to review very briefly the history of passive samplers other than those described above. At the annual meeting of the American Industrial Hygiene Association in 1972, Palmes and Gunnison (1972) presented the first paper on this type of sampler; it described the quantitative application of the method to measurement of SO_2 and to water vapor in air. At the same meeting, Braun (1972) reported a mercury vapor sampler which was empirically calibrated and depended on diffusion of mercury vapor through a series of small holes where it was captured by a strip of gold foil and changed the resistance of the foil.

Goldsmith (1977) reported a proprietary dosimeter; this device was described in much greater detail, however, by Bamberger, et.al. (1978) and Mazur, et.al. (1978) for use in sampling organic vapors and ammonia respectively. Finally, at the 1978 meeting of AIHA, there were three samplers presented: Campbell (1978) described a dosimeter for aniline, Gosselink, et.al. (1978) reported a personal organic vapor sampler with an *in situ* sample elution feature. Finally, Palmes and Tomczyk (1978) presented a personal sampler for NO_x.

It is seen, therefore, that the history of use of these devices for the quantitative estimation of airborne gases has been very short. We believe, however, that there is a definite increase in interest in devices of this type. We also believe that such devices may obviate some of the problems of both weight and expense as well as improve accuracy and precision in determination of airborne gases in industry and the community. In other words, we feel that passive samplers have a very short past, but a very bright future.

REFERENCES

Bailey, A. and P.A. Hollingdale-Smith. A Personal Diffusion Sampler for Evaluating Time Weighted Exposure to Organic Gases and Vapours. *Ann. Occup. Hyg.*, *20*:345-356, 1977.

Bamberger, R.L., G.G. Esposito, B.W. Jacobs, G.E. Podolak and

J.F. Mazur. A New Personal Sampler for Organic Vapors. Am. Ind. Hyg. Assoc. J., 39:701-708, 1978.

Braun, D.L. Detection of Mercury Vapors as an Adjunct to Respiratory Protective Devices. Presented at AIHA Annual Meeting, San Francisco, 1972.

Campbell, J.E. The Development of a Passive Dosimeter for Airborne Aniline Vapors. Presented at AIHA Annual Meeting, Los Angeles, 1978.

Gosselink, D.W., D.L. Braun, H.E. Mullins and S.T. Rodriguez. A New Personal Organic Vapor Monitor with In-Situ Sample Elution. Presented at AIHA Annual Meeting, Los Angeles, 1978.

Mazur, J.F., R.L. Bamberger, G.E. Podolak and G.G. Esposito. Development and Evaluation of an Ammonia Dosimeter. Am. Ind. Hyg. Assoc. J., 39:749-753, 1978.

Nelms, L.H., K.D. Reiszner and P.W. West. Personal Vinyl Chloride Monitoring Device with Permeation Technique for Sampling. Anal. Chem., 49:994-998, 1977.

Palmes, E.D. and A.F. Gunnison. Personal Monitoring Device for Gaseous Contaminants. Presented at AIHA Annual Meeting, San Francisco, 1972.

Palmes, E.D. and A.F. Gunnison. Personal Monitoring Device for Gaseous Contaminants. Am. Ind. Hyg. Assoc. J., 34: 78-81, 1973.

Palmes, E.D., A.F. Gunnison, J. DiMattio and C. Tomczyk. Personal Sampler for Nitrogen Dioxide. Am. Ind. Hyg. Assoc. J., 37:570-577, 1976.

Palmes, E.D. and C. Tomczyk. Personal Sampler for NO_x. Presented at AIHA Annual Meeting, Los Angeles, 1978.

Reiszner, K.D. and P.W. West. Collection and Determination of Sulfur Dioxide Incorporating Permeation and West-Gaeke Procedure. Environ. Sci. & Technol., 7:526-532, 1973.

Tompkins, F.C., Jr. and R.L. Goldsmith. A New Personal Dosimeter for the Monitoring of Industrial Pollutants. Am. Ind. Hyg. Assoc. J., 38:371-377, 1977.

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A PORTABLE FLUOROMETRIC MONITOR TO DETECT PNA CONTAMINATION OF WORK AREA SURFACES*

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A PORTABLE FLUOROMETRIC MONITOR TO DETECT PNA CONTAMINATION OF WORK AREA SURFACES

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INTRODUCTION

Survey monitoring in coal conversion work areas for surface contamination caused by spill, leakage, or contact transfer of material containing carcinogenic polynuclear aromatic hydrocarbon (PNA) compounds or mutagenic acridenes is essential for the health and safety of personnel. A portable direct-reading instrument, similar in function to the familiar radiological survey devices, is required for this type of survey monitoring. The instrument must be capable of (1) functioning during actual plant operation in variable working environments; (2) detecting material spilled on various work surfaces, including machinery, plumbing, construction materials, and on personnel and clothing; and (3) being easily and reliably operated by all plant personnel (laborers, technicians, and staff).

The portable fluorescence spotter currently under development at ORNL has the desired capabilities. This instrument, which in final form will consist of an optical unit that contains fluorescence excitation and detection systems and is connected by an umbilical cable to a battery-powered electronics unit (see Figure 1), will enable remote monitoring of work area surfaces at distances of 0 to 2 meters.

PRINCIPLES OF OPERATION

The spotter induces and detects the fluorescence of PNAs such as perylene, whose structure and optical properties are shown in Figure 2. Like most PNAs,

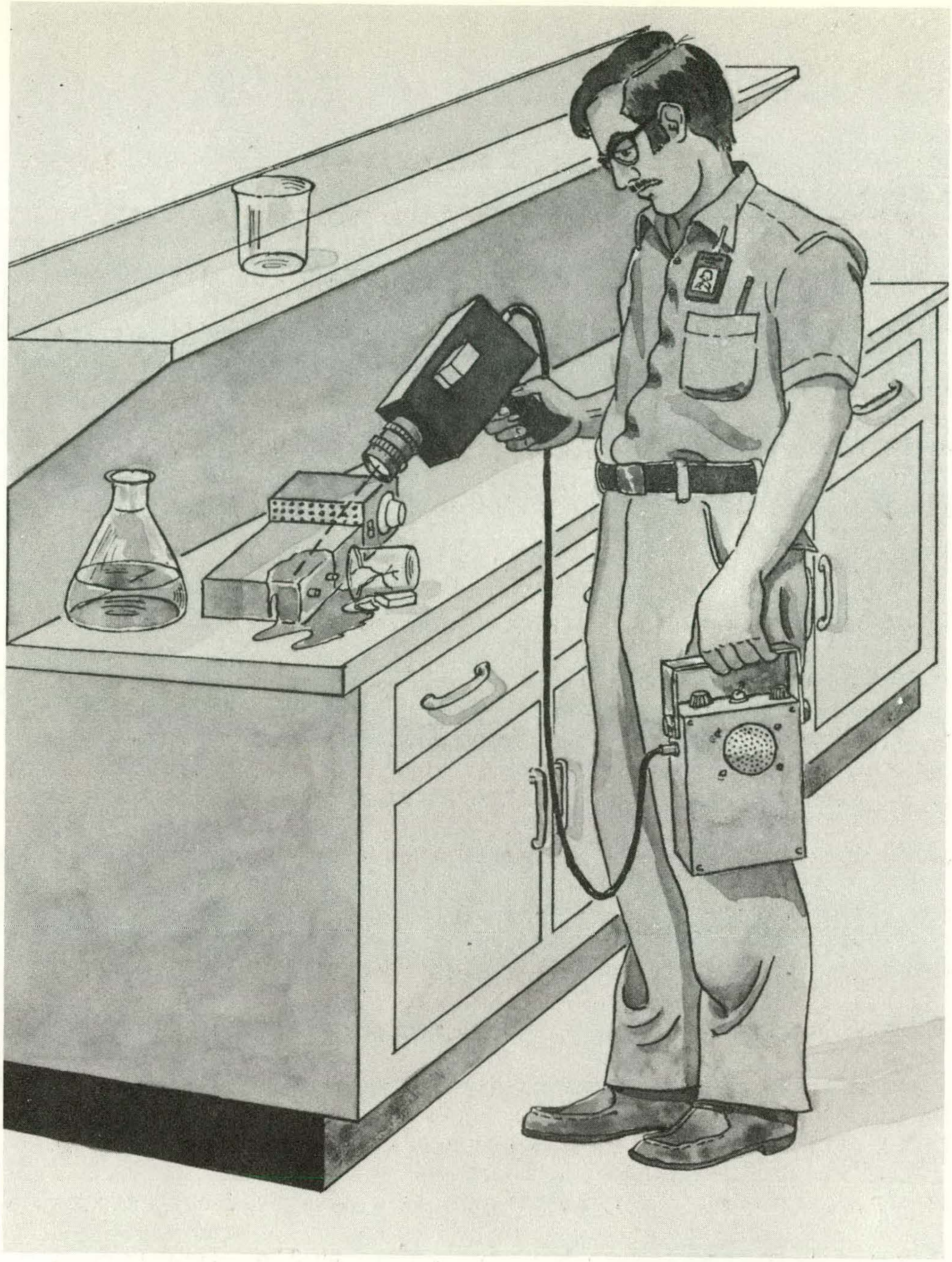

Figure 1. Portable fluorometric spotter concept.

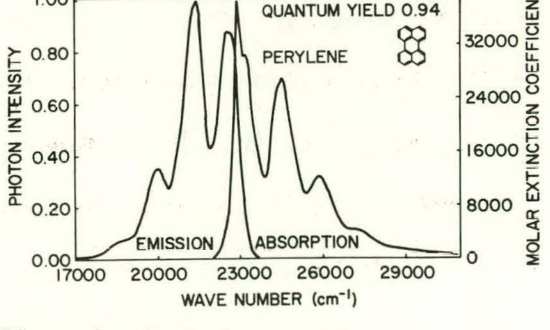

Figure 2. Optical properties of perylene.

perylene absorbs light in the 350- to 440-nm region of the spectrum and emits fluorescence with high efficiency in the blue-green region of the spectrum. Multiring heteroatom aromatics, including acridenes, are also fluorescent; however, they generally absorb light and fluoresce at longer wavelengths than do their pure hydrocarbon counterparts.

The initial effort involved construction and laboratory testing of a prototype device. The prototype optics unit consists of two subunits: (1) a uv illuminator which radiates a cone of amplitude-modulated, near-ultraviolet light; and (2) a fluorescence detector which detects the fluorescence induced by the uv light in a spill. The operation of the spotter is depicted in Figure 3, which also shows the signal traces corresponding to the radiated uv intensity and to the emitted fluorescence when a spill has been "sighted." The fluorescence signal sits atop a much higher signal due to background illumination of the viewed surface. The uv beam and, in turn, the fluorescence which it induces are modulated at 1 kHz. Since the electronic frequency spectrum of fluorescent or incandescent room lighting consists of a 120-Hz fundamental and its harmonics superimposed upon white noise, it is possible to separate the 1-kHz fluorescence signal from the background signal by electronic filtering. Demodulating and low-pass filtering this signal, which effectively averages each 1/2-msec pulse, enables detection of very low-level fluorescence (i.e., only 3% as intense as the background illumination in the optical wavelength band of interest).

A schematic diagram of the prototype spotter is shown in Figure 4. The illumination beam is produced by a high-pressure mercury arc lamp and modulated by an electromagnetic, tuning-fork chopper. A dichromatic beam splitter reflects the illumination beam to the telephoto output lens while it transmits the longer-wavelength fluorescence to the photomultiplier tube. The filters

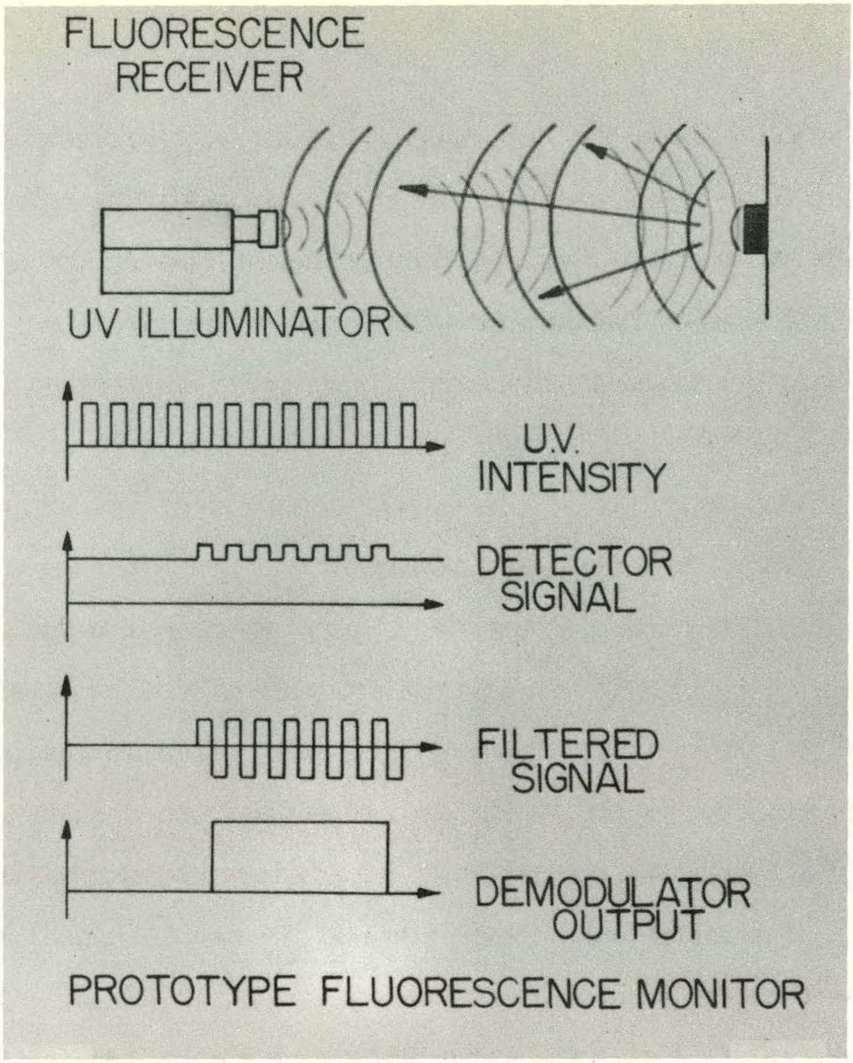

Figure 3. Principle of spotter's operation.

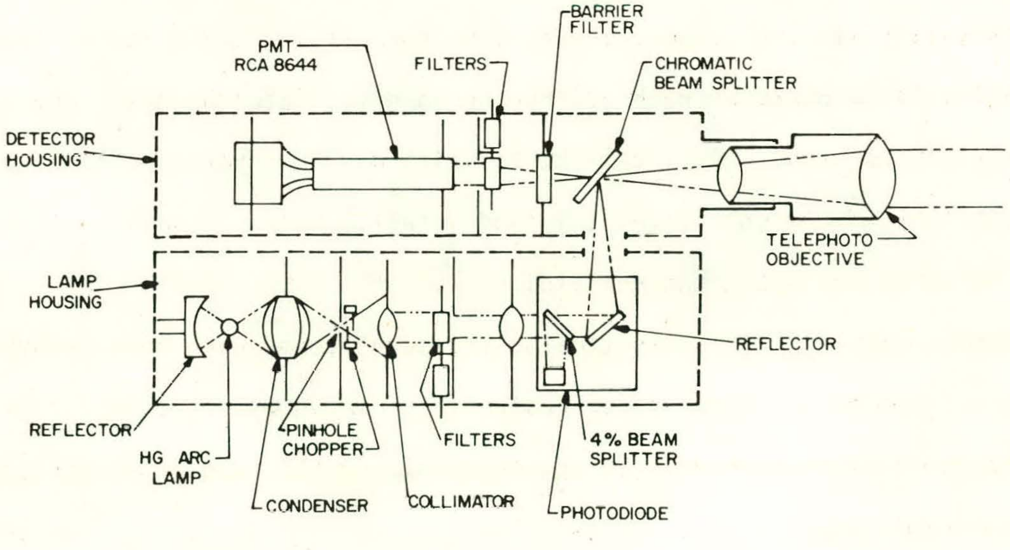

Figure 4. Schematic of the prototype spotter.

in both units are mounted in thumbwheels which project outside the housings, allowing for filter selection while the unit is in use. The telephoto lens is adjusted so as to focus the illumination beam 40 cm from the spotter (the cross-sectional area of the beam at focus is approximately 1 cm^2). This results in roughly distance-independent fluorescence measurements for distances ranging from 0 to 80 cm.

RESULTS AND DISCUSSIONS

The prototype spotter has been laboratory tested with a number of liquid samples and with films and smears of coal conversion oils on selected construction materials. Table 1 lists the sensitivity of the prototype spotter to various coal process liquids. The samples used in these measurements were 1- to 20-μ-thick films of the materials prepared on microscope slides with cover slips. The variation in sensitivity to the different coal liquefaction or oil shale products generally reflects the different PNA content of each; for some substances (e.g., ORNL hydrocarbonization oil), the sensitivity also apparently depends on the relative asphaltene-vs-light oil content of the material as will be discussed later. These figures are actually upper limits on sensitivity since they were computed by normalizing the measured fluorescence from milligram amounts of each oil by the observed detector noise and the amount of material observed. Milligram-level smears of ORNL hydrocarbonization oil and COED syncrude on both floor tile and metallic surfaces have also been examined in a less quantitative fashion.

The sensitivity of the spotter to solutions containing PNAs or acridenes, including some hydrocarbonization wastewaters, is shown in Table 2. Note that the spotter is sensitive to microgram amounts of pure compounds (perylene) in dilute solution.

Table 1

Sensitivity of the Spotter to Various Coal Conversion Oils and Solvents

SAMPLE	SENSITIVITY (MICROGRAMS)
SRC-I RECYCLE SOLVENT	27
SRC-I WASH SOLVENT	129
SRC-I PROCESS SOLVENT	34
SRC-I LIGHT ORGANIC LIQUID (RAW)	884
SRC-II FUEL OIL BLEND	17
CENTRIFUGED SHALE OIL (PROCESS I)	26
HYDROTREATED COAL DISTILLATE	38
PRODUCT DISTILLATE ($ZnCl_2$)	11
COED SYNCRUDE	20
ORNL HYDROCARBONIZATION OIL (HC-12)	790

Table 2

Sensitivity of the Spotter to Solutions and Aqueous Coal Conversion Liquids

SENSITIVITY TO VARIOUS SUBSTANCES

(EXCITATION = 350 nm, EMISSION CUT-ON = 420 nm)

SAMPLE	SENSITIVITY (MILLIGRAMS)	DISTANCE (cm)
HC-10 SCRUBBER H_2O	1.0	22
HC-8 BIOREACTOR FEED	10.0	22
W-41 BIOREACTOR EFFLUENT	250.0	22
UNH ($UO_2(NO_3)_2 \cdot 6H_2O$)	1.0	27
PERYLENE	.001	82

Coal liquefaction products may contain certain compounds which, in sufficient amounts, quench the fluorescence of PNAs and thus interfere with fluorometric monitoring techniques. Two classes of aromatic compounds that are abundant in coal conversion products are phenols and acridenes. We have tested for phenolic interference by adding large excesses of phenol to solutions containing perylene. As one might expect from the fact that there is no overlap between the optical absorption of phenol and the fluorescence emission of PNAs, phenol did not interfere with our fluorometric PNA determinations. However, heteroatom aromatic compounds such as acridenes, which are abundant in oils having a high asphaltene content, do apparently affect PNA fluorescence. The optical absorption of many acridenes overlaps the emission from PNAs, resulting in a shift of the fluorescence to longer wavelengths and a decrease in its intensity. Normal PNA fluorescence of materials such as ORNL hydrocarbonization oil is observed, however, upon fivefold dilution of the oil with aliphatic solvents or oils. We are examining the possibility of taking smear samples of potentially contaminated surfaces using porous materials such as plastics in situations where ultra-low-level monitoring of contamination by these heavy oils is required.

The prototype spotter provides the capability for crude discrimination among classes of organic contaminants, such as PNAs and BTXs (benzene, toluene, xylene), by selection of optimal excitation and emission wavelengths with optical filters. The spotter can also discriminate the fluorescence of uranyl nitrate (UNH) from the fluorescence of organic compounds, even though both have similar optical properties, because the luminescence lifetime of uranyl nitrate is comparable to the 1-msec beam modulated period. This results in a nonzero phase shift in the fluorescence signal from uranyl nitrate samples which can be discriminated electronically with a phase-sensitive demodulator. Since the spotter is sensitive to 1-mg amounts of UNH, it could conceivably be used in nuclear fuel and waste handling facilities to locate spills or leakage of UNH-containing liquids.

FUTURE DEVELOPMENTS AND ACTIVITIES

The characteristics of the prototype spotter which are important to its function as a survey device are:

1. Its high sensitivity, due to the strong native fluorescence of PNAs.
2. Its ability to operate in either illuminated or darkened work areas.
3. Its ability to yield a semiquantitative measurement of the amount of spilled material at variable spotter-to-surface distances.
4. Its ability to detect spills remotely at distances from 0 to 2 meters.

Portability is being incorporated into the design of an advanced version spotter (Figure 5) which is to be field tested in DOE coal conversion facilities. This version is approximately 25 cm long x 15 cm high x 5 cm wide (neglecting telephoto lens), a size comparable to that of many commercial home movie cameras. A portable, belt-pack-size, battery-powered electronics unit to be used with the advanced version spotter is also under development at ORNL in collaboration with the ORNL Instrumentation and Controls Division.

The most desirable characteristic of such an instrument is, of course, its utility. Toward this end, we have recently operated the prototype spotter in the ORNL hydrocarbonization facility, where we were able to locate PNA contamination in the experimental area. Our DOE-sponsored programmatic effects include fabrication of two advanced version spotters for comprehensive field testing in other DOE coal conversion facilities.

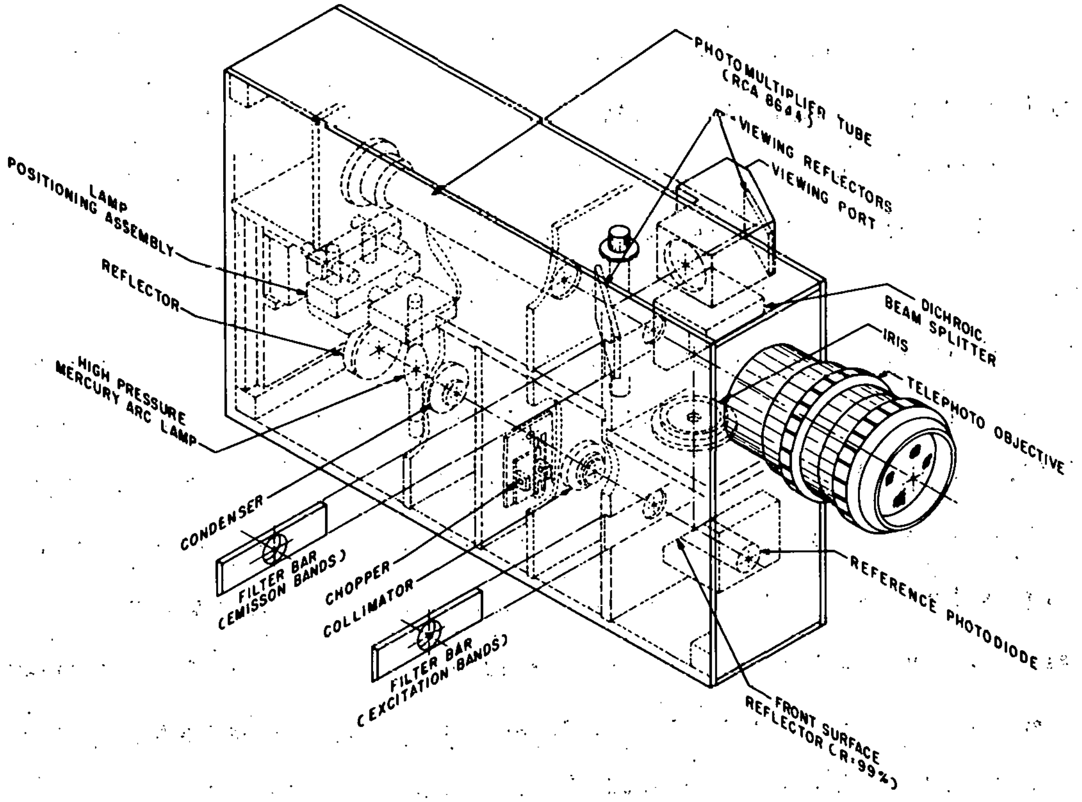

Figure 5. Advanced spotter assembly.

A POCKET-SIZED PERSONAL
AIR CONTAMINANT MONITOR

by

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Presented at:
The Symposium on Assessing the Industrial
Hygiene Monitoring Needs for the
Coal Conversion and Oil Shale Industries
November 6, 1978

ABSTRACT

A pocket-sized personal air contaminant analyzer is being developed to monitor a worker's exposure to toxic gases. The heart of this instrument is a miniaturized gas chromatograph, complete with carrier gas supply, pressure regulator, sample pump, and computer system. The instrument will be capable of automatically sampling the air at one minute intervals during an 8-hour shift, measuring the concentrations of up to 10 different gases, calculating and storing the average and peak concentrations of those gases, and sounding an alarm if potentially dangerous environmental conditions are detected. The miniature size of the package is due mainly to the use of integrated circuit processing techniques utilized in the fabrication of the major components of the chromatograph. This instrument, which is currently in the early prototype development phase, will allow the on-site monitoring of a mobile worker's exposure to multiple gaseous contaminant, which should have a significant impact on the field of industrial hygiene.

INTRODUCTION

Gas chromatography is a widely used technique to analyze air samples for contaminant gases. Gas chromatographs have been too massive, however, to be unobtrusively carried by a worker for the purpose of environmental monitoring. Recently the techniques of integrated circuit processing have been utilized to greatly reduce the size of all major components of a standard gas chromatograph (GC), so that a completely self-contained instrument weighing less than one kilogram is now possible. The prototype of such an air contaminant monitor containing an integrated GC is currently under development. It is anticipated that the final instrument will be capable of sampling the air at one-minute intervals during an eight-hour shift, analyzing the sample for up to ten selected contaminant gases, calculating and storing desired average exposures for each gas, and be capable of warning the wearer of dangerous environments by sounding an alarm when any concentration exceeds a preset maximum exposure limit.

The completely self-contained gas chromatograph system, as shown in Fig. 1, consists of a gas chromatograph for doing the actual separation of gaseous impurities from the air and a microcomputer system for both analyzing the separated components and controlling the operation of the complete instrument. The chromatograph separates gaseous contaminants from air by injecting a brief pulse of sample at the head of a long separating column. A carrier gas, which is continually flowing through the column, transports the sample past a column lining which is capable of absorbing and desorbing the constituents of the sample mixture. Different impurities are retained in the lining for different total amounts of time, so they will exit the column at characteristically different times. A detector placed at the column output measures the concentration of the now separated impurity peaks and the computer system determines the identity of the peaks using stored retention time data, calculates the present concentrations, updates the average concentrations, sounds an alarm if any concentration exceeds a stored maximum, and will display any concentration on demand.

DEVICE FABRICATION

The heart of the complete system is the integrated GC which consists of a sample injection valve, separating capillary column, and output detector. These elements are fabricated on a single 5-cm diameter silicon wafer using a sequence of photolithography and silicon etching steps. The etches were developed from integrated circuit processing techniques which allow very tight control over the locations and geometries of the etched features. The separating column is formed by etching a spiral groove in the top surface of the silicon wafer and then hermetically sealing the wafer to a piece of Pyrex glass. A photograph of such a wafer and glass assembly is shown in Fig. 2. The column is 1.5 meters long with a cross section of 150 x 30μm. Etched holes through the wafer lead to the sample injection value and output detector which are located on the bottom surface of the silicon wafer. The sample injection valve is an extremely small solenoid operated diaphragm valve which is capable of reproducibly injecting samples of less than 10-nl volume. The detector is an integrated thermal conductivity detector which is batch fabricated using integrated circuit processing techniques and is capable of detecting impurity concentrations of about 500 ppb at the detector. The capillary column is lined with a thin layer of liquid stationary phase by passing a plug of the lining through the capillary and then blowing the column dry.

The complete chromatography system utilizes support components which have been miniaturized to roughly match the size of the integrated GC. Since the column cross sectional area is so small, the column operates on extremely small gas flows, which allows a significant reduction in the carrier gas supply. A 10cc high-pressure gas cartridge, for example, is capable of supplying the nominal 0.2 nl/min carrier gas flow rate for about 100 hours of operation. A pressure regulator prototype has been built using another miniature diaphragm valve and a 10cc surge tank to supply carrier gas at constant pressure to the chromatograph. Since the one valve injection scheme requires sample gas to be pressurized above the carrier gas input pressure, a miniature piston pump has been developed which draws in samples from the air on command from the computer and pressurizes them for the injection valve.

Recent advances in the field of large scale integrated circuits have allowed entire microcomputer systems to be built on silicon chips less than 5mm on a side. Without such a computer system a pocket-sized gas chromatograph would not be possible. The computer, with only a few small support circuits, handles the adjustment and sequencing of the pressure regulator, sample pump, input valve, and detector amplifier. In addition, it analyzes the detector amplifier output to do peak detection, integration, base line correction, impurity gas identification, and concentration calculations. Low power, low cost microcomputers are becoming available which will allow continuous operation of the instrument for an eight-hour shift on a small rechargeable battery.

A preliminary drawing of the final configuration of the instrument is shown in Fig. 3. The package size, 4cm x 8cm x 15cm, and the expected weight of 0.6 kg should allow for relatively convenient and unobtrusive use of the instrument.

SYSTEM PERFORMANCE

The performance of the instrument is now limited mainly by the rather short, 1.5m, column and the extremely small sample injections. The short column requires extremely efficient column linings in order to provide good separations in the short times available and at ambient temperature. Since the amount of column lining is limited by the available column surface area, the injected samples must be limited to about 10nl in order not to overload the lining. An injection of 10nl of 10ppm hexane, which is now at the limit of detection, represents only 0.4pg of impurity.

The work on column linings to this point has been somewhat limited due to the lack of complete, working chromatographs. Recent work with the stationary phase Squalane, for example, has given some beginning indications of the performance of the instrument. One such separation, with a rather thin column lining is shown in the oscilloscope photograph of Fig. 4. The air peak is mostly off screen, and hexane, heptane, and octane impurity peaks can be seen. The peak on the far right, octane, was injected at a concentration of about 4000ppm.

The height equivalent to a theoretical plate (HETP) of this column is less than 0.1mm. A thicker lining tends to increase the HETP but also increases the separation factor. A thicker Squalane lining with a HETP of about 1.0mm was able to clearly separate air, acetone, pentane, hexane, and heptane.

It is not completely clear at this point what performance will be obtainable from the miniature columns. Many techniques which have been developed for increasing the surface area of standard GC columns should be applicable in the miniature columns and would substantially increase performance. The columns can now be fabricated with a high yield of working units, so that investigation of different lining schemes can now proceed. It seems highly probably that linings can be developed which will have the required performance to separate about ten different gases, but probably different column linings will be required for different classes of compounds, for example polar vs nonpolar substances.

Although the detector is capable of detecting impurities at about the 500ppb level, there is significant broadening of the impurity peaks from injection to detection, so it appears that the minimum level of detection of substances in air for this unit will be about 10ppm. It is hoped that improved detector systems and peak detection programs can be developed to reduce this limit, but the detection of gases under 1 ppm may never be possible for such a portable chromatograph.

CONCLUSION

A complete portable gas chromatograph has been designed and all major components built and tested. Some development work is still necessary to improve the performance of the column linings and to fully integrate all system components before the prototype phase will be completed. The final pocket-sized instrument will be capable of separating and measuring up to ten sample gases and calculating and storing their time weighted average concentrations. It will be fully self-contained and capable of unattended operation for an entire eight-hour shift. In addition, with minor software changes, the same instrument could be used as an initial survey device to quickly assess the concentrations of the programmed impurity gasses at many locations in a plant. As a personal monitor, the instrument should significantly expand the ability to measure workers' exposures and aid in the reduction of those exposures. In such an application, the device should prove to be a useful analytical tool and should have significant impact on the fields of industrial hygiene and occupational safety.

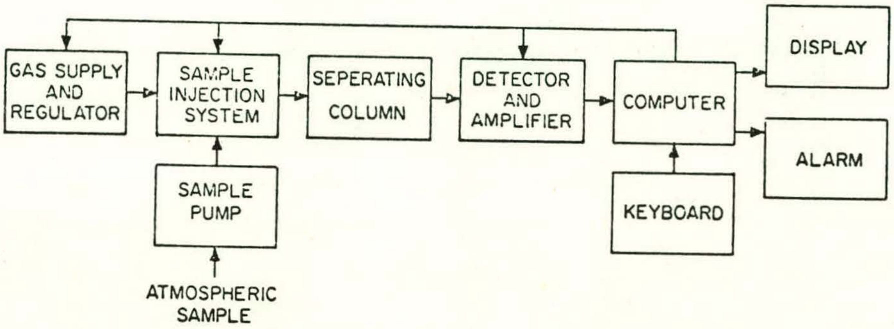

Figure 1. Block diagram of proposed gas chromatographic air analyzer.

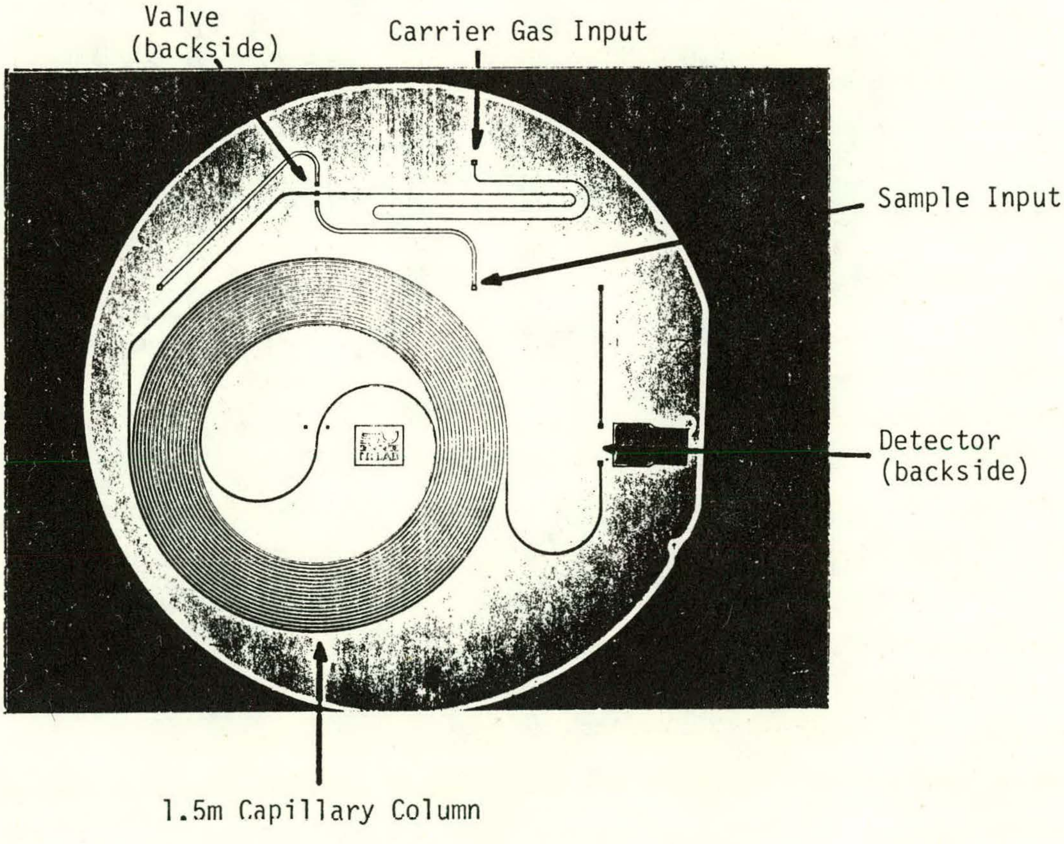

Figure 2. Photograph of 5-cm diameter etched silicon wafer. View is through Pyrex glass cover plate.

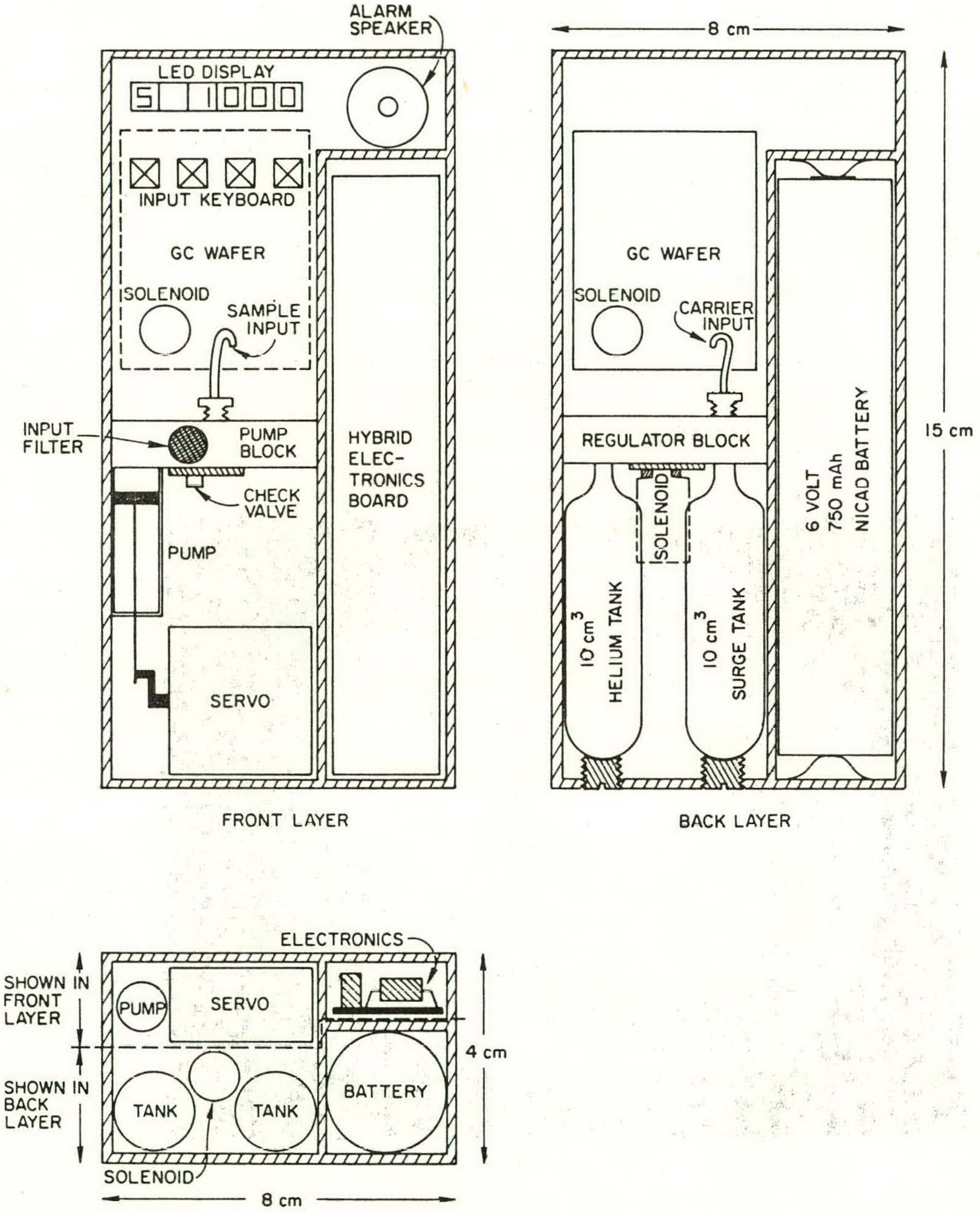

Figure 3. Proposed layout of pocket-sized gas chromatographic air analyzer system.

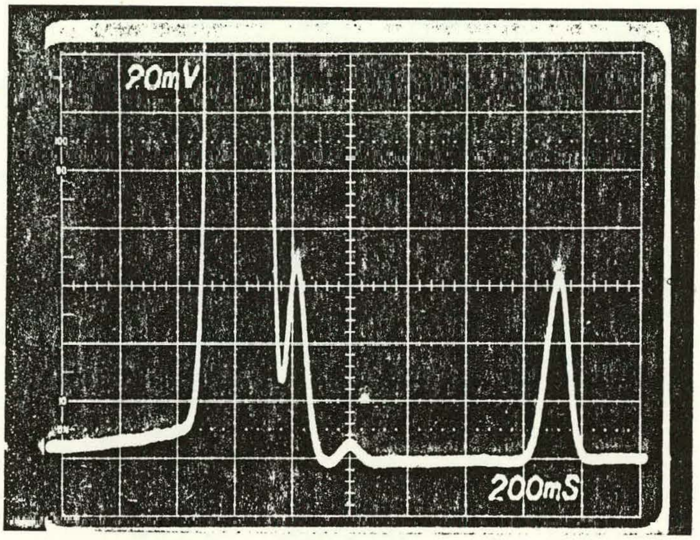

Figure 4. Oscilloscope photograph of amplified detector output showing, from left to right, air, hexane, heptane and octane peaks.

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RECENT ADVANCES - SOLID STATE GAS DETECTION

RECENT ADVANCES IN THIN SOLID FILMS FOR SOLID STATE GAS DETECTION

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Presented at the Symposium on Assessing the Industrial Hygiene Monitoring Needs for the Coal Conversion and Oil Shale Industries, Brookhaven National Laboratory, Upton, ~~NY~~ 11973, November 6-7, 1978.

RECENT ADVANCES IN THIN SOLID FILMS FOR SOLID STATE GAS DETECTION

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Abstract

Several materials systems have shown promise as thin films for solid state gas detection when incorporated in integrated devices using standard planar processing techniques[1]. Among the several active areas of pursuit, impressive recent advanced in thin film metal-oxide semiconductors, metals, and certain organic materials suggest a bright future for the development of highly intergradable solid state gas sensing devices. Recent developments in thin film metal-oxide semiconductors (ZnO) sensitive to CO and O_2, hydrogen and H_2S sensitive metal-gate MOS structures, and an organic thin film (phthalocyamine) sensitive to NO_2 are discussed in this, the first part of a two part presentation entitled "Recent Advances - Solid State Gas Detectors"

Introduction: ZnO as a Material for Gas Detection

Materials systems whose electrical properties are influenced directly by reactions with the gas ambient and which lend themselves to standard planer processing have received considerable attention recently. As a specific case ZnO was a likely candidate for study because of its long service record as an industrial catalyst. Electrical properties of ZnO surfaces are very sensitive to ambient conditions and high purity single crystal specimens are valuable for studying such processes. Gas-solid interactions by chemisorption processes involve charge transfer of electrons to or from surface layers. Figure 1 illustrates a specific example of oxygen chemisorption on n-type ZnO. Oxygen acts as an acceptor introducing surface acceptor states that deplete electrons from the solid. Energy band bending depicted in this figure has a spatial extent on the order of a Debye length, L_D into the solid.

$$L_D^2 = \varepsilon kT/q^2N_D$$

Conductivity measurements on single crystal specimens,however,will not reflect this surface sensitivity if its spatial extent is small compared to the sample thickness. In polycrystalline films the surface charge transfer process is still at play and with crystallite size small, the surface layers dominate the measured conductance. Figure 2 is an illustration of possible processes in polycrystalline films where individual grains are connected to form a conducting medium.

For the first situation we show adsorption of oxygen at free surfaces which establishes a depletion region accompanied by a large reduction in free charge. The depletion region can extend through the intergranular contact as shown pinching off the conduction path between grains. In the second figure oxygen is adsorbed along grain contacts as well resulting

ZnO Surface Band Bending

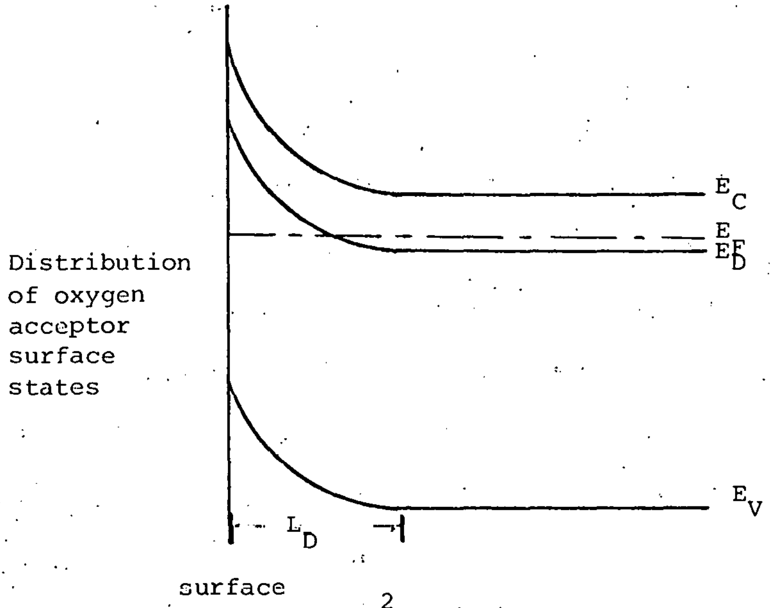
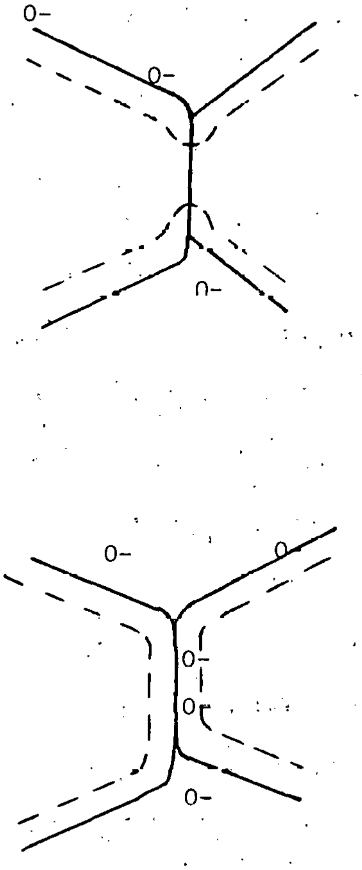


Figure 1

$$L_D^2 = \varepsilon kT/q^2N_D$$



$$R_{meas} = q/n_{eff}q\mu_{eff}$$

Figure 2

in a potential barrier to carrier flow between adjacent grains that is modulated by the amount of oxygen on the surface. The expression for the measured resistance of such films is

$$R_{meas} = g/_{n_{eff} q \mu_{eff}}$$

where n_{eff} is the effective carrier concentration in the individual grain, q is the electronic charge, μ_{eff} is the effective mobility in the intergranular region, and g is a geometrical parameter.

Studies by previous workers on films of this geometry have analyzed the situation by considering a highly conductive grain to be separated from its neighbors by a second high resistance phase that effectively determines the measured resistance. Such an oversimplification does not deal with the electronic processes directly and can not give more than qualitative information if applied to gas sensitivity.

A more fundamental approach recently applied to this situation has provided a semiquantitative description of electronic processes and a guide for materials processing to optimize gas sensitivity of polycrystalline metal-oxide semiconductors.

A chemisorption charge transfer model would be expected to depend critically on grain size and the corresponding number of free carriers which take part in conduction and surface reactions. For the case of small crystallites the volume concentration of surface acceptors can be comparable to or, even greater than the volume density of free carriers inside. Such a situation requires simultaneous solution of Poisson's equation and the charge neutrality equation for each grain. We apply this approach to determine crystallite surface potential and from this the effective carrier concentration as a function of the density of ionized surface acceptor states for a particular set of materials parameters (e.g., grain size and geometry, dopant concentrations, donor and acceptor energy levels distributed in the bandgap, capture cross section for surface acceptor states, etc.). For the case of ZnO the effective carrier concentration versus grain size is plotted in Figure 3 for a given surface acceptor density, N_{ss}. The results of the computer solution suggest the existence of a sharp transition in the effective carrier concentration between a highly conductive grain with large radius and a nearly fully depleted grain of small radius. The transition is for small changes in grain size and,for a given doping level,is a function of temperature and concentration of surface acceptor states. The result suggests that material parameters might be adjusted such that small changes in surface acceptor density could give rise to large changes in n_{eff} and the measured resistance of the film. The effect of a distribution in grain size about a mean and a distribution in energy of surface acceptor levels and bulk donor levels is shown to smear out this sharp transition.

The situation is illustrated in Figure 4 where n_{eff} is plotted from the computer solution versus N_{ss}, the surface acceptor concentration for ZnO material parameters as listed in the figure. For the parameters used, an optimum sensitivity of n_{eff} to N_{ss} is determined for a discrete grain size of 35nm at room temperature.

We have to some extend experimental confirmation using Hall and conductivity measurements that a high sensitivity region may indeed exist. We have been successful in fabricating and studying films that have a distribution in grain size and that would appear to lie in the upper and lower regions of the curve, but have failed to produce films to date that lie in the transition region. Fortunately, the RF Sputtering process employed for film deposition affords good control of doping and grain size.

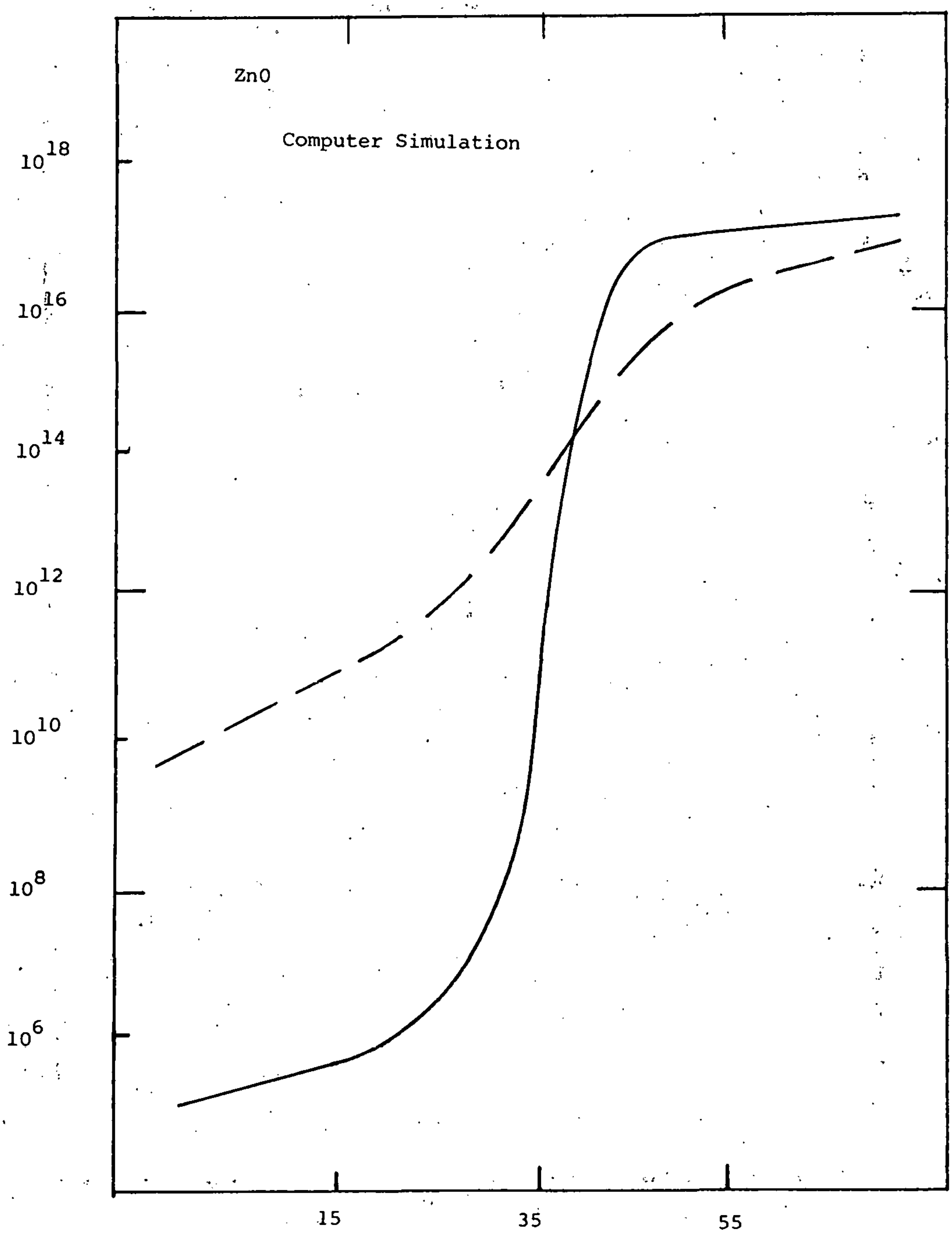

ZnO
Computer Simulation
10^18
10^16
10^14
10^12
10^10
10^8
10^6
15
35
55
Grain Size R (nm)

Figure 3.

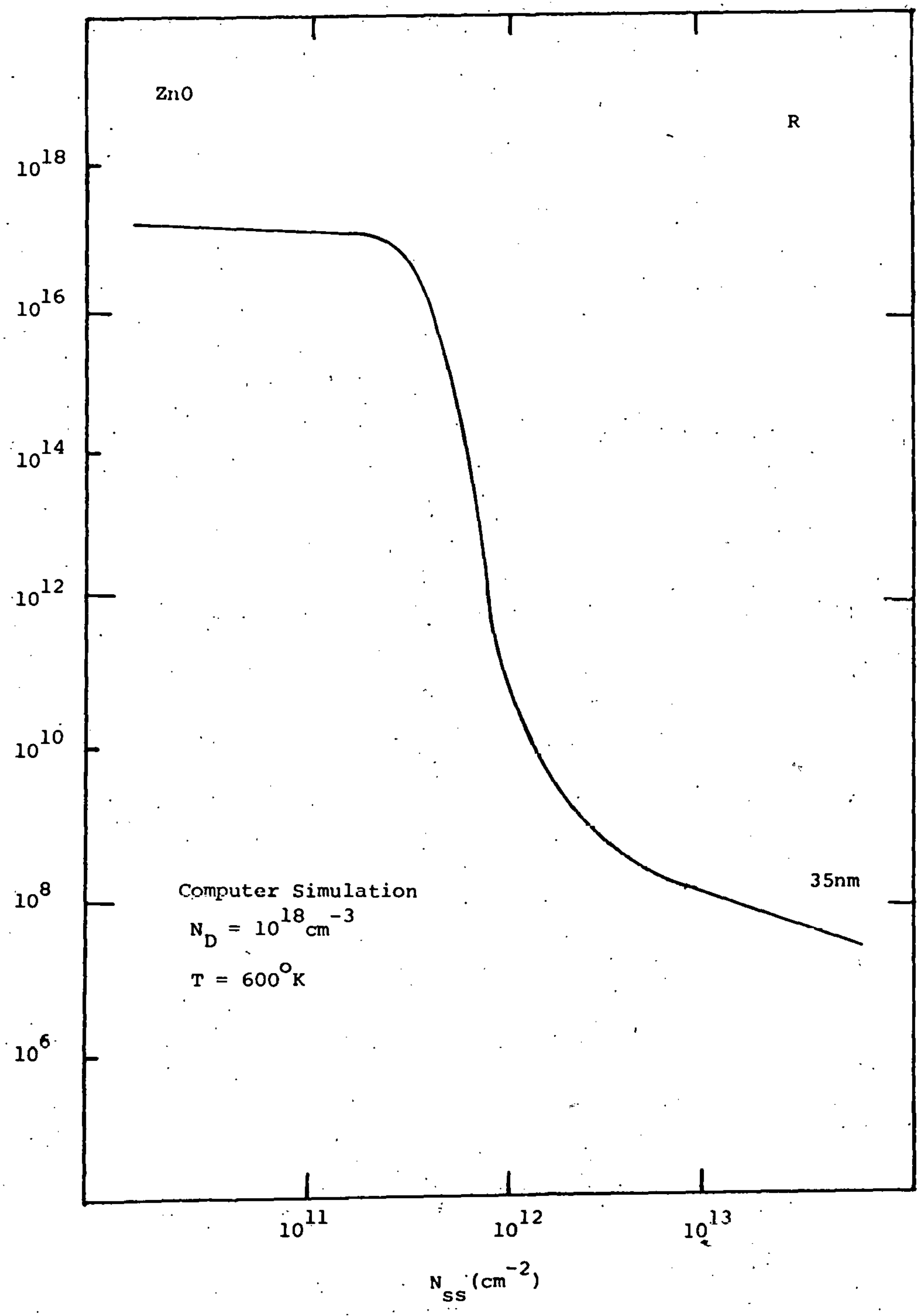

ZnO
R
10^{18}
10^{16}
10^{14}
10^{12}
10^{10}
10^{8}
10^{6}
35nm
Computer Simulation
$N_D = 10^{18} cm^{-3}$
$T = 600^{\circ}K$
10^{11}
10^{12}
10^{13}
$N_{ss} (cm^{-2})$

Figure 4.

Gas Sensitivity: ZnO

Figure 5 illustrates the sensitivity of ZnO to CO in air. Plotted is the change in resistance of a ZnO thin film resistor operated at elevated temperatures versus CO concentration in parts per thousand. The response of the film is due to interaction of gaseous CO with ionized adsorbed oxygen in the oxidation reaction of CO of CO_2. The net process donates an electron to the conduction band at the surface and the film resistance decreases.

If an isobar from this figure for 5ppt CO is plotted with temperature as a parameter the curve of Figure 6 results. The bell shape in the response versus temperature suggests a temperature distribution for the form of ionized oxygen on the surface,where in the region of highest sensitivity the predominant adsorbed form is O^-. It is well known that certain catalytically active metals such as Pd and Pt are used in oxidation and hydrogenation reactions[3]. Incorporation of such a metal in small quantities as a dopant in ZnO is observed to increase the sensivitity of thin films to chemisorption and catalytic charge transfer processes. Additionally, the response curve for these films in Figure 6 is shifted to lower temperatures. This is a desirable feature in integrated devices on silicon where thermal isolation of adjacent devices is a significant developmental problem.

H_2 and H_2S Sensitive MOS Structures

Thin metal films which dissociatively dissolve H_2 such as Pd and Pt have been incorporated in integrated diodes and capacitors on passivated silicon substrates[4,5]. Changes in work function at the metal-SiO_2 interface induced by ionized H_2 and gases such as H_2S and NH_3 can give rise to large changes in the reverse leakage current of a Schottky diode or changes in the flat band voltage of MOS capacitors. H_2 sensitivity is shown in Figure 7 with the structures operated at room temperature. The figure

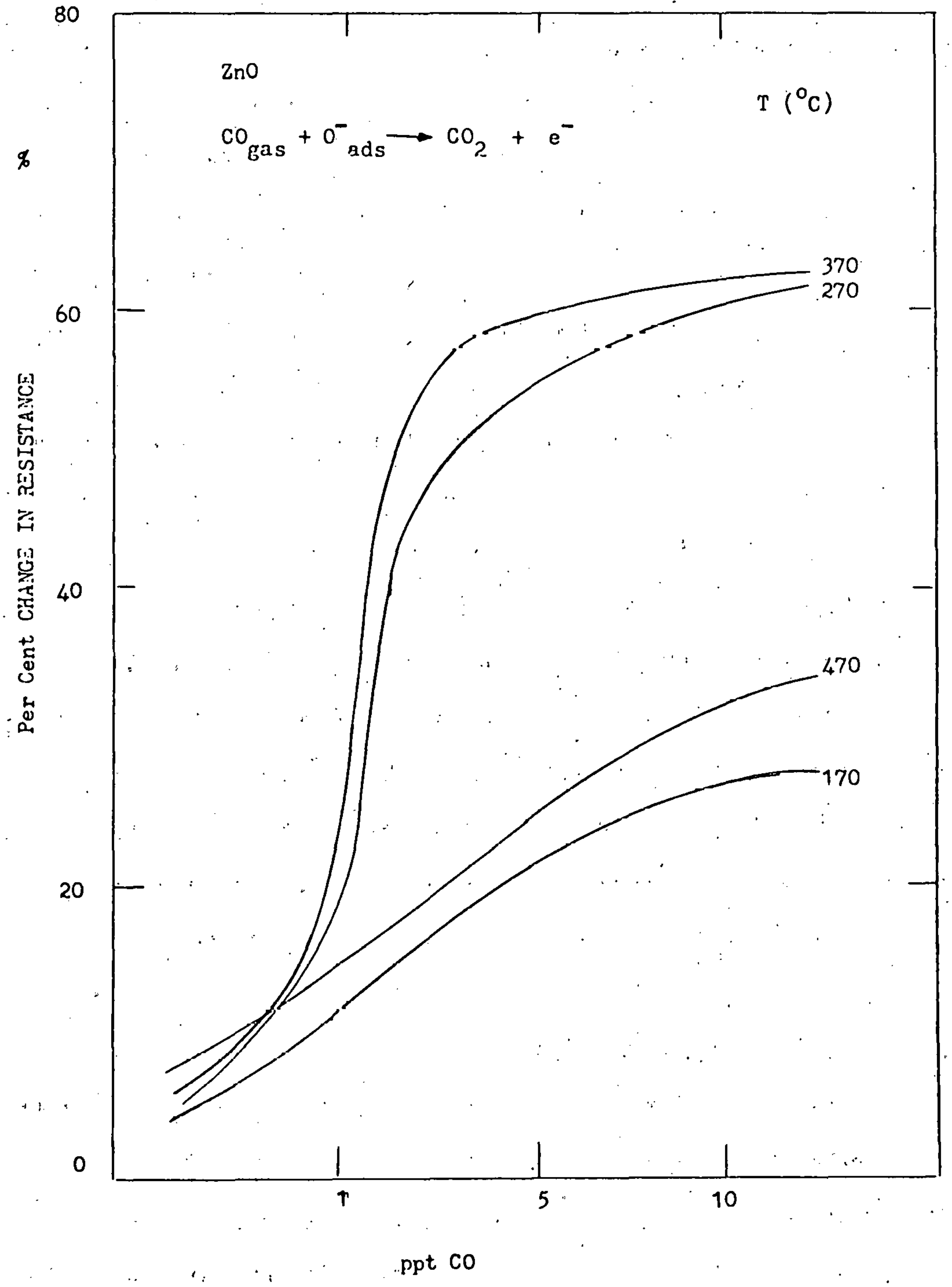

80
60
40
20
0
%
Per Cent CHANGE IN RESISTANCE
ZnO
$CO_{gas} + O^-_{ads} \rightarrow CO_2 + e^-$
T (°C)
370
270
470
170
1
5
10
ppt CO

Figure 5.

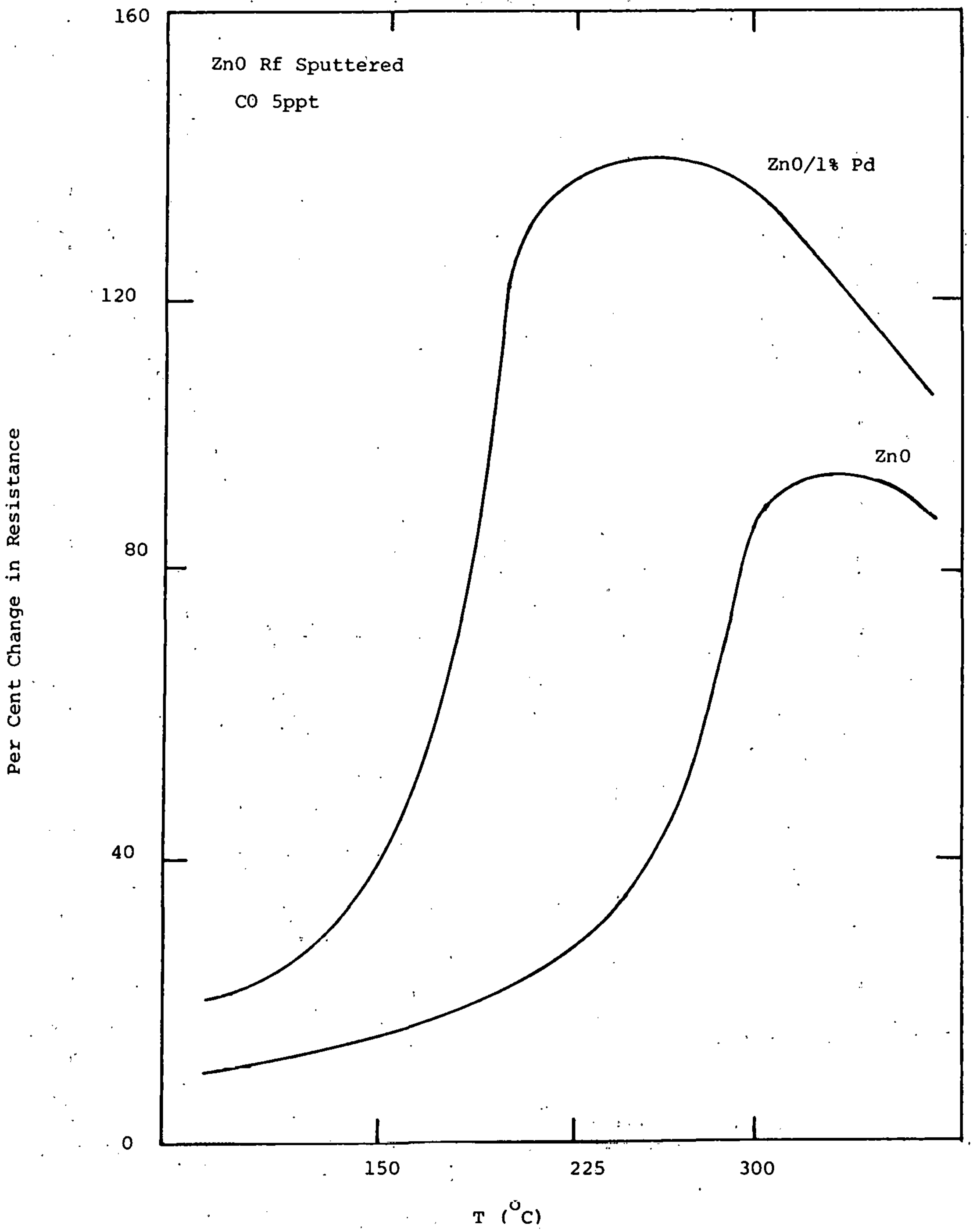

160
120
80
40
0
ZnO Rf Sputtered
CO 5ppt
ZnO/1% Pd
ZnO
Per Cent Change in Resistance
150
225
300
T (°C)

Figure 6.

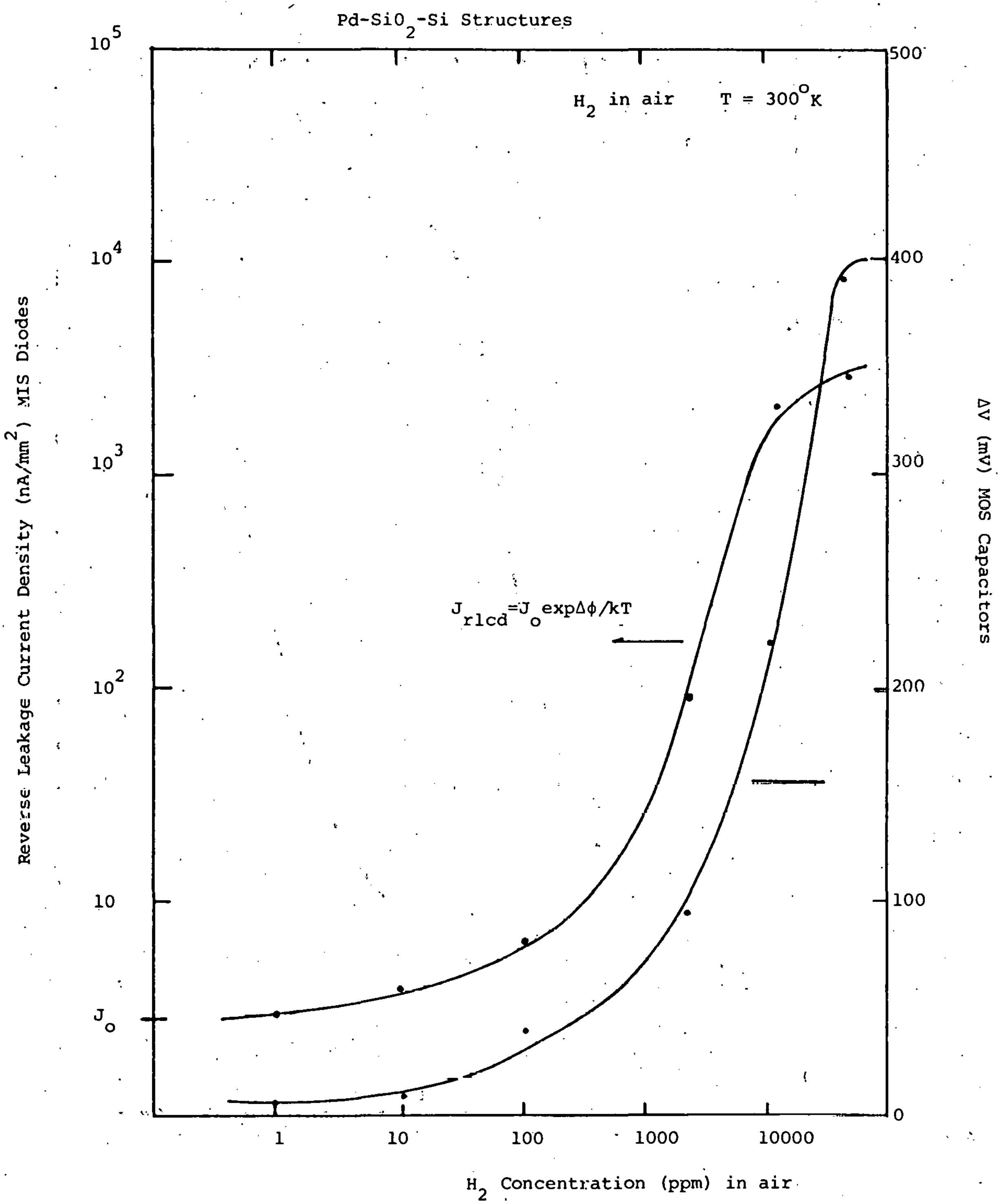

Pd-SiO_2-Si Structures
H_2 in air
T = 300°K
10^5
10^4
10^3
10^2
10
J_o
Reverse Leakage Current Density (nA/mm^2) MIS Diodes
500
400
300
200
100
0
ΔV (mV) MOS Capacitors
$J_{rlcd}=J_o\exp\Delta\phi/kT$
1
10
100
1000
10000
H_2 Concentration (ppm) in air

Figure 7.

illustrates diode sensitivity in terms of changes in reverse leakage current and changes in capacitor flat band voltage versus hydrogen concentration. 1 to 10 ppms H_2 in air are detected with the upper limit on sensitivity being near 1% H_2.

MOS capacitors can be operated at elevated temperatures improving response times and the sensitivity to H_2 is perverved. Both structures are sensitive to H_2S, but operation at room temperature results in a short term deterioration in response due to sulfur poisoning of the metal surface. However, the sensitivity is entirely reversible at elevated temperatures above 160°C in air. Diode structures can not be used at elevated temperatures whereas MOS capacitors retain their characteristics substantially in this temperature range. As an alternative to measurements of changes in flat band voltage with H_2 or H_2S, the actual change in capacitance can be measured at a given gate voltage. Figure 8 illustrates the result of such a measurement plotting changes in differential capacitance versus H_2S concentration at elevated temperature in air. 1 to 10 ppm H_2S can be determined. Device sensitivity can be improved by minimizing the SiO_2 dielectric thickness.

Detection of NO_2 with Organic Semiconductor

Recent interest in organic semiconducting thin films sensitive to various gas species has produced some impressive results[6]. As a specific example, a thin film polymeric material, phthalocyamine, has been shown extremely sensitive to NO_2 and Cl operated at elevated temperatures. A change in film resistance is measured with detection in the parts per billion range for NO_2. A sensitivity curve of measured resistance versus NO_2 concentration is shown in Figure 9 (after reference 6). The attractive aspect is that the material can be processed with conventional planar techniques.

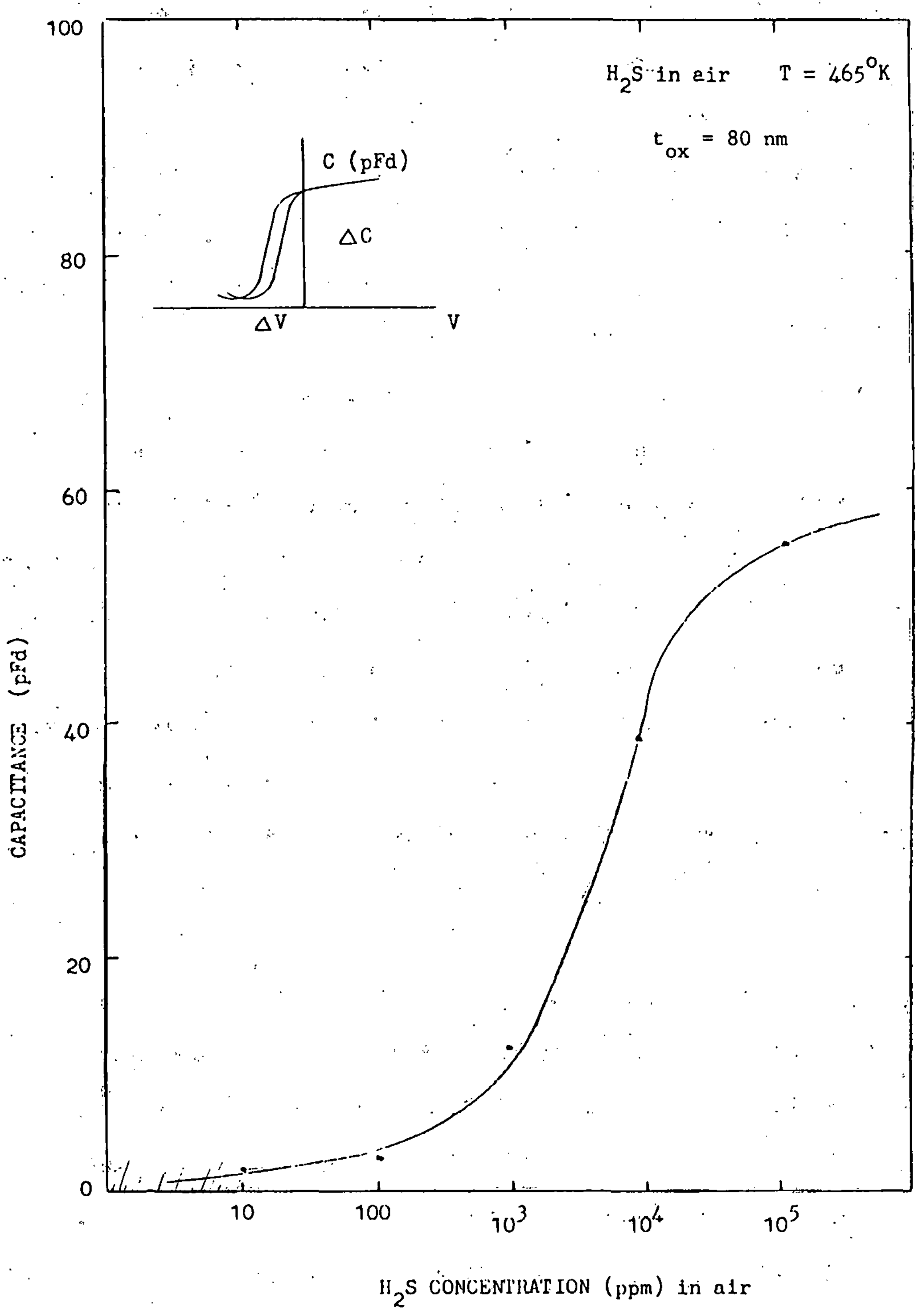

100
80
60
40
20
0
CAPACITANCE (pFd)
H_2S in air
$T = 465^\circ K$
t_{ox} = 80 nm
C (pFd)
ΔC
ΔV
V
10
100
10^3
10^4
10^5
H_2S CONCENTRATION (ppm) in air

Figure 8.

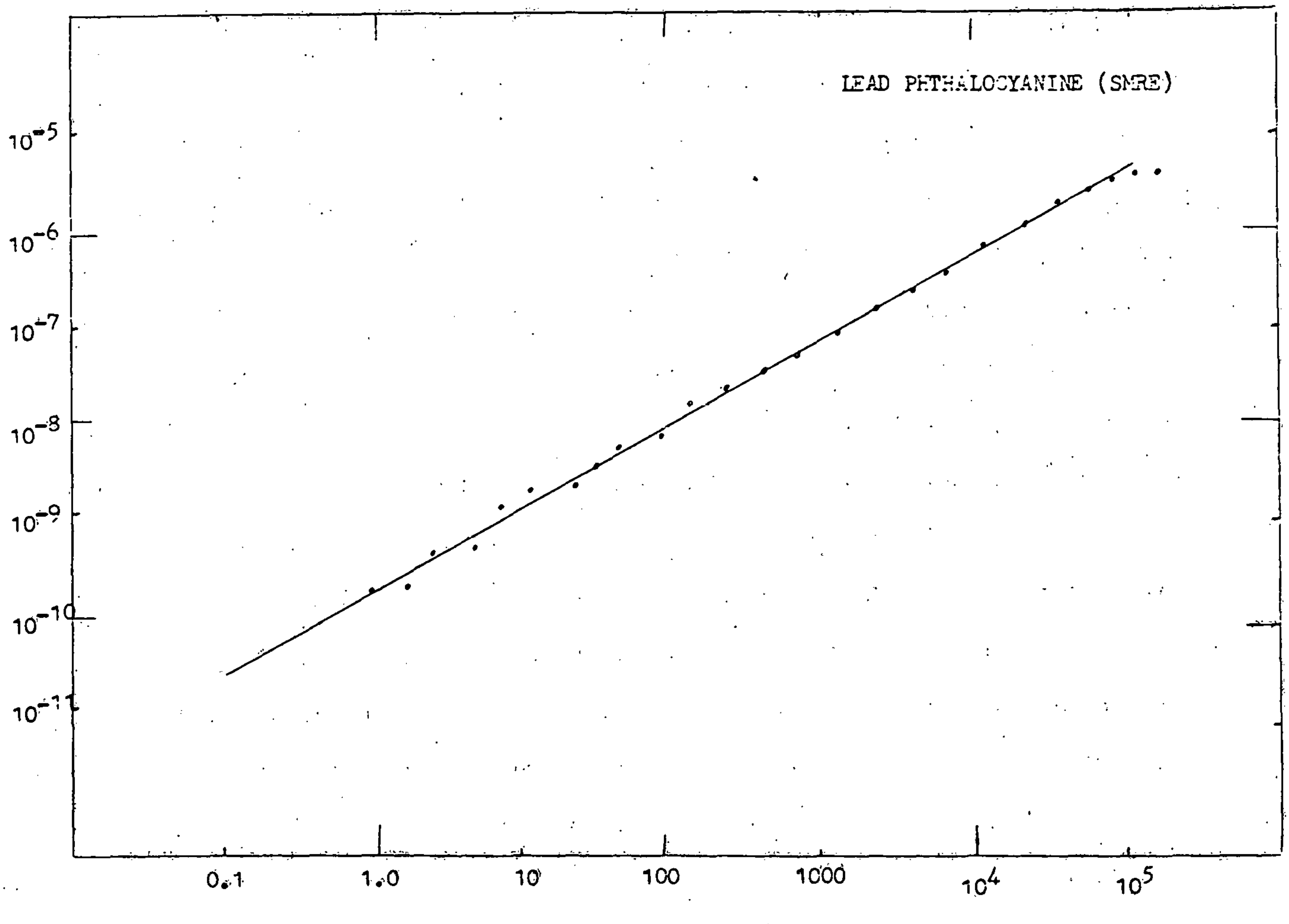


Figure 9. After ref. (6).

The aspect of selectivity has been approached from several angles. Figure 6 was one specific illustration where the addition of a catalyst as a dopant impurity shifted the ZnO temperature distribution for the response of the film in the case of CO. In general, the sensitivity of a metal-oxide is temperature dependent and conceivably an array of devices operating at different temperatures with the associated signal processing could be used to discriminate several gas constituents. Alternatively, pre-processing of the gas ambient by filtering of the gas components, analogous to pre-processing of communications waveforms before detection, can provide selectivity as well. We have been working to incorporate Zeolite molecular sieves with commercially available devices and with our own integrated versions. Figure 10 demonstrates the results of the use of a 3 angstrom pore size Zeolite deposited on ZnO as a filter for CO. H_2S, which is a poison to ZnO, is screened out because its molecular size is too large to pass through the Zeolite. Responses to H_2S without the Zeolite are shown. With the filter, H_2S is effectively screened from the sensor. The currently employed deposition process for the Zeolite is not fully compatible with standard planar processing techniques and before this technology can be fully implemented, thin film deposition of molecular sieve material must be developed.

Figure 11 illustrates the utility of 3A Zeolite for separation of H_2 and H_2S. The results shown here are for a commercially available SnO_2 based detector. Two identical detectors, with one incorporating the Zeolite, can effectively descriminate the response to H_2S from that of H_2. This is also of interest for the diode and capacitor structures referred to earlier.

Finally, separation in time with the chromatography column described in this symposium[7] incorporating our sensors at the end of the column is

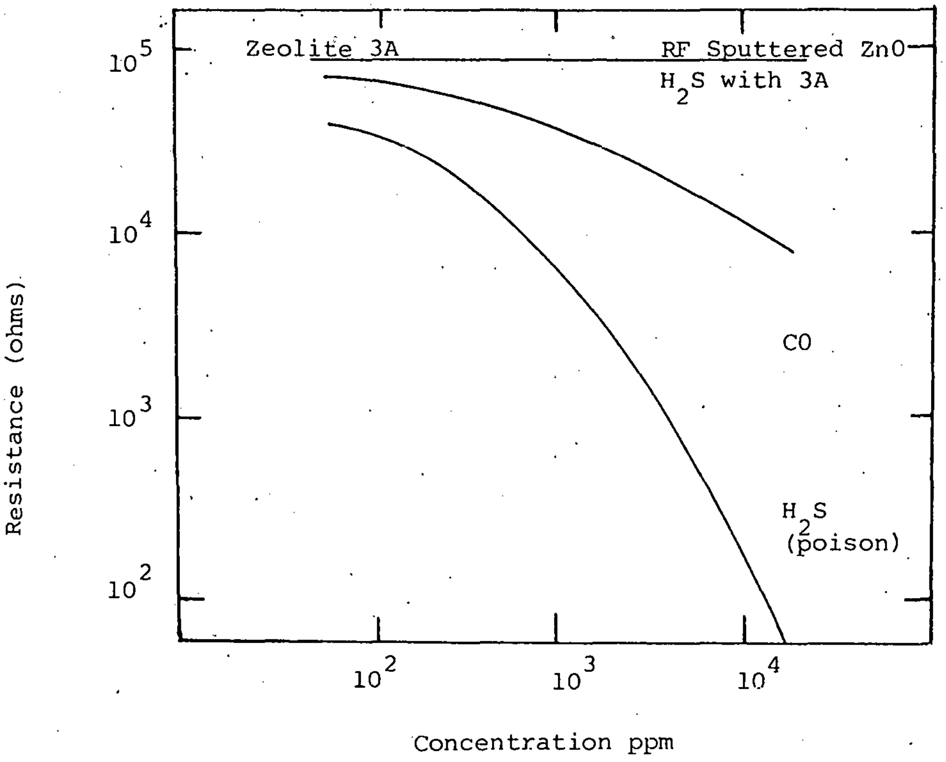


Figure 10

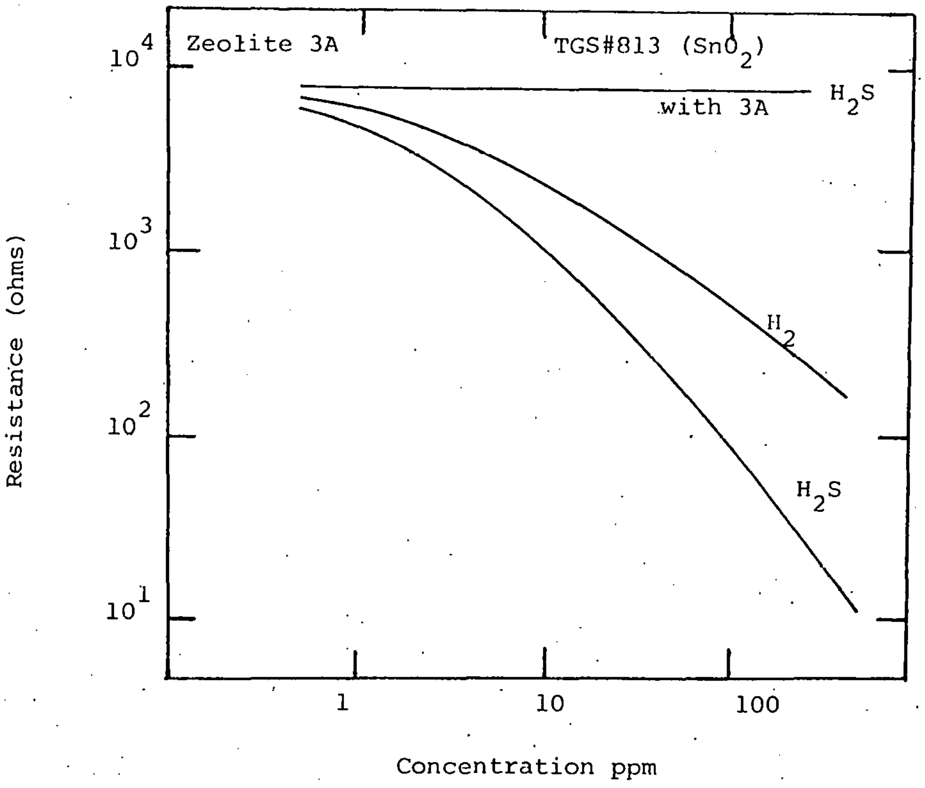


Figure 11

possible. The high degree of integrability and success of implementing standard processing to these materials have given some results that so far appear promising.

We have concerned ourselves in the first section of the presentation with recent developments of materials and devices around which some solid state detectors are based. Part II discusses developments with the associated signal processing and development of algorithms making the best use of already existing sensor technology.

References

Morgan, M.G. and Morris, S.C., "Individual Air Pollution Monitors -- An Assessment of National Research Needs", Brookhaven National Laboratory, Upton, New York, July (1975).

Bednarczyk, D. and Bednarczyk, J., "The Carrier Concentration in Thin Polycrystalline Films As a Function of Crystallite Size", Thin Solid Films, Vol. 44, 137 (1977).

Dabill, D.W., et.al., "The Oxidation of Hydrogen and CO Mixtures Over Platinum Catalysts", submitted to J. Catalysis, January (1977).

Lundstrom, I., et.al., "A Hydrogen Sensitive MOS Field Effect Transistor", Applied Physics Letters, Vol. 26, 510, (1975).

Lundstrom, I., et.al., "Hydrogen in Smoke Detectors by Pd-Gate-Field-Effect Transistor", Rev. Sci. Instru., Vol. 47, 738 (1976).

Bott, B., Jones, A. and Jones, T., unpublished work.

Jerman, T. - this conference.

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PORTABLE GAS DETECTION:
ENHANCEMENT OF SEMICONDUCTOR
SENSOR CAPABILITIES BY
MICROCOMPUTER CONTROL AND SIGNAL
PROCESSING

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Presented at the Symposium on Assessing the Industrial Hygiene Monitoring Needs for the Coal Conversion and Oil Shale Industries, Brookhaven National Laboratory, Upton, NY 11973, November 6-7, 1978.

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INTRODUCTION

A primary goal of our research is the eventual development of a portable pollution monitor. The ideal monitor would be small, light weight, safe, rugged, inexpensive and capable of continuous operation throughout the workday. As a gas detection system it would need to respond reliably to combustible and polluting gases over a dynamic range of several orders of magnitude, with a time resolution of a few minutes and a typical accuracy of 10-20%. A gas detection technology that seems suited to the eventual fulfillment of these goals is that of semiconductor detectors. However, to date, semiconductor detectors have been characterized by low reproducibility, drift, and very poor gas selectivity. These limitations cannot be overcome until much more is known about the nature of the detection mechanism in the semiconductor material. Some of these limitations though appear to be inherently tied to the nature of the materials used in such a way that it is unlikely that they will be completely overcome by materials research in the near future. If the computational power which is now becoming available at low cost in microcomputers can be used to compensate for the imperfections of present solid state detectors then the development of a portable gas detection instrument may be possible. This is made possible only by the significant decrease in both size and cost of computer systems over the past few years.

To aid the theoretical understanding of the basic mechanisms of the detection process, an empirical foundation must be established dealing with the response of existing detectors to various gases under various conditions. An experimental effort satisfying such needs should be able to accomplish the following tasks.

1) Investigate the basic response mechanism of the detectors. (e.g. determine empirically the dependence of the semiconductor material on temperature, gas concentration, fouling, etc.).
2) Provide insight into the characteristics which would be desirable in future detectors, thereby aiding in the development of higher performance detectors.
3) Determine the extent to which a synergistic cooperation between semiconductor and microcomputers is able, by using innovative signal processing techniques, to overcome the inherent limitations of existing detectors, and, therefore, make the genesis of a <u>truly personal, portable gas detection system feasible</u>.

In our preliminary efforts to meet the above goals, we have designed and constructed a microcomputer-based data acquisition and analysis system. To determine the necessary functional attributes of the system, we have studied a detector which typifies the state of the art in solid state gas detection. That detector is the Taguchi Gas Sensor (TGS), which is manufactured by Figaro Manufacturing Company of Japan. The TGS is constructed of a highly porous n-type, tin oxide semiconductor whose conductivity is greatly affected by the gases present at its surface. The surface reactions which determine the sensor's detection properties are strongly temperature dependent. To control the sensor temperature, a heating coil is imbedded within the sensor. A power of 600 mw dissipated in this coil is capable of heating the TGS to about 400 C. Heating in order to achieve reasonable sensitivities to gases is a method likely to be used by most detectors we plan to test.

Preliminary study of the TGS yielded the following characteristics which we expect to be in common with those of other semiconductor gas detectors:

1. Concentration Response: The conductivity of the sensor can change over an order of magnitude when exposed to just a few hundred ppm of combustible gas. The data acquisition system has been developed to measure conductivities over a six decade range in magnitude.
2. Resistance Drift and Stabilization Times: When the detectors are heated up after a long period of inactivity they may take up to a week before stable resistances are obtained. Even then there are changes in resistance with time that are not correlated with changes in environment. The data collection system has the capability to take data over long time periods so that drift and detector lifetimes can be analyzed.

3. Temprature Variation: The resistances of the detectors and their sensitivities to gas concentrations change dramatically with temperature in a very complex way. If the temperature is changed the response depends on the previous history of the detector. The detector has a memory that extends from a few hours to a few days, that causes a hysteresis loop to be produced in a resistance vs. temperature plot. The data acquisition system changes, in real time, detector temperature and gas concentration so that the detectors' response to the three variables temperature, concentration, and time can be determined.

RESULTS

A. Steady State Response

When TGS sensors operating at 5V heater voltage are placed in pure N_2 their resistances drop from "air" values of approximately 10-20 KΩ to very low values (.5-2 KΩ). In addition, the sensors resistances are observed to drift over a large range (of up to a factor of 2) over time periods of hours to days in a constant environment. This drift in resistance at constant temperature over long time periods does not seem to be related to ambient gas concentrations. If 0_2 is added, the resistances increase, nearly following a power law relationship, until in pure 0_2 they are the greatest observed (500 KΩ to 1 mΩ). Fig. 1 shows this power law response for several sensors. Resistances of individual sensors start at vastly different values but all show similar power law slopes.

If one starts with a high 0_2 concentration (for instance pure 0_2 or Air) and adds either CH_4, CO or H_20, very similar curves are produced. The resistance vs. concentration is again described by essentially a power-law, but now the resistance decreases. The remarkable feature of these curbes is that their slope is the negative of the slope for increasing resistance in 0_2 concentrations.

An equation which fits these curves very well is found to have the following form

$$R = (K_o + K[C])^{-\beta}$$

for CH_4, CO, H_20; and for 0_2 replace $-\beta$ by $+\beta$.

where R = resistance of sensor

K_o = a detector dependent constant which describes the finite resistance at zero gas concentration

K = a constant which is specific to a sensor and the type of gas

$[C]$ = concentration of gas (ppm)

β = power-law slope.

In the above equation the β is very similar from sensor to sensor or gas to gas, but changes sign for concentrations of 0_2. Values of K, the gas sensitivity coefficient, change from sensor to sensor, gas to gas, and temperature to temperature. It is this variation that will need to be exploited if these sensors are to be used to selectively identify a gas. Imbedded in the K_o term are the drift effects.

For a single sensor, operating at constant temperature, there is a day to day variation in resistance even in a very "clean" atmosphere. If the dependence of sensor resistance on CH_4 concentration in air is measured on different such days a family of curves is obtained, each with a different starting point but with other essential features much the same as can be seen in Fig. 2. If these curves are optimally fit to

$$R = (K_o + K[C])^{-\beta}$$

β is found to be constant to ± 25% and K constant to ± 10%. Almost all variation is found in the K_o term.

Based on preliminary results, we feel that the dependence of a sensor resistance on the simultaneous presence of concentrations of several reducing gases can be expressed by

$$R = (K_o + \sum_i K_i [C_i])^{-\beta}$$

where $[C_i]$ is the concentration of the i^{th} reducing gas, and K_i is a strongly temperature dependent gas sensitivity coefficient for the i^{th} gas.

This expression suggests that if there is enough temperature variation among the sensitivity coefficients K_i then it may be possible to produce gas specificity by varying the temperature. Long stabilization times and hysteresis effects greatly complicate data collection when the temperature is varied. If, however, at different temperatures, the resistance vs. concentration characteristic is measured, and then the corresponding relationship between resistance and temperature at constant concentrations is obtained, then a graph similar to that shown in Fig. 3 would be obtained. Here we can see that temperature dramatically affects the zero concentration resistance as well as the sensitivity to the gas. If such curves for different gases show different sensitivity functions vs. temperature, then conceptually at least, we have a means of improving the specificity of the sensors to various gases. It is in this area that a coupling of the control and computational power of microcomputers to the limited selectivity of the solid state gas detector could lead to an acceptable gas detection system.

CONCLUSION

We have shown that, at constant temperature in an oxygen rich ambient, the TGS resistance, R, varies with reducing gas concentration [C] as $R \sim K[C]^{-\beta}$, where K is a sensitivity coefficient peculiar to the reducing gas and the operating temperature, and β is a power law exponent. It seems possible that the dependence of the sensitivity constants K for various gases on detector temperature can be utilized to enhance the TGS selectivity in gas detection. The major complication to this scheme would be the long stabilization times involved when temperature is changed. Nevertheless, a synergistic combination of semiconductor sensors and microcomputer-based signal processing is expected to help overcome the most significant limitation of present sensors: their lack of selectivity.

ACKNOWLEDGEMENT

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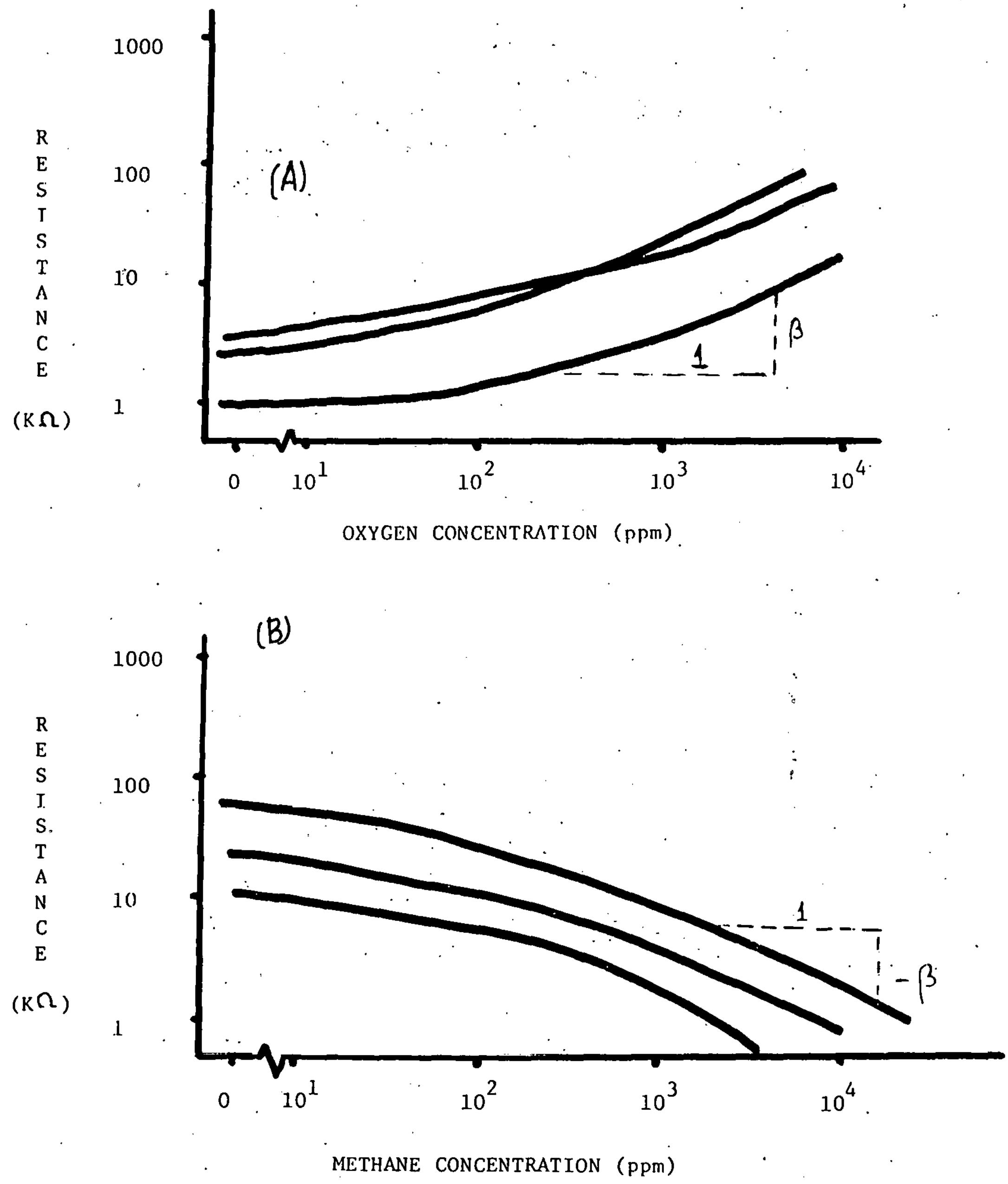

Figure 1a. Dependence of the resistance of three detectors on oxygen concentration in a nitrogen ambient.

Figure 1b. Dependence of the resistance of three detectors on methane concentration in air.

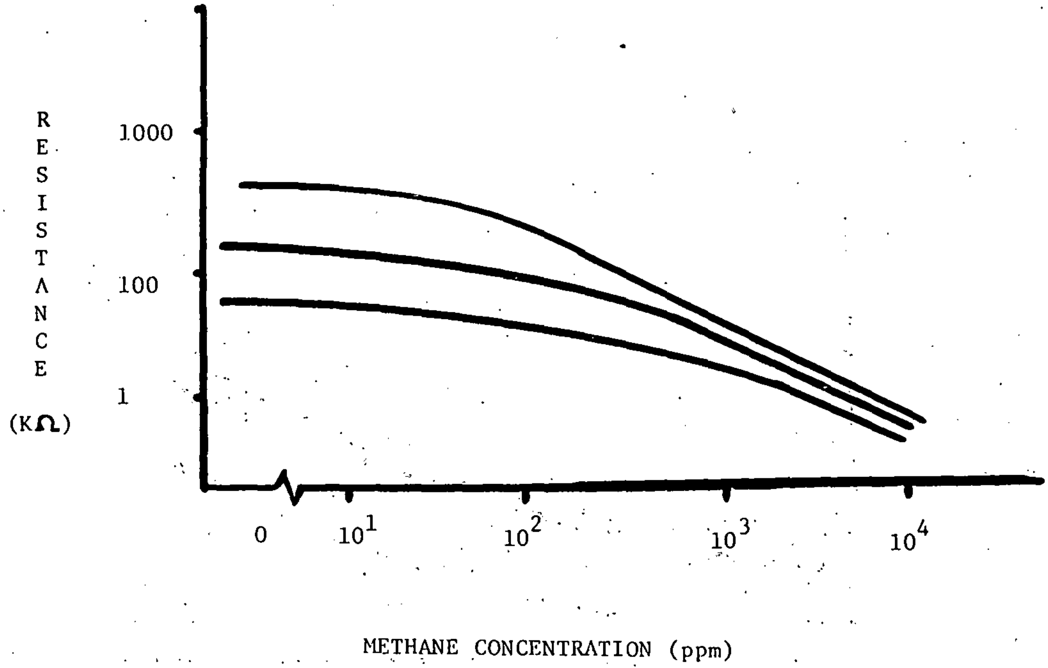

Figure 2. Resistance of a single detector vs. methane concentrations in air for separate trials.

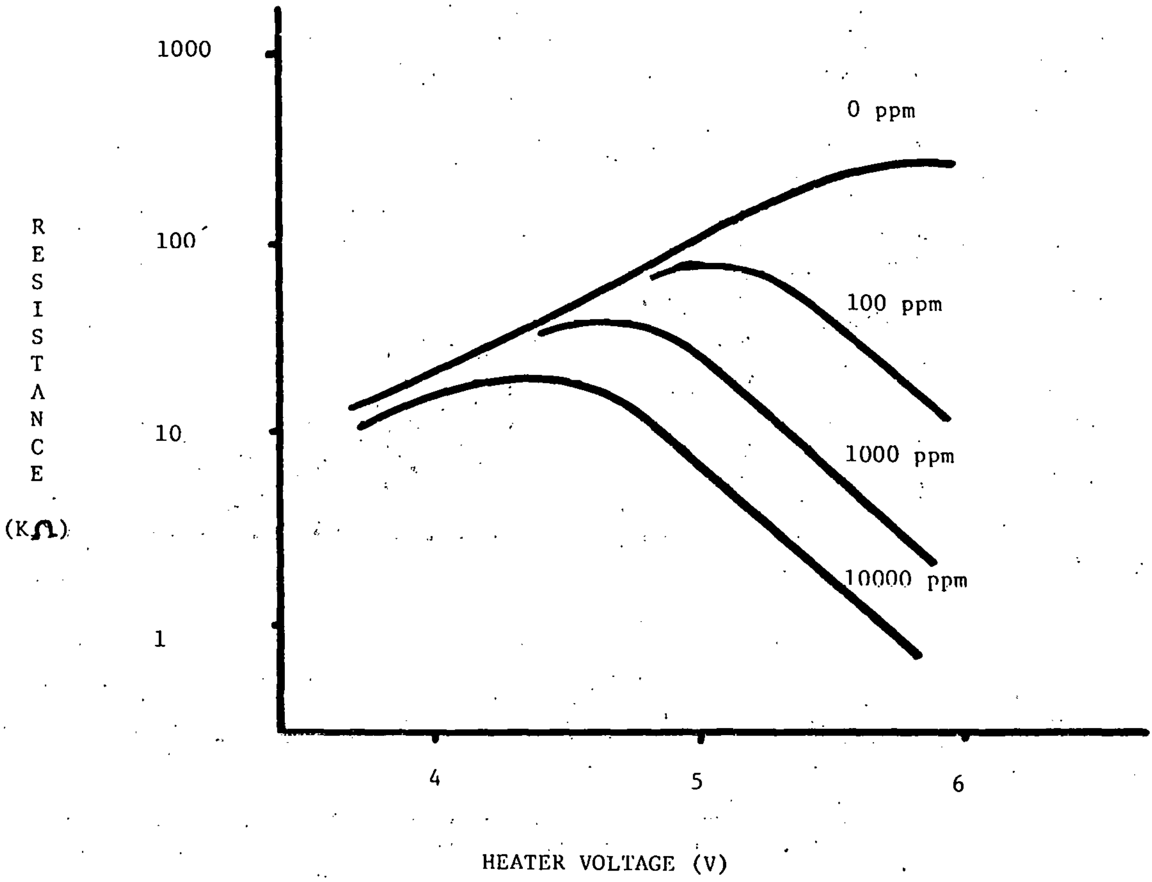

Figure 3. Detector resistance vs. heater voltage in various concentrations of methane in air.

Dup

RAPID ANALYSIS OF PNA COMPOUNDS IN COMPLEX SAMPLES BY ROOM TEMPERATURE PHOSPHORIMETRY*

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Presented at the

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Hygiene Monitoring Needs for the
Coal Conversion and Oil Shale Industries"

Brookhaven National Laboratory
Upton, NY 11973

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*Research sponsored by the Division of Biomedical and Environmental Research, U.S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corporation

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The characterization and detection of polynuclear aromatic (PNA) compounds is an extremely important problem involving numerous fields of research ranging from petroleum and coal technology to carcinogenisis research and health hazards assessment studies. Room Temperature Phosphorimetry (RTP) is a relatively new technique that has recently gained considerable interest among analytical spectroscopists (1-6). This technique is based on the phosphorescence at room temperature of organic compounds adsorbed on various solid substrates including asbestos, silica gel, sodium acetate, and filter paper and provides a simple and sensitive tool for monitoring PNA compounds in fossil fuels and coal conversion products.

Methodology of the RTP technique.

A RTP assay consists generally of four steps:

1. substrate preparation (optional pretreatment),
2. sample delivery,
3. drying process, and
4. spectroscopic measurement.

Filter paper was cut into 0.25-in. circles using a standard office hole punch. Three microliters of sample solution were then spotted

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*Research sponsored by the Division of Biomedical and Environmental Research, U.S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corporation.

on the support using syringes with a volume of 3 microliters. Predrying was achieved with infrared heating lamps. The subsequent drying process during the measurement was accomplished by blowing warm and dry air through the sample compartment. Phosphorimetric measurements were performed with a commercial Perkin-Elmer spectrofluorimeter equipped with a rotating phosphoroscope.

Concerning sampling procedures, the RTP technique is characterized by the simplicity and versatility of its methodology. The use of filter paper as direct sample support offers an extremely large choice of the types of samples which can be monitored, such as liquid or gas samples collected on filter membranes.

<u>The external heavy atom effect</u>.

Since the first report of the solvent heavy atom effect was given by Kasha (7), it has been confirmed that the presence of heavy atoms, either as substituents (internal heavy atom effect) or in the environment (external heavy atom effect), can enhance significantly the process of intersystem-crossing and, therefore, the phosphorescence emission. Significant progress has been achieved recently in the RTP method by the extensive use of the heavy atoms. For PNA compounds a large variety of heavy atom salts such as CsI, NaI and Pb(oAc) (lead acetate) have been found to be very efficient in enhancing the phosphorescence quantum yields. The presence of heavy atom salts offers considerable advantage in quantitative analysis since the limits of detection can be decreased, in some cases by several orders of magnitude (Fig. 1). The detection limits of the PNA compounds investigated are in the nanogram and sub-nanogram range (Table 1). Preparation of phosphorescent substances can be accomplished not only by adding heavy atoms to the solvent but also by incorporating these perturbers directly in the adsorbent material prior to sample delivery. The use of commercially available, pretreated adsorbents is also possible.

Recent studies have shown that the technique based on selective triplet emission enhancement could extend considerably the specificity of the RTP technique in multicomponent analysis. It was possible to selectively enhance the phosphorescence emission of a given compound (or group of compounds) in a complex mixture (8).

Analysis of hazardous PNA compounds.

The RTP technique has a great potential as a rapid and simple tool for monitoring PNA compounds. It will have useful application in many cases of analysis of environmental samples. It is most valuable in situations where the analysis time and cost per sample are important factors.

A practical example of application is the characterization and semiquantitative determination of PNA compounds in a Synthoil sample that has been coarsely fractionated. For compounds that are abundant in the Synthoil, such as pyrene, direct identification by RTP could even be performed with the crude sample (9). Figure 2 illustrates an example of rapid identification of pyrene in Synthoil by RTP analysis using the synchronous scanning technique by which both excitation and emission wavelengths were scanned simultaneously with a constant wavelength interval $\Delta\lambda$ between them (10,11).

The RTP technique can offer a rapid and simple method for differentiating isomeric PNA compounds. Precise identification of PNA isomers is extremely important in environmental studies and health hazards assessment because the toxicity varies strongly with the structure of isomers. Benzo[a]pyrene (BaP) and benzo[e]pyrene (BeP) are well known examples; whereas BeP is relatively innocuous, BaP is a hazardous compound (12). Isomeric benzopyrene can be easily and unambiguously differentiated in RTP analysis by exploiting the difference of their singlet-triplet energy splitting (10).

It is believed that RTP can provide a rapid and practical method for monitoring BaP because its phosphorescence occurs at about 690 nm and is not interferred with by its isomer BeP or by a large number of other multiring PNA compounds (8). Another example of interest involves 1,2,5,6-DBA (dibenzanthracene) and 1,2,3,4-DBA. These are two isomers that exhibit strikingly different carcinogenic activities and can be differentiated easily by synchronous RTP analysis (Fig. 3).

Potential applications.

In the area of occupational health hazard assessment, RTP can offer several advantages as an analytical monitoring tool. The technique should provide a simple, rapid, and sensitive method for identifying major PNA components in samples from coal conversion and oil shale industries.

Since RTP is essentially a surface detection technique, it can be applied to monitoring organic compounds on contaminated surfaces in coal procession locations (working areas, spills, clothing, etc...).

The versatility of its sampling procedures is one of the main advantages of the method. Various sample collection methods are possible: spotting, leaching, swipe techniques, liquid and gas filtration. The use of filter paper or filter membranes as direct sample support greatly broadens the type of samples that can be monitored. For example, the use of RTP to monitor PNA vapors and particulates has the obvious advantages in many applications, especially with regard to field sampling and real-time or nearly real-time organic trace analysis.

The possibility of automation is another main advantage of the RTP technique. An automatic device using the RTP method for continuous analysis was previously developed for clinical applications (Fig. 4) (4). This instrument demonstrated that the RTP technique could possibly be utilized on a routine basis. Such an automated system could be developed for field monitoring of PNA compounds, offering, therefore, various advantages including rapidity and lower cost of analysis.

REFERENCES

1. Vo-Dinh T.; Winefordner J.D.; *Appl. Spectrosc. Rev.*, 1977, 13(2), 261.
2. Wellon S.L.; Paynter R.A.; Winefordner J.D.; *Spectrochemica Acta*, 1974, 30A, 2133.
3. Vo-Dinh T.; LueYen E.; Winefordner J.D.; *Anal. Chem.*, 1976, 48, 1186.
4. Vo-Dinh T.; Walden G.; Winefordner J.D.; *Anal. Chem.*, 1977, 49, 1176.
5. Jakovljevic I.M.; *Anal. Chem.*, 1977, 49, 2049.
6. A von Wandruska R.M.; Hurbituse R.J.; *Anal. Chem.*, 1976, 48, 1784.
7. Kasha M.; *J. Chem. Phys.*, 1952, 20, 71.
8. Vo-Dinh T.; Hooyman J.R.; 1978, submitted for publication.
9. Vo-Dinh T.; to be published.
10. Vo-Dinh T.; Gammage R.B.; *Anal. Chem.*, 1978, in press.
11. Vo-Dinh T.; *Anal. Chem.*, 1978, 50, 396.
12. Searle C.E.; Ed. " Chemical Carcinogens" ACS Monogr., 173, Library of Congress, Washington, D. C., 1976, p. 253.

Table 1 Limits of optical detection (L.O.D.) of several PNA compounds by RTP[a]

Compound	λ_{ex}[b] [nm]	λ_{em}[b] [nm]	L.O.D. [ng]
Acridine	360	638	0.4
BaP	395	688	0.5
BeP	335	543	0.01
2,3-Benzofluorene	343	505	0.03
Carbazole	296	415	0.005
Chrysene	330	518	0.03
1,2,3,4-DBA	295	567	0.08
1,2,5,6-DBA	305	555	0.005
Dibenzocarbazole	295	475	0.002
Fluoranthene	365	545	0.05
Fluorene	270	428	0.2
α-Naphthol	310	530	0.03
Phenanthrene	295	474	0.007
Pyrene	343	595	0.1
Quinoline	305	505	0.04

[a] Source: Vo-Dinh T.; Hooyman J.R.; 1978, submitted for publication.

[b] λ_{ex} = excitation wavelength, λ_{em} = emission wavelength.

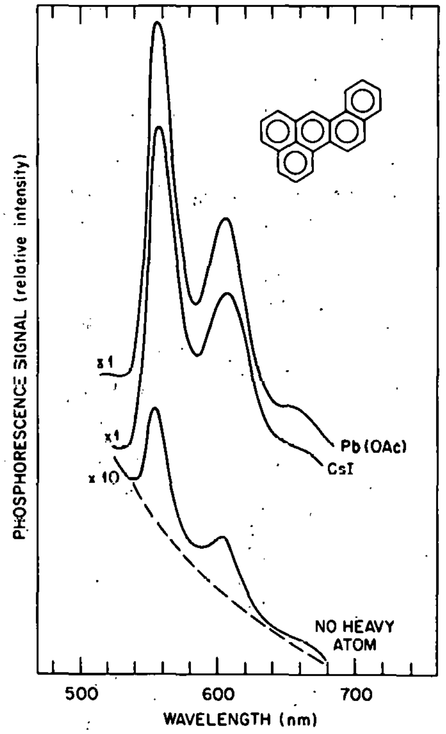

Figure 1. The external heavy atom enhancement for 1,2,5,6-dibenzanthracene.

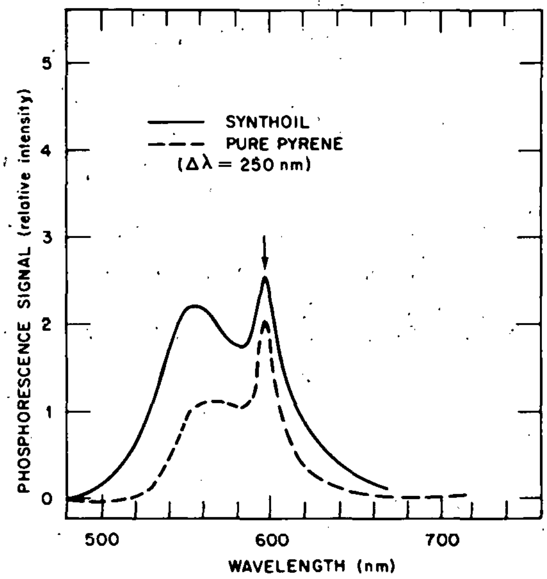

Figure 2. Identification of pyrene by RTP using the synchronous excitation scanning technique.

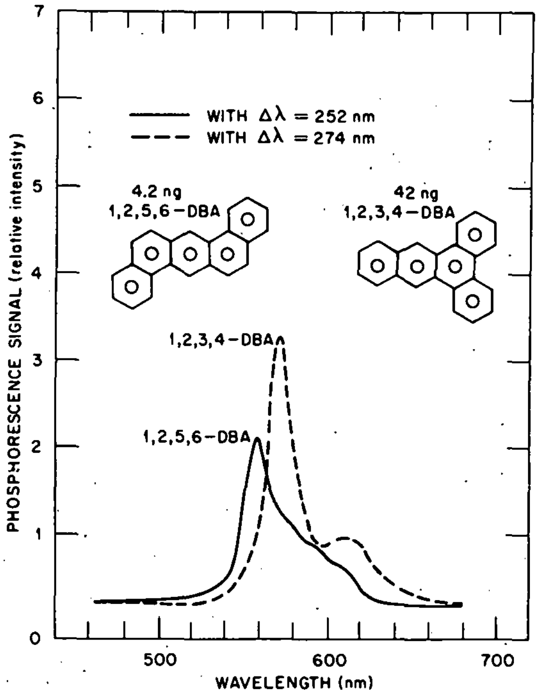

Figure 3. Differentiation of 1,2,3,4,-DBA and 1,2,5,6-DBA in a binary mixture.

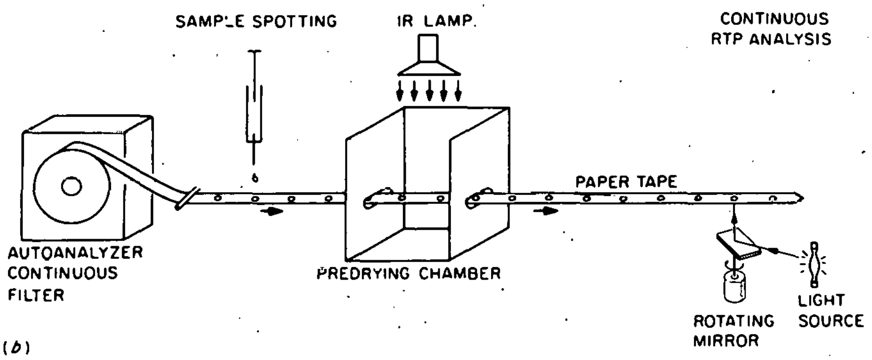

Figure 4. Schematic diagram of automated RTP analysis.

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SCREENING TECHNIQUES FOR BIOLOGICAL ACTIVITY

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INTRODUCTION

Increasing demands for energy and a desire for domestic self-sufficiency are anticipated to lead to a much greater utilization of our coal and shale oil resources before the end of this century. To minimize the harmful effects which often accompany new technology, an effort is being made to anticipate health hazards which may arise. Studies of materials from coal processing pilot plants (1,2) have indicated that the organic materials to which workers may be exposed are similar in kind to those found in crude oil and coal tar, although their relative amounts differ.

The compound classes in these materials which are of concern include the polycyclic aromatic hydrocarbons, heteocyclic compounds, aromatic amines and phenols and naphthols (1,2). Routine and complete chemical analysis for those compounds which are biologically active is not practical at present. Thus, the recommended standards (3) for occupational exposures in coal tar industries are based on the measurement of total cyclohexane extractable mass in a sample of suspended particulate matter. Changes in the levels of biologically active materials may not be reflected by such measurements and such standards may not adequately protect workers.

Short-term bioassay could provide a practical method of monitoring industrial environments for the presence of biologically active and potentially hazardous materials. Such tests can readily detect changes in the levels of these materials and some can be completed within a few days.

This paper will discuss some of the *in vitro* bioassays which are presently available, and consider their applicability to the evaluation of occupational exposures in the coal conversion and shale oil industries. As no direct assessment of the degree of human hazard can be made from the results of such tests, the choice of appropriate standards for comparison will be discussed. The advantages and limitations of such systems will be considered and research needs for the application of industrial monitoring will be suggested.

SHORT TERM BIOASSAYS

Although this paper will focus on work which has been done with the Ames mutation assay (4,5), many other short-term bioassays have been developed as shown in Table 1.

The tests, in general, detect agents which cause damage to DNA. Both prokaryotic and eukaryotic organisms have been used, and the damage to the DNA has been detected by a wide variety of methods. The bioassays presently available, as well as some of those being developed, have been reviewed (6-8) and are currently being evaluated (9,10). Some of those *in vitro* bioassays which may have application to industrial hygiene will be described.

Repair Deficiency Assays

Damage to DNA in prokaryotic systems, such as *Escherischia coli* and *Salmonella typhimurium*, has been detected by several methods. In repair deficiency assays (4,6-8), the killing effects of the test material on normal and/or repair deficient strains of bacteria are determined. The test is frequently performed as a plate test with the chemical deposited in the center of a Petri dish containing a "lawn", i.e., a small background growth of the tester strain. Killing effects are measured as zones of inhibition of bacterial growth.

Mutation Assays

Mutation assays, such as the Ames test (4) have been widely used for screening purposes. The Ames assay employs mutant strains of *S. typhimurium* which cannot biosynthesize histidine. Upon exposure to a chemical which causes a mutation, these strains revert back to a histidine independence, i.e., they grow in media with little or no histidine. The original mutant strains of *S. typhimurium* bacteria have been modified to increase sensitivity to mutagens, making this assay one of the most sensitive.

Metabolic Activation

Many mutagens and carcinogens are the metabolites of inactive chemicals and, because of differences in metabolism between bacteria and mammals, may not be detected in bacterial tests. For example, the 7,8-diol-9,10-epoxides of benzo(a)-pyrene which are derived metabolically from microsomal mixed function oxidases in mammals appear to be the major mutagenic and carcinogenic metabolites of benzo(a)pyrene (11,12). Ames and co-workers (4), therefore, incorporate microsomal enzymes derived from livers of rats treated with Aroclor 1254 in order to provide a metabolic activation system in their bacterial assays.

SOME PRIOR CONSIDERATIONS

There are a number of considerations in selecting a short-term bioassay for application to personnel sampling in an industrial setting. The tests should be relatively easy to use, require only modest investments in equipment and personnel, and preferably need but a few days for completion. A high level of sensitivity is desirable as the samples collected will be of a limited mass. The test system should be capable of detecting the classes of compounds which are anticipated in the coal and shale oil processing plants. Further, it must be able to detect biologically active compounds in a complex mixture.

Although more appropriate bioassays may be available in the future, the bioassay which best meets these criteria at present is the Ames test (4). It is highly sensitive, typically showing response to materials tested in the microgram to milligram range. It is an _in vitro_ test which can be completed within a few days and thus is very inexpensive in comparison to most bioassays. It has been used successfully to indicate the presence and aid in the separation and identification of biologically active compounds in a number of complex mixtures such as cigarette smoke (13), particulate matter in the ambient air (14-17), coal derived fuels from pilot plants (18), and urine (19).

APPROPRIATE STANDARDS FOR BIOASSAYS IN INDUSTRIAL HYGIENE

No direct assessment of the degree of human health hazard can be made from the results of bioassays of samples collected in industrial environments. Thus, standards or reference points are needed for the practical purpose of determining ranges of response which might be of concern. The ambient aerosol provides a very practical reference. The classes of organic compounds which are anticipated in the atmosphere of the coal and oil shale processing plants, i.e., polycyclic aromatic hydrocarbons, aza-arenes, phenols and naphthols (1,2), are found in ambient particulate matter (20). They are present in urban air at levels which probably do not pose a long-term health hazard to non-smokers (21). Levels at rural sites are even lower than for urban areas (20). In addition, sample collection and handling are very similar.

AMBIENT AEROSOL MEASUREMENTS

Organic fractions of suspended particulate matter collected in New York City and in Tuxedo, New York, a rural site about 50 miles northwest of the city, have been tested for the presence of biologically active material using the Ames assay (4).

Experimental

The particulate samples were sequentially extracted with increasingly polar solvents--cyclohexane, dichloromethane and acetone--in a Soxhlet apparatus, for eight hours with each solvent. Extracts were filtered and then reduced to a 10 ml volume using a rotary evaporator (35-40°C) and stored in a freezer at -20°C until use. The cyclohexane and dichloromethane extracts were evaporated just to dryness under argon on a slide warmer kept at 35-40°C and redissolved in acetone for testing. The acetone extracts were reduced in volume. Final sample concentrations were determined by weighing duplicate 100 μl aliquots (which were taken to dryness) on a Cahn Electrobalance. Test solutions were generally in the range of about 1-5 mg/ml. Testing was carried out at levels ranging from 50-500 μg per plate (0.1 ml).

The organic fractions were generally screened for the presence of direct-acting (no microsomal activation) mutagens using the Ames Salmonella typhimuriam plate assay system. As preliminary investigations indicated that strains TA-98 and TA-100 were the most sensitive, these were used in all subsequent tests. Aroclor 1254-induced rat liver, microsomal fraction S-9, and co-factors were used in tests employing microsomal activation. Bacterial mutagenicity was calculated in terms of net (control subtracted) revertant colonies per microgram of organic material using the linear portion of the dose-response curve.

Results

Several aspects of the results of our tests of organic fractions of particulate matter are pertinent to the possible application of bioassays to industrial hygiene. Typical results are shown in Tables 2 and 3. The non-polar (containing the polycyclic aromatic hydrocarbons) and polar fractions all exhibit mutagenic activity with no microsomal activation. This indicates the presence of active compounds other than polycyclic aromatic hydrocarbons as these require activation. As moderately polar and polar organic compounds of interest may also be present in samples collected in an industrial setting, it may be appropriate to use a sequential solvent extraction or a binary (non-polar and polar) solvent system to separate all biologically active organic compounds for testing.

Microsomal activation reduced the activity of all three fractions by 30-100%. Although microsomal enzymes do permit the detection of mutagens such as benzo(a)pyrene which must be metabolically activated, they can also deactivate other materials (22). Enzymes can also be deactivated by other compounds which may be present in a mixture. Thus, the use of microsomal enzyme preparations in this assay may present complications.

The Ames assay does permit the detection of differences in the biological activity of samples collected in different areas, as shown in Table 2, and in samples collected on different days, shown in Table 3.

The biological activity of organic fractions of ambient particulate matter cannot be directly compared with that of particulate samples collected in a coal or shale-oil processing plant at this time. However, Epler and co-workers (18) have tested various fractions of crude oils and synthetic oils derived from coal for mutagenicity using the Ames test. The mutagenic activity of crude oil and synthetic oil, determined as a mass weighted activity of the fractions tested, is compared to that of organic fractions of respirable particulate matter in Table 4. Values for the neutral fractions of the oils, which are probably similar in composition to the non-polar fraction of particulate matter, are also included. The levels of activity of the synthetic fuels are within an order of magnitude of those of the particulate matter, indicating that approximately the same amounts of material must be collected for bioassay. This assumes, of course, as a first approximation, that aerosol samples collected in the workplace will be similar in composition to the fuel oils.

The protocol used in our laboratory for testing the cyclohexane-soluble fraction of particulate matter requires the use of two strains of S. typhimurium, a determination of the response at four different doses and the use of duplicate plates for each dose tested. The mass requirements for a significant response above background is about 2-3 milligrams. Assuming that coal and shale-oil processing plants will be required to meet occupational exposure standards similar to those proposed for coal tar products (3), personnel samplers presently available (1.6 l/min. sampling rate) would collect less than 0.1 mg total mass. If this is all organic material, the amount available is probably sufficient for testing with only one strain of bacteria at only one dose with the most sensitive bioassay presently available. Thus, personnel samplers capable of sampling a much larger volume of air would be required for monitoring personnel exposure.

ADVANTAGES AND LIMITATIONS OF IN VITRO BIOASSAYS

In vitro bioassays are more sensitive than animal tests. They are also faster and cheaper than either animal tests or chemical analyses. They can detect the presence of biologically active materials in mixtures and indicate differences in the levels of these materials which may originate from changes in raw materials or in processes.

Bioassays, such as the Ames test, cannot be directly and quantitatively extrapolated to predict human health effects. Comparisons of the biological activity and the chemical composition of samples collected in pilot plants, in petroleum refineries and in the ambient atmosphere, however, can provide reference points for judging levels of activity which may pose a health hazard. The microsomal activation system which is presently in use may not be adequate. As there are variations in the activity of these enzymes from laboratory to laboratory, some standardization of method would be required. Liver microsomes are presently used in the Ames test system. Some mutagenic and carcinogenic compounds may be reductively activated or may be metabolized by organs other than liver or by other cell components in humans and would not be detected by this bioassay. Further, none of the presently available short-term bioassays can indicate co-carcinogens or promoters which are present in particulate matter and may potentiate the action of a carcinogen.

RESEARCH NEEDS

A better understanding of relationships between the chemical composition of mixtures, long-term in vivo bioassays and the response of short-term bioassays to variations in chemical composition is needed for the application of such tests to industrial hygiene monitoring. Bioassays of organic fractions of aerosols in coal and shale oil pilot plants and in closely related indistries should also be compared.

Improved sampling techniques are needed as larger samples are required for the most sensitive bioassay presently available than can be collected by personnel samplers currently in use. More efficient sampling substrates are needed for organic compounds with lower molecular weights, which may be wholly or partially in the vapor state.

ACKNOWLEDGEMENT

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REFERENCES

1. Office of Assistant Director for Environment and Safety, Carcinogens Relating to Coal Conversion Processes, Report prepared by TRW Energy Systems under Contract No. E(49-18)-2213 for the Energy Research and Development Administration, June 14, 1976.

2. Guerin, M. R., J. L. Epler, W. H. Griest, B. R. Clark and T. K. Rao, "Polycyclic aromatic hydrocarbons from fossil fuel conversion processes," In: Carcinogenesis, A Comprehensive Survey, Vol. 3. Eds., P. W. Jones and R. I. Freudenthal, Raven Press, New York, N. Y. (1978).

3. U.S. Dept. of Health, Education and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health. Criteria for a Recommended Standard - Occupational Exposure to Coal Tar Products. DHEW(NIOSH) Publication No. 78-107, Sept. (1977).

4. Ames, B. N., J. McCann and E. Yamasaki. "Methods for detecting carcinogens and mutagens with the Salmonella/mammalian-microsome mutagenicity test," Mut. Res. 31: 347 (1975).

5. McCann, J., E. Choi, E. Yamasaki and B. N. Ames. "Detection of carcinogens as mutagens in the Salmonella/microsome test. Assay of 300 chemicals," Proc. Nat'l. Acad. Sci. USA 72:4135 (1975).

6. Bridges, B. A. "Short-term screening tests for carcinogens," Nature 261:195 (1976).

7. Committee 17, Council of the Environmental Mutagen Society: Environmental Mutagenic Hazards. Science 187:503 (1975).

8. Working Group of the Subcommittee on Environmental Mutagenesis. "Approaches to determining the mutagenic properties of chemicals: Risk to future generations," J. Environ. Path. Toxicol., 1:301 (1977).

9. International study of short-term carcinogenicity tests. Nature, 274:740 (1978).

10. Purchase, I. F. H., E. Longstaff, J. Ashby, J. A. Styles, D. Anderson, P. A. Leferre and F. R. Westwood, "Evaluation of short-term tests for detecting organic chemical carcinogens," Br. J. Cancer, 37:873 (1978).

11. Sims, P., P. L. Grover, A. Swaisland, K. Pal and A. Hewer, "Metabolic activation of benzo(a)pyrene proceeds by a diol epoxide," Nature, 252:326 (1974).

12. Yang, S. K., D. W. McCourt, J. C. Leutz and H. V. Gelboin, "Benzo(a)pyrene diol-epoxides: Mechanism of enzymatic formation and optically active intermediates," Science, 196:1199 (1977).

13. Mizusaki, S., H. Okamoto, A. Akiyama and Y. Fukuhara, "Relation between chemical constituents of tobacco and mutagenic activity of cigarette smoke condensate," Mut. Res., 48:319 (1977).

14. Daisey, J. M., I. Hawryluk, T. J. Kneip and F. Mukai, "Mutagenic activity in organic fractions of airborne particulate matter," Presented at the Conference on Carbonaceous Particles in the Atmosphere, March 20-24, Berkeley, California, 1978.

15. Talcott, R. and E. Wei, "Brief communication: Airborne mutagens bioassayed in Salmonella typhimurium," J. Nat'l. Cancer Inst., 58:449 (1977).

16. Teranishi, K., K. Hamada and H. Watanabe, "Mutagenicity in Salmonella typhimurium mutants of the benzene-soluble organic matter derived from airborne particulate matter and its five fractions," Mut. Res., 56:273 (1978).

17. Pitts, Jr., J. N., D. Grosjean and T. M. Mischke, "Mutagenic activity of airborne particulate organic pollutants," Toxicol. Lett., 1:65 (1977).

18. Epler, J. L., J. A. Young, A. A. Hardigree, T. K. Rao, M. R. Guerin, I. B. Rubin, C.-H. Ho and B. R. Clark, "Analytical and biological analyses of test materials from the synthetic fuel technologies. I. Mutagenicity of crude oils determined by the Salmonella typhimurium/micrsomal activation system," Mut. Res., 57:265 (1978).

19. Yamasaki, E. and B. N. Ames, "Concentration of mutagens from urine by adsorption with the non-polar resin XAD-2: Cigarette smokers have mutagenic urine," Proc. Nat'l. Acad. Sci. USA, 74:3555 (1977).

20. Hoffmann, D. and E. L. Wynder, "Organic particulate pollutants--chemical analysis and bioassays for carcinogenicity," In: Air Pollution, 3rd ed. Vol. II. Ed., A. C. Stern, Academic Press, New York, N.Y. pp. 361-455 (1977).

21. Cederlöf, R., R. Doll, B. Fowler, L. Friberg, N. Nelson and V. Vouk, "Air pollution and cancer: Risk assessment methodology and epidemiological evidence," Environ. Health Pers., 22:1 (1978).

TABLE 1. SOME IN VITRO SHORT-TERM BIOASSAYS[(a)]

BIOASSAY	BIOLOGICAL SYSTEM
PROKARYOTIC ORGANISMS	
Repair deficiency	S. typhimurium, E. Coli, B. Subtilis
Point mutations	S. typhimurium, E. Coli, B. Subtilis
EUKARYOTIC ORGANISMS	
Mitotic recombination	Saccharomyces cerevisiae
Reversions	Saccharomyces cerevisiae
Forward mutations	Schizosaccharomyces pombe
Unscheduled DNA synthesis	Human fibroblasts
Sister-Chromatid exchange	Chinese hamster cells, bone marrow cells
Chromosome aberrations	Hamster and rat cells
Cell transformation	Hamster kidney fibroblasts, human diploid lung fibroblasts

(a) References 6-8

TABLE 2. COMPARISON OF BACTERIAL MUTAGENICITY OF ORGANIC FRACTIONS OF URBAN AND RURAL PARTICULATE MATTER[(a)]

Fraction	New York City	Tuxedo Park, N.Y.[(b)]
	Net Revertant Colonies/Microgram	
Non-polar	0.87±0.15	0.7±0.1
Moderately polar	4.5±0.2	1.2±0.4
Polar	0.7±0.1	0.2±0.4

(a) Quarterly composites of weekly respirable suspended particulate matter, winter, 1978; Salmonella typhimurium TA-98 used with no microsomal activation.

(b) Sampling site is located in a heavily wooded area about 50 miles northwest of New York City.

TABLE 3. DAILY VARIABILITY OF BACTERIAL MUTAGENICITY OF MODERATELY POLAR ORGANIC FRACTIONS OF SUSPENDED PARTICULATE SAMPLES COLLECTED IN NEW YORK CITY(a)

Date	Net Revertant Colonies per Microgram(b) TA-98	TA-100
8/11-8/12/76	1.0±0.1	1.1±0.1
8/27-8/28/76	2.9±0.2	3.0±0.3
8/28-8/29/76	1.3±0.2	2.3±0.2

(a) Dichloromethane extractable fraction of 24-hr. total suspended particulate samples.

(b) Tested with S. typhimurium bacterial strains with no microsomal activation.

TABLE 4. A COMPARISON OF THE MUTAGENICITY(a) OF SOME SYNTHETIC AND NATURAL FUEL OILS(b) WITH ORGANIC FRACTIONS URBAN PARTICULATE MATTER(c)

Sample	Net Revertant Colonies per Microgram(a)	
Respirable Particulate Matter(c):		
Non-polar fraction	0.23±0.06	(0.78)(e)
Moderately polar fraction	0.5±0.1	(0.21)(e)
Crude Oil Composite -		
Total activity(d)	0.24	
Neutral fraction	0.35	
Synfuel A - Total activity(d)	4.11	
Neutral fraction	0.60	
Synfuel B - Total activity(d)	0.50	
Neutral fraction	0.51	

(a) Determined with S. typhimurium TA-98 using Aroclor 1254-induced rat liver S-9 preparation and co-factors.

(b) Epler et al., Mut. Res. 57:265 (1978).

(c) Quarterly composite of samples collected in NYC from Oct.-Dec., 1977.

(d) Weighted activity of all fractions.

(e) Net revertant colonies per cubic meter of air.

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PORTABLE OPTICAL PARTICLE COUNTERS

by

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PORTABLE OPTICAL PARTICLE COUNTERS

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Introduction

Under contract with the Bureau of Mines, we have in the past several years been investigating the feasibility of using optical particle counters (OPCs) to measure dust size distributions and concentrations that may be found in mining operations. As a result of this research, two OPC systems have been developed and calibrated specifically for measuring this type of dust, and a third system is currently under development.

The first system to be developed used a Bausch and Lomb 40-1A OPC as the sensor and a Hewlett-Packard multichannel analyzer (MCA) data acquisition system. This system is currently being used by Bureau of Mines personnel to study the particle size distributions of aerosols generated in coal fragmentation studies under laboratory conditions. Since both the Bausch and Lomb 40-1A OPC and the data acquisition system are rather large and require a 110 volt power supply, the system is not portable and not easily moved from one project to another.

The second system was designed specifically for field use, and has thus been designed with portability in mind. The sensor for this system is a battery-powered Royco 218 portable OPC, and the data acquisition system consists of a specially-built battery-powered eight-channel analyzer. Since both the OPC and MCA of this system can be powered by batteries as well as 110 volt AC power, the system is as suitable for use in remote locations as it is in the laboratory. This system, weighing approximately 60 pounds and being housed in three separate units, was essentially a two-man operation, even though the system was portable. In addition, the OPC uses an incandescent light bulb as a light source, which has two disadvantages when used in coal mines. First, it is difficult to design a system to be intrinsically safe with the incandescent bulb being present, and second, the incandescent light bulb draws sufficient current to require a sizable battery if long-term operation is desired.

To bypass the shortcomings of the incandescent light bulb source in the OPC, a third OPC system using a laser diode light source was designed, and is currently under development. In this system, the receiving optics of the Royco 218 OPC are to be used with the laser diode light source. The electronics are also being redesigned so that less power will be required than the present system. It is expected that this OPC can be packaged into a volume of about 30 cm x 20 cm x 10 cm.

It can be seen from these three systems that the direction of our OPC system development has been to go from a large stationary system to a very portable light-weight system. It may be possible, by using the laser diode light source and by completely redesigning and miniaturizing the optical system, to develop a personal sampler based on the OPC principal.

In this paper, the portable system using the Royco 218 OPC will be described, since this is a system which is currently in use. Also described will be the method by which impactors have been used to calibrate the OPC to give a calibration based on the aerodynamic diameter of the particle. Next, the system which uses the laser diode light source will be described, and the progress of the current research on this system presented.

The Portable OPC/MCA System Using the Royco 218 OPC Sensor

The portable optical particle counter/multichannel analyzer (OPC/MCA) system is shown in Figure 1, and has been described in detail in Reference 1.

This system consists of an OPC, an MCA, and a battery pack, separated into three units to aid in the portability of the system. The OPC is a Royco Model 218 portable particle monitor (Royco Instruments, Inc., 141 Jefferson Drive, Menlo Park, CA 94025). The MCA and the battery pack are units which have been designed and built in our laboratory.

In operation, the OPC/MCA system functions in the usual manner of an optical particle counting system (2). Aerosol flows through the eluminating volume within the OPC, and the light scattered by a single particle is collected and focused by an optical system onto a photo diode, where an electrical pulse is generated. The amount of light scattered, and thus, the magnitude of the electrical pulse from the photo diode is a function of the particle size, with larger particles generating pulses of larger magnitude. These pulses are classified according to their magnitude in the MCA, which stores the data in the appropriate channels. After a preset time, the number of pulses that have been recorded in each channel of the MCA are read. Then, by use of a calibration curve, relating the particle size to the pulse magnitude, a particle size distribution can be obtained.

For this system, two modifications were made to the OPC as purchased from the manufacturer. First, an electrical output jack was installed, so that signals from the OPC electronics would be available for analysis by the MCA. Secondly, a new inlet was installed in the OPC which provided a sheath of clean air around the particles passing through the optical view volume. The purpose of this modification was to eliminate the recirculation of particles in the view volume, which was noticeable in the unmodified unit. Also, by providing a sheath of clean air around the aerosol stream, the flow rate of the OPC was increased from .28 lpm to 2 lpm, which dictated the use of a larger pump and a different flow system. The details of these modifications are described in Reference 1.

One of the major tasks in developing an OPC system for measuring mining-related dust particle size distributions is obtaining a calibration curve relating the signal pulse height to the particle diameter of that particular dust.

As received from the manufacturers, the OPCs are calibrated on transparent spheres (ideal aerosols), which are a good approximation to many atmospheric aerosols. However, the aerosols generated by mining-related activities consist of irregular particles of varying indices of refraction and shapes (non-ideal aerosols), which may act entirely different in an OPC than an ideal aerosol. For the systems which have been mentioned in this paper, we have used a calibration method employing an inertial impactor, which provides a relationship between the OPC signal output and the aerodynamic diameter of the dust particles.

The impactor calibration procedure has been described in general in Reference 3, and its application to the portable OPC/MCA system has been described in Reference 1. Briefly, this calibration technique consists of making two size distribution runs with the OPC. For the first run, the OPC samples through an impactor on its inlet, while in the second run, the impactor is removed. A ratio, R, for each channel is then found by dividing the number of particles in each channel of the MCA for the first run by the number of particles in the corresponding channel of the second run. The channel number, or corresponding OPC voltage, where R = 0.5 corresponds to the 50% cut-off point of the impactor. Not only does the curve of R vs. the OPC voltage yield a calibration point, but it also provides an indication as to whether or not the OPC can resolve the size distribution of that particular aerosol. For example, the impactor has been designed to have a sharp cut-off characteristic. Thus, if the resolution of the OPC is good, there will be a sharp drop from 1 to 0 in the value of R as a function of the OPC voltage. If the resolution is poor, the decrease from 1 to 0 will be gradual.

Some typical graphs of the ratio R vs. the OPC voltage are presented in Figure 2 for the particles of approximately the same physical size (Stokes diameter). In this figure, the OPC voltage has been normalized by dividing by the OPC voltage at R = 0.5 for each curve, V_{50}. It can be seen from Figure 2 that the decrease of R from 1 to some value less than 0.5 is fairly sharp for all of the dusts tested.

Calibration curves obtained by using the impactor calibration technique for coal, silica, potash, rock, and Arizona road dust aerosols are shown in Figure 3 for the portable OPC/MCA systems. The individual points shown on the calibration curves correspond to impactors with different cut-off sizes which were obtained by using nozzles of different diameters on the impactor.

It should be noted that the data points in Figure 3 were calibrations made in the laboratory with dust generated in a fluidized bed type of dust generator (4). However, three data points are shown for silica which was obtained in the field, and this data agrees well with the silica data obtained in the laboratory. Also shown in Figure 3 is the calibration curve for oleic acid particles, which are spherical oil droplets and are considered to be ideal aerosols. The "average" calibration curve in Figure 3 is the average of all of the dust data presented.

This method of calibrating OPC sensors has two advantages. First, impactors classify particles by their aerodynamic diameters, which is the diameter considered to be important in governing the motion of respirable dust particles. Secondly, the OPC system can be calibrated in the field on any unknown aerosol, which is important if the chemical compound or physical shape of the particles are of such a nature as to be difficult, if not impossible, to duplicate in the laboratory.

The OPC System Using the Laser Diode Light Source

Since it is difficult to make an OPC with an incandescent light bulb light source safe for use in a gaseous atmosphere, which may exist in a coal mine, it was decided to investigate the feasibility of using a laser diode for the light source. Although the development of the OPC is currently in the feasibility study stage, the small size of the laser diode may make it possible to develop an OPC small enough to be a personal sampler and it is, thus, described in this paper.

The laser diode, as shown in Figure 4, is about one-half the size of a dime. The source of light is a slit .25 µm x 13 µm in size and thus is effectively a line source.

To test the feasibility of using this light source, an adapter for the Royco 218 OPC optical tube was made, as shown in Figure 5. This adapter is designed to connect directly to the receiving optics of the Royco 218 OPC and has access holes for the aerosol inlet and outlet tubes. Thus, with this adapter, it is possible to test the feasibility of using the laser diode while using the rest of the electronics of the Royco 218 OPC.

Since the laser diode is a line light source, the light intensity will be different at the view volume parallel to and transverse to the slit, as shown in Figure 6. This shows that the light beam width is much greater parallel to the slit than transverse to it. Thus, the particles can pass through a fairly wide view volume and still experience essentially the same light intensity. In addition, the resulting electrical pulse will be short, allowing for relatively high particle concentrations to be sized without coincidence losses.

Conclusions

It has been shown that OPCs can be a useful tool in determining the size distribution and concentration of dust aerosols. Two systems have been built and are currently being used for studying these types of dust. It has also been shown that by using inertial impactors for calibration, it is possible to obtain a calibration of the OPC based upon the aerodynamic diameter of the particles, which is an important parameter in determining the quantity of respirable dust.

Although the feasibility study of using the laser diode as a light source in an OPC is currently in progress, it appears as though this light source may be an alternative to the incandescent bulb. Since the laser diode is very small, and the photo diode sensor is also small, it should be possible to make the entire optical tube, including the light source, optics, and detector, into a package small enough to be used as a personal sampler. Considerable electronics are also required for an OPC. However, with the miniaturization of electronic circuits, they should also be small enough to be compatible with a personal sampler. In addition, the electronics and laser diode require little power and should be compatible with the type of power that is currently used by personal samplers.

Acknowledgement

This work was supported under Bureau of Mines Contract H0177026 through the Twin Cities Mining Research Center. The financial support of the Bureau is gratefully acknowledged.

References

1. Marple, V. A. and K. L. Rubow, "A Portable Optical Counter System for Measuring Dust Aerosols", Am. Ind. Hyg. Assoc. J. 39:210-218 (March, 1978).
2. Willeke, K. and B. Y. H. Liu, "Single Particle Optical Counter: Principle and Application", Fine Particles: Aerosol Generation, Measurement, Sampling, and Analysis (B. Y. H. Liu, ed.), pp. 697-729, Academic Press, New York (1976).
3. Marple, V. A. and K. L. Rubow, "Aerodynamic Particle Size Calibration of Optical Particle Counters", J. Aerosol Sci. 7:425-433 (1976).
4. Marple, V. A., B. Y. H. Liu and K. L. Rubow, "A Dust Generator for Laboratory Use", Am. Ind. Hyg. Assoc. J. 39:26-32 (Jan., 1978).

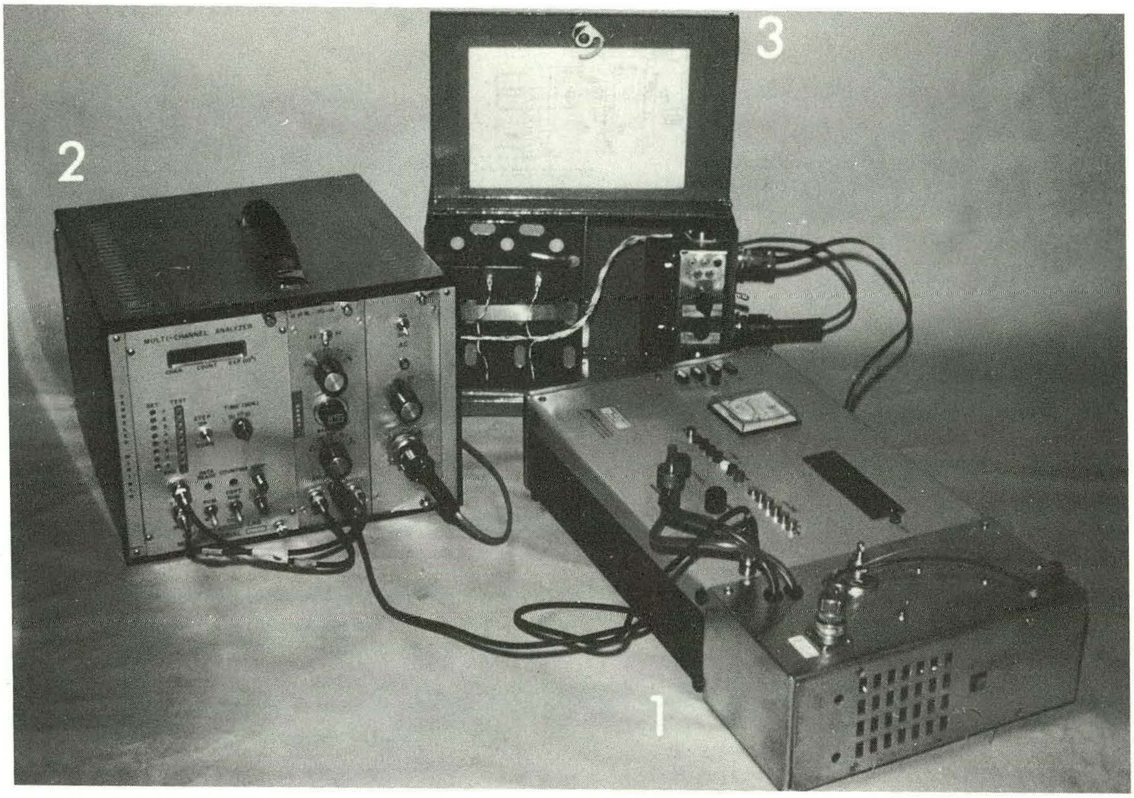

Figure 1. Portable optical particle counter/multichannel analyzer system. 1) Modified Royco 218 portable optical particle counter. 2) Multichannel analyzer. 3) Battery pack.

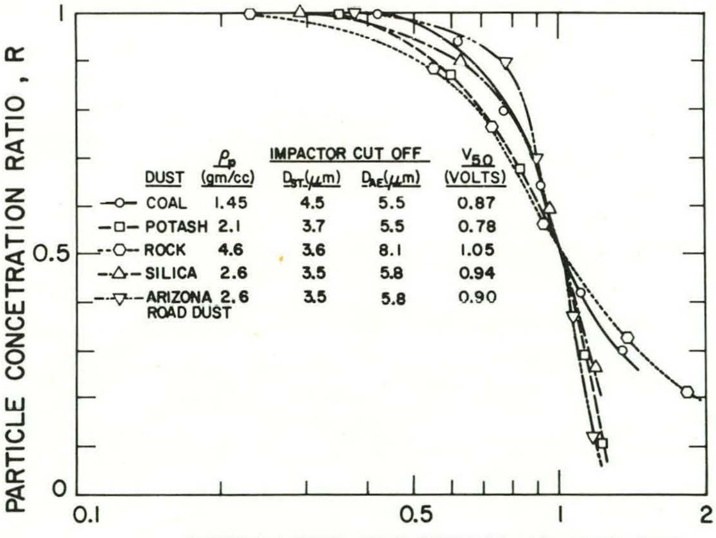

Figure 2. Typical graphs of particle concentration ratio versus OPC output.

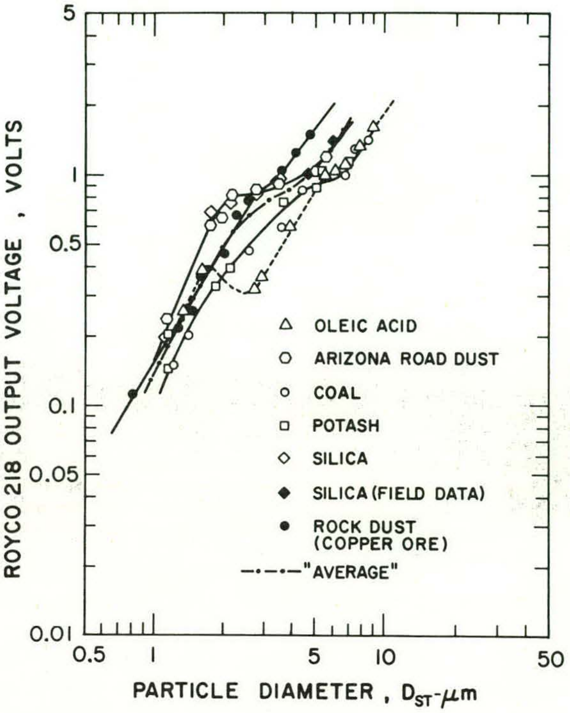

Figure 3. Modified Royco 218 OPC calibration curves.

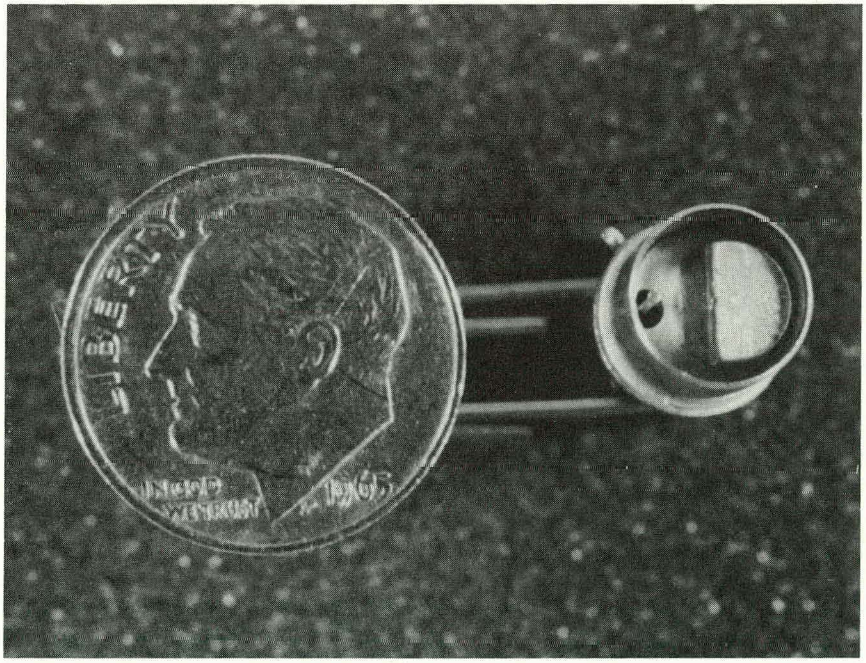

Figure 4. Laser diode light source.

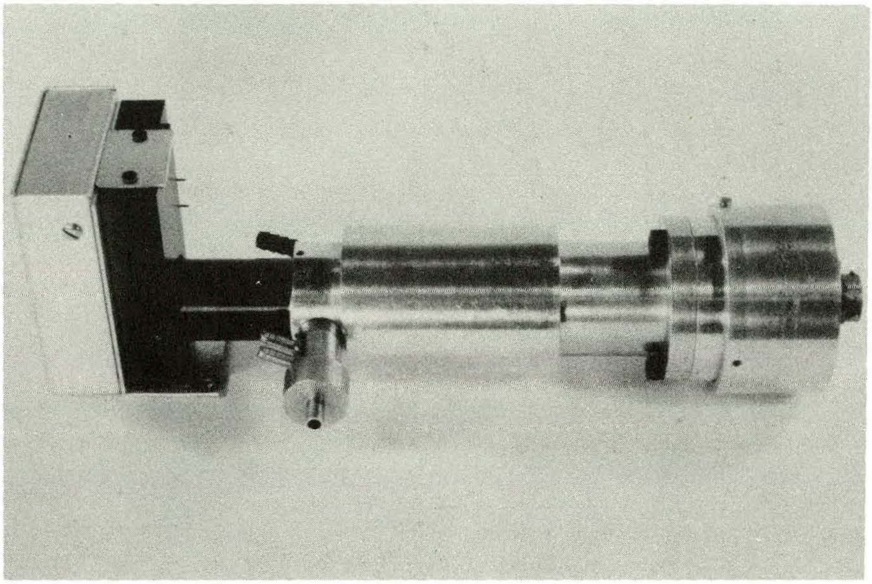

Figure 5. Modified Royco 218 optical tube (light-colored portion of tube is adaptor to hold the laser diode light source).

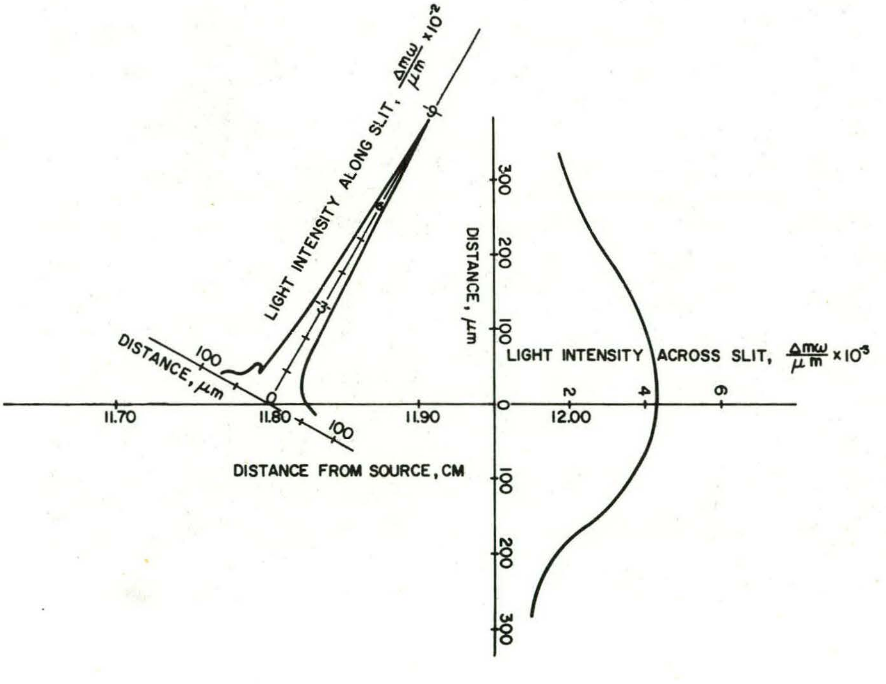

Figure 6. Light intensity along and across light beam at viewing volume using laser diode.

SURFACE ANALYSIS TECHNIQUES AND THEIR USE IN POLLUTION DETECTION AND MEASUREMENT

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Surface Analysis Techniques and Their Use in Pollution Detection and Measurement*

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ABSTRACT

Surface analysis techniques such as Auger electron spectroscopy (AES), electron spectroscopy for chemical analysis (ESCA), secondary ion mass spectrometry (SIMS) and ion scattering spectrometry (ISS) are reviewed. The advantages and limitations of these methods are compared with bulk analysis techniques such as x-ray fluorescence spectroscopy, atomic absorption and emission spectroscopy, gas chromatography, and neutron activation analysis. Results obtained using ESCA, AES, SIMS, ISS and x-ray fluorescence analysis from auto exhaust, laboratory prepared, clean air and biological samples are discussed. Possible future areas of research using surface techniques are discussed.

Introduction

In recent years the energy crisis has focused attention on using coal in vast quantities for liquification and gasification. Also, alternate energy sources such as solar, fusion, fission and other exotic fuels are being proposed. All these forms of energy generation will require characterization and detection of environmental pollution for regulatory purposes as well as for understanding the sources, environmental pathways, reservoirs, distribution and biological effects of these pollutants.

The usual bulk analysis techniques employed for detection and measurement of environmental pollutants are atomic emission spectroscopy, x-ray fluorescence spectroscopy, chemical analysis, gas chromatography and neutron activation analysis. Properties of these techniques are compared in Table 1 with those of recently developed techniques employed in areas of "surface" science, namely Auger spectroscopy, ESCA, ISS and SIMS. The minimum quantity detectable is generally less for the surface techniques since only a single layer of atoms is needed for analysis. On the other hand, when the contaminant is dispersed

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*Work performed at Brookhaven National Laboratory under contract with the U. S. Energy Research and Development Administration.

throughout a thicker sample, bulk techniques are more sensitive since a larger sample volume can be examined. The surface techniques can detect a broader range of elements; however, molecular species can be detected using gas chromatography.

A principal advantage of the surface techniques is the capability they provide for studies of spatial distributions of pollutants. For example, concentrations can be studied as a function of nanometer depths in environmental or biological samples.

In the present study, surface techniques were examined to demonstrate the feasibility and usefulness of using these techniques in the area of pollution detection, measurement and characterization.

We have analyzed samples from auto exhaust, a laboratory prepared sample and a clean air sample by surface techniques. An auto exhaust sample was also analyzed by x-ray fluorescence spectroscopy. The differences observed by these two techniques are discussed. The biological samples, (i) fish scale and (ii) fish otolith from commercial fish, were also analyzed to demonstrate the possibility of using surface techniques to study biological samples. Since our group did not have the analytical instrumentation, samples were analyzed by 3M Company, Varian Associates and Physical Electronics, Inc. X-ray fluorescence analysis was provided by the Instrumentation Division of Brookhaven National Laboratory. Principles and details of bulk analysis are not discussed here and can be found in (1,2,3). Basic principles of surface techniques are included and references are provided for detailed description of instrumentation.

Basic Principles in Surface Analysis

A. Auger Electron Spectroscopy (AES): Auger Spectroscopy is an analytical technique used to identify the elemental composition of a sample surface. The electron beam incident on the surface of the material has a fixed energy, eg. 1.5 keV. These electrons have sufficient energy to knock out an electron from an inner shell of an atom, and resultant vacancy is immediately filled by an electron from an outer shell. The difference in energy can be released in the form of a photon or by knocking out another electron from an outer shell called the Auger electron. These electrons are then analyzed using a standard Auger spectrometer (4). Auger electron energies are characteristic of the element from which they originate. Thus, the Auger spectrum gives a qualitative analysis of elements present on the surface. The number of Auger electrons emitted is proportional to the number of atoms of the element present on the surface, thus, the intensity of Auger peaks provides quantitative measurements (5). The energy of Auger electrons are low so that only those electrons produced in the first few layers (5 - 20 Å) of sample can leave the surface. Thus, the method is sensitive only for the elements present on the surface. More recently, Varma, et al. (6) have modified the standard Auger spectrometer to improve the sensitivity of this technique. Figure 1 (a) shows schematically the process of Auger electron production. The Standard Auger spectrometer can detect elements in concentration of the order of 0.1 atomic percent, and can detect all elements above helium. No Auger transitions exist for hydrogen or helium.

B. Electron Spectroscopy for Chemical Analysis (ESCA): In this method, a monoenergetic beam of x-rays is used to bombard the sample surface. Absorption of these x-ray photons by the atoms of the sample results in the emission of electrons which originate from the inner or core shells. The energy of the incident x-ray photon is shared between the energy of the emitted electron and the binding energy of this electron in its orbital. The energy spectrum of emitted electrons is measured by a spectrometer (7). Since the atomic structure of each element is unique, the measurement of energy of the emitted electrons from one or two orbitals of each element is sufficient to identify the elemental composition of the sample. All the elements have electrons that can be detected in this manner except for hydrogen. Chemical bond information can also be obtained from analysis of peak shapes, multiline structure and shifts in energy of the ejected electrons in an ESCA spectrum.

Free electrons produced in a solid are scattered by bound electrons in the solid and thus lose part of their energy before leaving the solid. These electrons, although they reach the spectrometer, are counted as background. Only those photoelectrons generated in the first few monolayers of sample have sufficient probability to escape the sample with negligible loss of energy. Thus, this is also a surface technique which samples depths of the order of 5-20Å of the specimen. Exact sampling depth depends on the sample being analyzed. Detection sensitivity of this method is about the same as that for AES. A schematic of the ESCA process is given in Figure 1(b).

C. Secondary Ion Mass Spectrometry (SIMS): In this technique, a sample surface is bombarded by a monoenergetic ion beam. The ion beam has sufficient energy and intensity to sputter ions from the sample surface. These sputtered ions are also called secondary ions. These secondary ions are mass analyzed using a standard mass spectrometer. By choice of appropriate electronics, both positive and negative secondary ions can be mass analyzed. The sampling depth in this technique is of the order of a monolayer, however, the sampling depth depends on other parameters such as sputtering rate, etc. (8). A schematic representation of SIMS is shown in Figure 1(c). All elements and isotopes in the periodic table can be analyzed using this technique. The sensitivity of SIMS depends on the scan rate and sputtering rate and can vary by about three orders of magnitude showing a general decrease in sensitivity for heavy elements. For some elements, sensitivity of parts per billion or less have been achieved.

D. Ion Scattering Spectrometry (ISS): In this method, the sample surface is bombarded by monenergetic noble gas ions as was the case for SIMS. (As a matter of convenience, the same ion beam can be used for simultaneous analysis of SIMS and ISS). Some of the incident ions undergo binary elastic collision with atoms in the first monolayer of the sample and will be scattered from the surface. For a scattering angle of 90° classical collision theory gives a relationship between the mass M_1 of the atom on the surface, and energy E_1 of the scattered ion in terms of the incident ion mass M_o and its initial energy E_o,

$$E_1 = \frac{M_1 - M_o}{M_1 + M_o} E_o.$$

In normal ISS spectroscopy the ions scattered at 90° are energy analyzed and thus a spectrum of intensity versus energy of scattered ion is obtained. The spectrum can then be analyzed for various elements present on the surface. The sampling depth for ISS is a single monolayer, because incident ions that penetrate the monolayer have a high probability of being neutralized by the matrix. Thus, even though these ions may be scattered at 90°, they will not be detected by ISS since they are neutral ions. A schematic representation of the ISS process is given in Figure 1(d). Details about the method can be found in (9).

Experimental

Sample Preparation: Nickel substrates 6mm x 12mm and 0.8 mm thick were prepared from ultrapure nickel sheet. These substrates were cleaned first using Alconox and then rinsed in ordinary tap water. Final rinse was done using deionized distilled water. The nickel substrate was then attached near the tailpipe of a 1971 automobile. The exhaust was collected by direct impact of exhaust gases onto the substrate. The automobile was driven for approximately 20 miles. Regular leaded gasoline was used in the automobile. After exposure to exhaust fumes, the substrate was carefully removed from the tailpipe and the sample analyzed. This sample will be referred to as auto exhaust in further discussions. For x-ray fluorescence analysis a 35 second sample of exhaust gasses from a 1969 Volkswagen was collected by impingment on filter paper to avoid interference which would be contributed by the thick Ni substrate employed in the surface analysis techniques.

To check the effect of the presence of several elements in the sample on analysis, known quantities of various salts were deposited onto a clean nickel substrate. This sample is referred to as Laboratory prepared sample. Reagent grade LiCl (1.5 g), $Li_2\ SO_4 \cdot H_2O$ (1.66 g) and Pb $(No_3)_2$ (3.22 g) were first dissolved in 100 ml of distilled water. From this assay, 5 microliters of solution was evaporated on the nickel substrate using an infrared lamp. The amounts of various materials present on the substrate were calculated to be Cl (.063 mg), SO_4 (.062 mg), NO_3 (.060 mg), Li (.021 mg) and Pb (.101 mg). Other impurities in this sample were Ca (100 ppm), Fe (15 ppm), Cu (2 ppm) and Na (10 ppm).

Clean nickel substrates were also exposed to outdoor environmental air at Brookhaven National Laboratory. This sample is referred to as clean air in further discussion. This sample was exposed at location P-9 (approximately 2.5 km from the central complex of research buildings in the northeasterly direction) where routine environmental monitoring samples are obtained. The exposure was for approximately 5½ hours from 9:00 a.m. to 2:30 p.m. on March 26, 1976.

Biological Samples: Two biological samples (i) fish scales from a dead fish (presumed to have died from copper contamination), and (ii) fish otolith from a commercial fish, were prepared by the Biology Department of Brookhaven National

Laboratory. No cleaning, except for rinsing with tap water, was done on these samples.

Auto exhaust, laboratory prepared and clean air samples were analyzed by SIMS (both positive and negative), ISS, AES and x-ray fluorescence spectroscopy. SIMS and ISS were done by 3M Company, AES by Varian Associates using commercially available equipment. X-ray fluorescence spectroscopy was done by the Instrumentation Division of Brookhaven National Laboratory using a low power, high sensitivity laboratory-developed system. The biological samples were analyzed by AES, ESCA and x-ray fluorescence. AES and ESCA were performed by Physical Electronics Industries, Inc., and Varian Associates using commercially available systems. No SIMS or ISS was performed on these samples.

Results and Discussion

A. Auto Exhaust: Figures 2 and 3 show spectrum obtained by positive SIMS and negative SIMS, respectively. Mass-range scanned was from 1-100 atomic mass units. Figure 4 and 5 show ISS spectra. For figure 4, the incident beam was 2 keV neon ions and for figure 5 it was 1 keV $^{3}He^{+}$. Figure 6 shows an Auger spectrum for this sample. X-ray fluorescence analyses results for the Volkswagon auto exhaust sample and a blank filter paper are shown in figures 7 and 8 respectively. From figure 2, which shows positive SIMS results, one can clearly see the variety of elements present in auto exhaust fumes (e.g., Li, B, Na, Ag, Al, Si, Cl, K, Ca, Ti, Fe, Ni, Cu, Zn, etc.). From the negative SIMS analysis shown on figure 3, other elements such as O,F,S and Br can be identified. Note that in this spectrum (fig. 3) two isotopes of chlorine and bromine were clearly identified. Some of the elements, such as Ti, may have been present due to impurities present in the nickel substrate.

ISS results are shown on figures 4 and 5. Here heavy elements such as Br and Pb are apparent. Figure 4 shows variation in concentration of bromine and lead in this sample as a function of depth. One can clearly see that concentration of bromine and lead reach a constant level after the first few angstroms of the surface has been removed by sputtering. In the ISS analysis with low mass $^{3}He^{+}$ions, as shown in figure 5, other elements such as Cl, S, O, C, etc., can be identified. The AES spectrum from the sample (figure 6) shows the presence of elements like S, Cl, C, O, etc., but surprisingly does not show any lead or bromine. This could have been due to mishandling of the sample during shipment or sample preparation. The x-ray fluorescence spectrum of the Volkswagon exhaust sample (Figure 7) reveals the presence of Pb, Br, Cu, Zn, Fe and probably Se. Of these, Fe, Cu and Zn are also present on the blank filter paper (Figure 8) though probably in smaller quantities, especially for Fe. Thus, this technique readily detected Br, Pb and Fe, but not some of the lighter elements (Li, B, Na, Al, K, Cl, C, O and S) detected by surface techniques. (Some of these latter elements may be contributed by the Ni substrate used for the surface technique samples).

B. <u>Laboratory Prepared Sample</u>: Figure 9 shows a positive SIMS spectrum of the laboratory prepared sample at low and high sensitivity. In this spectrum, Li, B, Li_2, Ne, Na, Mg, Al, Li_2O, Li_2OH, K, Ca, Fe, Ni, Cu were detected. The mass scan was from 1-100 atomic mass units, thus heavy elements like lead, etc., are not seen in the spectrum. Figure 10 shows negative SIMS for the same sample, in this case elements C, CH, O, OH, F, C_2H_2. S and Cl were observed. Figure 11 is a depth profile of this sample over approximately 1000Å and shows concentration variation of three elements O, Cl and C. Figure 12 shows an ISS spectrum with the incident ion being $^3He^+$. In this spectrum elements C, O, S, Cl, Ni, and Pb were observed. Figure 13 shows an AES spectrum of this sample and shows the presence of Ni, Pb, S, Cl, and O. A comparison of SIMS, ISS, and AES suggests that SIMS identified all the elements that were present on the sample including the impurities, ISS and AES detected some of the elements. Thus, SIMS appears to be a more sensitive technique than ISS or AES.

C. <u>Clean Air Sample</u>: Figure 14 and 15 show ISS spectra from the clean air sample when Ne and $^3He^+$ incident ions were used, respectively. One surprising finding was the presence of bromine in this sample. Figure 16 shows the AES spectrum for this sample. No bromine was detected in this spectrum.

D. <u>Biological Samples</u>: The fish scale and otolith samples were analyzed by AES, ESCA, and x-ray fluorescence. AES was difficult to perform due to charging of the sample surface by the incident electron beam, especially for fish scales. The qualitative results obtained using AES and ESCA showed the presence of calcium and oxygen in otolith and mostly silicon in fish scales. An in-depth analysis of the otolith sample showed a calcium to oxygen ratio, which generally increased with depth. No other heavy elements were detected. X-ray fluorescence detected only Ca in otolith and Si in fish scales.

Conclusions

It thus appears from these analyses that, for the environmental samples, SIMS has higher sensitivity than AES or ISS. But SIMS does not identify chemical composition, thus AES or ESCA in tandem with SIMS might be an excellent analytical technique. However, with AES, charging of the sample surface can be a problem since electrons are used as the excitation source. Also, the electron beam is somewhat damaging to biological surfaces. Thus, for biological samples, we feel ESCA which uses low energy x-rays as the excitation source is preferable to AES.

Applications of Surface Analysis Techniques

The basic difference between surface and bulk techniques is the ability to analyze, with the surface techniques, elemental composition present on the surface, i.e., the first few monolayers of the sample. By suitable sputtering techniques, known amounts of sample surface can be removed, thus depth profiling is possible. This depth profiling has an advantage in that pollution deposited as a function of time can be studied. If the pollutants have a tendency to segregate to the surface, or surface concentration is higher than bulk, then surface analysis is apt to give results more closely related to biological hazard for low solubility particles. It has been shown by Linton, et al. (10) that, for small particles (such as fly ash from coal burning), the surface concentration of toxic trace elements can be much greater than the concentration determined by bulk analysis.

Sensitivities as high as one part per trillion can be achieved by surface techniques if the impurities can be concentrated on the surface. For example, there are about 10^{15} atoms per square centimeter on a surface. Analyzing one square centimeter of the surface at sensitivity of 100 parts per million, one can detect 10^{12} atoms. If we can scavenge these 10^{12} atoms from 100 ml of solution, we can achieve a bulk sensitivity of about one part per trillion for most metals. The problem of scavenging and depositing 10^{12} atoms on the surface is not an easy one, however, Hercules' (11) recent technique employing chelating agents shows great potential in this regard. This procedure is not required for those samples in which impurities are already present on the surface.

Identification of chemical forms of these elements in pollution samples can shed some light on the concentration of those compounds which are more biologically reactive. This, for example, will include identification of various oxides, nitrides or carbides. The chemical composition information is lost when wet chemical analysis or bulk analysis is performed on these samples.

Surface chemical reaction rates can also be studied with these techniques, to determine production or decrease in various chemical compounds as a function of concentration of environmental insults.

These techniques are also capable of providing valuable information on marine samples. For example, transfer of pollutants from fly ash or other objects to the marine waters and sediments.

The measurement of trace element concentrations in biological samples (like hair, nails, teeth, etc.) as a function of distance along the growth direction can provide a measure of the body's uptake of heavy metals or other chemical constituents as a function of time. Historical and baseline data can be obtained from museum pieces, stones and other antiques and can be correlated to environmental insults, epidemiological data and medical data, for application in health effects studies.

Acknowledgment

We would like to thank 3M Company, Varian Associates and Physical Electronics Industries for providing analysis of these samples. We would also like to thank Dr. H. W. Kraner, Instrumentation Division, for x-ray fluorescence analysis of these samples, J. R. Steimers, Safety and Environmental Protection Division, for sample preparation, and Drs. R. B. Setlow and A. D. Woodhead, Biology Department, for advice and assistance in measurements on biological samples.

References

1. Applied Spectroscopy Reviews, Vol. 6, Edited by E. G. Brame, Jr., Maycel Dekker, Inc., New York (1973).

2. Johansson, S. A. E., and Johansson, T. B., Analytical Application of particle induced x-ray emission, Nucl. Instrum. Meth., 137, 473-516 (1976).

3. Trace substances in Environmental Health - V, Proceedings of Unversity of Missouri's 5th Annual Conference on Trace Substances in Environmental health, edited by D. D. Hemphill, June 29 - July 1 (1971).

4. Methods of Surface Analysis, edited by A. W. Czanderna, Vol. 1, Elsevier Scientific Publishing Co., New York (1975).

5. Weber, R. E., and Johnson, A., Determination of Surface Structures using LEED and Energy Analysis of Scattered Electrons, J. Appl. Phys., 40, 314-318 (1969).

6. Varma, M. N., Joshi, A., Strongin, Myron and Radeka, V., Difference Auger Spectroscopy for studying small quantities of elements on metallic surfaces, Rev. sci. Instrum., Vol. 44, No. 11 (1973).

7. Electron Spectroscopy, edited by R. Caudano and J. Verbist, published by Elsevier Scientific Publishing Company, New York (1974).

8. Riach, G. E., and Goff, R. E., Electrons or Ions, Industrial Research, 83-92, June 1974.

9. Goff, R. E., Ion scattering Spectrometry - A new technique for Surface Composition Analysis, Proceedings of the 6th National Conference on Electron Probe Analysis, Pittsburgh, July 1971.

10. Linton, R. W., Loh, A., Natush, D. F. S., Evans, C. A., and Williams, P., Surface Predominance of Trace Elements in Airborne particles, Science, Vol. 191, 852-854 (1976).

11. Hercules, D. M., Cox, L. E., Onisick, S., Nichols, G. D., and Carver, J. C., Electron Spectors Copy (ESCA); Use for Trace Analysis, Anal. Chem., 45, 1973-1975 (1973).

TABLE - 1

Comparison of Various Properties of Surface and Bulk Analysis Techniques

Techniques	Minimum Detection (gm)	Chemical Information	Depth Analysis	Elements Detected	Destructive (D) Nondestructive (ND)	Surface (S) Bulk (B)	Temperature Dependence
Atomic Absorbtion	$10^{-8} - 10^{-10}$	None	No	All, except rare gases, C,H,O,N,S,P and Halogens	D	B	Small
Atomic Emission	$10^{-8} - 10^{-10}$	None	No	Same as above	D	B	Extreme
X-ray Fluorescence	$10^{-7} - 10^{-12}$	None	No	$Z > 12$	ND	B	None
Auger Spectroscopy	$10^{-12} - 10^{-13}$	Some	Yes	$Z > 2$	ND-maybe	S	None
ESCA	$10^{-12} - 10^{-13}$	Moderate	Yes	$Z > 1$	ND	S	None
ISS	$10^{-12} - 10^{-13}$	Some	Yes	Except H, He	ND	S	None
SIMS	$10^{-9} - 10^{-14}$	None	Yes	All	D	S	None
Chemical	10^{-9}	None	No	All	D	B	None
Gas Chromatography	$10^{-9} - 10^{-12}$	None	No	Organic Compounds	D	B	Extreme
Neutron Activation	$10^{-6} - 10^{-13}$	None	No	Many	ND	B	None

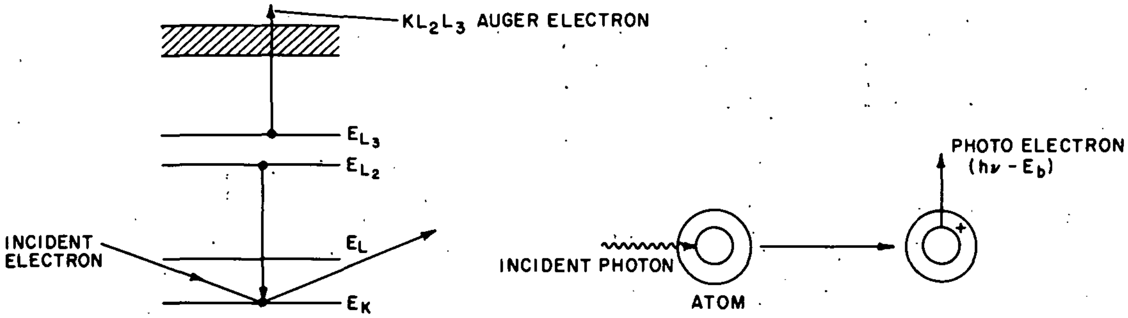

Figure 1(a). Schematic representation of Auger process.

Figure 1(b). Schematic representation of ESEA process.

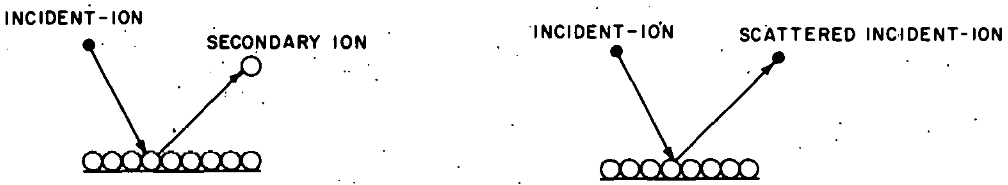

Figure 1(c). Schematic representation of SIMS process.

Figure 1(d). Schematic representation of ISS process.

Figure 1

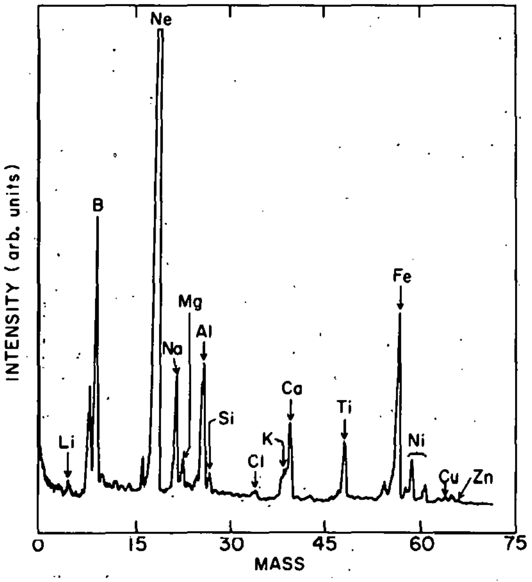

Figure 2. Positive SIMS spectrum of auto exhaust sample.

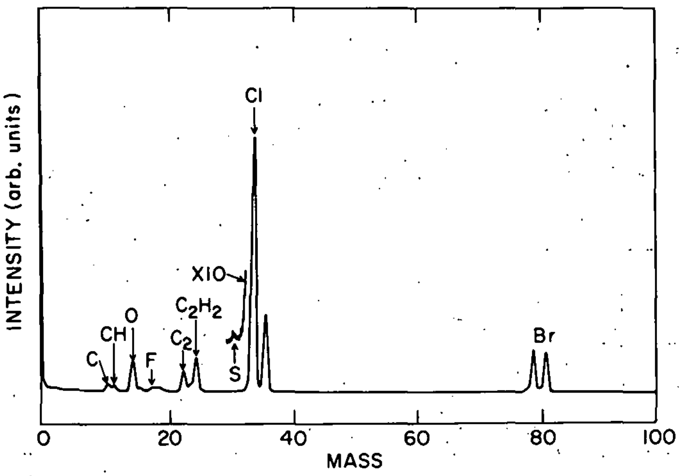

Figure 3. Negative SIMS spectrum of auto exhaust sample.

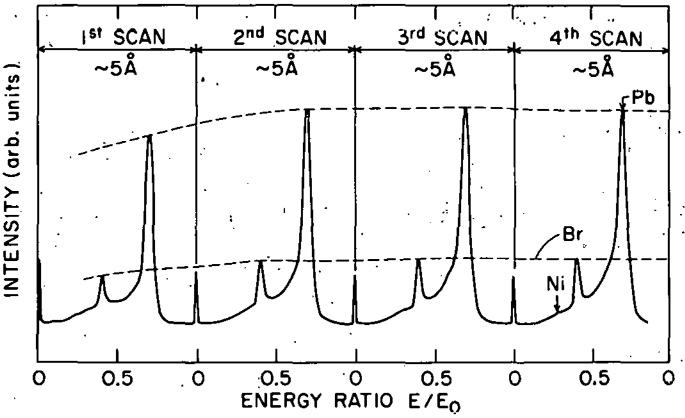

Figure 4. ISS spectra of auto exhaust sample for incident beam of 2 keV neon ions.

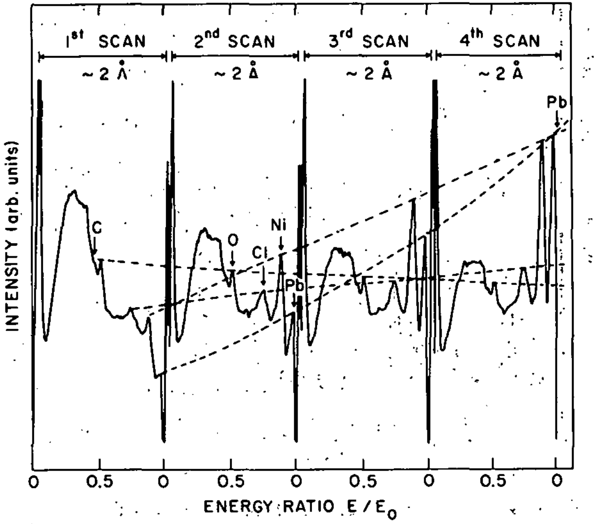

Figure 5. ISS spectra of auto exhaust sample for incident beam of 1 keV $^3He^+$ ions.

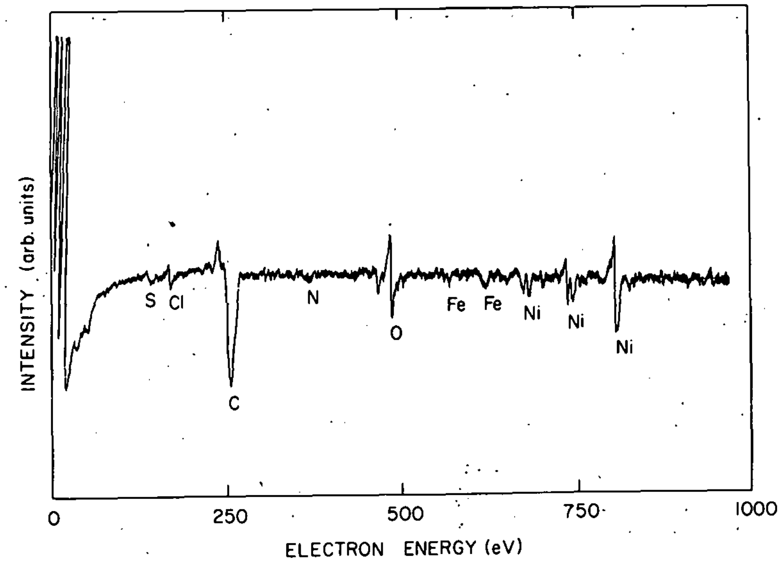

Figure 6. Auger spectrum of auto exhaust sample.

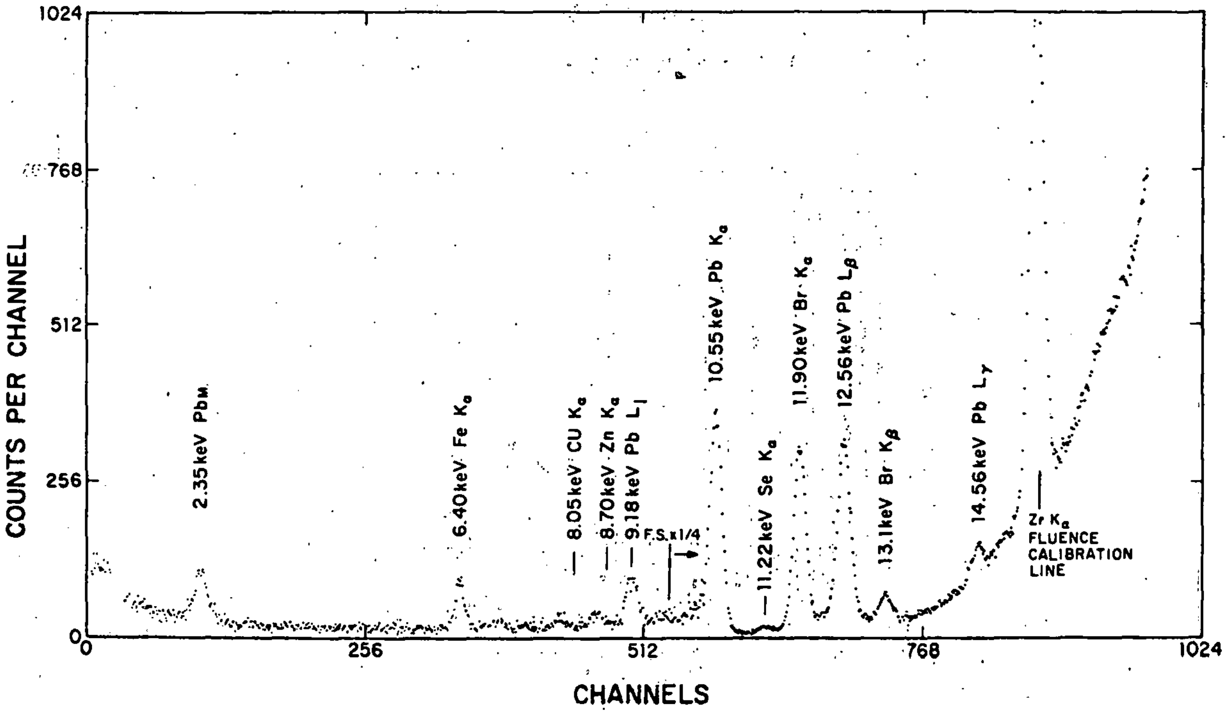

Figure 7. X-ray fluorescence spectrum of auto exhaust sample.

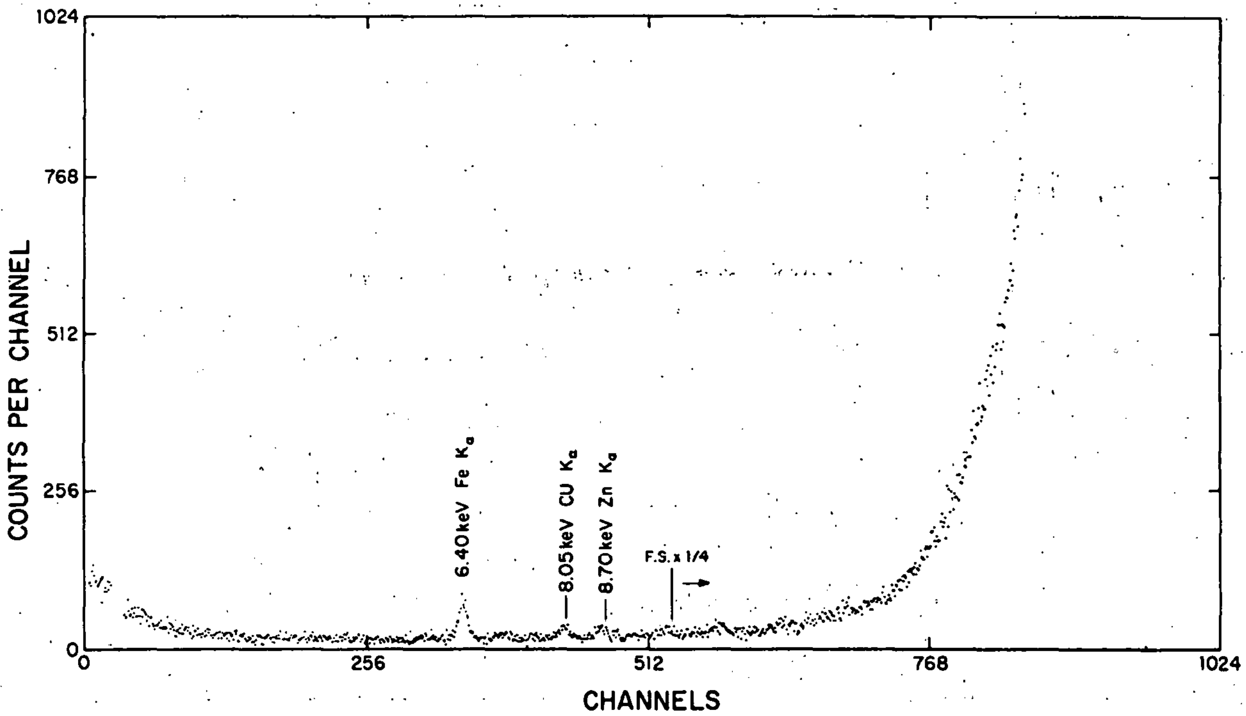

Figure 8. X-ray fluorescence spectrum of blank filter paper.

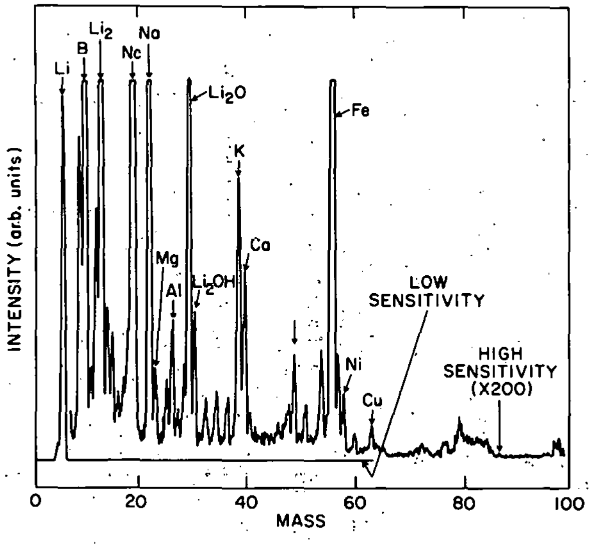

Figure 9. Positive SIMS spectrum of laboratory prepared sample (both at high and low sensitivity).

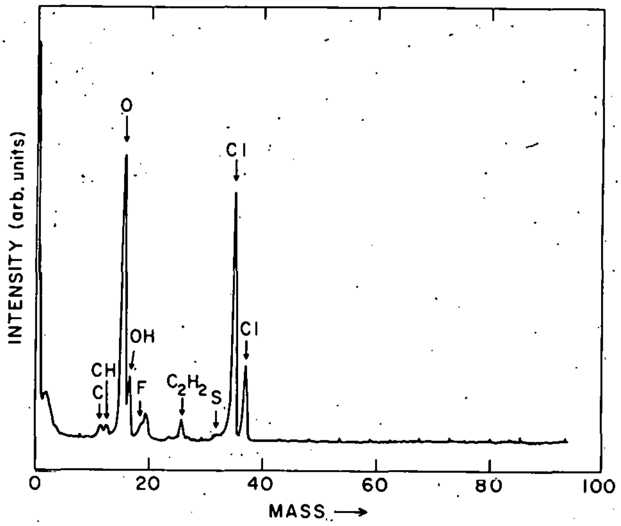

Figure 10. Negative SIMS spectrum of laboratory prepared sample.

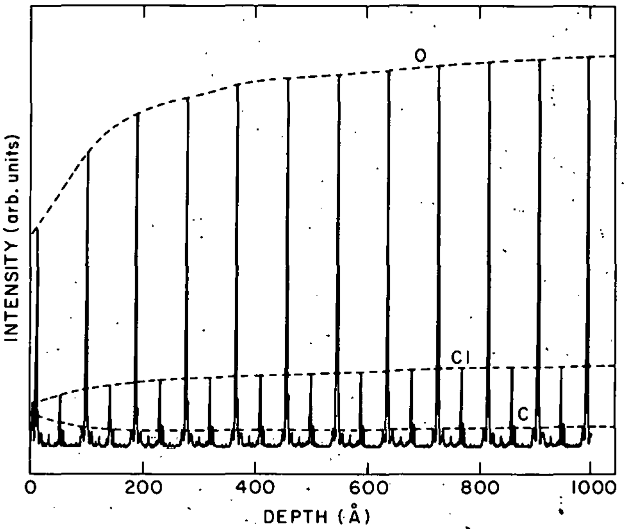

Figure 11. SIMS spectrum of laboratory prepared sample showing a depth analysis from 0 - 1000Å.

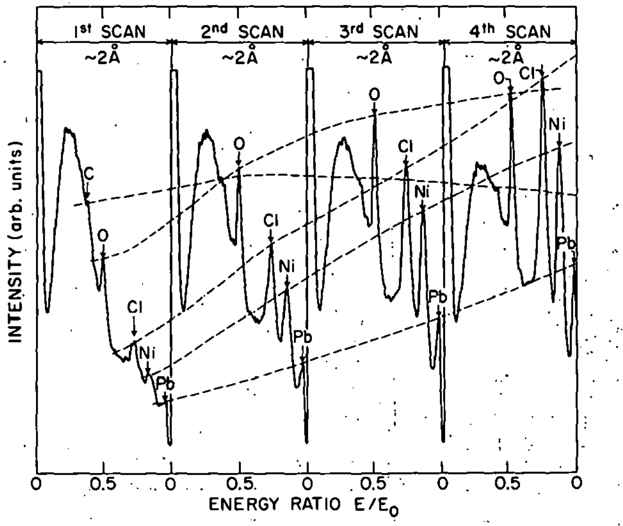

Figure 12. ISS spectrum of laboratory prepared sample for incident beam of $^3He^+$.

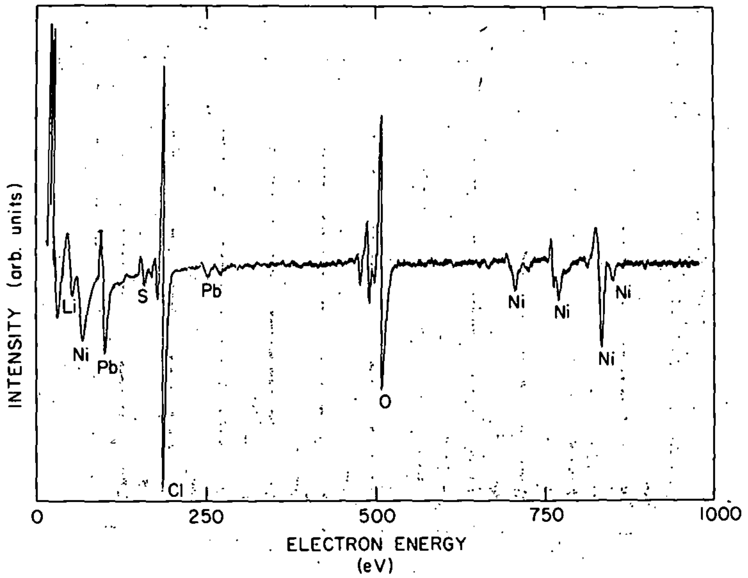

Figure 13. Auger spectrum ot laboratory prepared sample.

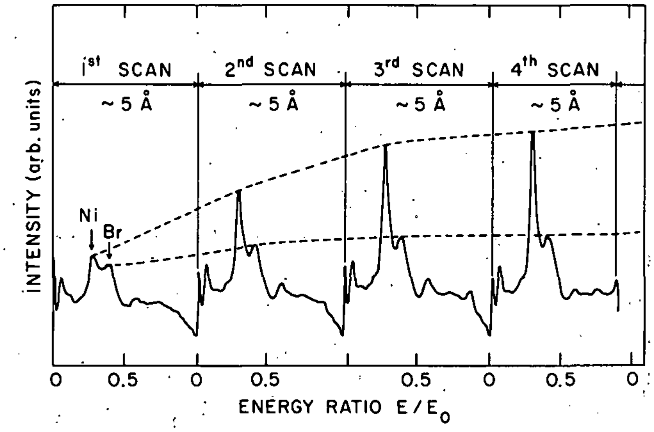

Figure 14. ISS spectra of the clean air sample for incident beam of neon ions.

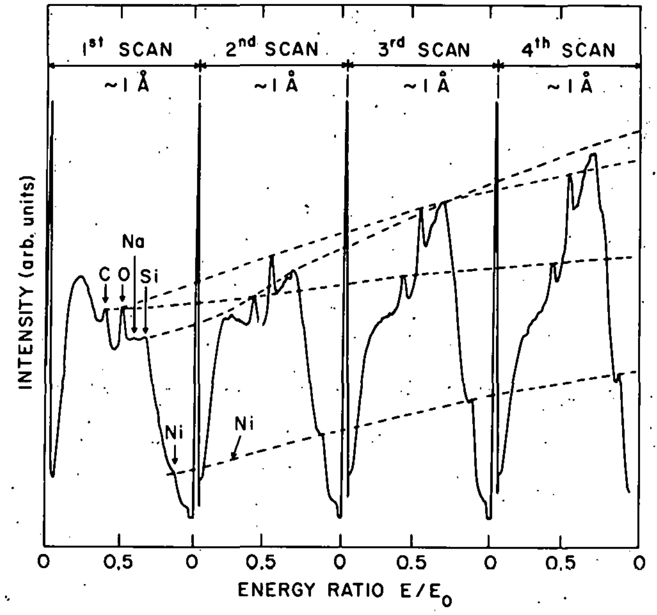

Figure 15. ISS spectra of the clean air sample for incident beam of $^3He^+$ ions.

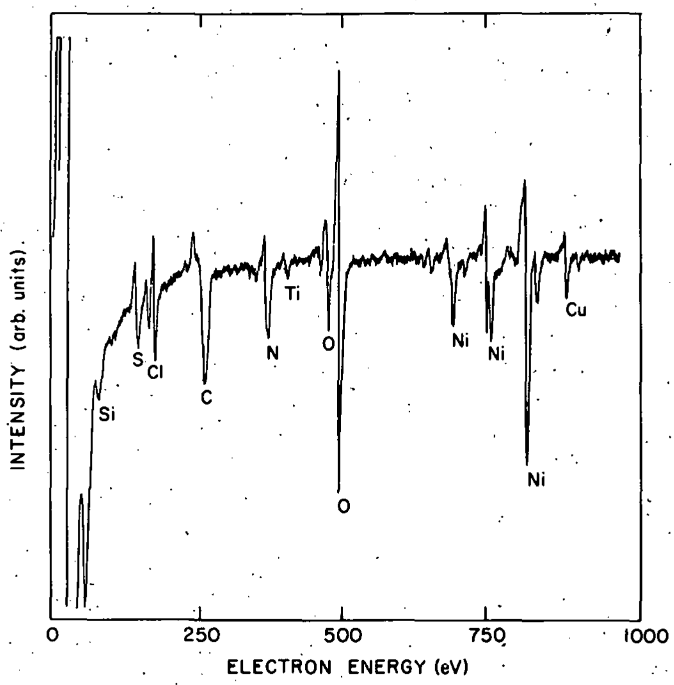

Figure 16. Auger spectrum of clean air sample.

OPEN DISCUSSION

(Samuel Morris - Chairman)

Baum: Well, I'd just like to comment in light of the complexity of the biological responses and possible synergistic effects that it may be very fruitful to do more of the biological Ames types of analyses in the near future. I think that's probably as close as we can come to evaluating hazards and perhaps the combination of how to concentrate the samples so that they can be presented to the Ames test suitably may be important in the short term.

Morris: I had a couple of questions on biological testing. My impression was that you were talking about this as a possible routine monitor in an industrial situation. Even the original purpose of the Ames test wasn't for that. It seemed to me that obviously you're going to have to do a lot of pretesting in order to know what you're working with before you can do routine testing. Once you are in a phase where you're doing your routine sampling, I wonder if you really need such a big sample? One of the problems was that the sample size you were collecting wasn't enough, and it seemed to me that once you know the kind of thing you're looking for, all you will be checking perhaps is, "Are you going above normal level or something like that?" Maybe just one dose is enough.

Daisey: I would never do the testing for one dose. Certainly you need to do duplicate plates. It's to some extent like radiation, a random process. The other thing is that when you start testing these materials, you can have toxic effects. And you can see those pretty readily with the dose response curve because when you start seeing toxicity, the response tends to be lower. The curve flattens out and you can't really see that with one dose.

Morris: Even in a routine situation where you know what you're working with, you still want to get a couple of points on the dose response curve?

Daisey: Yes, I think so.

Baum: Would it make sense to develop the control of the system such that, in general, a person could wear a personnel monitoring device for a month, let's say, and you would extract a sample and do a simple spot test and hopefully you would get a negative response if the control procedures were adequate? Is that true and enough?

Daisey: You can take longer samples and have enough material to do the testing. The spot test is useful because you would determine whether or not there is any activity, but you really don't know what the level of activity is. Where if you do a dose response curve, you can make comparisons to measurements that were done previously.

Runion: There is one thing that I think this committee might consider doing and that is in this matter of sampling for a PNA particulate material and operating within the framework of current criteria for coke oven emissions. I think it is generally recognized that the silver membrane and glass fibers do not catch all the material of interest. Somebody else mentioned that it is very likely that the silver membrane which is an expensive little gizmo is unnecessary. So if there is a little project that this group might want to consider, it might be an extra extension of the work that has already been done, keeping in mind the terms of a research project so that we can finally zero in on the combination of glass fiber and a backup medium which seems to be satisfactory. There may be some questions regarding brea through problems of this sort that the projects might embrace, but with the end-point objective of making this system generally acceptable to everyone and maybe a little less expensive.

Campbell: Another thing that I forgot to mention this morning is shelf life. The problems associated with those samples which have never really been quantified should be looked at in the program.

Daisey: I have another comment on the shelf life of samples. There is a good deal of information on polycyclic aromatic hydrocarbons collected in the air. The data suggest that you lose these materials from the filter when you store it, and a very good practice is to take them from the filter and extract them as soon as possible. One question I have is: What is the purpose of the silver membrand backup filter?

Campbell: I think the way it started is that silver membrane originally was chosen because there was a little problem in weight gain from water vapor. Since a gravimetric technique was used, that problem was eliminated. Then when filter study was begun in the coke oven industry, the silver membrane clogged up and someone slapped a glass fiber filter on top of it and all of a sudden it became standard technique. That is my opinion. I don't know if that is really how it happened.

Brief: There is another factor that had to do with the fact that the silver membrane is free of any benzene-soluble material and when they did the first extraction, they got a section zero where, if you took other filtering material, you tended to get something.

White: I would just like to put into perspective that what we are trying to focus on is the availability of monitoring tools for the future as opposed to what is available to handle problems today. We're pretty well trapped into using what tools are available to look at current problems, and we're talking about five and ten years into the future. I think we need to key in on what are the time restraints in terms of needing this technology. We're talking about future monitoring equipment and having that available so that we can do more in-depth analysis in the work place environment. One of the things that I think I'd like to hear a comment on is the advisability of going to bioassay samples. That's an area where there may be some activity.

Campbell: It kind of scares me as an industrial hygienist to see a test like the Ames test which started out as a screening method all of a sudden be stuck in a guy's lapel and to have it compared to human exposure.

White: In defense of biological test systems, I think Martha Radike made the comment that with these systems you are selecting species which are extremely sensitive and the fact that you can do that may indeed provide some safety margin that we may be concerned with in industrial hygiene.

Campbell: Well, it might increase the sensitivity, but I think the greatest problem is that it is still a screening mechanism. The general public may look at it otherwise and the work person may look at it otherwise and draw their own conclusions.

White: I would just indicate that bioassays, and not biological test systems, would not be different from doing urinalysis for people working around tritium, and that seems to be a useful tool for the health physicist.

Runion: You know you have to ask a question in the real world out there, and we're talking about the real world of coal conversion operations, an industrial enterprise. Are we going to come up with the tools to measure, assess, and monitor the environment within the framework of our contemporary views as to what is too much? We need both. Of course we need both. I view this conference as one of trying to be satisfied that the tools we have are the tools in the immediate future, not 10 years from now, are going to be in place, are in place to satisfy that need. The application of bioassay vehicles like the Ames test is to me a research project, not an item for assessment on whether you are or are not in some sort of compliance. We are mixing a little bit of science with law and with the practicalities of working and relating with people as employers and employees. We can't get this all too mixed up.

Morris: Well, to some extent, I think that there is an interest here in what the routine monitoring ten years from now may look like. What instruments will be available ten years from now? Research is clearly needed because everyone recognizes that the standards today really have an inadequate basis.

Brief: But if we use New York City air for comparison, we'll have to ban a lot of people, I suspect, from working at all. This will pose some real hard problems in making definitions of when the level is and when it's not. I suspect that we're living in an environment that is biologically active. I think any air pollution sample will show that kind of activity. I was curious about the results because it seemed to me that it might be safer to be working perhaps in a coal conversion plant than breathing New York City air, and yet the perception would be just the opposite. Now what do we do with the 8 million people in New York City? I think you're opening up a very huge can of worms unless you have some good basis for a steady standard. So in terms of a research tool, fine, but in terms of a monitoring scheme at this point I think it would be very premature.

Morris: But you're never going to have a basis for setting standards until you begin to get some of those data.

Daisey: I don't think you can go out and use it to monitor tomorrow. I don't think there are any questions about that. As far as New York City vs industrial plants, all those numbers were revertants per microgram.

Brief: I realize the distinction.

Daisey: The other thing is if you're talking about exposures in an industrial plant, you can usually accept levels that are maybe one hundred times higher than what people are exposed to in the ambient atmosphere.

Brief: It's like raising the issue of motherhood and the flag. When you talk about biological activity and cancer, it is a very hysterical type of a situation. I don't think any worker would accept the principle that he is working in a more biologically active environment than he has to go home and live in.

Daisey: What alternative do you have?

Brief: Well, I can see the legal restraints on industry. I can see an awful lot of additional legislation. I can see an awful lot of extra regulation. I see opening up a box of additional controls and restraints. It may make it difficult to actually operate a facility, which would be a shame.

Baum: I think that's a mistake because the worker working with radiation knows it causes cancer. You educate him to the problem and the relative risks and so on, I think he'll be reasonable about it.

Lippman: If there was a better or easier choice, I think we all would have come to a conclusion by now. We have some feeling that we can't go to a single indicator specie even if it is a known carcinogen like benzo(a)pyrene and feel that that is giving us a good index. Now, we really don't know what to look for, and yet we want to have some relatively simple, relatively inexpensive monitor of what people are exposed to when we're only interested in these materials because they are mutagens. I mean if they weren't carcinogens/mutagens, we would say forget about them altogether. So, we have a quick and dirty approach, biological activity. Admittedly, it's not any great thing but perhaps it's the least bad of the alternatives. In my mind it is probably better than benzene soluble mass. It is better than beno(a)-pyrene as an indicator. So, as crude as it is, it might be the best thing to give us information. I recognize that the regulators are liable to screw it all up. This is something we have to face in our recommendations perhaps. How to recommend it without letting it get into the regulatory situation.

Runion: Sounds like the TLV committee 25 years ago, doesn't it?

Lippman: We all have been subject to deja vu in industrial hygiene. It seems the wheel has been invented many times in the last 20 years, 25 years. What is a rational posture to take at this point? It comes down to what do we feel is the best way to prevent unnecessary exposure of the workers in these plants, that we can apply not 10 years from now, but next year and the year after. If it isn't a crude biological index, well, what should it be?

Runion: May I respond to that question? I spoke about it several times this week, and I don't have the answer to all this but I do think that one approach is to use some of the tools we now have and add some of these new tools, like the Ames test, some of the more sensitive analytical procedures that were discussed this morning in terms of narrowing in on some of the preferred PNA species that you think might be good common denominators. When the toxicologist does a study on the SRC1 liquid substance in which they're going to expose the mice in an atmosphere where they will reside until they die, these atmospheres should be tested, using these various means of assessment. So, when you finally get the bioassay result in higher forms of life, which we all one time or another can refer to in making these decisions, we have that information then as a reference. I don't think you can come up today in all fairness to our society and throw on it the potential burden of the Ames test as the means of saying it is or isn't a good situation. Maybe five years from now as a result of some concerted effort, say taking a systems approach, we'll begin to see that these other tools can be introduced into the criteria-setting mechanism that we now are not happy with. That's my suggestion. It's not predicted. It can't be done in a month.

Campbell: One quick comment I have about the Ames test is that perhaps it can show us whether the cyclohexane or benzene fraction is the right fraction to look at.

Morris: That's very interesting. Is there anyone here who's done work from chemical tests that relates to that? That is, using other extractions?

Campbell: I think Jim Eppler has been looking at the Ames test with different fractions. I don't know his results.

Morris: Otto, do you have any closing comments?

White: No. If there are no further comments and discussions, I would like to thank everyone for participating and contributing to the exchange of information during this symposium.

Thank you again.

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APPENDIX I

Agenda

SYMPOSIUM
ON
ASSESSING THE INDUSTRIAL HYGIENE MONITORING NEEDS
FOR THE
COAL CONVERSION AND OIL SHALE INDUSTRIES

BERKNER HALL
Brookhaven National Laboratory
Upton, New York 11973

November 6, 1978

Theme: "Recognition of Occupational Health Monitoring Requirements for the Coal Conversion and Oil Shale Industries"

Agenda

9:00 Opening Ceremonies

Introductory Remarks - O. White - Brookhaven National Laboratory
C. B. Meinhold - Brookhaven National Laboratory

Welcome Address - V. P. Bond - Brookhaven National Laboratory

Session Chairman: A. Sharkey - Pittsburgh Energy Research Center

9:10 Overview from Fossil Energy - J. Abrahams - U.S. Department of Energy, FE/ET

9:30 Significance of Trace Constituents in Coal - R. Ruch - Illinois State Geological Survey

9:55 Coal Gasification: Process Description and Effluent Characterization - J. C. Craun - Environmental Research & Technology, Inc.

10:20 Coal Liquefaction: Process Description & Effluent Characterization - F. K. Schweighardt - Pittsburgh Energy Research Center

10:45 Coffee Break

11:10 Oil Shale: Process Description & Effluent Characterization - R. Merril Coomes - Tosco Corporation

11:35 Relative Chemical Composition of Selected Synthetic Crudes - W. H. Griest, M. R. Guerin, B. R. Clark, C. -h. Ho, I. B. Rubin & A. R. Jones - Oak Ridge National Laboratory

12:00 Lunch

Session Chairman: N. Bolton - Union Carbide

1:30 Toxicology and Carcinogenicity of Oil Shale Products - W. Barkley, D. Warshawsky, & N. Radike - University of Cincinnati

1:55 LASL Industrial Hygiene Experiences in the Oil Shale Industry - L. L. Garcia - Los Alamos Scientific Laboratory

2:20 Industrial Hygiene Experience in Coal Liquefaction (An Overview) - H. E. Runion - Gulf Oil Corporation

2:45 Occupational Safety and Health in Coal Gasification - J. Evans - Enviro Control, Inc.

3:10 Coffee Break

3:30 Panel Discussion - All Speakers

November 7, 1978

Theme: "Status of Dosimetry Technology for Occupational Health Monitoring Requirements for the Coal Conversion and Oil Shale Industries"

Agenda

Session Chairman: D. Fraser - University of North Carolina

9:00	Adequacy of Current Dosimetry Tools for the Coal Conversion and Oil Shale Industries - J. Campbell & W. Porter - Oak Ridge National Laboratory
9:25	Criteria for Occupational Health Monitoring in the Fossil Fuel Conversion Industries - O. White - Brookhaven National Laboratory
9:50	Preliminary Thoughts on Proxy PNA Compounds in the Vapor & Solid Phase - R. B. Gammage - Oak Ridge National Laboratory
10:15	DUVAS: A Field Portable Second-Derivative UV-Absorption Spectrometer for Monitoring PNA Vapors - A. Hawthorne - Oak Ridge National Laboratory
10:40	Coffee Break
11:10	Passive Dosimeters for Gases - E. D. Palmes - N.Y. University Medical Center
11:35	A Portable Fluorometric Monitor to Detect PNA Contamination of Work Area Surfaces - D. D. Schuresko & G. Jones, Jr. - Oak Ridge National Laboratory
12:00	Lunch

Session Chairman: S. Morris - Brookhaven National Laboratory

1:15	A Pocket-Sized Personal Air Contaminant Monitor - H. Jerman & S. Terry - Stanford Electronics Laboratories
1:40	Recent Advances - Solid State Gas Detection: Recent Advances in Thin Solid Films for Solid State Gas Detection - D. J. Leary & A. G. Jordan and Portable Gas Detection: Enhancement of Semiconductor Sensor Capabilities by Microcomputer Control and Signal Processing - D. T. Tuma & P. K. Clifford - Carnegie-Mellon University
2:05	Rapid Analysis of Complex PNA Compounds in Complex Samples by Room Temperature Phosphorimetry - T. Vo-Dinh - Oak Ridge National Laboratory
2:30	Screening Techniques for Biological Activity - J. M. Daisey & F. Mukai - N.Y. University Medical Center
2:55	Coffee Break
3:10	Portable Optical Particle Counters - V. Marple - University of Minnesota
3:35	Surface Analysis Techniques and Their Use in Pollution Detection and Measurement - M. N. Varma & J. W. Baum - Brookhaven National Laboratory
4:00	Open Discussion

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APPENDIX II

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