DOE/EV-0058

Industrial Hygiene Monitoring Needs for the Coal Conversion and Oil Shale Industries

Study Group Report

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Assistant Secretary for Energy Environment
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FOREWORD

This document reports the conclusions of a study group organized to assess the need for research and development of instrumentation for monitoring occupational exposures in the coal conversion and oil shale industries. Following the traditions established during the development of nuclear energy, the Department of Energy (DOE) formed the working group as part of its overall efforts to recognize and evaluate hazards to health concurrent with the development of new energy technologies. The Department of Energy is committed to the protection of the work force with the same degree of dedication as it devotes to developing alternative energy systems and supplies. It is hoped that early efforts to identify and monitor hazards to health will improve the data base for epidemiological studies and prevent such situations as the current one billion dollar annual compensation payments to victims of black lung disease.

The members of the study group designated to assess the industrial hygiene monitoring needs for the coal conversion and oil shale industries are:

	Affiliation
Otto White, Jr., Co-Chairman	Brookhaven National Laboratory
Samuel Morris, Co-Chairman	Brookhaven National Laboratory
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David Fraser	University of North Carolina
Morton Lippman	New York University
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* Present affiliation is Diamond Shamrock Corporation.

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

The third meeting of the group was held at Brookhaven National Laboratory (BNL) in conjunction with a two-day symposium on "Assessing the Industrial Hygiene Monitoring Needs for the Coal Conversion and Oil Shale Industries." The symposium program (Appendix) 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). This information proved to be invaluable when the study group met following the symposium for a third day (November 8, 1978) to draft its report to DOE.

The Office of Health and Environmental Research/DOE is grateful to the Chairmen and members of the study group for their contributions both in time and effort to the production of this document. Any questions or comments with respect to the report should be addressed to Dr. Daniel Lillian, Office of Health and Environmental Research. The proceedings of the BNL Symposium are available through the National Technical Information Center (BNL Report 51002, March 1979).

I. INTRODUCTION

Procedures involved in converting solid coal and oil shale into more usable liquid or gaseous fuel result in the utilization and generation of many hazardous substances with potential emission into the environment and the workplace. These substances range from simple inorganic compounds, such as carbon monoxide, to complex organic compounds, such as 7,12-dimenthylbenz(a)anthracene. The health effects resulting from exposure to these compounds range in severity from nuisance and mild irritation to cancer and death, while the response interval can range from immediate to 25 and 30 years. To add to the complexity of the problem, many of these compounds enhance or accelerate the action of other compounds when present together. The Department of Energy formed this study group to assess instrumentation needs to assure the work force of these emerging industries a safe and healthful working environment.

The primary purpose of environmental monitoring in the workplace is to evaluate exposures so that controls can be instituted to protect the health of the worker. There are a number of specific ways monitoring is used, and instrumentation needs often depend on a specific purpose. Examples of ways in which environmental monitoring is used include:

1. Evaluating hazards to health
2. Monitoring the performance of engineering controls
3. Monitoring trends in engineering controls
4. Developing design requirements for new engineering controls
5. Documenting exposure levels
6. Testing for compliance purposes
7. Measuring process losses to the environment
8. Selecting suitable respiratory protection devices
9. Identifying contamination sources
10. Assessing emergency conditions

A more in-depth evaluation of future instrumentation requirements can be made by concentrating specifically on monitoring needs for evaluating hazards to health. For example, at least four different criteria can be used in evaluating health hazards. These include conditions that are:

1. Immediately hazardous to life and health
2. High risk, but not immediately hazardous
3. Moderate risk and not immediately hazardous
4. Short-term, nonroutine high hazards

For each of these conditions, the following questions must be answered before a priority can be affixed:

1. What compounds are represented in this class?
2. Is monitoring technology available for present needs?
3. Is current technology compatible with future needs?
4. If not, is technology being developed to meet the projected needs?
5. When will the technology be needed?
6. When will that technology be available?

II. TECHNOLOGY REVIEW

The increased emphasis on occupational safety and health initiated by legislative action in the early 1970's has resulted in some significant gains in the development of monitoring tools for occupational health surveillance. Requirements for more precise and accurate evaluation of workplace exposures have led to the production of noise dosimeters, passive dosimeters for certain gases and vapors, portable real-time monitors for organic vapors, new low flow rate pumps, more sensitive and accurate detector tubes, more specific analytical methods, heat stress monitors, and direct reading dust monitors.

These improvements in monitoring technology have simplified the task of those involved in monitoring employee exposures. These instruments have met that need rather well. Unfortunately, most advances have been made in areas where traditional monitoring techniques already existed, rather than in areas recently identified as potential health hazards. The emerging fossil conversion industries represent such an area since the base materials may contain most of the elements found in the periodic table and the processes and conditions required to produce the crude material can concurrently synthesize a host of highly toxic by-product chemicals. Although these industries have been shown to be similar to the petroleum industry, studies have shown that some of the products, depending on the process, are potentially more toxic than their petroleum counterparts. Avoidance of exposures to vapors, liquids and airborne particulates is the desired goal—even for those compounds exhibiting similar toxicity to their petroleum counterparts.

A review of industrial hygiene efforts at the pilot and demonstration plant levels indicates that current activities are mainly focused on monitoring traditional contaminants— silica dust, carbon monoxide, oxides of nitrogen, coal dust, hydrogen sulfide, and sulfur oxides. Contaminants which are somewhat unique for these industries and which pose a high potential long-term risk are not being monitored to the extent desirable because of lack of technology, high costs, long analytical procedures, lack of specificity, inadequate sampling methods, and inefficient recovery procedures. Additionally, many critics of detailed industrial hygiene involvement at the pilot and demonstration plant levels suggest that, because of scaling problems associated with upgrading pilot and demonstration units to the commercial plants, the contaminants of concern may differ. The study group believes that efforts to learn as much as possible about the hazards associated with these emerging industries should grow concurrently with the developing technology. Although current occupational health monitoring is locked into using technology and tools that are presently available, future assessments of occupational health problems in commercial fossil fuel conversion plants will require additional, more sophisticated monitoring tools.

Future trends in occupational health monitoring will require more accurate assessment of individual dose to adequately predict health response. Accurate dose assessment will not only require personnel monitoring, but also a determination of individual exposure rate. A review of analytical techniques adaptable to personnel monitoring was reported by Morgan and Morris in 1976. Although the authors were concerned almost exclusively with air pollutants such as SO_2, NO_x, CO, O_3 and particulates, their ranking of techniques in order of payoff probabilities is appropriate for this report (Tables 1 and 2).

It was against this background that the study group embarked upon its task of assessing the occupational health monitoring needs for the coal conversion and oil shale industries, with particular attention given to exposures to fugitive toxic materials.

III. RESEARCH AND DEVELOPMENT REQUIREMENTS FOR ASSESSING POTENTIALLY HAZARDOUS EXPOSURES

A. Immediately Hazardous to Life and Health

This category includes those materials which are present in sufficient quantities such that acute exposure could occur and the associated health and/or safety effects could result in immediate and serious impairment to life and health.

Six compounds have been identified as representatives of this class:

1. H_2S - acute poison (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

The study group believes that technology is available to provide equipment which can be used as personal and area monitors with continuous direct reading and/or alarm capabilities for H_2S, CO, O_2, and H_2. Technology is presently lacking for monitoring explosive levels of coal and shale dust and for NO_x-NO_2 personal alarming devices.

Future needs may require personal monitors capable of transmitting a signal to bring outside assistance in emergencies.

Phenols, hydrogen cyanide, metal carbonyls and carbon disulfide would also be included in this category if potential concentrations in the workplace were sufficiently high.

In most cases, exposure to life-threatening concentrations should occur only as the result of a leak. Rather than relying on individual monitoring of several hazardous materials, a single indicator might be monitored to give warning of a leak. In gasification plants where the process stream includes high concentrations of CO, this gas has been suggested as an indicator. The indicator must be present in sufficient concentration to give warning in all process streams carrying immediately hazardous substances. CO may not be suitable as an indicator in certain processes utilized in liquefaction and shale plants.

For each type of plant, it will be necessary to determine which indicators are appropriate for leak detection for each work area. Fixed alarm monitors are most appropriate together with survey meters.

B. High Risk, but not Immediately Hazardous

This category is reserved for substances which may cause irreversible effects to body organs or systems, but which are not present in sufficient quantities to produce acute toxicological effects. Carcinogenic, mutagenic and teratogenic organic compounds are included in this category, as well as trace metals, silica dust and asbestos fibers.

There is the potential for exposure to so many of these substances that the study group believes it to be impracticable to monitor them routinely except when dictated by regulatory requirements. The evaluation of one or more indicator compounds is a logical approach. Unfortunately, there is general agreement that indicators now frequently used, such as benz(a)pyrene and/or the benzene or cyclohexane soluble fraction are of marginal or little value in many cases. No single indicator may be adequate and certainly different indicators or groups of indicators may be needed in different situations. Further research is needed to study unit operations and process streams from both the chemical and biological standpoints and to identify indicators that are representative of the biological effect from the expected exposure. The strategy recommended is to identify a variety of potential indicators (perhaps six or eight) and the place where each is likely to be useful and the kind of monitoring required. In general, personal or survey instruments will be appropriate. The state-of-the-art for monitoring each compound by the methods needed should be assessed and finally, if necessary, new instruments should be developed. Since the final selection and evaluation of specific indicators can not be made until commercial plants are built, it is necessary to have available, at that time, a number of indicators to choose from, for which instrumentation is available. Since this instrumentation will probably be group selective, a common line of development will lead to instruments capable of measuring several indicator compounds.

The instruments needed now are portable monitors—survey instruments and personal exposure monitors. It is desirable that these instruments be inexpensive.

Further research is needed on direct biological indicators of hazard such as the Ames Salmonella Typhimurium test and the Tradescantia test system. There is a need to refine protocols and to develop standard biological test systems. These test systems must be compared with chemical indicators; they have the potential of being used as one means of evaluating chemical indicators. It is not possible to judge the value of biological tests as direct indicators of the level of risk of occupational exposures. The study group recognizes the problems associated with nonprofessional interpretation of results from such tests and recommends that consideration be given to develop endpoints which minimize the potential for misinterpretations.

C. Moderate Risk and not Immediately Hazardous

The study group anticipates increasing demands to provide a comprehensive record of all hazardous compounds to which a worker is exposed; this will require increased use of personal monitors, automated chemical analyses and computerized data-handling systems. The appropriateness of using area monitors to assess potential health hazards of individual workers should be evaluated since most operations will occur out-of-doors. Contaminant releases are likely to be localized, suggesting possible limited use of area monitors to measure exposures to individuals.

D. Short-Term, Nonroutine High Hazards

The availability of portable survey instruments for evaluating hazards to health during emergencies involving Condition A (immediately hazardous to life and health) compounds appears to be adequate for present and future needs. Unfortunately, much R&D effort is required to reach this status for Condition B (high risk, but not immediately hazardous) compounds and potential Condition A compounds (e.g., hydrogen cyanide, carbon disulfide, metal carbonyls, and phenols).

IV. SPECIFIC RESEARCH SUGGESTIONS

A. Personal Monitors for Gases

1. Current Instrumentation

a. The study group encourages additional evaluation of current instrumentation under various conditions of interferences, temperatures, pressures, humidity, and related variables to ascertain their appropriateness for future needs.

b. It is likely that passive monitors will become a primary monitoring tool. An improvement needed is the development of new substrates to expand the diversity of measurable compounds and to allow for greater sensitivity. This area of investigation is likely to provide high payoff within a few years.

c. Current personal sampling pump flow rates need to be improved to provide higher collection capabilities (5 to 10 lpm).

2. Second Generation Instrumentation

The study group encourages the development of new sampling instruments which will facilitate automated analysis and data recording to permit handling large amounts of data generated during routine monitoring, e.g., personal gas chromatography units capable of multiple compound analysis, miniaturization of existing devices, and simplified analytical procedures.

"Real-time" data reporting is necessary only for Condition A (immediately hazardous) exposures. In other cases, the most attractive approach seems to be through personal samplers which either internally record the results of real-time analysis over the course of the day, or collect an integrated sample over a day. The latter sampler could be inserted into a device at the end of the day, which analyzes and records the exposure automatically.

DOE should support the development and application of personal gas chromatography devices for monitoring vapor-phase polycyclic hydrocarbons. Potential problems such as condensation in the sampler and long retention time on gas chromatograph columns need to be investigated.

B. Nitrogen Compounds

There is a need to develop reliable and rapid readout sampling techniques for NH_3, HCN, and nitrogen heterocyclic compounds.

C. Aerosols

This is an area where there are many needs. For example, there is a need to do in situ characterization, but no immediately promising avenues for research in this area are evident.

Since tar and oil particulates which collect in the nasopharyngeal region may provide a significant exposure, a size cut of particulates known as inhalable particulates may be useful in characterizing aerosols containing polynuclear material. For comparison purposes, size cuts of 15 μm and 2.5 μm consistent with recent EPA dichotomous sampler performance in sampling of outdoor suspended particulate matter should be explored. Current technology appears to be adequate for sampling with a variety of particle size separators, and development of more sophisticated devices is not recommended at this time.

Research support would be productive if directed toward:

1. Improving extraction efficiency and separation techniques for organic components absorbed or adsorbed by particulates.
2. Chemical specification by compound, rather than by anion and cation, as a function of particle size.
3. In situ separation of soluble and insoluble particulates.
4. Improving collection capacity of pumps used with personal particulate samplers.

D. Metals

Five metals were identified for which exposure in coal conversion plants may be a problem. These are:

1. Arsenic
2. Beryllium
3. Cadmium
4. Chromium
5. Nickel

The toxicity of metals seems to vary with valence (e.g., Cr^{+6} vs Cr^{+3}) and with chemical compound (e.g., $CoCO_3$ vs $CoSO_4$). Current analytical technology generally does not provide insight into these factors. Research is needed to provide this additional information. In addition, organometallics are a potential hazard in fossil fuel conversion for which improved instrumentation is necessary.

E. Fibers and Dust

Although exposures to fibers (e.g., asbestos) and dusts (e.g., silica) are not unique to the fossil conversion industry, the need to develop an inexpensive, in situ method for assessment of fibers was apparent to the study group.

F. Surface Contamination

Worker contact with contaminated surfaces appears to be a very important mode of exposure. The need to develop reproducible, simple, and significant means for measuring surface contamination was quite evident to the study group. Research in this area should be encouraged.

G. Skin Contamination

Research should be directed toward developing tools which evaluate skin contamination. Furthermore, research is required to determine whether the carcinogenic hazard is enhanced by the use of UV as a screening tool for skin contamination.

H. Analytical Development

The study group encourages the refinement and development of analytical tools and techniques for materials which are identified via characterization studies and are directly amenable to industrial hygiene applications.

I. Industrial Hygiene Surveys/Research

The pilot plant and the demonstration plants represent excellent opportunities to characterize the work atmosphere for the various processes, evaluate the appropriateness and durability of various indicators and sampling tools, define appropriate sampling strategies and techniques, and evaluate the stability of collected contaminants. In-depth industrial hygiene surveys for monitoring the pilot and demonstration plant worker exposure should provide invaluable information even if many processes and procedures are not scalable.

J. Bioassays

The study group expresses the desirability of developing and evaluating a) bioassay tests which are sensitive to chemical/physical features associated with hazardous effects from toxic agents, i.e., determining and characterizing alkylating activity with a colorimetric test, and b) bioassay procedures to identify body burden resulting from several routes of exposure.

V. THE FUTURE

Fossil fuel conversion technology and knowledge of associated hazards to health are both advancing rapidly. The working group recommends that it reconvene for a short single session in approximately one year to re-evaluate the situation with respect to instrumentation needs and identified potential health hazards.

Table 1

Gas-Sensitive Instrumentation Techniques

	< 3 yr	3 to 6 yr
Outstanding probability of payoff	Sorption methods Gel-tape colorimetry Electrochemical cells Coulometric and amperometric devices Nondispersive spectroscopy (CO) Fluorescence devices (SO_2) Chemiluminescence (O_3,NO_x)	Sorption methods Colorimetry (tape based) Electrochemical cells Coulometric and amperometric devices Fluorescence devices (SO_2) Nondispersive spectroscopy (CO) Chemiluminescence (O_3,NO_x)
Good probability of payoff	Microwave devices (CO)	Electronic solid state devices Nondispersive spectroscopy (gases other than CO) Piezoelectric gas sensors Microwave devices (CO) Gas chromatography
Fair to Poor probability of payoff	Gas chromatography Cryogenic sampling Electronic solid-state devices Nondispersive spectroscopy (gases other than CO) Piezoelectric gas sensors Microwave devices (gases other than CO)	Cryogenic sampling Bioluminescent methods Optoacoustic methods Microwave devices (gases other than CO)

Adapted from: Morgan, M.G. and Morris, S.C., Individual Air Pollution Monitors: An Assessment of National Research Needs, BNL 50482, January 1976.

Table 2

Particle-Sensing Instrumentation Techniques

	< 3 yr	3 to 6 yr
Outstanding probability of payoff	Virtual impactor (M,2D,C) Filters (M,~N,~D,C) Diffusion batteries with filters [C(D)] β meter (M)	Virtual impactor (M,2D,C) Filters (M,~N,~D,C) Diffusion batteries with filters [C(D)] Optical Scattering (N,D) β meter (M)
Good probability of payoff	Diffusion battery with condensation nuclei counter (N,D)	Virtual impactor (M,2>2D,C) Diffusion battery with condensation nuclei counter (N,D) Piezoelectric mass balance (M,~N,~D)
Fair to poor probability for payoff	Piezoelectric mass balance (M) Optical scattering (~N,D)	

M - device appropriate for measurement of total suspended particulate mass
N - device appropriate for measurement of total number of particles
D - device appropriate for measurement of particle "size" distribution. The notation 2D indicates that sizing into two categories such as $\geq 3\ \mu m$ and $\leq 3\ \mu m$ is possible.
C - device appropriate for collecting samples of particles for chemical analysis. The notation C(D) indicates that chemical composition can be estimated for two or more separate ranges of particle size.
Other candidate technologies that were considered but viewed as unsatisfactory or inappropriate for use in individual air pollution monitors included:
- liquid impingers
- centrifugal separation
- conventional impactors
- thermal precipitation
- electrical mobility
- microwave

Adapted from: Morgan, M.G. and Morris, S.C., Individual Air Pollution Monitors: An Assessment of National Research Needs, BNL 50482, January 1976.

APPENDIX

Symposium 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 Technology 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 and Technology, Inc.
10:20	Coal Liquefaction: Process Description and Effluent Characterization F. K. Schweighardt - Pittsburgh Energy Technology Center
10:45	Coffee Break
11:10	Oil Shale: Process Description and 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, and 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, and 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 and 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 and 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 and 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 and 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 and A. G. Jordan and Portable Gas Detection: Enhancement of Semiconductor Sensor Capabilities by Microcomputer Control and Signal Processing - D. T. Tuma and 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

Agenda (Continued)

2:30 Screening Techniques for Biological Activity - J. M. Daisey and F. Mukai - New York 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 and J. W. Baum - Brookhaven National Laboratory

4:00 Open Discussion

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