MINING SURVEILLANCE STUDY OF COAL PREPARATION AND RELATED LABORATORY FLOAT-SINK OPERATIONS

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Richmond, California 94804

NIOSH Contract 210-80-0027

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health
Environmental Investigations Branch
Morgantown, West Virginia 26505

August 1983

PB84-182831

REPORT DOCUMENTATION PAGE	1. REPORT NO.	2.	3. Recipient's Accession No.

4. Title and Subtitle
Mining Surveillance Study of Coal Preparation and Related Laboratory Float-Sink Operations

5. Report Date

6.

7. Author(s)
Anonymous

8. Performing Organization Rept. No.

9. Performing Organization Name and Address
NIOSH, Public Health Service, U.S. Department of Health and Human Services

10. Project/Task/Work Unit No.

11. Contract(C) or Grant(G) No.
(C) 210-80-0027
(G)

12. Sponsoring Organization Name and Address
Same as box 9

13. Type of Report & Period Covered

14.

15. Supplementary Notes

16. Abstract (Limit: 200 words)

A survey of techniques used to control occupational exposures to various trace metals, frothing agents, and organic solvents at coal preparation sites and laboratories was conducted at the EAL Corporation (SIC-1211) in Richmond, California, Carbon County, Utah, Jefferson County, Alabama, and Washington County, Pennsylvania in 1981. The laboratories were located at Clarksburg and Wheeling, West Virginia. The coal preparation facilities relied principally on natural ventilation and work practices to control employee exposure. The laboratories used ventilation and local exhaust systems as well as work practices to reduce the concentration of contaminants. Analysis of environmental and breathing zone samples at the coal preparation facilities showed that the concentration of trace metals and frothing agents were controlled to below acceptable limits. Analyses at the laboratories showed similar results except for ethylene-dibromide (106934) (EDB). Although the measured concentrations of EDB were consistently below the OSHA limit of 20 parts per million (ppm), they were above the NIOSH standard of 0.13ppm. The authors recommend that a less hazardous solvent be substituted for EDB.

17. Document Analysis a. Descriptors

b. Identifiers/Open-Ended Terms
NIOSH-Publication, NIOSH-Contract, Coal-processing, Toxic-vapors, Laboratory-workers, Occupational-exposure, Employee-exposure, Industrial-hazards, Safety-practices, Air-quality-measurement

c. COSATI Field/Group

18. Availability Statement:	19. Security Class (This Report)	21. No. of Pages
		161
	20. Security Class (This Page)	22. Price

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PREFACE

Section 101(A)(6)(B) of the Federal Mine Safety and Health Act of 1977 states that the Secretary of Health and Human Services or his duly appointed representative "...shall for each toxic material or harmful agent which is used or found in a mine, determine whether such material or agent is potentially toxic at the concentrations at which it is found in a mine." The Act designates the National Institute for Occupational Safety and Health (NIOSH) as the agency in the Department of Health and Human Services responsible for occupational health research investigations in the mining industry.

Part of the NIOSH effort in this area has been a surveillance program of conducting preliminary investigations into specific agents found or used in mining, which little is known about or which creates concern with respect to potential occupational health hazard. These investigations are limited in scope to literature reviews and preliminary industrial hygiene surveys. The findings of these preliminary investigations are used to identify health hazards, and to aid the direction of NIOSH research efforts in the occupational mine health field. This report represents one such mining surveillance investigation project.

This report was submitted in partial fulfillment of Contract #210-80-0027 by EAL Corporation under the sponsorship of the National Institute for Occupational Safety and Health.

ABSTRACT

Worker exposures to potential occupational health hazards associated with coal preparation and related laboratory float-sink operations were evaluated. The three types of hazards studied were:

(1) Trace metals, such as Be, Cd, Co, Cr, Li, Ni, and V, potentially found as natural contaminants in coal dust;

(2) Frothing agents (principally, methylisobutyl carbinol) used in flotation cleaning; and

(3) Organic solvents (including perchloroethylene, ethylene dibromide, xylene, and VM&P naphtha) used in laboratory float-sink operations.

Detailed industrial hygiene surveys were conducted at 5 facilities. Three of these were coal preparation plants and two were commercial coal laboratories with laboratory float-sink operations. Survey methods included area sampling for trace metals, and both area and personal sampling for frothing agents and organic solvents. The organic solvents in float-sink operations were sampled for ceiling levels as well as 8-hour time weighted averages. In addition to air sampling, indepth walkthrough surveys of each facility evaluated the following items: (1) operating procedures, (2) chemicals in use, (3) exposure hazards, (4) work forces, (5) engineering control measures, and (6) in-plant programs for medical, industrial hygiene and safety.

Of the three hazard categories investigated in this study, the use of ethylene dibromide (EDB) in laboratory float-sink operations yielded the most important study findings. Although the EDB sampling results were consistently below the current OSHA PEL of 20 ppm, the results indicated that the involved employees were exposed to airborne concentrations exceeding the NIOSH-recommended guideline of 0.13 ppm. This was found to be true regardless of the relative scale of operations and the availability of standard

engineering controls. It should also be noted that there were only a very small number of employees directly involved with this operation at each facility.

Based on the other personal and area air monitoring conducted during the five surveys, the employees involved in the various study operations were not overexposed to (1) trace metals, (2) the chemicals used in frothing agents, and (3) the other organic solvents (i.e., xylene, VM&P naphtha) used for float-sink operations.

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PURPOSE AND NEED FOR THE STUDY

Little information exists on the potential health hazards associated with coal preparation generally, and with float-sink operations in particular. A modest but significant base of information on the potential risk of coal preparation as a control technology for source generated sulfur oxide emissions and other potentially toxic substances produced from coal has been developed as a result of the Environmental Protection Agency Industrial Environmental Research Laboratories comprehensive environmental assessment program (Versar 1978a;1978b;1980). However, there has been comparatively little information generated in the past several years concerned with occupational health aspects of coal preparation. Until recently coal dust exposure assessments had largely been restricted to underground coal operations. A review of chemical exposures either below or above ground in the coal industry apart from the new coal conversion technologies has not been conducted.

Information gaps in the occupational health area are largely explained by the lack of a legislative mandate for health research inquiry into surface coal operations prior to the enactment of the Federal Mine Safety and Health Act of 1977. Prior to March 1977 the health research performed by NIOSH in assisting the then Mining Enforcement and Safety Administration (MESA) in review of health hazards in the coal industry was limited, under MESA legislation, to underground coal operations. Only with the creation of the Mine Safety and Health Administration (MSHA) and the enactment of the FMSH Act of 1977 were health research responsibilities further expanded to encompass a review of surface coal operations and coal preparation.

Trace Metal Contaminants in Coal Dust

Coal preparation is essentially a physical or mechanical process for cleaning coal. Apart from the limited use of certain types of chemical substances in advanced levels of coal cleaning such as those chemicals used

in froth flotation, potential health hazard are essentially limited to the processed material itself - coal and associated impurities.

Respirable coal dust levels were not studied in this survey because the Mine Safety and Health Administration (MSHA) routinely evaluates worker exposure to coal dust (MSHA, 1978).

Trace metal contaminants in airborne coal dust were chosen for study because of their potential for adverse health effects. No prior studies had been done on trace metals in coal preparation facilities. The seven targeted agents included: Be, Cd, Co, Cr, Li, Ni, and V.

Froth Flotation Reagents: Methylisobutyl Carbinol (MIBC) and Dowfroth M-222

Froth flotation is a combination chemical/physical process which resolves ultrafine coal particles from noncoal impurities via selective adhesion of some particles to air bubbles finely disseminated through a feed coal slurry with concurrent adhesion of other particles to the slurry media. Air adhering particles, usually coal, are separated from nonadhering particles as a concentrate or froth at the surface of the slurry.

Froth flotation involves the use of various reagent chemicals to assist selective adhesion of certain particles to either the air or water/slurry interfaces. There are three general classes of reagents used which are described as: frothers, collectors or promotors, and modifying agents. Table 1 is a list of various kinds of chemical substances that serve to facilitate the process.

Table 1. Flotation reagents.

Frothers	Modifying Agents
amyl alcohol	sodium and potassium cyanides
butyl alcohol	potassium permanganate
terpinol	sodium sulfite

cresol	potassium chromate
methylisobutyl carbinol (MIBC)	sodium disulfate
kerosene	sodium phosphate
crude oil	sodium bicarbonate
coal tar products	sodium silicate

Collectors

methylisobutyl carbinol (MIBC)
kerosene

Source: Leonard, 1979

There is little available monitoring data in the literature documenting exposure among coal preparation workers to flotation reagents. Two reagents used as frothers in the froth flotation process were chosen for this study: methylisobutyl carbinol (MIBC) and Dowfroth M-222 Flotation Frother (a mixture of polypropylene glycol monomethylethers). MIBC was of interest because it is used extensively throughout the industry as a frother/collector in flotation units processing bituminous coal. Limited sampling showed MIBC levels to be below the current OSHA permissible exposure limit of 100 mg/m^3 (Enviro Control, Inc. 1980). Dowfroth M-222 was chosen as an example of a brandname substitute for MIBC, which was presumed to be relatively non-toxic. (See Appendix C: Material Safety Data Sheet for Dowfroth M-222)

Float-Sink Operations: Organic Liquids

Float-sink or specific gravity fractionation of coal is an operation or laboratory procedure involving the separation of a coal into various specific gravity factions by immersion in heavy organic liquids. The fractions of a certain topsize coal are obtained for specific gravity gradients and are evaluated according to percent weight, ash and Btu value to describe the coal's amenability to cleaning. The data obtained is referred to as Washability Data.

A wide variety of organic liquids may be used in float-sink testing, these may include:

Acetylene tetrabromide
Benzene
Bromoform
Carbon tetrachloride
Certigrav - a mixture of Cl and Br halogenated solvents
Ethylene dibromide
Gasoline
Methyl iodide
Pentachloroethane
Perchloroethylene or tetrachloroethylene
Tetrabromoethane
Toluene
1,1,1-trichloroethane
VM&P Naphtha
Xylene

There are two potential occupational health hazards which are readily identifiable with float-sink operations. One involves the exposure to the various organic liquids used in the float-sink procedure. The other involves the exposure to coal dust associated with raw coal sample preparations prior to float-sink testing.

In general, there is a fairly abundant information base regarding the acute and chronic toxicity as well as other health information for the various heavy organic liquids used in fractionation (NIOSH 1976a;1976b; 1977c; 1978). There is, however, very limited available information describing the nature or extent of exposure among laboratory workers performing float-sink testing. Therefore organic liquids used in float-sink operations were selected as a third focus for this study. The specific agents studied were: ethylene dibromide, perchloroethylene, xylene, and VM&P naphtha.

SCOPE OF STUDY

The overall objective of this study was to evaluate worker exposure to potential occupational health hazards associated with coal preparation and

related laboratory float-sink operations. Detailed industrial hygiene surveys were conducted at five facilities (three of which were coal preparation plants and two of which were commercial coal laboratories with laboratory float-sink operations) in order to assess the potential health hazards associated with occupational/environmental exposure to:

- Trace metals, such as Be, Cd, Co, Cr, Li, Ni, and V, potentially found as natural contaminants in coal dust;

- Frothing agents (principally, methylisobutyl carbinol) used in flotation cleaning; and

- Organic solvents, including perchloroethylene, ethylene dibromide, xylene, and VM&P naphtha, used in laboratory float-sink operations.

DI SCRIPTION OF WORK PROCESSES

Overview of Coal Preparation

Coal preparation is basically concerned with improving the quality of a coal to meet the needs of a specific end use or to achieve a specific purpose, e.g., pollution abatement. In recent years the growing concern for the potential environmental and health consequences of expanded coal utilization in this nation has encouraged recognition of the potential role of coal preparation as a viable and cost-effective control technology in reducing sulfur oxide emissions and other potentially toxic substances produced from coal.

Coal preparation, in standard practice today, is a physical process where impurities, such as rock, shale and pyritic materials are removed from the coal by essentially gravimetric methods. Basically, the differences in the relative densities of a coal and the impurities in a coal allow separation or cleaning to be achieve in water, air and dense-media in various process steps.

There are five generally recognized levels of coal cleaning and/or coal preparation that describe the degree to which a coal may be processed. Each level is largely characterized by the type of cleaning performed and the type of process steps or equipment in use. A brief description of the various levels of coal preparation is presented in Table 2.

There are two types or levels of coal preparation plants of basic importance in profiling the coal preparation industry overall. The bulk of coal preparation plants in the United States today are Level III installations producing coals for the steam coal markets. These plants wash both coarse and fine coal products either using jigs for washing unsized coal with a controlled topsize or using jigs, dense media and jigs, tables or hydrocyclones to wash coarse and fine coals separately in two circuits.

Level IV installations, which total about 168 facilities in fourteen (14) states nationwide, represent the other major portion of the industry. Level IV plants are the ultimate commercial level of coal cleaning. They further clean untrafine coal particles via a process termed "froth flotation" and produce coal for metallurgical purposes.

The 1978 Keystone Coal Industry Manual (Nielsen, 1978) includes a Directory of Mechanical Coal Cleaning Plants that identifies nearly 500 coal preparation plants throughout the United States. These plants represent the wide variety of cleaning processes in use today. For this study, however, consideration was limited to coal preparation plants employing froth flotation cleaning, or Level IV installations. Within this group there is adequate representation of coal preparation industry characteristics and potential occupational health hazards.

Table 2. Five levels of coal preparation.

	I	II	III	IV	V
Kind of cleaning	Crushing only(crusher or rotary breaker)	Coarse coal cleaning only	Coarse coal cleaning and simple fine coal cleaning	Coarse and flue coal cleaning plus froth flotation closed circuit	Cleaning all sizes multiple stage, two products, fine crushing, closed circuit
Scope	Crushing to a given topsize. If rotary breaker used, some impurities are removed. Used for lower ash and sulphur run-of-mine coals.	Coarse coal,usually + 10mm, washed only, with fines bypassed and added raw to product. Partial cleaning only required to meet specifications.	Coarse and fine coal cleaning down to 0.5mm with latter size recovered raw or discarded. No closed water circuit. Total wet washing of easy coal to meet required specifications.	Standard complete plant washing all sizes including -0.5mm by froth flotation or other means. Closed water circuit. Complete washing required for difficult coals or market conditions.	Crushing coal to increase liberation using low relative density of separation, retreating middlings. Froth flotation. Three product separation. Closed water circuit.
Range of Recovery	95 to 100 percent	80 to 95 percent	60 to 80 percent	60 to 80 percent	25 to 40 percent primary 20 to 30 percent secondary

Source: Zimmerman, 1978

Coal Preparation Operations: Cleaning, Finishing

Coal preparation involves two distinct operational areas. The equipment or operations used in these areas provide distinctively characteristic functions. The first area, coal cleaning, includes operations or processes involved in removing refuse and foreign material from the raw coal. Coal cleaning generally employs the use of separators, washers, sizing screens and flotation processes.

The second operational area, coal finishing, includes processes or unit operations concerned with final preparation of the cleaned coal. Coal finishing generally makes use of desanding screens, centrifuges and thermal dryers, and clean coal crushers.

The section below provides a brief summary of the various types of equipment or unit operations involved in coal preparation along with a brief definition or description of purpose or function.

Equipment Definitions—

Airtable	Separates coal from refuse by pulsating air up through a rack of coal. The lighter coal rises to the top and is withdrawn. The heavy refuse settles to the bottom and is removed.
Breaker	Reduces the size of the coal by impaction forces. These forces can be mechanical or gravitational. Rotary breakers pick up coal and drop it.
Crusher	Reduces coal size by wedging the coal and applying pressure. Common types include hammermills, jaw, single and double roll crushers.
Centrifuge	A tank that spins and throws the water off of the coal, much like a washing extractor. Used for

dewatering fine coal.

Cyclone	A separator that depends upon centrifugal force to separate particles of different specific gravity. The centrifugal force is supplied by the shape of the cyclone and the pressure drop across the cyclone.
Dryer	Removes excess moisture from coal by natural drainage, screening, centrifugal dewatering, thickening and filtering, and thermal drying.
Filter	Separates particles from a fluid stream by passing the stream through a porous material upon which the particles collect.
Flotation Unit	Froth flotation separates fine coal from refuse by a chemical process. In a tank, water is bubbled to which coal particles selectively adhere. Simultaneously, a wetting agent wets the refuse which sinks. The froth (coal) is removed from the top and the refuse from the bottom.
Heavy Media Washer	Separates coal from refuse by means of a specific gravity principle - when coal which is placed in a medium that has a specific gravity between that of itself and that of refuse sinks and is removed.
Jig	Separates coal from refuse by stratifying the coal by specific gravity. Water is pulsated upward through a bed of coal and refuse. The light coal forms the layer on the top and the dense refuse migrates and forms a layer on the bottom.
Magnet	Picks iron refuse such as nails, spikes, and rails

from the incoming coal; also reclaims magnatite.

Pick Table — A slowly moving conveyor which is loaded with a coarse feed coal to the preparation plant. Large rocks and pieces of wood are hand picked from this coal.

Screen — Separates coal by size; is often shaken to enhance separation. Small particles fall through holes in the screen, while large particles are retained.

Thickener — Separates settleable solids from separate settleable solids from process water. The slurry enters a usually round tank in the center and overflows around the edges. The long residence time allows the solids to settle and be removed from the bottom. Flocculants may be used.

Wash Table — Separates fine coal from refuse. Raw coal slurry is fed onto an upper corner of a tilted table with a series of ridges. The table is shaken so as to move dense refuse along the ridges perpendicular to the water flow. Light coal is carried down the table by the water over the ridges. As a result, the fine coal is separated due to a difference in specific gravity.

Froth Flotation

Froth flotation marks a characteristic departure from the exclusive reliance on physical methods alone in coal cleaning. Froth flotation is a combination chemical/physical process. Ultrafine coal particles are resolved from noncoal impurities via selective adhesion of some particles to air bubbles finely disseminated through a feed coal slurry with concurrent adhesion of other particles to the slurry media. Air adhering particles,

usually coal, are separated from nonadhering particles as a concentrate or froth at the surface of the slurry.

Froth flotation involves the use of various reagent chemicals to assist selective adhesion of certain particles to either the air or water/slurry interfaces. There are three general classes of reagents used which are described as: frother, collectors or promotors and modifying agents. (See Table 1.)

Float-Sink

Float-sink or specific gravity fractionation of coal is an operation or laboratory procedure involving the separation of a coal into various specific gravity factions by immersion in heavy organic liquids. The fractions of a certain topsize coal are obtained for specific gravity gradients and are evaluated according to percent weight, ash and Btu value to describe the coal's amenability to cleaning. The data obtained is referred to as Washability Data.

The preparation method and the type of equipment used in coal preparation are dependent on the physical properties of a coal. Therefore, collecting Washability Data on various coals by float-sink plays an important role in determining how much coal, of what quality, can be produced at a specific gravity and with what difficulty. Washability Data is also used to determine the combination or layout of unit operation that can best achieve the quality of coal desired.

The float-sink procedure itself involves floating a coal sample of a particular topsize in solutions of increasing specific gravity and reconveying "floats" at each step for analytical evaluation. On a large scale a series of suitable holding tanks (for example, 15 gallon polyethylene containers) of specific gravity gradients are used. The method has been described by the Bureau of Mines (Anon., 1967).

Laboratory float-sink procedures can also be applied to coarse or fine

particles. Here, separations can be carried out in beakers, with coarse materials, in separatory funnels, with intermediate size samples, and separatory tubes with centrifuge for fine sizes (those less than 200-mesh).

A wide variety of organic liquids may be used in float-sink testing, these include:

- Acetylene tetrabromide
- Benzene
- Bromoform
- Carbon tetrachloride
- Certigrav - a mixture of Cl and Br halogenated solvents
- Ethylene dibromide
- Gasoline
- Methyl iodide
- Pentachloroethane
- Perchloroethylene or tetrachloroethylene
- Tetrabromoethane
- Toluene
- 1,1,1-trichloroethane
- Xylene
- VM&P Naphtha

There are two potential occupational health hazards which are readily identifiable with float-sink operations. One involves the exposure to the various organic liquids used in the float-sink procedure. The other involves the exposure to coal dust associated with raw coal sample preparations prior to float-sink testing.

For a complete description of the work processes or unit operations at each of the five facilities surveyed in this study, see Appendix A. Facilities 1,2 and 3 are coal preparation plants, while Facilites 4 and 5 are commercial float-sink laboratories.

POTENTIAL EXPOSURE HAZARDS

Trace Metal Contaminants in Airborne Coal Dust

Trace metals, which are recognized potential contaminants in coal, are associated with a variety of adverse health effects. These effects range in severity from simple irritant effects to the induction of cancer. Table 3

summarizes currently recognized occupational exposure limits and health effects of the seven targeted agents (Be, Cd, Co, Cr, Li, Ni, and V).

Respirable Dust

Respirable dust is the predominant occupational health concern associated with coal preparation. Excessive exposure has long been recognized as a cause of pulmonary disease, specifically, coal workers' pneumoconiosis or "black lung". For more than a decade the Mine Safety and Health Administration (MSHA) and its predecessor, the Mining Enforcement and Safety Administration (MESA), have placed particular emphasis on limiting worker exposure. Over this time, extensive monitoring has been conducted.

Although recent MSHA data has indicated that only 3 percent of the respirable dust samples taken for surface coal operations were above the 2 mg/m^3 standard, other information continues to suggest that the potential for significant occupational exposure in coal preparation may still exist. A 1980 NIOSH study showed that nearly 30 percent of the "high dust" operations monitored at eight coal preparation plants had workplace or environmental concentrations of dust above 2 mg/m^3.

MSHA data as recent as 1978 showed that as many as 10 to 20 percent of coal preparation workers in "high risk" work categories, such as scalper screen operator and fine coal plant operator, were exposed to dust above 2 mg/m^3. Respirable dust exposures were not evaluated in this study because of the extensive monitoring program currently being carried out by MSHA.

Crystalline Silica

Respirable free silica (SiO_2) is also a possible health exposure in coal preparation. As part of its respirable dust monitoring program, MSHA routinely examines the silica composition of general respirable dust samples. MSHA's approach is to first process dust samples for compliance/non-compliance with the 2 mg/m^3 standard and then analyze for percent free silica.

Table 3. Summary of health effects of trace metals.

AGENT	CURRENT FEDERAL OCCUPATIONAL EXPOSURE STANDARD (up to an 8-hr TWA (unless otherwise noted)	NIOSH RECOMMENDATION FOR PERMISSIBLE EXPOSURE LIMIT (up to 10-hr TWA unless otherwise noted)	HEALTH EFFECTS
Be - Beryllium	2 $\mu g/m^3$ 5 $\mu g/m^3$ acceptable ceiling 25 $\mu g/m^3$ maximum ceiling (30 min.)	0.5 $\mu g/m^3$ (130 min.)	Tracheobronchitis, Pneumonitis, Dermatitis, Berylliosis, Lung Cancer
Cd - Cadmium	0.1 mg/m^3; fumes = 0.3 mg/m^3; ceiling 0.2 mg/m^3; dust = 0.6 mg/m^3 ceiling	40 $\mu g/m^3$ 200 $\mu g/m^3$ ceiling (15 min.)	Emphysema, Renal bubular injury Anemia
Cr - Chromium (VI)	100 $\mu g/10m^3$ ceiling	1 $\mu g/m^3$ for carcinogenic Cr (VI); 25 $\mu g/m^3$ for other chromium; 50 $\mu g/m^3$ ceiling	Dermatitis, Nasal Irritation, Lung Cancer Kidney damage
Co - Cobalt	0.1 mg/m^3 fume and dust		Chronic interstitial pneumonitis, Pulmonary hypersensitivity, Dematitis
Li - Lithium	0.025 mg/m^3		Irritant, Nasal Irritant, Symptoms referable to nervous system.
Ni - Nickel, inorganic and compounds	1 mg/m^3 (metal & soluble compounds as Ni)	15 $\mu g/m^3$	Asthma, pulmonary fibrosis, Lung/sinus cancer, contact dermatitis (sensitization)
V - Vanadium	Vanadium pentoxide: dust = 0.5 mg/m^3 ceiling; fume = 0.1 mg/m^3 ceiling	Vanadium compounds 0.05 mg/m^3 ceiling (15 min.)	Severe respiratory tract irritation, conjumtivitis, tracheobronchitis, dermatitis, emphysema

Review of limited data indicates that silica exposure in coal preparation is primarily associated with raw coal processing operations. Existing data indicate that percent silica at these operations can exceed the 5 percent level and range as high as 12 percent.

Crystalline silica exposures were not evaluated in this study because of the extensive monitoring program currently being carried out by MSHA.

Noise

Noise is also typically a potential problem throughout most areas of a coal preparation plant. Average environmental noise exposures ranging between 95 and 100 dBA are not uncommon. Major noise sources in a plant include noise from process material impacting on the inside surfaces of steel chutes and other plant equipment, from vibrating screens, coal crushers, pumps, motors, fans and blowers.

Because noise is another widely recognized potential health hazard in coal preparation, it is also closely monitored by MSHA. Noise exposure was, therefore, not evaluated in this study.

Methylisobutyl carbinol (MIBC) in Froth Flotation

The current permissible exposure limit (PEL) for methylisobutyl carbinol is 25 ppm, averaged over an 8-hour workshift. MIBC can affect the body if it is swallowed, inhaled, or comes in contact with eyes or skin.

The most important effects of MIBC are narcosis and eye irritation. Unacclimatized individuals exposed to airborne concentrations as low as 50 ppm have experienced irritation to the eyes. Symptoms of headache and drowsiness are also associated with overexposure. Although chronic systemic effects have not been reported in humans, medical screening and surveillance of employees with a history of either impaired liver or kidney function is recommended by NIOSH where an individual might be exposed to MIBC at

potentially hazardous levels.

Because MIBC is a defatting agent it can also cause skin irritation (dermatitis) on prolonged exposure. To reduce the possibility of dermal irritation, direct contact should be minimized. Whenever liquid MIBC comes in direct contact with skin, one should promptly wash the affected area with soap and water.

Flotation Frothing Agent: Dowfroth M-222

Dowfroth M-222 Flotation Frother (a mixture of polypropylene glycol monomethyl ethers, with an average molecular weight of about 280) is a dark brown liquid, low in volatility, with a slight, pleasant, etherial odor. It is low in single dose oral toxicity (LD_{50} = >5000 mg/kg in female rats), transiently irritating (conjunctiva) and very slightly damaging (cornea) to the eye, and mildly irritating to the skin with repeated or prolonged exposure. It is not likely to be absorbed through the skin in acutely toxic amounts. Because of its low vapor pressure and toxicity, it is an unlikely inhalation hazard under ordinary conditions of handling and use. There are currently no known human effects for excess exposure; systemic effects have not been established. There are currently no established guidelines on permissible exposure limits. Overall, the potential health hazard of polypropylene glycol monomethyl ethers appears to be negligible. (See Appendix C: Material Safety Data Sheet for Dowfroth M-222.)

Float-Sink Operations: Ethylene Dibromide

The Occupational Safety and Health Administration's (OSHA) current standard for work exposure to ethylene dibromide (EDB) is 20 ppm as a time-weighted average (TWA) concentration, with an acceptable ceiling concentration of 30 ppm. Since 1977 NIOSH has recommended in a Criteria document for EDB that occupational exposure be limited to a ceiling concentration of 0.13 ppm as determined over any 15-minute sampling period. NIOSH concluded that chronic occupational exposure to EDB poses a serious hazard that may result in an increased risk of adverse reproductive, carcinogenic and other effects

(liver, kidneys, heart and other internal organs and systems). In California, EDB has been regulated as a carcinogen since 1981 with a PEL of 0.13 ppm as a TWA and ceiling concentration.

Float-Sink Operations: Perchloroethylene

Clinical evidence accumulated over the years clearly demonstrates that perchloroethylene is toxic to the liver and kidneys in humans. Perchloroethylene vapor is irritating to the eyes and upper respiratory tract, and may cause frontal sinus congestion and headache. Contact with the skin can cause burns, blistering, and erythema due to a "degreasing" effect. Over time this can produce serious dermatitis and associated infections.

Perchloroethylene exposure can also result in altered physiological and behavioral responses generally related to depression of the central nervous system (CNS). These symptoms include vertigo, impaired memory, confusion, fatigue, drowsiness, irritability, loss of appetite, nausea and vomiting. Reduced motor skills, mental acuity and symptoms of fatigue have important implications for worker safety. Severe depression of the CNS from excessive exposure can result in coma, collapse of cardiopulmonary function and death.

Concern for carcinogenic potential of perchloroethylene arises in part from the basic structural similarity of perchloroethylene to vinyl chloride and other chlorinated olefins (chloroethylenes) known to be carcinogenic. More importantly the results of initial animal studies conducted by the National Cancer Institute have shown perchloroethylene to be carcinogenic in mice. Although at present there are limited available epidemiologic data to associate perchloroethylene directly with cancer in humans, the potential for producing these effects is indicated. Since January 1978, NIOSH has recommended that perchloroethylene be handled in the workplace as if it were a human carcinogen. Perchloroethylene currently appears on the OSHA "Candidate List" of chemicals being considered for further scientific review.

OSHA's current standard for occupational exposure to perchloroethylene is

100 ppm as a TWA concentration for an 8-hour work shift, with an acceptable ceiling concentration of 200 ppm, and a maximum peak above the acceptable ceiling concentration of 300 ppm for not more than 5 minutes in any 3-hour period. In 1976 NIOSH recommended that exposure be limited to 50 ppm as a TWA for up to a 10-hour work day, 40-hour work week and a ceiling concentration of 100 ppm. The American Conference of Government Industrial Hygienists (ACGIH) have recommended a Threshold Limit Value (TLV-TWA) of 50 ppm. The current standards and recommended limits were selected on the basis that they would prevent serious narcotic effects and that chronic intoxication involving hepatic or central nervous system effects would also be unlikely.

Float-Sink Operations: Xylene

Xylene vapor is principally an irritant to eyes, nose and throat. Because its irritating properties are perceivable at air concentrations less than three times the permissible exposure limit, it is considered to have fairly good warning properties. However, olfactory fatigue does occur rapidly. At high exposure concentrations xylene can produce anorexia, nausea, vomiting and abdominal pain, as well as chemical narcosis. As with the other two solvents, the liquid is a skin irritant capable of causing erythema, dryness and defatting. Additionally, contact with the liquid is a potential contributor to overall work exposure by dermal absorption.

Float-Sink Operations: VM&P Naphtha

VM&P naphtha is regarded principally as a sensory irritant capable of affecting the eyes and throat. VM&P naphtha produces olfactory fatigue in airborne concentrations ranging from 140-880 ppm. Few studies in the literature report effects from dermal exposure to VM&P naphtha. However, since it is a refined petroleum product similar to stoddard solvent and mineral spirits, which are considered primary irritants, VM&P naphtha is also considered a dermal irritant.

The current federal occupational health standard for VM&P naphtha is defined under petroleum distillates (naphtha) as 500 ppm (2000 mg/m^3) determined as

an 8-hour TWA concentration. NIOSH has recommended an identical limit for all common petroleum solvents, which is defined on a weight basis, of 350 mg/m^3. For VM&P naphtha, which has a mean molecular weight range of from 87 to 114, the NIOSH recommended TWA ranges in ppm from about 75 to 100 ppm. The NIOSH limit is designed for up to a 10-hour workshift, 40-hours workweek. The NIOSH limit is believed to be sufficiently low to prevent sensory irritation (eye and throat) and long-term toxicity. The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned VM&P naphtha a TLV-TWA of 300 ppm and a TLV-STEL (short-term exposure limit) of 400 ppm. The STEL is a 15-minute time weightted average exposure which should not be exceeded at any time during a work day. As many as four excursions up to the STEL are permissible in a day provided there are at least 60 minutes between each exposure and the daily TLV-TWA is not exceeded.

Exposure information and guidelines for the four float-sink operation solvents targeted in this study are summarized in Table 4.

Table 4. Exposure information for float-sink solvents.

	Ethylene Dibromide	Perchloroethylene	VM&P Naphtha	Xylene
Vapor Pressure (mmHg) @ 20°C	11	14	2 - 20	7(ortho-) 9(meta-) 11(para-)
Dermal Hazard	yes	yes	yes	yes
Potential Carcinogen	yes	yes	no	no
OSHA PEL's (ppm)				
TWA	20	100	500*	100
Ceiling	30	200	--	--
Peak	50 (5-min.)	300 (5-min./3-hr. period)	--	--
NIOSH Recommended Limits (ppm)				
TWA	--	50	**(350 mg/m^3)	100
Ceiling	0.13	100	--	200 (10-min.)
ACGIH TLV's (ppm)				
TWA	A2***	50	300	100
STEL	A2***	--	400	150

*Petroleum distillates (naphtha)
**PPM varies from 75-100 ppm according to the mean molecular weight of the VM&P naphtha mixture (typically from 87-114).
***A2 Classification. "Industrial Substance Suspect of Carcinogenic Potential For Man." Chemical substance or substances associated with industrial processes, which are suspect of inducing cancer hazard on either (1) limited epidemiological evidence, exclusive of clinical reports of single cases, or (2) demonstration of carcinogenesis in one or more animal species by appropriate methods.

METHODS OF STUDY

Identification and Selection of Facilities for Study

Evaluation of suitability for inclusion of a facility in this study was based primarily on how well it addressed the three surveillance priorities. These priorities were to evaluate 1) trace metal contaminants in coal dust; 2) potential health hazards for chemicals used in froth flotation; and 3) potential health hazards for chemicals used in laboratory float s i n k operations.

Additional consideration was also given to the following criteria:

- the types of cleaning
- equipment in use
- plant layout
- production capacity
- size of work force
- geographic location
- facility age
- in-plant chemical usage

The study was structured in three progressive phases to enable the development of a meaningful yet manageable study plan. Following is a brief description of each phase.

- Phase I: A detailed literature search was performed in order to gather and evaluate available information on the industrial hygiene aspects and the potential occupational health problems associated with coal preparation and associated laboratory float-sink operations. From this information, a study protocol was prepared which recommended 1-day walkthrough surveys of eight coal preparation and laboratory float-sink facilities.

- Phase II: Walkthrough surveys of eight facilities were conducted to accumulate initial site information and to determine the suitability of the facilities for detailed study.

- Phase III: The objective of this main phase of the study was to characterize worker exposures to the potential hazards identified in Phase II. Five detailed surveys, utilizing personal and area monitoring were performed in this phase.

In Phase I an initial selection of 25 coal preparation plants and eight float-sink laboratories was made. Selection of coal preparation facilities was initially limited to those facilities listed in the 1978 Keystone Coal Manual's Directory of Mechanical Coal Cleaning Plants (Neilsen, 1978), as employing froth flotation. Of the approximately 489 coal preparation plants listed, approximately 167 were readily identified as employing or having the design capability for flotation cleaning. Of these, 163 process bituminous coals and 4 process anthracite coals. From the 25 plants identified as potentially suitable facilities for study, five coal preparation plants were selected for Phase II, the walkthrough survey. Of these, three plants were chosen for the Phase III indepth survey.

In addition, three float-sink laboratories were selected for the Phase II walkthrough survey. The decision to survey non-producer coal laboratories was based on the difficulty in identifying groups of workers performing float-sink testing in coal preparation plants. Identification of workers and exposure associated with float-sink testing apart from coal preparation--specifically in coal producer, consumer, commercial or coal preparation/design engineering laboratories--seemed to be the more appropriate emphasis in evaluating potential exposure risks to the heavy organic solutions. Eight companies were readily identified through the consultant listings in the 1978 Keystone Coal Industry Manual. From these, three companies were chosen for the Phase II walkthrough. From these three

facilities, two were chosen for the Phase III indepth survey.

Sampling and Analytical Methods

General Methods--

The general methods of sampling and analysis employed for each of the three surveillance priorities are described in this section. The complete NIOSH P&CAM analytical methods are included in Appendix B.

Specific sampling protocol used for each of the five facilities surveyed are described in the next section. Table 5 lists the agents sampled and type of sampling done for each facility.

Trace metal contaminants--In order to evaluate the potential health hazard associated with trace metal contamination of airborne coal dust, area air samples were collected at selected locations during a representative production run at each of the three coal preparation plants. The metals sampled were Be, Cd, Co, Cr, Li, Ni, and V.

Samples were collected on 0.8-micron pore-size mixed cellulose ester membrane filters, housed in a standard 3-piece filter cassette, using an MSA Model G portable high flow sampling pump. Samples were collected at a rate of approximately 2 liters per minute (Lpm) Flows were established using a precision rotameter. Sampling durations were approximately five (5) hours with sample volumes of about 650 liters.

Sample analysis for trace metals was accomplished using a modified version of NIOSH Method No. P&CAM 173. Instead of using atomic absorption (AA) spectroscopy, samples were analyzed by inductively coupled plasma atomic emission spectroscopy (ICPAES), which has two advantages: it is more sensitive than AA for the metals indicated above and is less expensive. A detailed description of the Method No. P&CAM 173 is found in Appendix B.

Froth flotation: Methylisobutyl carbinol (MIBC)--Two of the coal preparation plants were monitored for MIBC in froth flotation. Industrial

TABLE 5. Agents sampled at each of 5 facilities.

AGENT	TYPE OF SAMPLING*	FACILITY 1	FACILITY 2	FACILITY 3	FACILITY 4	FACILITY 5
		Coal Preparation Plant	Coal Preparation Plant	Coal Preparation Plant with float-sink	Float-Sink Laboratory	Float-Sink Laboratory
I. Trace Metal Contaminants	Area-TWA	X	X	X		
II. Froth Flotation Chemicals						
methylisobutyl carbinol	Personal-TWA	X	X			
	Area-TWA	X	X			
Dowfroth M-222	Personal-TWA			X		
	Area-TWA			X		
III. Float-Sink Solvents						
Perchloro-ethylene	Personal-TWA				X	X
	Personal-CL			X	X	X
	Area-TWA				X	X
Ethylene Dibromide	Personal-TWA				X	X
	Personal-CL				X	X
	Area-TWA				X	X
VM&P Naphtha	Personal-TWA					X
	Personal-CL					X
	Area-TWA					X
Xylene	Personal-TWA				X	†
	Personal-CL				X	
	Area-TWA				X	

*TWA = the time-weighted concentration for a normal 8-hour workday.
CL = the ceiling level; a 15-minute time weighted average taken during a period of highest anticipated exposure level.

hygiene sampling, employing both personal and area sampling strategies, was performed. Partial period consecutive sample measurements were made at Facility 1, while both full period (8-hour) and partial period consecutive measurements were made at Facility 2.

All air samples collected for MIBC were collected on standard size activated charcoal sampling tubes using MSA low flow portable air sampling pumps. Sampling rates were established at 0.2 liters of air per minute (Lpm) or less, and average sample volume ranged from about 6 to 30 liters at Facility 1 and 8 to 80 liters at Facility 2. Sampling pumps were pre- and post-survey calibrated using the standard soap bubble burette procedure. Air sample analysis was accomplished using gas chromatography equipped with flame ionization detection (GC-FID). A detailed description of the analytical method used in determination of methylisobutyl carbinol, NIOSH Method No. S-60, is presented in Appendix B.

Froth Flotation: Dowfroth M-222--At coal preparation Facility 3, personal and area air monitoring was performed for froth flotation to characterize the potential for worker inhalation exposure to Dowfroth M-222. Samples were collected on standard-size activated charcoal sampling tubes, using MSA low flow portable sampling pumps. Samples were collected at a rate of approximately 0.05 liters per minute (Lpm) and volumes ranged from about 18 to 24 liters. A bulk sample of the commercial frother (Dowfroth M-222) was collected for use as an analytical reference. Sample analysis was accomplished using gas chromatography and flame ionization detection (GC-FID) per NIOSH Method No. P&CAM 127 (Appendix B). Calculation of airborne concentrations were based on an average molecular weight estimation of 280.

Laboratory Float-Sink Solvents: Perchloroethylene--In characterizing current worker exposure to perchloroethylene for routine testing operations, short-term personal ceiling samples were utilized at coal preparation Facility 3 while full period consecutive personal samples as well as ceiling samples were taken at the two float-sink laboratories (Facilities 4 and 5). Area monitoring was carried out at Facilities 4 and 5.

All samples were collected on standard size activated charcoal sampling tubes, using MSA low flow portable sampling pumps. Samples were analyzed by gas chromatography with flame ionization detection according to NIOSH Method No. P&CAM 127 (Appendix B).

Laboratory Float-Sink Solvents: Ethylene dibromide (EDB)--In order to characterize worker exposure to EDB, both area and personal monitoring was done at the two float-sink laboratories (Facilities 4 and 5). Ceiling or peak exposure levels were obtained during periods of anticipated high exposure.

All samples collected were obtained with standard activated charcoal sampling tubes, using MSA low flow portable sampling pumps. Because of differences in desorption modes between perchloroethylene/xylene or VM&P naphtha, and ethylene dibromide, it was necessary to collect perchloroethylene, xylene and naphtha on separate sampling tubes from EDB. Analysis of EDB was per NIOSH P&CAM 260 via gas chromatography with electron capture detection. Detailed sampling and analytical procedures are presented in Appendix B.

Laboratory Float-Sink Solvents: VM&P Naphtha—In order to characterize worker exposure to VM&P naphtha, both area and personal monitoring was done at Facility 4, a commercial float-sink laboratory. All samples were collected on standard size activated charcoal sampling tubes, using MSA low flow portable sampling pumps. Because of the different desorption modes involved in analyzing EDB versus perchloroethylene and VM&P naphtha, EDB was collected on separate sampling tubes from perchloroethylene/naphtha. Analysis was accomplished using gas chromatography equipped with flame-ionization detection according to NIOSH Method No. P&CAM 127(Appendix B).

Laboratory Float-Sink Solvents: Xylene--In order to characterize worker exposure to xylene, both area and personal monitoring were done at Facility 4, a commercial float-sink laboratory. All samples were collected on

standard size activated charcoal sampling tubes, using MSA low flow portable sampling pumps. Because of the different desorption modes involved in analyzing EDB versus perchloroethylene and xylene, EDB was collected on separate sampling tubes from perchloroethylene/xylene. Analysis was accomplished using gas chromatography equipped with flame-ionization detection according to NIOSH Method No. P&CAM 127 (Appendix B).

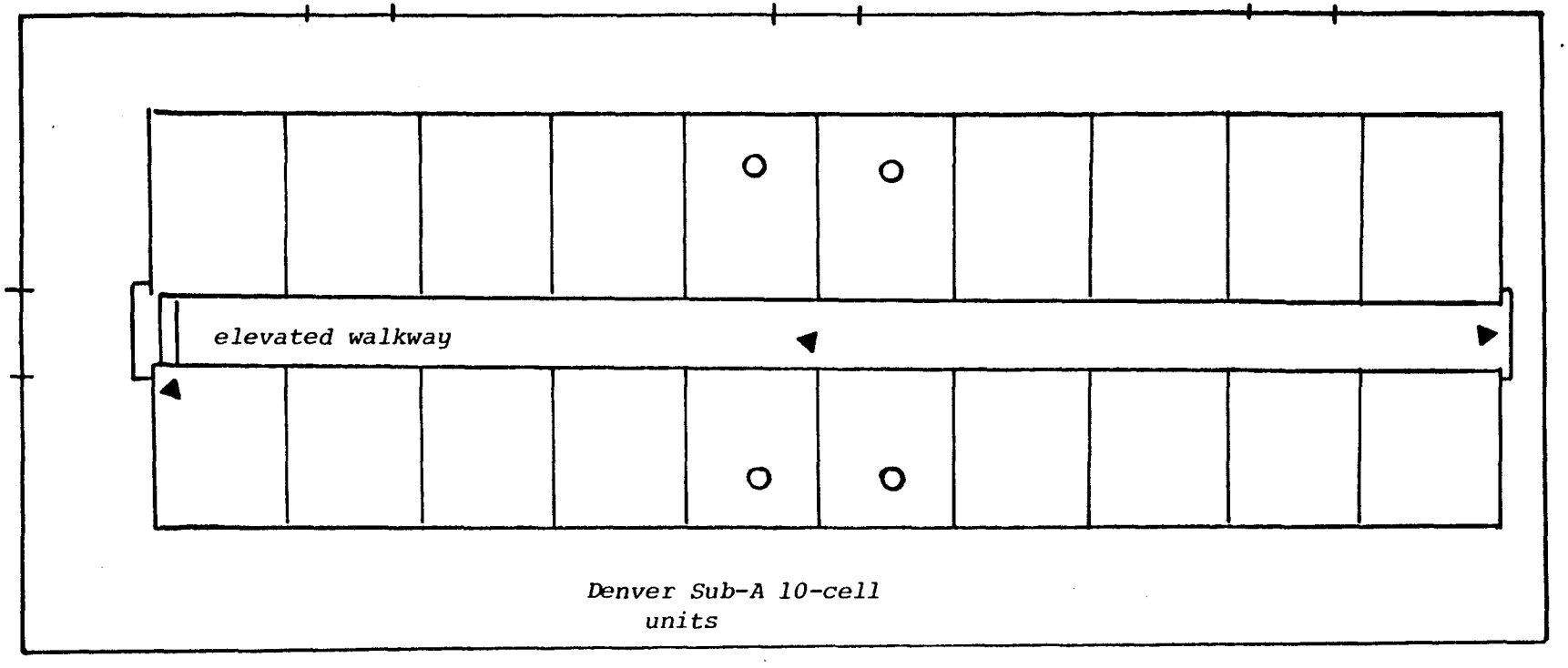
Specific Sampling Protocol for Each Facility

Facility 1: Coal preparation plant--
Froth Flotation: Methylisobutyl carbinol (MIBC)--To assess the potential health hazard associated with the use of MIBC in froth flotation, industrial hygiene monitoring, employing both personal and area sampling strategies, was performed. Personal monitoring was limited to the flotation/filter operator, who has primary responsibility for monitoring unit operations and who was initially identified as the plant employee routinely at the greatest risk of exposure to MIBC. Area sampling was carried out at both the fine and coarse coal flotation operations. The sampling locations chosen for each operation (Figures 2 and 3) were selected so as to allow a determination of potential "worst case" environmental exposure concentrations near each unit under normal operating conditions. The sampling performed was limited to a single representative day shift.

For fine flotation, the sampling sites have been designated as far end, middle and near end. These were positioned along an elevated walkway, located between the two 10-cell Denver Sub-A Units, at a height of between 4 and 5-1/2 feet. The "middle" sampling location was chosen particularly for its proximity to the two frother reagent inlets located in the middle two flotation cells of the 10-cell unit. (See Figure 1.)

For coarse flotation, two sampling sites were chosen; one was positioned in the middle of the 4-cell Denver unit, the other was positioned on the access end. The sampling pump, positioned in middle of the unit, was fastened to a hand railing, at a height of about 3 feet above the froth take off. The "end" location was positioned about 5-1/2 to 6 feet in height above the

Figure 1. Facility No. 1: Area sampling location for fine coal flotation.



floor level and about 1-2 feet from the froth discharge. (See Figure 2.)

Under normal plant conditions, both 10-cell Denver Sub-A fine flotation units are in operation at the same time. For coarse coal flotation, however, only one 4-cell flotation bank is necessary. Therefore,at the time of the survey, only the 4-cell Denver unit was in operation.

The personal and area samples collected were partial period consecutive sample measurements. Personal monitoring involved collection of split shift samples, with sampling durations of about 120 and 240 minutes. Area monitoring also involved the collection of partial period samples, with sampling durations of approximately 130, 165 and 90 minutes. Personal and area monitoring were performed coincidentally. The personal samples collected covered an exposure duration in excess of 85 percent of the full work shift period (420 minutes); while the area samples collected were in excess of 90 percent of the 7-hour day shift period.

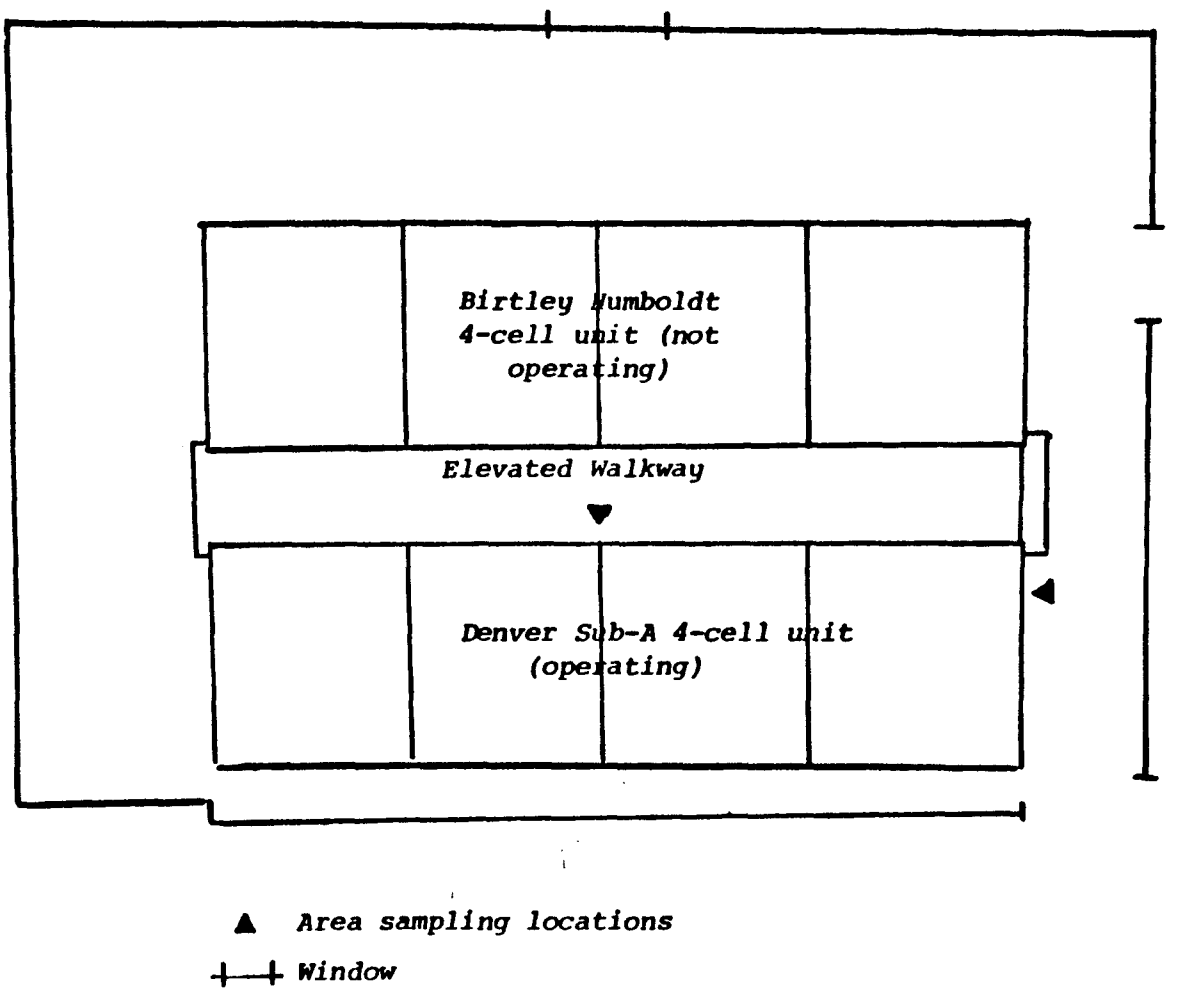
All air samples were collected on standard size activated charcoal sampling tubes, using MSA low flow portable air sampling pumps. Sampling rates were established at 0.2 liters per minute (Lpm) or less and sample volumes ranged from about 6 to 30 liters in size. Sampling pump flow rates were checked for proper calibration both before and after the survey visit using a soap bubble meter.

Air sample analysis was accomplished by gas chromatography using flame ionization detection (GC-FID) per NIOSH Method No. S-60. (See Appendix B.)

Over the single day visit, a total of 18 personal and area samples were collected for MIBC: four samples were personal samples collected for the flotation/filter operation; five samples were area samples collected at the coarse coal flotation operation; and, the remaining nine (also area samples) were collected for the fine coal flotation operation.

Trace Metals—In order to evaluate the potential health hazard associated with trace metal contamination of airborne coal dust, area air samples were

Figure 2. Facility No. 1: Area sampling locations for coarse coal flotation.



collected at the following locations during a representative production run:

- Rotary Dump
- Rotary breaker
- Blending bins
- Clean Coal Crusher
- Vacuum Filters

Samples were collected on 0.8 micron pore-sized mixed cellulose ester membrane filters, housed in a standard 3-piece filter cassette, using an MSA Model G portable high flow sampling pump. Samples were collectd at a rate of approximately 2 liters per minute (Lpm). Flow rates were established using a precision rotameter. Sampling durations were approximately five (5) hours with sample volumes of about 650 liters.

Sample analysis for trace metals was accomplished using a modified version of NIOSH Method No. P&CAM 173. Instead of using atomic absorption (AA) spectroscopy, samples were analyzed by inductively coupled plasma atomic emission spectroscopy (ICPAES), which has two advantages: it is more sensitive than AA for the metals indicated above and is less expensive. A detailed description of the Method No. P&CAM 173 is found in Appendix B.

Facility 2: Coal preparation plant--
Froth Flotation: Methylisobutyl carbinol (MIBC)--To assess the potential health hazard associated with the use of MIBC in froth flotation, an industrial hygiene monitoring strategy involving both personal and area monitoring was employed. The Deister Table Operator, was identified as the "maximum risk employee" and was chosen for personal monitoring.

To obtain information about potential "worst case" exposure concentrations in the vicinity of the flotation units, area air monitoring was also conducted.

The personal and area monitoring conducted for MIBC involved full period occupational and environmental exposure monitoring. Approximately one-half

of the samples collected were full period (8-hour) single sample measurements and the other half were partial period consecutive 4-hour sample measurements. Personal and area sampling was performed coincidentally.

Over the two-day sampling period, a total of 20 personal and area samples were collected for MIBC analysis. Three samples were collected for the Deister Table Operator and the remainder were for environmental exposure measurements at respective flotation units. Personal monitoring was limited to the single unit operator responsible for routinely monitoring flotation unit operations. Area sampling locations were chosen at each of the four flotation banks in general to assess potential "worst case" exposure concentrations in immediate proximity to the individual units. Four sampling locations (one at each of four separate flotation units) were chosen to determine airborne concentrations of MIBC in breathing zone areas around the frother feed inlets. Three other sampling locations were chosen on separate flotation units in areas thought to be representative of general airborne concentrations in the vicinity of the respective units. Sampling positions on each unit were in general 4-1/2 to 6 feet above the floor level. Figure 3 provides a general illustration of flotation unit layout and area sampling locations.

Trace Metals--In order to evaluate the potential health hazard associated with trace metal contamination of airborne coal dust, area air samples were collected at the following locations in the operation during a representative production run:

- Rotary Breaker
- Raw Coal Screens
- Raw Coal Storage
- Vacuum Filters

Because clean coal crusher operations had been discontinued, area monitoring performed in the raw coal storage area was substituted.

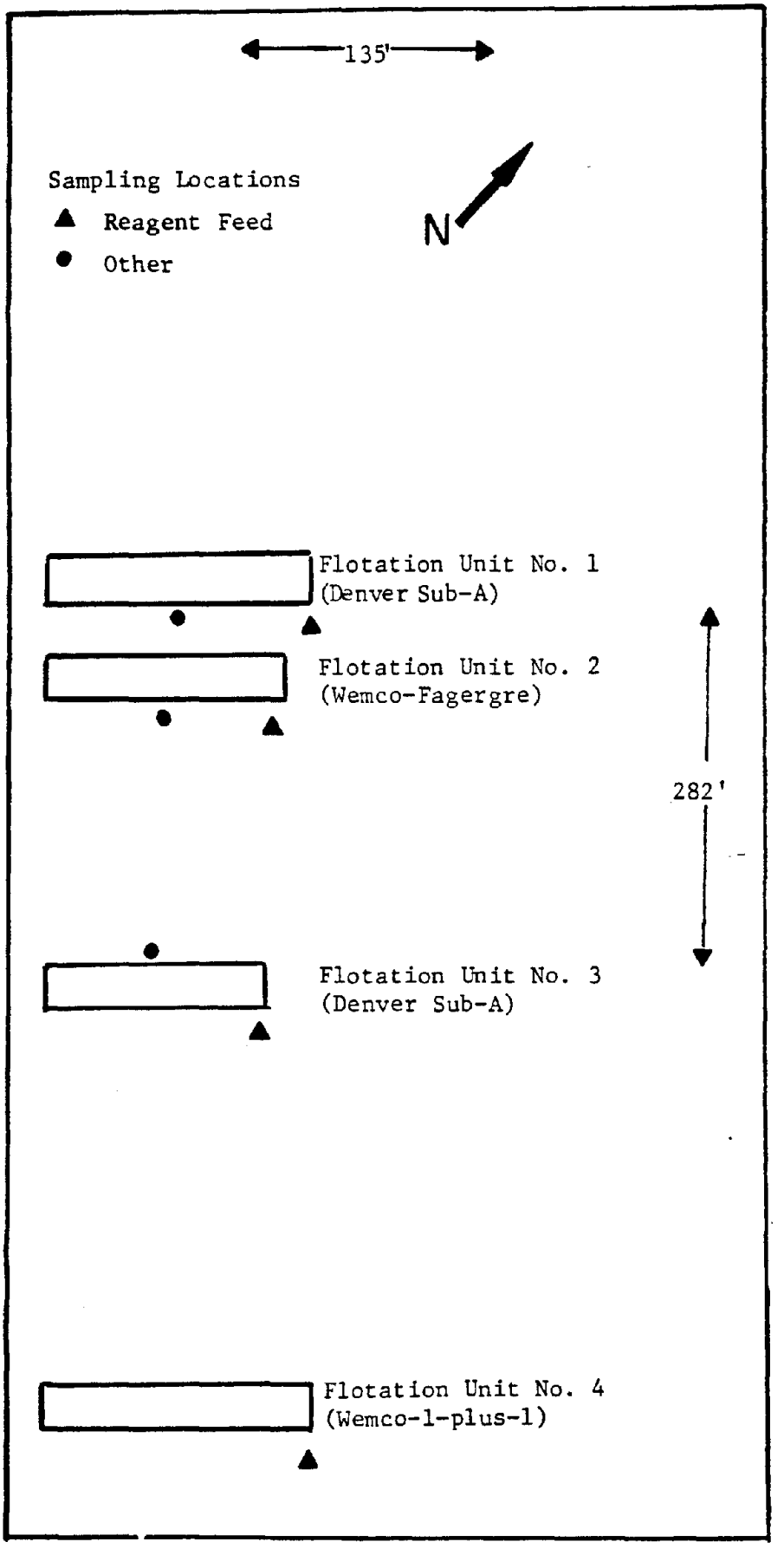


Figure 3. Facility 2:
Flotation unit lay-out and area sampling locations.

Samples were collected on 0.8 micron pore-sized mixed cellulose-ester membrane filters, housed in a standard 3-piece filter cassette, using a portable MSA Model G high flow sampling pump. Samples were collected at a rate of approximately 2 liters per minute. Flows were checked in the field using a precision rotameter. Sampling durations averaged about 5-1/2 hours with approximate sample volume of 660 liters.

Sample analysis for trace metals was accomplished using a modified version of NIOSH Method No. P&CAM 173. Instead of using atomic absorption (AA) spectroscopy, samples were analyzed by inductively coupled plasma atomic emission spectroscopy (ICPAES), which has two advantages. It is more sensitive than AA for the metals indicated above and is less expensive. A detailed description of Method No. P&CAM is found in Appendix B.

Facility 3: Coal preparation plant with float-sink laboratory--
Froth flotation: Dowfroth M-222--Personal and area air monitoring were performed for froth flotation to characterize potential worker exposure to Dowfroth M-222. The personal monitoring performed was restricted to the fine coal attendant who is primarily responsible for monitoring flotation operations and who is identified as the "maximum risk employee." The area monitoring performed was conducted to allow an evaluation of potential "worst case" environmental exposure concentrations in the vicinity of froth flotation operations. Area samples were collected from five locations in the process area to achieve this objective. Three of the locations chosen were within close proximity (approximately 3 feet) of the frothing reagent feed system inlets, while two others were set away from the reagent feed inlets at the opposite ends of the flotation unit. Figure 4 illustrates the special arrangements of unit area sampling locations.

The occupational and environmental exposure measurements obtained for froth flotation were based on the collection of single full period samples. The sampling period covered, on the average, was approximately 90 percent of the full workshift period (approximately 380 of 420 minutes). A total of 2 personal and 10 area samples were collected over the two-day period.

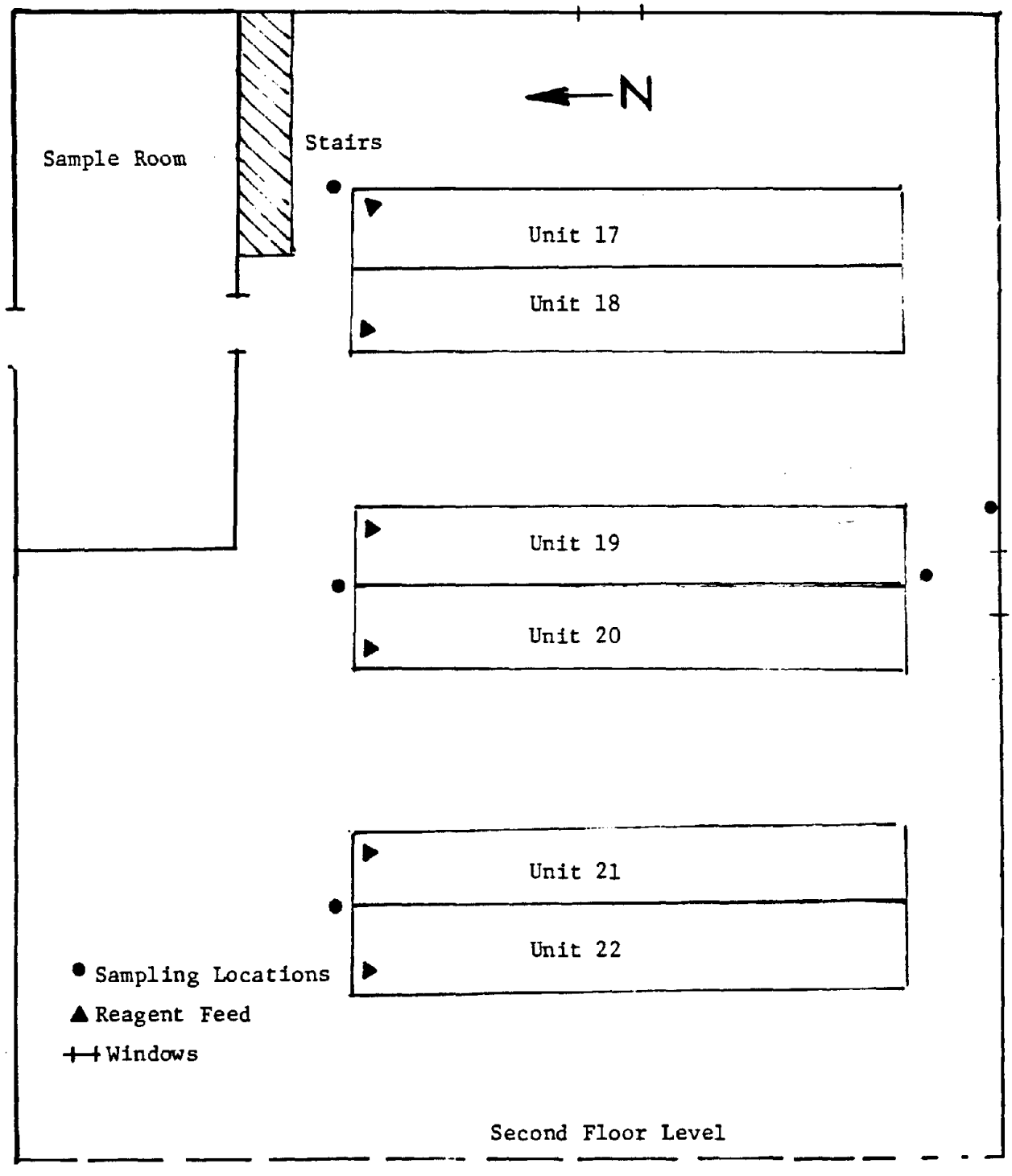


Figure 4. Facility 3: Froth flotation sampling locations for Dowfroth M-222

Sample analysis was accomplished using gas chromatography with flame-ionization detection according to NIOSH Method No. P&CAM 127. It should be noted that P&CAM 127 was chosen originally as the most appropriate sampling and analytical method for characterizing occupational and environmental exposure concentrations to Aerofroth 77-A (a frothing agent cpmprised of a mixture of aliphatic alcohols, including n-butyl alcohol) at froth flotation. However, on the first day of the detailed survey, it was learned that Facility 3 was making a last minute change-over from Aerofroth to Dowfroth M-222 (a frothing agent comprised of a mixture of polypropylene glycol monomethyl ethers). It was felt that in the absence of a more suitable sampling and analytical method, this method would be able to generate initial data at least generally indicative of relative exposure risks. These data, however, must be qualified since P&CAM 127 (a general method for organic solvents) has not been validated specifically for polypropylene glycol monoethyl ethers. Calculations of airborne concentrations were based on an average molecular weight of 280 for the product mixture.

Laboratory Float-Sink Operations: Perchloroethylene--Float-sink operations at Facility 3 are carried out on a periodic but limited scale. Testing is performed exclusively by a single employee, the coal sampler, and is limited to fractionating coal samples at one specific gravity level. Operations typically involve only about twenty minutes of activity, repeated twice weekly.

In characterizing current worker exposure to perchloroethylene for routine float-sink testing operations, a sampling strategy which emphasized collection of short-term personal samples was utilized. Personal samples for the coal sampler (the "maximum risk employee") were collected on standard size activated charcoal sampling tubes, set at a flow rate of about 0.20 liters per minute (Lpm), using MSA low flow portable sampling pumps. The sampling period was limited to the duration of float-sink activities (approximately 20 minutes) and the sample volumes collected were about 4 liters in size. For convenience, a bulk sample of the test solution was collected for analytical reference. Samples were analyzed by gas

chromatography and flame-ionization detection per NIOSH Method No. P&CAM 127. The number of samples collected to characterize worker exposure to perchloroethylene for these operations was limited to two.

Trace Metals--General area air samples were collected for trace metal analysis in five coal preparation plant locations during a representative day shift. These locations were near the:

- scalper/crusher
- raw coal storage
- raw coal screen
- clean coal crusher
- vacuum filters

Samples were collected on 0.8-micron pore-sized mixed cellulose-ester membrane filters, housed in a standard 3-piece filter cassette, using a portable MSA Model G high flow sampling pump. Samples were collected at a rate of approximately 2 liters per minute. Flow rates were checked in the field with a precision rotameter. Sampling durations averaged about 5-1/2 hours with approximate sample volume of 660 liters.

Sample analysis for trace metals was accomplished using a modified version of NIOSH Method No. P&CAM 173. Instead of using atomic absorption (AA) sectroscopy, samples were analyzed by inductively coupled plasma atomic emission spectroscopy (ICPAES) which has two advantages. It is more sensitive than AA for the metals indicated above and is less expensive.

Facility 4: Float-Sink Laboratory--

EDB, Perchloroethylene and Xylene--The monitoring objective was to characterize worker exposure to the various solvent mixtures used routinely in laboratory float-sink operations. Both personal and area monitoring strategies were employed to achieve this end. Personal sampling was limited to the single laboratory technician directly involved with float-sink testing. The monitoring performed was full period consecutive sampling. Both time weighted average (TWA) and ceiling or peak (COP) exposure

measurements were obtained. The area sampling performed allowed for determination of "worst case" breathing zone concentrations at the hood face for both fine and intermediate float-sink operations and determination of "background" or general room air concentrations.

Monitoring performed on the first day of the detailed survey included both fine and intermediate scale float-sink operations, although chemical exposure was limited to perchloroethylene and xylene since the float-sink separations carried out were run at specific gravities of 1.60 or less. Monitoring on day 2 emphasized determination of occupational/environmental exposure to ethylene dibromide, with fine coal float-sink operations carried out at specific gravities of 1.70 and 1.80. COP levels were obtained during laboratory float-sink set-up operations. As indicated previously, no monitoring was performed for bulk coarse float-sink operations, which are performed outside the building.

All samples collected were obtained with standard activated charcoal sampling tubes, using MSA low flow portable sampling pumps. Sampling rates were approximately 0.05 liters per minute. Sample volumes ranged from about 1 to 20 liters. Because of differences in desorption modes between perchloroethylene/xylene and ethylene dibromide, it was necessary to collect perchloroethylene and xylene on separate sampling tubes from EDB. Analysis of perchloroethylene and xylene was per NIOSH P&CAM 127 via gas chromatography with flame ionization detection (GC-FID). Analysis of EDB was per NIOSH P&CAM 260 via gas chromatography with electron capture detection. Detailed sampling and analytical procedures are presented in Appendix B.

Facility 5: Float-Sink Laboratory—

EDB, Perchloroethylene and VM&P Naphtha—The monitoring objective was to characterize routine worker exposure to the heavy gravimetric liquids or coal fractionation solvents (perchloroethylene, ethylene dibromide and VM&P naphtha) used by Facility 5 in laboratory float-sink testing. To achieve this end, both personal and area monitoring strategies were utilized. Personal monitoring involved laboratory floatsink technicians directly

involved with washability testing and was carried out over two consecutive representative 8-hour workshifts. Eight-hour time-weighted average (TWA) exposure concentrations were determined by collecting full period consecutive air samples for each worker. To determine personal ceiling or peak (COP) exposure concentrations, 15-minute samples were obtained during periods (activities) of anticipated high exposure.

Area monitoring was also conducted. The area monitoring performed was carried out to: (1) assess potential "worst case" breathing zone solvent vapor concentrations at the enclosure faces for both fine and intermediate float-sink operations, and (2) characterize "background" or general room air concentrations away from immediate float-sink work stations.

Monitoring performed on the first day of the survey involved sampling during fine coal float-sink operations carried out at specific gravities of 1.40, 1.45, 1.55 and 1.60. On day 2, sampling involved personal and area monitoring carried out during both fine and intermediate float-sink operations. Fine coal testing was carried out at specific gravities of 1.45 and 1.60; intermediate testing involved float-sink at specific gravities of from 1.40 to 1.60 in 0.05 increments.

COP (ceiling or peak) exposure levels for perchloroethylene, ethylene dibromide and VM&P naphtha were obtained during periods of anticipated high exposure, such as during float-sink set up, gravity adjustment and entry into coal drying areas.

All samples collected were obtained with activated charcoal sampling tubes, using MSA low flow portable sampling pumps. Sampling rates were in a range of from 0.05 to 0.10 liters per minute (Lpm). Sample volumes ranged from about 0.5 to 20 liters. Because of the different desorption modes involved in analyzing ethylene dibromide versus perchloroethylene and VM&P naphtha, it was necessary to collect perchloroethylene and naphtha on separate sampling tubes from EDB. Analysis of perchloroethylene and naphtha was accomplished using gas chromatography equipped with flame ionization detection (GC-FID) per NIOSH approved sampling and analytical method No.

P&CAM 127. Analysis of EDB was accomplished using gas chromatography equipped with electron capture detection (GC-EC) per NIOSH Method No. P&CAM 260. Detailed descriptions of the analytical methods employed in the sample collection and analysis of perchloroethylene, VM&P naphtha and ethylene dibromide are presented in Appendix B.

FINDINGS AND DISCUSSION

The overall objective of this study was to evaluate worker exposure to potential occupational health hazards associated with coal preparation and related laboratory float-sink operations. Detailed industrial hygiene surveys were conducted at five facilities (three of which were coal preparation plants and two of which were commercial coal laboratories with laboratory float-sink operations) in order to assess the potential health hazards associated with occupational/environmental exposure to trace metals, frothing agents used in flotation cleaning, and organic solvents used in laboratory float-sink operations.

The following sections provide a summary of study findings according to the hazard categories listed above. Tables providing a complete summary of monitoring results for each facility visited are also included.

TRACE METALS

A limited amount of area air sampling was conducted at the three coal preparation plants (Facilities 1, 2 and 3). Of the six area samples analyzed (two from each plant), none had detectable amounts of any of the targeted metals. Table 6 shows the detection limits of the sampling and analytical method used.

FROTHING AGENTS: METHYLISOBUTYL CARBINOL (MIBC) AND DOWFROTH M-222

Study findings for frothing agents indicated that the potential for adverse exposure among coal preparation workers, specifically flotation unit operators, is generally quite limited. Personal and area monitoring conducted at two coal preparation plants (Facilities 1 and 2) using MIBC showed a low potential for worker inhalation exposure compared with the OSHA permissible exposure limit (PEL) of 25 ppm. Personal time-weighted average exposure measurements (Personal TWAs) for flotation operators, at respective plants, were both calculated at 0.05 ppm. Area exposure measurements were generally higher, ranging from 0.05 to 4.4 ppm. The principal factor

Table 6.

Detection limits for the area trace metal samples.

Metal	Airborne Detection Limit ($\mu g/m^3$)
Be	0.01
Cd	0.08
Co	0.1
Cr	0.7
Li	0.1
Ni	0.4
V	0.03

affecting personal exposure was worker mobility through the workplace. Possible factors affecting area concentrations included the type of flotation units in use, the location of these units within the plant, the location of the sampler relative to the unit, workplace ventilation, and other general plant characteristics.

Personal and area monitoring for the single coal preparation plant using Dowfroth M-222 (a mixture of polypropylene glycol monomethyl ethers) showed similar trends. Personal exposure measurements (TWAs) ranged from 2.3 to 3.6 ppm, while area measurements were higher, ranging from 5.1 to 33 ppm. There are currently no recommended guidelines on inhalation exposure to Dowfroth M-222.

The potential for dermal exposure to frothing agents among coal preparation workers, again specifically flotation unit operators, was also considered to be quite low. Since a frothing agent is typically delivered to froth flotation by an essentially closed system, there is little likelihood of direct worker contact with either pure or dilute concentrations of a frother under normal operating conditions.

No information is available that documents adverse health effects from exposure to methylisobutyl carbinol (MIBC) at concentrations lower than the PEL. Because of this, and since the potential for dermal exposure was determined to be low, the study concluded that use of MIBC does not pose a health hazard to coal preparation workers for routine conditions of use at the present time. Although there are no exposure standards for Dowfroth M-222, these compounds are considered to be relatively non-toxic. The findings of this survey indicated that this frothing agent is not to be regarded as a potential health hazard in coal preparation at the present time.

Monitoring results for MIBC are summarized in Table 7. Monitoring results for Dowfroth M-222 are summarized in Table 8.

ORGANIC SOLVENTS USED FOR LABORATORY FLOAT-SINK OPERATIONS

During the study, three different laboratory float-sink operations were evaluated. Two of these operations were performed by commercial coal laboratories (Facilities 4 and 5) and one was an operation performed on-site by a coal preparation plant (Facility 3). At all three facilities, only one or two employees (i.e. float-sink technicians) were directly involved. Float-sink operations were carried out using a total of four different organic solvents: ethylene dibromide, perchloroethylene, VM&P naphtha and xylene. Monitoring results for each facility are summarized in Tables 9, 10 and 11. The range of occupational/environmental exposures for individual solvents during the study are summarized in Table 12. Table 13 presents a detailed listing of pertinent exposure standards and guidelines for the above solvents.

Results for ethylene dibromide (EDB) were the most significant. In operations where EDB was used, personal and area monitoring consistently showed airborne concentrations in excess of the NIOSH-recommended exposure limit of 0.13 ppm. This was true regardless of the scale of operation and the engineering controls in use. Personal TWAs for EDB ranged from 0.15 to 4.5 pm, while area TWAs ranged from 0.15 to 4.2 ppm. Within a given work area, personal and area exposures were found to be comparable and quite consistent. In comparing results between facilities, both personal and area exposure concentrations obtained for Facility 5 were higher than those for Facility 4. This was not unexpected based on the relative scale of operations at the two facilities.

In operations where perchloroethylene, VM&P naphtha, and xylene were used, personal and area monitoring consistently showed airborne exposure concentrations below established exposure standards. Personal TWAs for perchloroethylene ranged from 1.5 to 25 ppm and area TWAs ranged from 1.0 to 37 ppm; the OSHA permissible exposure limit (PEL) is 100 ppm. Personal TWAs for VM&P naphtha ranged from 2.7 to 4.9 ppm and area TWAs ranged from 5.0 to 8.5 ppm; the TLV is 300 ppm. For xylene, personal TWAs ranged from 0.07 to

0.12 ppm and area TWAs ranged from 0.05 to 0.1 ppm; the PEL and TLV are both 100 ppm. In comparing results for perchloroethylene among all operations, exposure concentrations for perchloroethylene (as for EDB) were found to vary according to the scale of operations observed, the amount and range of fractionation solvents used, the engineering controls used, and according to variations in individual work practices.

Ceiling exposure measurements were also obtained at each facility, in an attempt to identify and/or quantitate operations or activities which might be associated with peak solvent exposure. Monitoring results provided a general indication that float-sink "setting up" operations may result in higher worker exposure to solvent vapors than routine float-sink activities. However, certain inconsistencies in these results also suggested that peak exposures may occur randomly and may not be specifically associated with a given operation or activity.

In monitoring conducted at Facility 5, one area in particular was identified as a major source of worker exposure to airborne vapors. This was the "small sample drying area." Despite the use of general exhaust ventilation to control solvent concentrations in this area, short-term sampling indicated that workers were potentially exposed to hazardous concentrations of EDB and perchloroethylene during routine sample drying operations. Area ceiling concentrations of 90 and 560 ppm for EDB and perchloroethylene, respectively, indicated that even brief residence in this area could expose a worker to a concentration in excess of recommended exposure guidelines. To reduce the potential hazard associated with solvent vapors given off during routine sample drying operations, improved ventilation controls were recommended.

The float-sink operations at Facility 3 were very limited. It was estimated that this operation lasted only about 15 minutes twice a week. Even though Table 11 shows short-term concentrations as high as 38 ppm, the overall duration is so brief that occupational exposure did not pose a problem.

Table 7. Sampling results for methylisobutyl carbinol.

	Facility No. 1	Facility No. 2	
	Day 1	Day 1	Day 2
Personal Samples Flotation Operator	0.05 ppm (1)	0.05 ppm (1)	0.05 ppm (1)
Area Samples	0.10 - 0.31 ppm (5)	0.41 - 3.1 ppm (6)	0.06 - 4.2 ppm (5)

( ) denotes number of TWA samples.

Table 8. Sampling results for Dowfroth M-222 (polypropylene glycol monomethyl ethers).

	Facility No. 3	
	Day 1	Day 2
Personal Samples Flotation Operator	3.6 ppm (1)	2.3 ppm (1)
Area Samples	3.0 - 11.6 ppm (5)	5.1 - 33.0 ppm (5)

( ) denotes number of TWA samples

Table 9.

Summary of monitoring results for Facility 4, a commercial coal laboratory performing laboratory float-sink (F-S) operations.

	Concentration (ppm)					
	Day 1			Day 2		
	PERC	XYL	EDB	PERC	XYL	EDB
Personal TWA						
F-S Technician	2.2	0.12	—	1.5	0.07	0.40
Personal Ceiling						
F-S Technician Short-term Exposure (setting up operation)	5.0	0.2	—	—	—	0.16
Area TWA						
Fine Coal F-S	1.0	0.1	—	2.0	0.05	0.15
Intermedial F-S	0.8	0.05	—	—	—	—
General Room	1.0	0.1	—	—	—	—

Table Key: PERC = Perchloroethylene
XYL = Xylene
EDB = Ethylene Dibromide
TWA = Time-weighted Average

Table 10.

Summary of monitoring results for Facility a commercial coal laboratory performing laboratory float-sink (F-S) operations.

	Concentration (ppm)					
	Day 1			Day 2		
	PERC	VMP	EDB	PERC	VMP	EDB
Personal TWA						
Technician I	22	3.2	1.7	16	3.1	3.2
Technician II	17	2.7	1.5	25	4.9	4.5
Personal Ceiling						
Technician I Short-Term Exposure (setting up operation)	—	—	—	11	3	—
Technician II Short-Term Exposure (setting up operation)	—	—	—	—	—	4.7
Area TWA						
Fine Coal F-S	37	7.3	1.4	12	5	4.2
Intermediate F-S	—	—	1.4	10	6	1.1
General Room	31	8.5	—	—	—	—
Area Ceiling						
Small Sample Drying Room	—	—	—	560	76	90

Table Key: PERC = Perchloroethylene
EDB = Ethylene Dibromide
VMP = VM&P Naphtha
TWA = Time-weighted Average

Table 11.

Summary of monitoring results for perchloroethylene during routine laboratory float-sink (F-S) operations at Facility 3.

	Perchloroethylene Concentration (ppm)
Personal Ceiling Samples	
Coal Sampler (float-sink testing)	38
Coal Sampler (coal grinding/sample preparation)	3

Table 12.

Range of monitoring results
for organic solvents used in laboratory float-sink (F-S) operations.

	Airborne Concentrations (ppm)			
	PERC	EDB	VMP	XYL
Personal TWAs				
F-S Technicians	1.5 - 25	0.15 - 4.5	2.7 - 4.9	0.07 - 0.12
Personal Ceilings				
F-S Technicians	5.0 - 38	0.14 - 4.7	3	2
Area TWAs				
Fine Coal F-S Operations	1.0 - 37	0.15 - 4.2	5.0 - 7.3	0.05 - 0.1
Intermediate Operations	0.8 - 10	1.4	6	----
General Room Levels	1.0 - 31	---	8.5	0.1
Area Ceilings				
Small Sample Drying Area	560	90	76	----

Table Key: PERC = Perchloroethylene
EDB = Ethylene Dibromide
VMP = VM&P Naphtha
XYL = Xylene
TWA = Time-weighted Average

Table 13.

Exposure standards and guidelines (ppm).

	Ethylene Dibromide	Perchloroethylene	VM&P Naphtha	Xylene
OSHA PEL's				
TWA	20	100	500*	100
Ceiling	30	200	--	--
Peak	50 (5-min.)	300 (5-min./3-hr. period)	--	--
NIOSH Recommended Limits				
TWA	--	50	**(350 mg/m^3)	100
Ceiling	0.13	100	--	200 (10-min.)
ACGIH TLV's				
TWA	A2***	50	300	100
STEL	A2***	--	400	150

*Petroleum distillates (naphtha)

**PPM varies from 75-100 ppm according to the mean molecular weight of the VM&P naphtha mixture (typically from 87-114).

***A2 Classification. "Industrial Substance Suspect of Carcinogenic Potential For Man." Chemical substance or substances associated with industrial processes, which are suspect of inducing cancer hazard on either (1) limited epidemiological evidence, exclusive of clinical reports of single cases, or (2) demonstration of carcinogenesis in one or more animal species by appropriate methods.

CONCLUSIONS

Worker exposures to potential occupational health hazards associated with coal preparation and related laboratory float-sink operations were evaluated. The three types of hazards studied were trace metals, frothing agents used in flotation cleaning, and organic solvents used in laboratory float-sink operations.

ORGANIC SOLVENTS

Of the three hazard categories investigated in this study, the use of ethylene dibromide (EDB) in laboratory float-sink operations yielded the most important study findings. Although the EDB sampling results were consistently below the current OSHA permissible exposure limit (PEL) of 20 ppm, the results indicated that the involved employees are exposed to airborne concentrations exceeding the NIOSH-recommended guideline of 0.13 ppm. This was found to be true regardless of the relative scale of operations and the availability of standard engineering controls. It is strongly recommended that a less hazardous solvent be substituted for ethylene dibromide in all laboratory float-sink operations.

Personal 8-hour time weighted averages (TWAs) for EDB ranged from 0.15 to 4.2 ppm, while area TWAs ranged from 0.15 to 4.2 ppm. Within a given work area, personal and area exposures were found to be comparable and quite consistent. It should also be noted that there were only a very small number of employees directly involved with this operation at each facility.

At one float-sink laboratory (Facility 5), airborne concentrations of EDB and perchloroethylene above the PELs were recorded in the sample drying room. Although employees spend a very limited amount of time in this room, it was recommended that engineering control measures (e.g., ventilation) be improved.

In operations where perchloroethylene, VM&P naphtha, and xylene were used, personal and area monitoring consistently showed airborne exposure

concentrations below established exposure standards. Highest personal time-weighted average exposure measurements for perchloroethylene were 25% of the OSHA PEL of 100 ppm; highest personal samples for VM&P naptha were <2% of the OSHA PEL of 300 ppm; and highest personal samples for xylene were <1% of the OSHA PEL of 100 ppm.

In comparing results for perchloroethylene among all operations, exposure concentrations for perchloroethylene (as for EDB) were found to vary according to the scale of operations observed, the amount and range of fractionation solvents used, the engineering controls used, and according to variations in individual work practices.

Ceiling exposure measurements for each of the four organic solvents were also obtained at each of the three float-sink laboratories in an attempt to identify and/or quantitate operations or activities which might be associated with peak solvent exposure. Monitoring results provided a general indication that float-sink "setting up" operations may result in higher worker exposure to solvent vapors than routine float-sink activities. However, certain inconsistencies in these results also suggested that peak exposures may occur randomly and may not be specifically associated with a given operation or activity.

TRACE METALS

Study findings showed that employees involved in coal preparation are not overexposed to trace metals. Area sampling for trace metal contaminants in coal dust at three coal preparation plants showed no detectable amounts of any of the targeted metals.

FROTHING AGENTS

The study concluded that employees involved in froth flotation are not exposed to levels of methylisobutyl carbinol (MIBC) or Dowfroth M-222 in excess of the OSHA permissible exposure limits (PELs). Personal time-weighted average exposure measurements for MIBC showed average worker

inhalation exposure of <1% of the OSHA PEL of 25 ppm. The highest area exposure measurements were <20% of the PEL. Although there is no exposure standard for Dowfroth M-222, it is considered to be relatively non-toxic.

The potential for dermal exposure to frothing agents among coal preparation workers was also considered to be quite low. Since a frothing agent is typically delivered to froth flotation by an essentially closed system, there is little likelihood of direct worker contact with either pure or dilute concentrations of a frother under normal oprating conditions.

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APPENDIX A

DESCRIPTION OF FACILITIES SURVEYED
FACILITY 1: DESCRIPTION OF COAL PREPARATION PLANT

GENERAL INFORMATION

Facility 1, a coal preparation plant, is located in Carbon County, Utah. The plant processes lower and upper Sunnyside Seam coal, mined underground by continuous mining and longwall methods, for metallurgical applications. Designed in the early 1950's by the McNally-Pittsburg Manufacturing Corporation, the plant is a Baum Jig Type Washer with a 10,000 ton-per-day capacity. Aside from the addition of unit train loadout station in 1969 and the more recent changeover from CMI rotary dryers to Wemco Centrifugal dryers, there have been no significant changes in plant operations from the original design.

COAL PREPARATION PLANT OPERATIONS

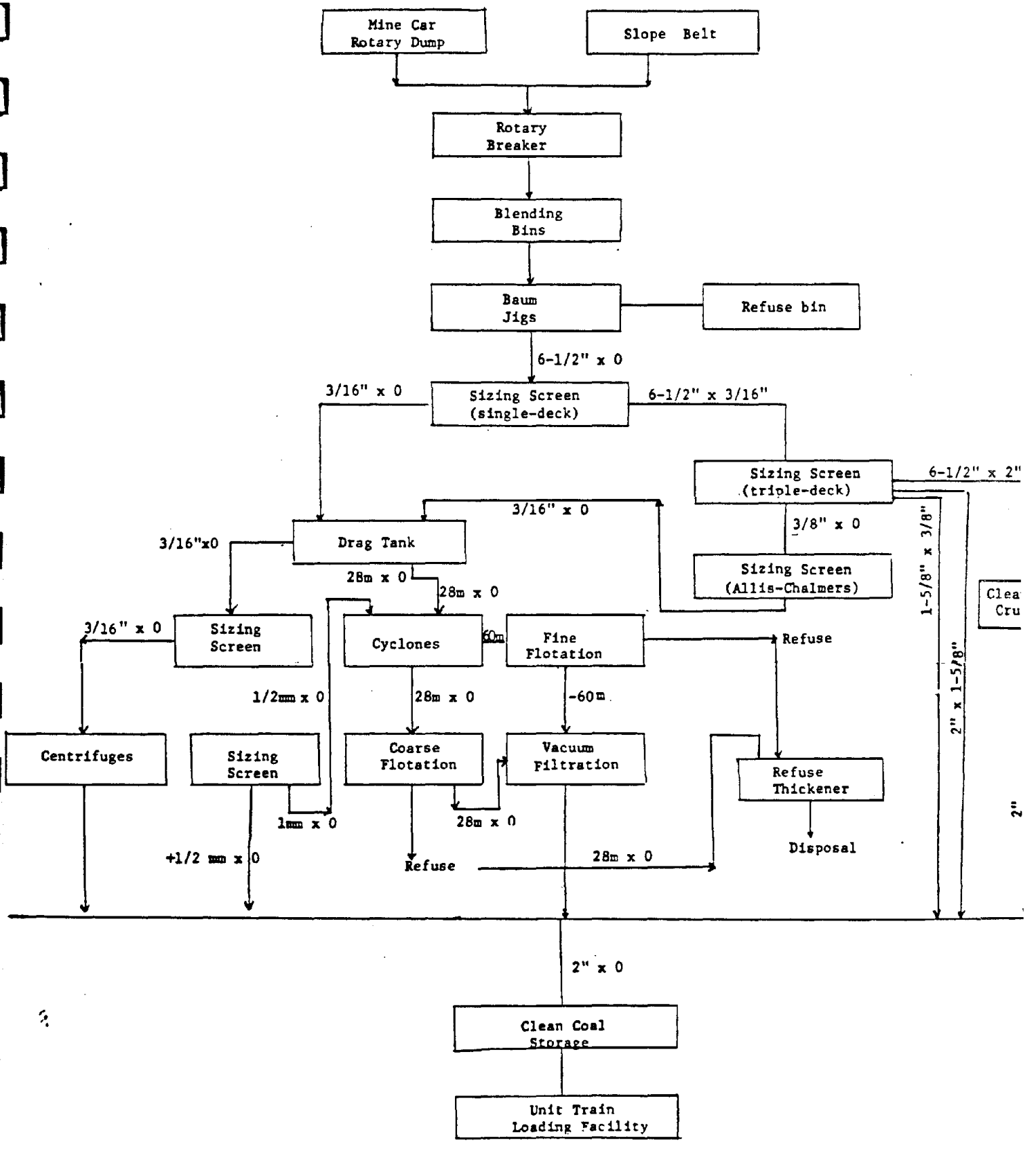
The coal preparation plant flow is illustrated in Figure 1. Run-of-mine (ROM) coal is delivered to a rotary breaker by either a mine car rotary dump system or a mine slope conveyor. The rotary breaker reduces ROM coal to a 6-1/2" topsize and delivers it to a raw coal storage feed belt. The raw coal storage feed belt conveys the raw product to 3500-ton capacity storage. Here, the raw coal feed is distributed by means of an automatic tripper car to eight 2-compartment blending and surge bins. Eight Jeffrey Feeders located at the bottom of each compartment control the rate of raw coal feed to the cleaning plant.

In the cleaning plant, a rotary feeder distributes raw coal between two McNally-Pittsburg 6-cell Baum Jigs. After the coal is washed, washed product is discharged to a single-deck sizing screen, where it is dewatered and separated into two process flows: 6-1/2" x 3/16" and 3/16" x 0. Refuse material, at the same time, is discharged to an oscillating and dewatering conveyor and then to a refuse bin for ultimate disposal.

Coarse Coal Circuit (6-1/2" x 3/16")

In the 6-1/2" x 3/16" circuit, washed coal product from the single-deck sizing screen is sent to a triple-deck sizing screen and separated into

Figure 1. Facility I
Central Preparation Plant
Sunnyside, Utah



four product streams:

- 6-1/2" x 2"
- 2" x 1-5/8"
- 1-5/8" x 3/8"
- 3/8" x 0

The 6-1/2" x 2" product is routed through a clean coal crusher and reduced to a final product topsize of 2". The 2" x 1-5/8" and 1-5/8" x 3/8" products are discharged directly to a mixing conveyor, then to a clean coal stockpile belt, and are conveyed to final coal loadout. The 3/8" x 0 product is sent to an Allis-Chalmers low head vibrating screen where it is separated into a plus 3/16" product and a minus 3/16" product. The plus 3/16 product is sent to the mixing conveyor where it is combined with 2" x 0 finished coal. It is then delivered to the clean coal stockpile belt and transported to clean coal loadout. Minus 3/16" product, in the meantime, is sent to a drag tank unit for further processing in the 3/16" x 0 wash circuit.

3/16" x 0 Cleaning Circuit

In the 3/16" x 0 coal cleaning circuit, underflow from the single-deck screen and the Allis-Chalmers low head vibrating screens is introduced into a drag tank. Here, coal is separated into two flows: 3/16" x 1/2 mm and 1/2 mm x 0. While 3/16" 1/2 mm product is dewatered in Wemco centrifuges and discharged to clean coal loadout, the 1/2 mm x 0 product is sent to a single-deck sizing screen where plus 1/2 mm x 0 overs are discharged to clean coal loadout and the underflow (1mm x 0) is collected in a cyclone sump and is pumped, as slurry feed, to the fine coal cleaning circuit.

Fine Coal Cleaning Circuit

In the fine coal cleaning circuit, 28 mesh x 0 product from a cyclone feed sump is pumped to two 24" McNally concentrating cyclones. Here product is separated into "fine" and "coarse" streams. Cyclone overflow (minus 60 m) passes through a conditioner unit to two Denver Sub-A 10-cell fine coal flotation units. Cyclone underflow (28 mesh x 0) passes through a conditioner

unit to a 4-cell Birtley-Humbolt or a 4-cell Denver Sub A coarse coal flotation unit. The froth concentrate or product from coarse and fine flotation are collected together in a primary cone and subsequently dewatered at a EIMCO 8-disc vacuum filter. The 28 m x 0 filter cake recovered at the vacuum filter is dropped onto the mixing conveyor where it is blended with a 2" x 0 finished coal. And finally, it is conveyed via a clean coal stockpile belt, to clean coal loadout. Final coal loadout occurs at a unit train loading facility located beneath the clean coal storage pile.

Refuse from the flotation circuits is discharged to a 120-ft diameter Dorr static thickener before being discharged to a tailings pond for ultimate disposal.

CHEMICALS USED IN FROTH FLOTATION

Two reagents are used in the plant's flotation units. These are methyl amyl alcohol [syn: methyl isobutyl carbinol (MIBC)], used as a frothing agent, and kerosene, used as a collecting agent. Approximate addition rates for each reagent to fine and coarse circuit flotation units are given in Table 1.

TABLE 1.

Flotation Reagent Addition Rates for Fine and Coarse Units

Fine Flotation (Denver Sub-A 10-cell Units)

Reagent	*Rate (cc/min)*
• *methyl isobutyl carbinol (MIBC)*	*9*
• *kerosene*	*220*

Coarse Flotation (4-cell Birtley Humboldt Unit or 4-cell Denver Unit

Reagent	*Rate (cc/min)*
• *methyl isobutyl carbinol (MIBC)*	*6*
• *kerosene*	*140*

POTENTIAL EXPOSURE HAZARDS

Froth Flotation - Methyl Isobutyl Carbinol (MIBC)

Methyl isobutyl carbinol (MIBC) is a potential health hazard if it is swallowed, is inhaled or comes in contact with the eyes or skin. Over-exposure may cause eye and skin irritation as well as headache or drowsiness.

To date, only limited observations of the effects of MIBC have been reported. The most important effects have been narcosis and eye irritation. Eye irritation has occurred to unacclimated persons at exposure levels as low as 50 ppm. Although chronic systemic effects have not yet been reported in humans, concern for the possible target effects of MIBC on liver and kidney function is indicated. The current permissible exposure limit for MIBC in air is 25 ppm, determined as a time-weighted average exposure concentration.

Trace Metal Contaminants in Airborne Coal Dust

Trace metals, which are recognized potential contaminants in coal, are associated with a variety of adverse health effects. These range in severity from simple irritant effects to the induction of cancer. Table 3 in the text summarizes currently recognized occupational exposure limits and the potential health effects associated with excess exposure to the seven targeted agents (Be, Cd, Co, Cr, Li, Ni, and V).

WORK FORCE

Approximately twenty-two (22) employees work in the coal preparation plant over three shifts. There are approximately 12 workers on days, 6 on swing and 4 on graveyard shifts. The workforce distribution, by job category and shift, is presented below.

Workforce

Job category	Shift 1st	2nd	3rd	
• Preparation plant foreman	1			
• Shift Foreman		1	1	
• Dispatcher	1	1		
• Central Operator	1			
• Flotation/Filter Operator	1			
• Coal Bin Operator	1			
• Greaser	1			
• Unit train Operator	2			
• Refuse Truck Operator	1			
• Laborer	2	1		
• Maintenance (welder, mechanic, electrician)	1	3	3	
	12	6	4	= 22 total

Following is a brief description of worker responsibilities for the various job classifications:

- Preparation Plant Foreman: functions as the general plant foreman. He is responsible for supervising overall plant operation and plant personnel.
- Shift Foreman: has individual responsibility for shift maintenance work activities; supervise shift personnel.
- Dispatcher: is responsible for operating the rotary car dump and mine slope conveyor; delivering raw coal to the plant.
- Central Operator: is the main plant control operator. He monitors all major process equipment operation from a central control panel and is in control of plant start-ups and shutdowns.
- Flotation/Filtration Operator: is primarily responsible for monitoring the operation of fine and coarse coal flotation units and the vacuum disk filters.
- Coal Bin Operator: monitors coal distribution to coal blending and surge bins, checks on the operation of coal plant feed belts, removes debris from the tramp iron magnet.
- Greaser: is primarily responsible for lubricating and greasing equipment throughout the plant.
- Unit Train Operator: controls clean coal rail car loading.
- Refuse Truck Operator: delivers refuse product to the refuse pile.
- Laborer: is responsible primarily for general cleanup, plant utility functions.
- Maintenance (Welder, Mechanic, Electricians): are responsible for overall electrical and mechanical plant maintenance and repair.

ENGINEERING CONTROL MEASURES

There was neither general nor local mechanical exhaust ventilation in use in the flotation work areas at the time of this survey. This was typical of the froth flotation operations observed throughout the coal preparation industry. Air movement within the plant, particularly near the flotation operations, is the result of natural ventilation. Weather permitting, plant doors and windows are open to the outdoors. Ventilation flow through the workplace varies according to external wind conditions (i.e., direction, speed).

At the time of this survey, plant doors and windows were open to the outdoors and air movement through the work area (i.e., froth flotation) was variable.

MEDICAL, INDUSTRIAL HYGIENE AND SAFETY PROGRAMS

The medical program in effect at the Central Preparation Plant is administered by the company's Personnel Department. As a part of this program, pre-employment physical examinations are given to all employees prior to initial employment. First-aid and emergency medical assistance is available from registered emergency medical technicians on all shifts. Routine medical treatment for work-related injuries and illnesses is available at a nearby industrial medical clinic during normal business hours. Emergency care is available at an area hospital.

Industrial hygiene and safety are handled by the Mine/Plant Safety Department which employs four full-time safety staff. Routine health monitoring is primarily limited to evaluation of occupational exposure to airborne coal dust.

The safety program in effect for the plant emphasizes employee training and hazard awareness. Safety meetings on pertinent safety and health topics are held on all shifts on a weekly basis.

Personal protective equipment currently supplied to workers for their use includes hard hats, protective gloves, safety glasses, hearing and respiratory protection.

FACILITY 2: DESCRIPTION OF COAL PREPARATION PLANT

GENERAL INFORMATION

Facility 2, a coal preparation plant is located in Jefferson County, Alabama. The plant processes low and medium (Blue Creek and Pratt Seam) volatile bituminous coals for metallurgical uses. The plant was originally designed by the McNally-Pittsburg Manufacturing Corporation and built by the American Bridge Company. It has been in operation since the early 1950's. Since initial start-up, the plant has undergone several plant and process changes. The following table provides a chronology of the more notable ones.

Date	Event
ca. 1952	Start-up
ca. 1962-65	Addition of: • froth flotation units • hydroseparator units • refuse thickener Changeover: • vibrating centrifugal dryers (from dewatering screens used to recover product from the wash tables)
ca. 1977	Addition of: • overland conveyor • thermal dryer unit • clean coal storage silo • automated clean coal loadout station

The only process change noted from the previous walkthrough survey visit was the discontinued use of the 3/8" clean coal crusher. This was the result of: (1) a change in marker demand for 3/8" size coal; and (2) a means of reducing environmental dust for outdoor coal storage. The Concord Coal Preparation Plant is capable of processing between 750 and 800 tons of raw coal feed per hour under current desing specifications. Operating on a 14-1/2

hour per day schedule and obtaining a 65 percent recovery on clean coal, the plant is capable of producing about 7000 tons of metallurgical grade clean coal per day.

The main wash plant is an 8-story facility, approximately 275 x 150 feet in area, that houses three coal processing circuits: (1) the coarse coal circuit cleans 2" x 5/16" size raw coal in a Chance Cone Unit, (2) the middling coal circuit cleans 5/16" x 0 size raw coal with Deister tables, and (3) the fine coal circuit cleans raw coal fines with flotation units. Below is a list of other prominent structures which comprise the overall coal preparation plant facility. Additional description of other process units associated with the Concord Plant is provided in the section on plant operations.

- Overland conveyor (raw coal delivery system)
- Crushing unit (Dual system of Tyrock vibrating screens and Bradford Rotary Breakers)
- Blending unit (24-bin unit, 6000-ton capacity)
- Hydroseparators (75 ft. diameter units)
- Refuse thickener (170 ft. diameter unit)
- Muck Coal and Refuse Loadout stations
- Thermal Dryer Unit
- Clean Coal Storage Silo (10,000-ton capacity)
- Automated clean coal loadout station

COAL PREPARATION PLANT OPERATIONS

The coal preparation flow for the Concord Plant is illustrated in Figure 1. Following is a basic description of the preparation sequence and major process units in use.

Raw Coal Handling

Low volatile run-of-mine (ROM) coal is delivered to the coal preparation plant by overland conveyor. The overland conveyor dumps onto an ROM con-

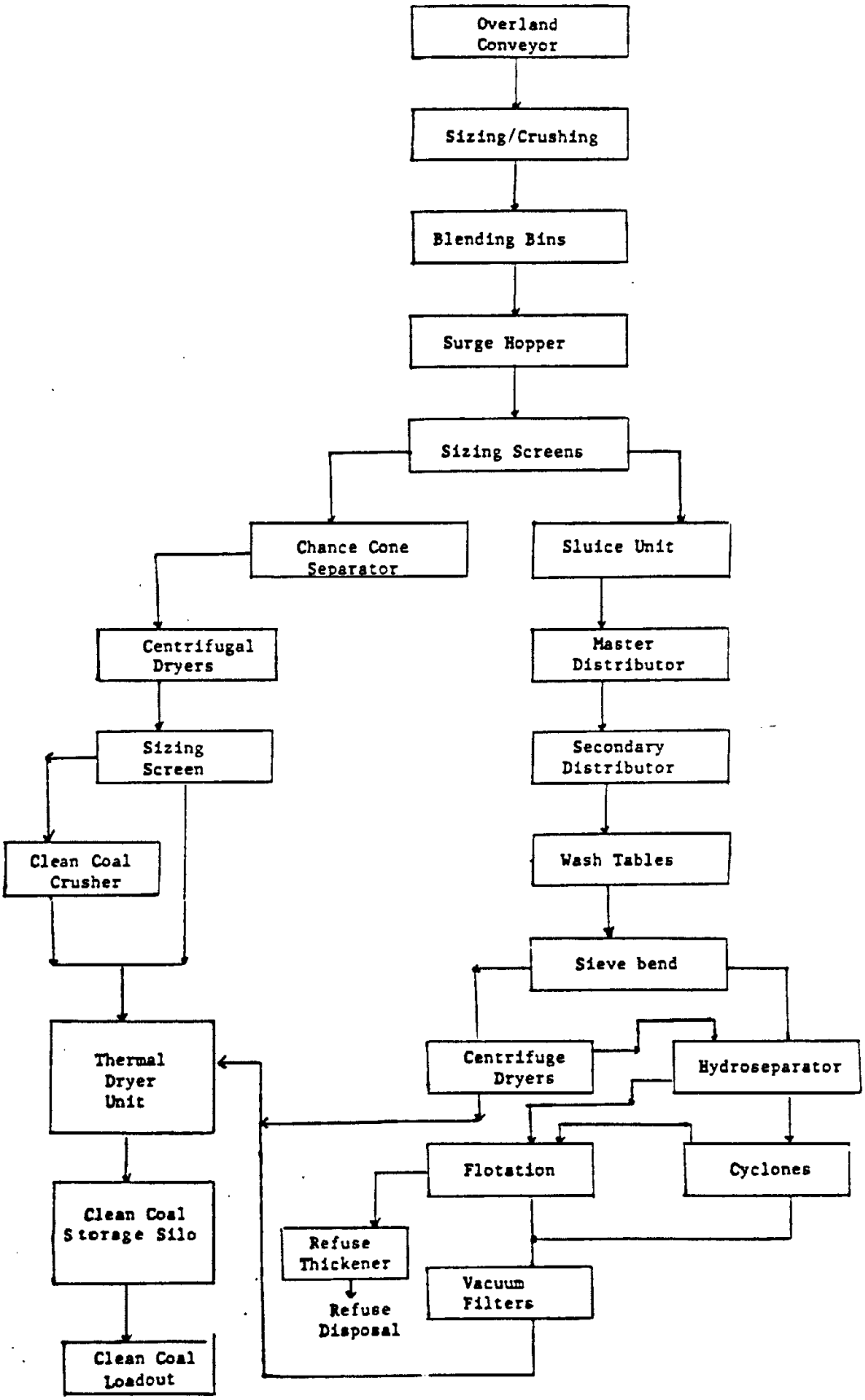


FIGURE 1. Facility 2

veyor which in turn, delivers ROM coal to the plant crushing section for initial processing. ROM coal is initially sized over vibrating screens to effect a product separation at 2". While oversize raw coal is routed through a rotary breaker and reduced in size, undersize product (2" x 0) is dropped onto a raw coal conveyor and transported to the blending plant.

In the blending plant, a tripper shuttle distributes raw coal to 24 blending bin compartments. Belt feeders at the base of individual blending bin sections control the discharge of raw coal to a collecting conveyor which in turn controls the rate of raw coal feed to the wash plant.

In the wash plant, the collecting conveyor delivers coal to a surge hopper. The hopper then feeds onto a scalper conveyor, which distributes coal to six double-deck sizing screens. Here raw coal feed is separated into two process streams: 2" x 5/16" and 5/16" x 0. The processing sequence for each are discussed in the following section.

Wash Plant Operation

2" x 5/16" Wash Circuit -- Raw coal feed, 2" x 5/16", is introduced into a 12-feet diameter Chance Cone Separator. Coal floats at or near the top of the fluid mass (a sand suspension) and overflows a weir together with a portion of the fluid mass with which it is mixed and a supernatant layer of water. Heavy impurities sink in the dense medium and are removed through a lock hopper system.

The clean coal, mixed with sand and water, passes over clean coal desanding and dewatering screens; the heavies from the refuse lock hopper pass over a refuse desanding and dewatering screen.

Dewatered clean coal passes to vibrating centrifuges for further drying. It then passes through a 3/4" sizing screen/crusher loop, is reduced to a final product size, and is finally routed through a thermal dryer unit to clean coal loadout. Refuse is discharged to a refuse conveyor for disposal.

5/16" x 0 Wash Circuit -- Raw coal (5/16" x 0) from the sizing screens is collected in a sluice unit and discharged to an 8-way master rotary distributor. The master distributor directs product flow to eight 8-way secondary distributors, which in turn direct flow to 63 Deister wash tables. Clean coal from the tables is subsequently delivered to sieve bend units for initial dewatering and fines separation; then, to vibrating centrifuges for initial drying; next, to a thermal dryer unit for final product finishing; and, finally to clean coal loadout for product shipment. Refuse is sent to settling tanks and then to a refuse conveyor for final loadout and disposal.

Fine Coal Circuit -- Fines that pass through the sieve bends and that are recovered from the vibrating centrifuges are sent to a hydroseparator unit for further processing. Here, hydroseparator underflow is pumped to concentrating cyclones, while overflow is sent to froth flotation. Underflow product from the concentrating cyclones and froth concentrate from flotation are delivered to vacuum disk filters for dewatering. The resulting filter cake is dropped onto a clean coal conveyor, routed through a thermal dryer unit for final product finishing and sent to clean coal loadout for final product shipment. Tailings from froth flotation are sent to a 175-foot diameter refuse thickener, where process water is clarified for reuse and thickened refuse is pumped to a settling pond for ultimate disposal. Final product shipment from the plant to market is by truck or railcar.

Two engineering control systems in the main wash plant were noted in the initial walkthrough survey. One was an enclosure and exhaust system set-up for the washed coal collection belt; the other was an enclosure and exhaust system set-up for the clean coal crusher.

LABORATORY FLOAT-SINK OPERATIONS

Laboratory float-sink operations are routinely performed on site in the plant coal laboratory (Fig. 2). Coarse coal separations are performed in a room set off from the main laboratory work area which is approximately 16 x 10 feet in size and is mechanically ventilated by a 36" axial exhaust fan.

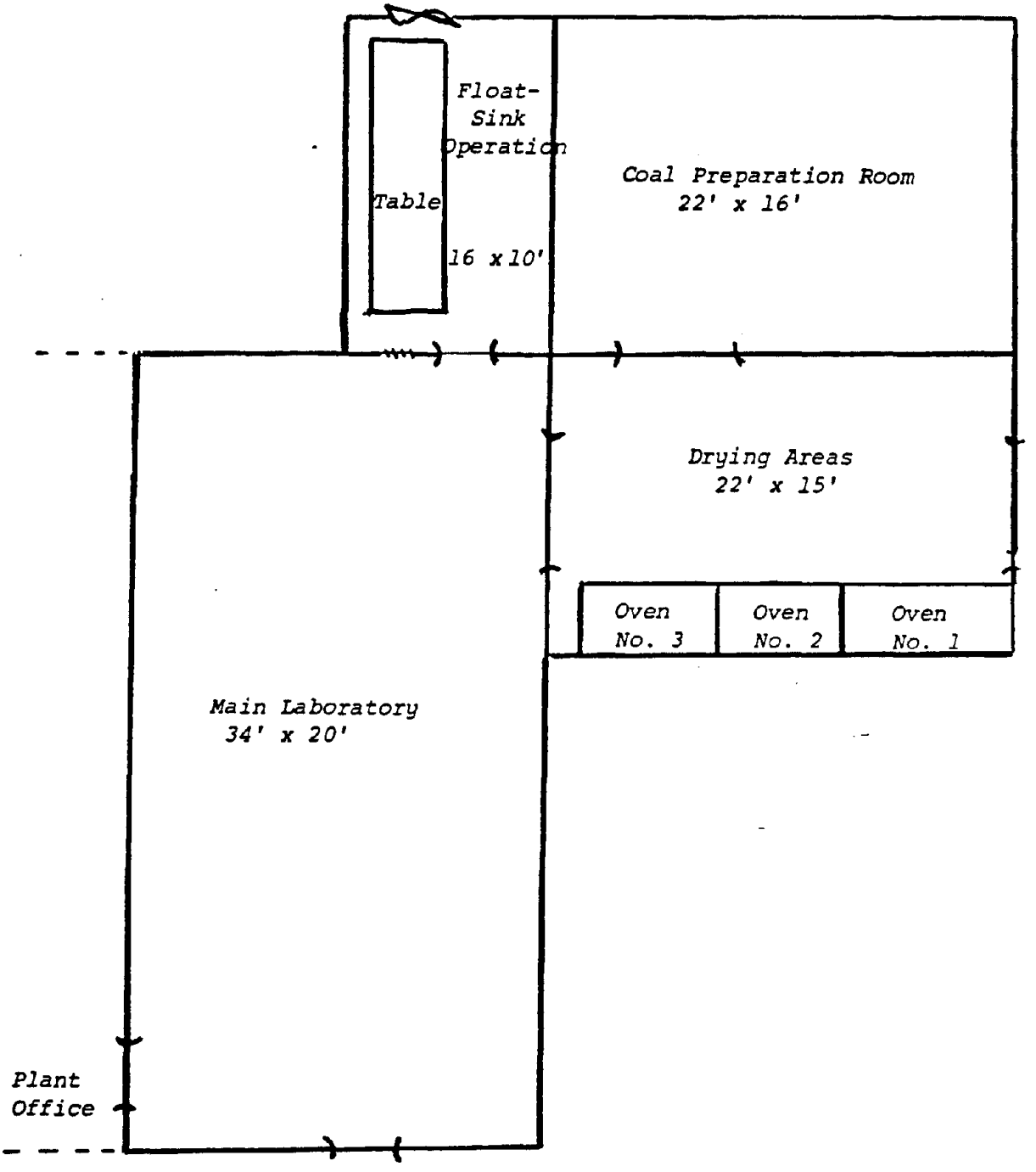


FIGURE 2. Plant Coal Laboratory

Coarse coal separations are performed daily on 6 process samples collected from the 3/8" and 3/8" x 28 mesh coal circuits: four of these are 3/8" refuse samples from the Chance cone; two are 3/8" x 28 mesh refuse from the Deister Tables. Zinc chloride solution at a specific gravity of 1.50 is routinely used to obtain the necessary refuse coal fractions. Perchloroethylene is used only on rare occasions where separation and recovery of coal fines or theoretical washability information is needed.

A conventional testing method is employed for coarse coal separations. Separations are obtained in 5-gallon capacity containers with zinc chloride solution at a specific gravity of 1.50. Samples, placed in a screen bottom sample container, are immersed in the test solution. Float-coal is recovered using a wire-screen strainer. Sink material is recovered with the removal of the screen bottom sample container from the test solution. Each sample fraction is then suitably dried, and is subsequently prepared for coal sample analyses.

Fine coal separations are not routinely performed by the Facility 2 coal laboratory and consequently, perchloroethylene is used only on rare occasions. According to the plant's coal preparation engineer, perchloroethylene had not been used at all for about 3 to 4 months.

CHEMICAL FROTHER

Methyl isobutyl carbinol (MIBC) is used by Facility 2 as the frothing agent for flotation cleaning. The chemical is delivered to the flotation units through a closed-line system from an outdoor storage tank at a regulated flow of about 50 to 60 milliliters per minute (mL/min.) per flotation tank. The per shift consumption of MIBC, based on an average delivery rate of 55 mL/min. for each of four flotation banks, is calculated as about 28 gallons for an 8-hour period.

POTENTIAL EXPOSURE HAZARDS

Methylisobutyl carbinol (MIBC) in Froth Flotation

The current permissible exposure limit (PEL) for methylisobutyl carbinol is 25 ppm, averaged over an 8-hour workshift. MIBC can affect the body if it is swallowed, inhaled, or comes in contact with eyes or skin.

The most important effects of MIBC are narcosis and eye irritation. Unacclimated individuals exposed to airborne concentrations as low as 50 ppm have experienced irritation to the eyes. Symptoms of headache and drowsiness are also associated with overexposure. Although chronic systemic effects have not been reported in humans, medical screening and surveillance of employees with a history of either impaired liver or kidney function is recommended by NIOSH where an individual might be exposed to MIBC at potentially hazardous levels.

Because MIBC is a defatting agent it can also cause skin irritation (dermatitis) on prolonged exposure. To reduce the possibility of dermal irritation direct contact should be minimized. Whenever liquid MIBC comes in direct contact with skin, one should promptly wash the affected area with soap and water.

Perchloroethylene in Float-Sink Operations

As mentioned, perchloroethylene is used only to a very limited extent at this facility. However, since it is associated with a variety of adverse health effects, the toxicity of this organic solvent is discussed here.

Clinical evidence accumulated over the years clearly demonstrates that perhcloroethylene is toxic to the liver and kidneys in humans. Perchloroethylene vapor is irritating to the eyes and upper respiratory tract, and may cause burns, blistering, and erythema due to a "degreasing" effect. Over time this can produce serious dermatitis and associated infections.

Perchloroethylene exposure can also result in altered physical and behavioral responses generally related to depression of the central nervous system (CNS). These symptoms include vertigo, impaired memory, confusion, fatigue, drowsiness, irritability, loss of appetite, nausea and vomiting. Reduced motor skills, mental acuity and symptoms of fatigue have important implications for worker safety. Severe depression of the CNS from excessive exposure can result in coma, collapse of cardiopulmonary function and death.

Concern for the carcinogenic potential of perchloroethylene arises in part from the basic structure similarity of perchloroethylene to vinylchloride and other chlorinated olefins (chloroethylenes) known to be carcino-

genic. More importantly results of initial animal studies conducted by the National Cancer Institute have shown perchloroethylene to be carcinogenic in mice. Although at present there are limited available epidemiology data to associate perchloroethylene directly with cancer in humans, the potential for producing these effects is indicated. Since January 1978, NIOSH has recommended that perchloroethylene be handled in the work place as if it were a human carcinogen. Perchloroethylene currently appears on the OSHA "Candidate List" of chemicals being considered for further scientific review.

OSHA's current standard for occupational exposure to perchloroethylene is 100 ppm as a TWA concentration for an 8-hour work shift, with an acceptable ceiling concentration of 200 ppm and a maxiumum peak above the acceptable ceiling concentration of 300 ppm for not more than 5 minutes in any 3-hour period. In 1976 NIOSH recommended that exposure be limited to 50 ppm as a TWA for up to a 10-hour work day, 40-hour work week amd a ceiling concentration of 100 ppm. The American Conference of Government Industrial Hygienists (ACGIH) have recommended a Threshold Limit Value (TLV-TWA) of 50 ppm.

The current standards and recommended limits were selected on the basis that they would prevent serious narcotic effects and that chronic intoxication involving hepatic or central nervous system effects would also be unlikely.

Trace Metal Contaminants in Airborne Coal Dust

Trace metals, which are recognized potential contaminants in coal, are associated with a variety of adverse health effects. These range in severity from simple irritant effects to the induction of cancer. Table 3 in the text currently recognized occupational exposure limits and the potential health effects associated with excess exposure to the seven targeted agents (Be, Cd, Co, Cr, Li, Ni and V).

WORK FORCE

Facility 2 employs approximately 69 workers over three shifts. There are 36 persons on day shift, 21 on evenings and 13 on nights. Day and evening shifts are operating shifts. The night shift is a maintenance shift. Distribution of the workforce by job category is indicated below.

Job Categories	1st Shift	2nd Shift	3rd Shift
Breaker Operator	1	1	
Sizing Screen Operator	1	1	
Chance Cone Operator	1	1	
Deister Tables Operator	1	1	
Panel Operator	1	1	
Dewatering Operator	1	1	
Thickener Operator	1	1	
Thermal Dryer Operator	1	1	
Wash helper	11	3	3
Electrician	4	5	5
Machinist	3	1	2
Welder			2
Railroad Car Loader Operator	1	1	
Dozer Operator	2		
Front-end Loader Operator	1		
Truck Driver	2	1	1
Clerk	1		
Chemist (stationary equipment operator)	1		
Laboratory Assistant-A	2	2	
	36	21	13

Brief descriptions of worker job responsibility by job category are provided below:

Main Plant Operators

- Breaker Operator is responsible for monitoring unit operation, greasing, checking belt alignments, looking out for chute plug ups and for unit switch over.
- Sizing Screen Operator is responsible for greasing conveyor belt lines in his area, monitoring the primary distributor to the Deister tables, and checking on the operation of all screens
- Chance Cone Operator is responsible for chance cone operation and accessory equipment.
- Deister Tables Operator is responsible for operating Deister Tables and Flotation Banks. Duties include: greasing, oiling, regulation of flow to flotation and maintenance of proper feed rate on the frother.
- Panel Operator controls overall plant operation, including: all major equipment, overland conveyor and thermal dryer.
- Dewatering Operator duties include monitoring and lubrication of the vacuum disk filters, centrifuges and accessory equipment.
- Thickener Operator is in charge of the hydroseparators and thickener. He monitors pump operation and thickener water levels. Is responsible for monitoring both the wash coal and refuse belts.
- Thermal Dryer Operator attends to thermal dry unit, assists with unit start up and performs unit lubrication and housekeeping.

General Plant Personnel

- Washer Helpers perform general plant housekeeping and sanitation, provide relief on various jobs if trained, assist plant operators in their duties.

- Electrician is responsible for overall plant electrical repair and maintenance.
- Machinist responsible for plant mechanical repair and maintenance.
- Welder responsible for fabrication and equipment repair.
- Railroad car loader controls coal loadout from the clean coal storage silo to unit car and train loading.
- Dozer Operator control disposal of refuse at refuse dump.
- Truck Driver delivers refuse from the loadout station to the refuse dump.
- End Loader Operator is responsible for general clean-up work and truck loading of coal.
- Clerk carries out clerical functions within the washer plant

Laboratory Personnel

- Chemist performs routine coal analysis such as ash, moisture sulfur, volatile matter, etc. on daily basis.
- Laboratory Assistant-A's duties include sample collection preparation of float-sink, laboratory clean-up and general laboratory housekeeping.

ENGINEERING CONTROL MEASURES

Facility 2 does not employ either general or local mechanical exhaust ventilation for froth flotation. Air movement within the plant is the result of natural ventilation. Weather permitting plant doors and windows are open to the out-of-doors. Air flow through the workplace (specifically, froth flotation) varies according to external conditions (i.e., wind speed and direction). At the time of the survey plant doors and windows were open to the out-of-doors and air flow through the work area was variable.

In the laboratory, mechnical exhaust ventilation was used to minimize worker exposure to solvent vapors associated with float-sink operations and

for dust for coal grinding. In the float-sink work area, a 36 inch wall fan, exhausting about 3800 cubic feet of air per minute (cfm), was used to limit the buildup of airborne contaminants. In the coal preparation area mechanical exhaust was also used to limit worker exposure to coal dust. In both cases, the placement of respective exhaust fans was consistent in drawing airborne contaminants away from worker breathing zones.

MEDICAL, INDUSTRIAL HYGIENE AND SAFETY PROGRAMS

The medical program for the preparation plant is administered by the Personnel Department. Medical examinations and health care are available through a company affiliated hospital. As part of the basic medical program, all company personnel are given a pre-employment physical examination. Routine first aid is provided by supervisory personnel.

Industrial hygiene and safety are handled by the joint mine/plant Safety Department. A full-time preparation plant Safety Inspector conducts routine safety and health inspections of the workplace to identify potential hazards. He informs the plant superintendent of these findings in writing to initiate corrective action. The Safety Inspector is responsible for monitoring noise and airborne dust and for compiling job-related illness and injury statistics.

Employee training is emphasized as a primary means for attaining company safety goals. Currently, all plant employees participate in a Job Safety Analysis Program which involves a weekly safety briefing and a twice monthly Personal Safety Observation (PSO). During a PSO, an employee is observed during routine job activities to evaluate the degree of safety associated with current work practices.

Personal protective equipment currently used includes hard hats, safety glasses and shoes, personal hearing protection (E.A.R. formable plugs) and respiratory protection for dust and organic vapors. Enforcement is prinicipally directed toward appropriate use of hats, glasses and shoes.

Housekeeping throughout the plant is carried out on a continuous basis. Plant operators are routinely responsible for performing general house-

keeping in their own areas. Washer helpers are assigned to general clean up activities in all other areas. Process spills or overflows are cleaned up promptly.

FACILITY 3: DESCRIPTION OF THE COAL PREPARATION PLANT

Facility 3, a coal preparation plant with laboratory float-sink, is located along the western bank of the Monogahela River in Washington County, Pennsylvania. Designed and constructed by the Link Belt Company in the middle 1960's, the plant start-up date for processing deep mined Pittsburgh seam coal for metallurgical use was 1968.

Designed to clean raw coal in three size ranges: coarse (4" x 1/2"), middlings (1/2" x 30 M) and fines (30 M x 0), the plant is set up in two independent parallel circuits for cleaning coarse and middling sizes and one single flotation circuit for cleaning fine sizes. Current production rate averages about 600 tons of raw coal feed per hour (TPH). This is approximately 92% of the design capacity of 650 TPH. With a fifty percent product recovery, typical clean coal production for an 8-hour work-shift is about 2400 tons per day (TPD).

Except for a few minor process changes such as the elimination of two coarse coal mechanical dryers and a paddle mixer at coal load-out, only one process change of note has occurred over the years. It is the most recent addition (1981) of a clean coal crusher placed in-line just prior to clean coarse coal load-out. The crusher reduces the final coal product (4" x 0) to a top size.

COAL PREPARATION OPERATIONS

Run-of-mine (ROM) coal is discharged to a ROM hopper at a mine car rotary dump. Raw coal is crushed to a 4" top size and conveyed to 2000 ton capacity raw coal storage bins, where by means of eight syntron feeders, raw coal feed to the plant is controlled to approximately 600 TPH.

Process flow is illustrated in Figure 1. Raw coal feed (4" x 0) from coal storage is delivered to the plant on two 325 ton-per-hour (TPH) plant feed belts. Raw coal is fed to two independent and parallel cleaning circuits, described as sides A and B, via dual vibrator feeders. Coarse

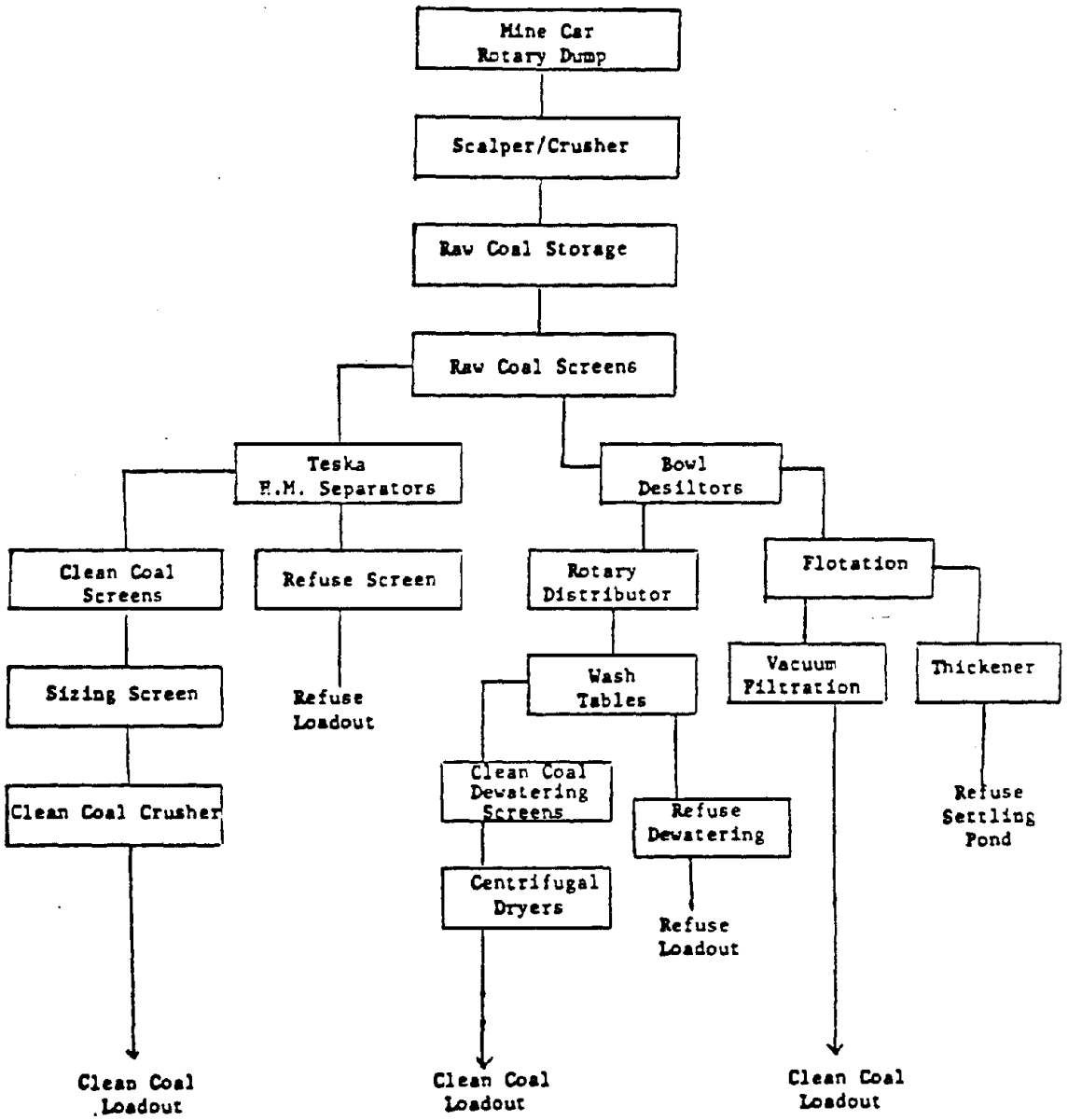


Figure 1. Facility 3
Coal preparation plant
Pennsylvania

raw coal, 4" x 1/2", and minus 1/2" middlings are separated by raw coal sizing screens and are diverted to the appropriate cleaning circuits. Coarse coal is delivered to A and B side Teska Heavy Media Separators (A and B side coarse coal cleaning circuits) while minus 1/2" middlings are delivered to A and B side 20'-diameter bowl desiltors (A and B side middlings coal cleaning circuits). Brief descriptions of each circuit follow.

Coarse Coal Cleaning Circuit (4" x 1/2")

In the coarse coal circuit, 4"x 1/2" feed from the raw coal sizing screens is diverted to a Teska Heavy Media Separator for washing. Float (clean coal) and sink (refuse) are separated at a specific gravity of approximately 1.50. Float coal is discharged to a clean coal screen while refuse is discharged to a refuse screen. Each is drained and rinsed to recover media and magnetite. Clean coal is reduced to a final 2" x 0 product size by a clean coal crusher and discharged to the loadout belt for barge transport shipment. Refuse is delivered to a refuse conveyor for outside disposal. A magnetite recovery circuit with a magnetic separator is used to recover and concentrate magnetite for reuse.

Middlings Coal Cleaning Circuit (1/2" x 30 M)

In the middlings coal circuit, minus 1/2" underflow from the raw coal screens is diverted to a 30'-diameter bowl desiltor where plus 30 M are separated from minus 40 M fines. Minus 30 M fines or desiltor overflow is sent to froth floation. The 1/2" x 30 M underflow is sent through a rotary distributor to Concenco 77 twin deck washing tables. Clean coal and refuse products from the tables are collected in respective sumps and then discharged to dewatering screens. Refuse is dewatered over 4' x 14' dewatering screens and conveyed to refuse disposal via a refuse belt conveyor, while clean coal is dewatered then dried before being discharged to the middlings clean coal belt and clean coal loadout.

Fine Coal Cleaning Circuit (30 M x 0)

In the fine coal circuit, minus 30 M raw coal overflow from A and B side bowl desiltors are combined into a single processing circuit. Passing through a single stationary distributor, slurry is delivered to six 4-cell Wemco flotation units for cleaning. Minus 30 M clean coal from flotation passes by gravity to two clean coal vacuum disk filters for drying. Minus 30 M refuse, in the meantime, is discharged to a 140' diameter refuse thickener. Dried clean coal, 30 M x 0 is ultimately combined with 1/2" x 30 M middlings on a clean coal belt and conveyed to coal loadout. Refuse from the thickener is pumped to a settling pond. Clarified water is recirculated to the plant for reuse.

Clean Coal Loadout

Final coal loadout can go either to railroad unit cars or river barges. Currently, coal shipment is exclusively by barge.

CHEMICAL FROTHER USED IN FLOTATION CLEANING

Dowfroth M-222 is the chemical frother currently being used by Facility 3 in froth flotation. Dowfroth replaces the plant's most recent use of an American Cyanamid Company product, Aerofroth-77A, which is a mixture of aliphatic alcohols. Dowfroth M-222 is a product of the Dow Chemical Company. It is a commercially manufactured mixture of polypropylene glycol monomethyl ethers (represented by the generalized chemical formula: $CH_3-(O-C_3H_6)_x - OH$. According to the Material Safety Data Sheet (Appendix C) the liquid frother can be irritating to the eye and skin, however, inhalation effects are said to be unlikely. Currently, there are no established systemic effects associated with overexposure to Dowfroth M-222.

LABORATORY FLOAT-SINK OPERATIONS

As part of an overall product quality assurance/quality control program, Facility 3 conducts routine coal testing on process streams throughout the plant. This includes both coal and refuse sample testing. For the most part, the analytical testing performed is carried out by a contract coal laboratory; however, some limited in-house testing is conducted. The testing performed in-house is primarily limited to a determination of percent moisture, ash, sulfur and volatile matter. Analyses are performed by the plant chemist. Sample collection and preparation are carried out by the coal sampler.

As part of the in-house testing program, raw coal feed to the plant is tested once each week. These samples require coal fractionation (laboratory float-sink testing), sample preparation and coal analysis. The coal sampler carries out coal fractionation with perchloroethylene (Certigrav at a specific gravity of ~ 1.60) in an open bath in the sample room, located on the second floor of the preparation building. The operation takes place about twice a week and typically involves only 15 to 30 minutes of float-sink separation.

The separation technique used is routine. Samples in screen bottom containers are immersed in 5 to 10 gallon-capacity vessels containing an appropriate test solution at a given specific gravity. The lighter coal fraction or "float" is removed from the surface with a wire screen strainer; the heavier material or "sink", which settles on the container bottom, is raised above the liquid to drain. The container is then reimmersed in a test solution of a higher specific gravity and the procedure repeated. This is continued until the initial sample is separated into the desired fractions. These are dried, weighed and analyzed.

Float-sink operations are carried out in the "sample room", a room of about 27 x 11 feet in area, which is located on the second floor level of of the main plant building, directly adjacent to froth flotation. The room is equipped with a floor level exhaust fan, which is located near the float-sink tank, to help control solvent vapors. The room is also equipped with a sample drying oven. The oven is not equipped with local exhaust ventilation. Figure 2 provides an illustration of room layout.

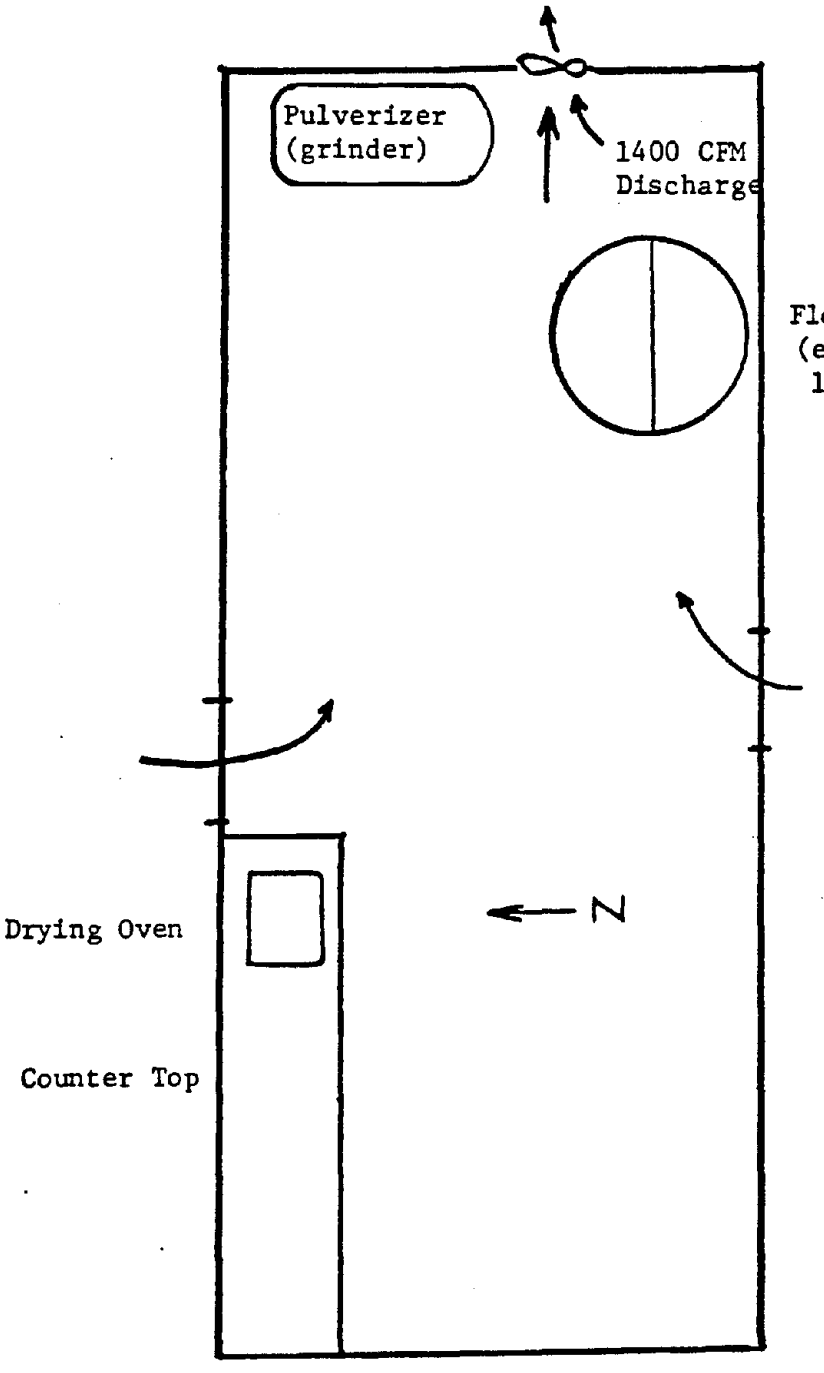


FIGURE 2. Sample Room Layout

POTENTIAL EXPOSURE HAZARDS

Flotation Frothing Agent - Dowfroth M-222

Dowfroth M-222 Flotation Frother (a mixture of polypropylene glycol monomethyl ethers, with an average molecular weight of about 280) is a dark brown liquid, low in volatility, with a slight, pleasant, etherial odor. It is low in single dose oral toxicity (LD_{50} = >5000 mg/Kg in female rats), transiently irritating (conjunctiva) and very slightly damaging (cornea) to the eye, and mildly irritating to the skin with repeated or prolonged exposure. It is not likely to be absorbed through the skin in acutely toxic amounts. Because of its low vapor pressure and toxicity, it is an unlikely inhalation hazard under ordinary conditions of handling and use. There are currently no known human effects for excess exposure; systemic effects have not been established. There are currently no established guidelines on permissible exposure limits. Overall, the potential health hazard of polypropylene glycol monomethyl ethers appears to be negligible.

Float-Sink Operations -- Perchloroethylene

Clinical evidence accumulated over the years clearly demonstrates that perchloroethylene is toxic to the liver and kidneys in humans. Perchloroethylene vapor is irritating to the eyes and upper respiratory tract, and may cause frontal sinus congestion and headache. Contact with the skin can cause burns, blistering, and erythema due to a "degreasing" effect. Over time this can produce serious dermatitis and associated infections.

Perchloroethylene exposure can also result in altered physiological and behavioral responses generally related to depression of the central nervous system (CNS). These symptoms include vertigo, impaired memory, confusion, fatigue, drowsiness, irritability, loss of appetite, nausea and vomiting. Reduced motor skills, mental acuity and symptoms of fatigue have important implications for worker safety. Severe depression of the CNS from excessive exposure can result in coma, collapse of cardiopulmonary function and death.

Concern for carcinogenic potential of perchloroethylene arises in part from the basic structural similarity of perchloroethylene to vinyl chloride

and other chlorinated olefins (chloroethylenes) known to be carcinogenic. More importantly the results of initial animal studies conducted by the National Cancer Institute which have shown perchloroethylene to be carcinogenic in mice. Although at present there are limited available epidemiologic data to associate perchloroethylene directly with cancer in humans, the potential for producing these effects is indicated. Since January 1978, NIOSH has recommended that perchloroethylene be handled in the workplace as if it were a human carcinogen. Perchloroethylene currently appears on the OSHA "Candidate List" of chemicals being considered for further scientific review.

OSHA's current standard for occupational exposure to perchloroethylene is 100 ppm as a TWA concentration for an 8-hour work shift, with an acceptable ceiling concentration of 200 ppm, and a maximum peak above the acceptable ceiling concentration of 300 ppm for not more than 5 minutes in any 3-hour period. In 1976 NIOSH recommended that exposure be limited to 50 ppm as a TWA for up to a 10-hour work day, 40-hour work week and a ceiling concentration of 100 ppm. The American Conference of Government Industrial Hygienists (ACGIH) have recommended a Threshold Limit Value (TLV-TWA) of 50 ppm. The current standards and recommended limits were selected on the basis that they would prevent serious narcotic effects and that chronic intoxication involving hepatic or central nervous system effects would also be unlikely.

Trace Metal Contaminants in Airborne Coal Dust

Trace metals, which are recognized potential contaminants in coal, are associated with a variety of adverse health effects. These range in severity from simple irritant effects to the induction of cancer. Table 3 in the text summarizes currently recognized occupational exposure limits and the potential exposure to the seven targeted agents (Be, Cd, Co, Cr, Li, Ni, and V).

WORK FORCE

There are approximately thirty-five (35) employees that work in the coal preparation plant over three shifts. There are nineteen (19) persons on the day shift, nine (9) on evening shift and seven (7) on night shift. The work force distribution for all three shifts, as well as shift schedules, are represented below:

Distribution of Workforce

Job title/Classification	Day Shift	Evening Shift	Night Shift
General foreman	1		
Operating foreman	1	1	1
Chemist	1		
Central Control Operator	1		
Coal Sampler	1		
Fine Coal Attendant	1		
Heavy Media Operator	1	1	
Greaser	1		
Slate Picker	1	1	
Car dumper	1	1	
Barge Loader	1		
Barge Mover	1		
Riverman Helper	1		
Utilityman	2		2
Repairman 1st Class (Mechanic)	3	4	4
Electrician	1	1	
	19	9	7

Total Workforce = 35

SHIFT SCHEDULE

Shift	Time
Day	8:15 a.m. to 3:15 p.m.
Evening	3:15 p.m. to 10:30 p.m.
Night	10:30 p.m. to 7:15 a.m.

The general foreman, operating foremen and plant chemist are management level personnel with overall responsibility for plant personnel, production and product quality. The remaining thirty (30) plant employees are production personnel organized under the United Mine Workers of America (Local No. 688 District 5). Following is a brief description of the primary job responsibilities associated with each of these job classifications:

- Central Control Board Operator (1): is responsible for monitoring overall plant operation, insuring that all plant equipment is operating normally. The central control board operator monitors all coal screens, all coal transport belts, the specific gravity of the Teska Heavy Media Separators and the refuse (Tram) loadout. He is in charge of coordinating plant start-ups. He is responsible for plant housekeeping in-and-around the central control panel work area.

- Coal Sampler (1): is responsible for collecting and processing coal and refuse samples as a part of the product quality assurance/quality control program. As a part of the coal processing regime, he periodically is involved with laboratory float-sink testing.

- Fine Coal Attendant (1): is responsible for monitoring the operation of the flotation units, the vacuum filters, the Deister tables, the centrifugal dryers and the heavy media sumps. The fine coal attendant controls the addition of chemical reagents to the froth flotation units and the addition of flocculent chemicals to the static thickener.

- Heavy Media Operator (2): is responsible for monitoring all process pumps. He monitors the operation of the static thickener and the slime remover, and has primary responsibility for clean up and general housekeeping on the ground floor level of the preparation building.

- Greaser (1): is responsible for overall equipment lubrication and greasing. His primary responsibility involves the tending of the plant's automatic greasing system. Periodically, the greaser will also remove debris from the tramp iron magnet on the No. 1 raw coal feed belt.
- Slate Picker (2): is responsible for monitoring the proper operation of the picking table, the raw coal crusher and distributing conveyor. The slate picker removes wood and metal debris as it enters the plant and breaks up large pieces of slate and sandstone before it enters the raw coal crusher.
- Car Dumper (2): operates the mine car haul and rotary dump.
- Barge Loader (1): supervises barge coal loading. He assures even coal distribution and loading by gauging the barge draft or freeboard.
- Barge Mover (1): controls barge movement and operates coal loading shutes.
- Riverman Helper (1): assists the barge loader and tows empty barges into place for coal loading.
- Utilityman (4): provides fill-in relief on all jobs except for the central control operator and mechanic; he is primarily responsible for plant clean-up and housekeeping in workareas not covered by unit operators.
- Mechanics (Repairman 1st Class)(11): are responsible for overall plant mechanical maintenance and repair.
- Electricians (2): are responsible for overall plant electrical maintenance and repair.

ENGINEERING CONTROL MEASURES

Although the preparation building is equipped with four 3-foot diameter roof exhaust fans, air movement within the plant is for the most part the result of natural ventilation. At the time of the survey, plant doors and windows were open to the outdoors and the air movement within the building was variable.

The sample room is equipped with a 9"-diameter floor level exhaust fan with a discharge rate of approximately 1400 cubic feet of air per minute (cfm). The two doors leading into the room are routinely open during float-sink testing. Given the position of the tank and the direction of air flow through the room, the mechanical exhaust ventilation and general dilution air provided offer practical controls for limiting worker exposure to test solution vapors (see Figure 2).

MEDICAL, INDUSTRIAL HYGIENE AND SAFETY PROGRAMS

Facility 3 has medical, industrial hygiene and safety programs which are administered jointly by the mine/plant personnel office. The medical program consists of pre-employment physical examinations for all employees, performed by a company physician, and on-site medical care and emergency assistance provided by a full time on-site staff nurse, shift emergency medical technicians and paramedics. Routine in-plant first aid is provided by supervisory personnel. Job injuries are reported to the preparation plant foreman. Accident reports are submitted to the Company safety supervisor.

Industrial hygiene and safety are handled by the Company's Safety Department, the staff of which includes a program administrator, the Safety Supervisor, and four staff assistants. The safety department is responsible for health and safety for all underground (mine) and surface (plant) personnel. The safety program in effect includes utilization of mine and plant safety committees, with labor and management representation, to both identify and correct potentially hazardous working conditions; compliance monitoring for worker exposure to coal dust; worker training; and the use of appropriate

personal protective equipment. The personal protective equipment currently required in all areas of the preparation plant includes safety glasses, safety shoes and hard hat. Additional protective equipment including protective gloves and outer wear are also provided to employees whenever a need is indicated.

FACILITY 4: DESCRIPTION OF FACILITY AND LABORATORY FLOAT-SINK OPERATIONS

GENERAL INFORMATION

Facility 4 is an independent commercial coal laboratory located in Wheeling, West Virginia that has been in the business of performing standard coal analyses for the coal mining industry since about 1975. Since about 1977, the laboratory has been performing coal washability testing, which for the purposes of this report will be referred to as laboratory float-sink (F-S) operations.

The laboratory's F-S operations include fine, intermediate, and bulk scale processes. Initially in 1977, the fine and some intermediate operations were performed in a laboratory located in the basement of the east wing of the Wheeling/Ohio County Airport Terminal Building. In 1982, just prior to this survey, all fine and intermediate F-S operations were relocated to the new project laboratory which is located on the second floor of the same building. This laboratory encompasses a work area of approximately 1700 square feet of which about 1350 square feet of area is utilized as laboratory workspace and the remaining area serves as office space. Figure 1 provides a plot plan for the present laboratory set-up.

Bulk scale operations were initially performed in the adjacent fire house building. To prevent the buildup of airborne solvent concentrations, a local exhaust ventilation system, adapted from the vehicle exhaust ventilation system, was used. The bulk operations were moved to an area outside the fire house around 1979-1980 where it is currently located.

The laboratory is organized into five service groups:

- Coal Laboratory Services
- General Laboratory Services
- Thermal Dryer Evaluation Group
- Hydrology Section
- Product Marketing Group

Including both technical and administrative personnel, the total staff numbers approximately 23 persons. Laboratory float-sink operations falls within the Coal Laboratory Services Group. Of the nine employees assigned to this department, only two are currently involved with laboratory float-sink analysis.

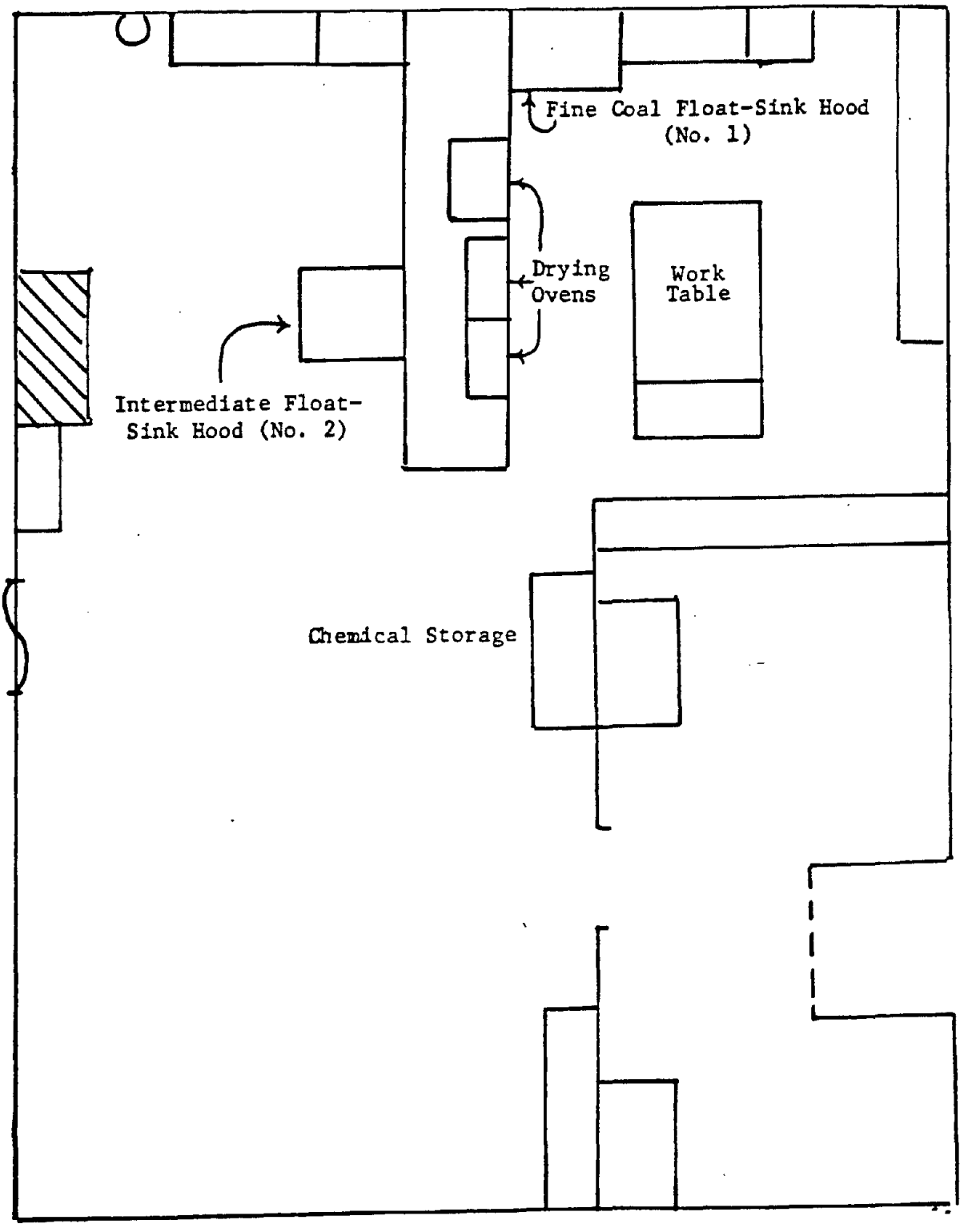


FIGURE 1. New Project Laboratory Plot Plan

LABORATORY FLOAT-SINK OPERATIONS

Laboratory float-sink testing is a procedure used to fractionate coal at pre-selected specific gravities. It is part of an overall analytical testing protocol, described as Washability Testing, which is performed to determine how well a coal can be cleaned or to what degree improvements can be made in the quality of a coal by improved preparation.

Basically, the testing procedure involves: sample immersion, float-coal recovery, reimmersion of the sink material and repetition of the procedure until the required sample fractions have been obtained. At each step, recovered fractions are dried and then prepared for subsequent analyses.

The particular manner by which the separation procedure is carried out depends on the particle top-size of the coal to be tested and the quantity requiring processing. For "fine" coal separations, a sample is placed into a glass separatory flask and funnel (joined by a standard ground glass taper joint) containing a test solution of a given specific gravity. After the sample separates a stopper is passed through the float layer and inserted into the neck of the separatory funnel. The products obtained are recovered by filtration. While the float is dried and prepared for coal analysis, the sink is reintroduced into another separatory flask arrangement, containing a heavier testing liquid, and the process is repeated. The procedure is carried out repetitively until coal fractions at all the required specific gravities have been obtained.

For "coarse" coal separations, a sample is placed in a wire screen container (of about 5 to 10 gallon capacity) which is inserted into a testing solution contained in a vessel of similar size. When the coal sample separates, the float fraction is recovered with a screen wire strainer; the heavier product is recovered with the removal of the screen bottom container. In the process, each product is carefully drained of excess solvent. Float-coal is dried prior to subsequent coal preparation and analysis; the heavier product is reimmersed in a test solution at the next higher gravity and the process is repeated. As for fine coal operations the procedure is repeated until the coal fractions, at all the required specific gravities, have been obtained.

Coarse coal separations can be performed either on an "intermediate" or "bulk" coal basis. The distinction here is primarily one of scale. Intermediate float-sink operations, like fine coal float-sink operations basically involve a bench-scale procedure and are carried out within a ventilated enclosure (laboratory hood) to minimize potential worker exposure to solvent vapors. Bulk float-sink operations, on the other hand, are performed on an appreciably larger scale, with the capability of handling much larger size coal samples.

At Facility 4 bulk coal operations are carried out at an outdoor location adjacent to the laboratory's coal preparation work area. Bulk coal samples are separated at a float-sink "table" comprised of ten 15-gallon tanks which contain test solutions over a full range of specific gravities (typically from about 1.30 to 2.00 in 0.05-0.10 increments). The tanks are arranged in a side-by-side fashion to allow convenient sequential float-sink separations to be made over a range of increasing specific gravities. To permit easy conveyance of sink material from one test solution to the next, the unit is equipped with an overhead hoist. Individual covers are placed over each holding tank to minimize both worker exposure to solvent vapors and changes in test solution gravities. At present, bulk float-sink operations at Tra-Det are performed without benefit of mechanical exhaust ventilation.

At Tra-Det, fine and intermediate float-sink operations are performed on a regular basis while bulk operations are performed infrequently. The majority of testing (about 75 percent) involves fine coal, while the balance is essentially intermediate. Over the past 4 to 5 months, it was estimated that Tra-Det had spent only a few days performing bulk coal operations.

CHEMICALS USED IN LABORATORY FLOAT-SINK OPERATIONS

Three chemical solvents are used by Facility 4 in making up float-sink test solutions at the appropriate specific gravities. These are:

- Perchloroethylene
- Ethylene dibromide (EDB)
- Xylene

The Table below provides a listing of the chemical suppliers used and the quantity of bulk solvent routinely ordered.

Fractionation Solvents

Chemical	Current Supplier	Container Shipment Quantity
• perchloroethylene	Vulcan Materials Co. Birmingham, Alabama	55-gallon drum
• ethylene dibromide	American Minechem Coriopolis, Pennsylvania	30-gallon drum
• xylene (Chemsol Diluent-C)	American Minechem Coriopolis, Pennsylvania	55-gallon drum

Because float-sink operations are routinely carried out over specific gravities that range from about 1.30 to 1.80, stock test solutions in appropriate specific gravity increments are pre-made and stored for use and reuse in the work area. Test solutions at specific gravities below 1.60 are comprised of perchloroethylene and xylene; those above 1.60 are comprised of perchloroethylene and ethylene dibromide, while those at 1.60 are primarily perchloroethylene. At the time of the survey, the laboratory had approximately 80 gallons of premixed and unmixed solvent on hand for fine and intermediate float-sink operations in the new project laboratory. There were approximately 13 six-gallon capacity covered stainless steel containers with test solutions at specific gravities of from 1.30 to 2.00 and three (3) five-gallon drums containing pure solutions of perchloroethylene, EDB and xylene (see Figure 2).

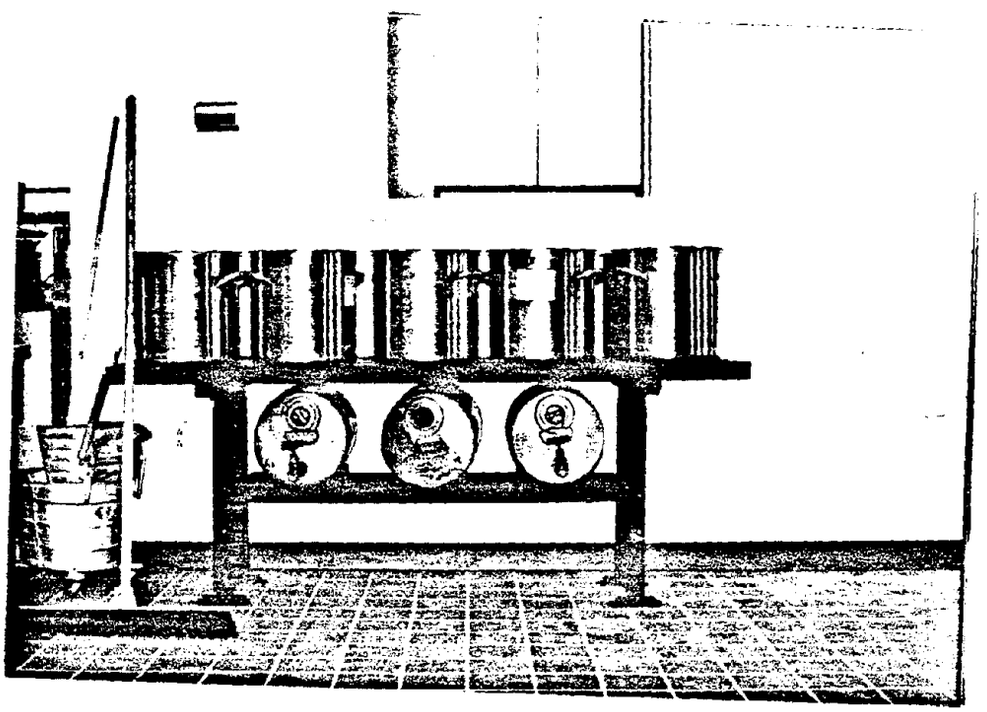


Figure 2. Solvent Storage for Fine and Intermediate Float-Sink Operations

EXPOSURE HAZARDS

Both chemical toxicity and degree of exposure (e.g., amount used) have to be evaluated when considering exposure hazards for this operation. Table 1 shows the Federal OSHA Permissible Exposure Limits (PELs) for the three solvents of concern and other relevant exposure information.

In terms of quantity used, perchloroethylene, with a specific gravity of about 1.60, is the most significant. Although the current Federal OSHA standard for perchloroethylene is 100 ppm (TWA), NIOSH has published in the 1976 Criteria Document on perchloroethylene a recommended permissible exposure level of 50 ppm averaged over a workshift of up to 10 hours, with a ceiling of 100 ppm averaged over a 15-minute period. In 1978, NIOSH further recommended that it is prudent to handle perchloroethylene as if it were a human carcinogen. This recommendation was based on the results of a National Cancer Institute study that indicated perchloroethylene causes liver cancer in laboratory mice.

Ethylene dibromide (EDB) and xylene are probably used in about the same quantities over a period of time. They are not used as frequently or in as large quantities as perchloroethylene.

Although the Occupational Safety and Health Administration's (OSHA) current standard for work exposure to EDB is 20 ppm as a time-weighted average (TWA) concentration, with an acceptable ceiling concentration of 30 ppm, since 1977 NIOSH has recommended in a Criteria Document for EDB that occupational exposure be limited to a ceiling concentration of 0.13 ppm as determined over any 15-minute sampling period. NIOSH concluded that chronic occupational exposure to EDB poses a serious hazard that may result in an increased risk of adverse reproductive, carcinogenic and other effects (liver, kidneys, heat and other internal organs and systems). In California, EDB has been regulated as a carcinogen since 1981 with a PEL of 0.13 ppm as a TWA and ceiling concentration.

Xylene vapor is principally an irritant to eyes, nose and throat. Because its irritating properties are perceivable at air concentrations less than three times the permissible exposure limit, it is considered to have fairly good warning properties. However, olfactory fatigue does occur rapidly. At high exposure concentrations xylene can produce anorexia, nausea, vomiting, and abdominal pain, as well as chemical narcosis. As with the other two solvents, the liquid is a skin irritant capable of causing eryethema, dryness and defatting. Additionally, contact with the liquid is a potential contributor to overall work exposure by dermal absorption.

TABLE 1. EXPOSURE INFORMATION FOR FLOAT-SINK SOLVENTS

	EDB	*Perchloroethylene*	*Xylene*
Vapor Pressure (mmHg) @ 20°C	*11*	*14*	*7/9/9 (ortho-, meta-, para-)*
Dermal Hazard	*yes*	*yes*	*yes*
Potential Carcinogen	*yes*	*yes*	*no*
PEL	*20 ppm*	*100 ppm* *200 ppm (ceiling)* *300 ppm (max. peak)*	*100 ppm*

WORK FORCE

Currently, there are two employees assigned to the 'new project lab'. Each is classified as a laboratory technician and each has interchangeable job responsibilities, which include performing laboratory float-sink separations, wet coal screening, and selected analytical testing. The testing performed routinely involves determining grindability, froth flotation efficiency and percent (consumption) magnetite. Overall, the level of effort devoted to each of these activities for an average work week has been estimated as follows:

Activity	Level of Effort (days per week)	Estimated man-hours per week*
Float Sink Operations	3	48
Wet Coal Screening	1 1/2	24
Analytical Testing	1/2	8

* Based on employment of 2 laboratory technicians in this work area.

Based on an estimate that approximately seventy-five percent of the float-sink testing performed for a given week is fine coal work, the average man-hour effort spent performing fine vs. intermediate size coal separations is given as:

Float - Sink Operation	Average Man - Hour Effort/Week
fine coal	36 hours
intermediate	12 hours

ENGINEERING CONTROL MEASURES

Engineering control measures are used as the primary means for limiting worker exposure to solvent vapors in fine and intermediate laboratory float-sink operations. At Facility 4, the principal control techniques employed are enclosure, mechanical exhaust ventilation and general environmental control of the workplace. At present, two mechanically ventilated enclosures (laboratory hoods) are used in the new project laboratory for controlling potential emissions from fine and intermediate float-sink operations. Figures and illustrate the two hoods in use. A notable difference between the two hoods is the sunken basin that has been incorporated into the design of hood No. 2 to accomodate the larger separatory vessels and space requirements necessary for processing intermediate coal samples. A design limitation noted for this hood was the lack of a basin-level exhaust to remove settled vapors.

Results of ventilation measurements taken for these two hoods showed the average face velocity for the fine coal float-sink operation hood (No. 1) was approximately 55 feet per minute (fpm) while the average face velocity for the intermediate float-sink operation hood (No. 2) was approximately 82 fpm. For control of high toxicity materials (TLV $\leq$ 10 ppm) in laboratory hoods, the American Conference of Governmental Industrial Hygienists (ACGIH) has recommended a hood exhaust volume of 150 cubic feet of air per minute per square foot of door area (150 cfm/sq.ft. of door area). This is equivalent to an average hood face velocity of 150 fpm.

The laboratory is also equipped with three ovens used for drying fine coal samples after coal washing. Each is fitted with a passive exhaust which is vented directly to the outdoors. The ovens in use are relatively new, with seals that appear to be in reasonably good shape. Overall the degree of control employed appears effective.

General room ventilation is provided in the new project lab by a HVAC (heating, ventilating and air conditioning) mechanical air supply system. The system maintains a controlled environment throughout the work area. The system provides both replacement air to the room and air temperature and humidity control. It is a recirculating system with a make-up air supply of about 25 percent by volume. Air is supplied to the room uniformly by multiple diffusers.

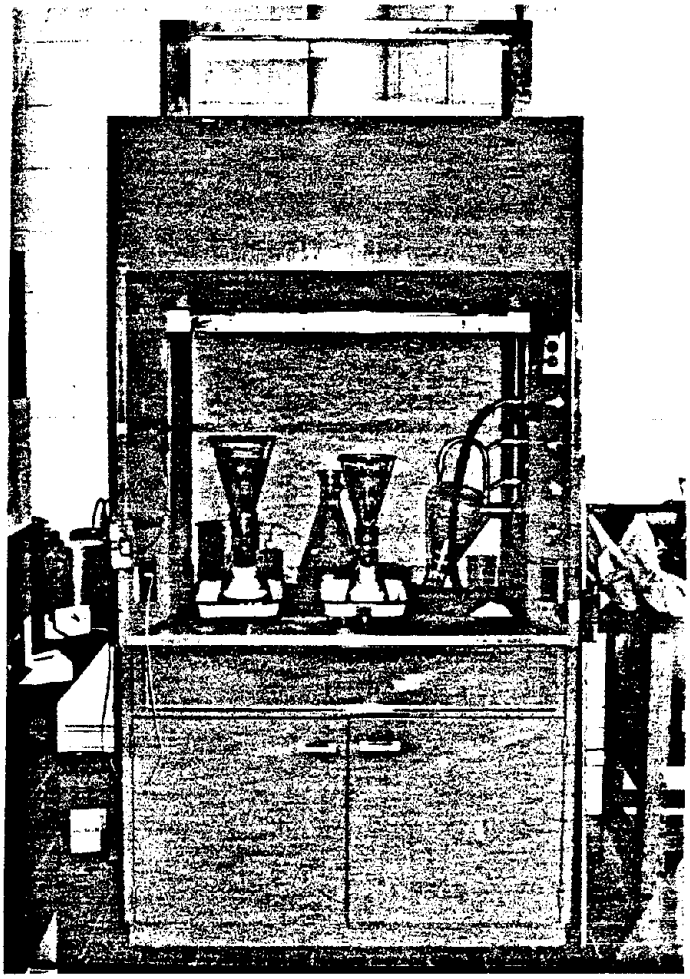


Figure 3.
Fine Coal Float-Sink
Hood (No. 1)

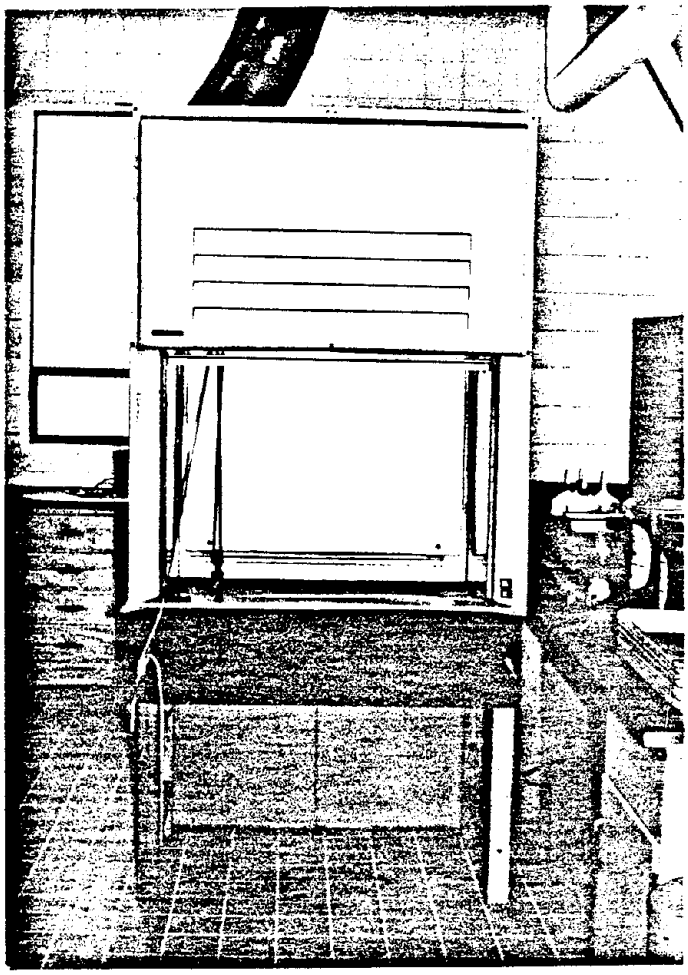


Figure 4.
Intermediate Float-Sink
Hood (No. 2)

MEDICAL, INDUSTRIAL HYGIENE, AND SAFETY PROGRAM

The only medical assistance available on-site is general first-aid administered by supervisory personnel. Pre-employment examinations are not currently given. There is currently no formal health or safety program in effect. Matters concerning safety and health are presently handled by laboratory supervisors. Although no formal program is in effect, periodic meetings on materials safety, chemical storage and handling and topics of concern are held on a lab by lab basis. Direction and implementation of acceptable safety and work practices, in conjunction with employee training, is the responsibility of laboratory supervisors in each work area.

The personal protective equipment currently available to employees in the new project lab, specifically for float-sink operations, includes safety glasses, protective gloves (elbow length), protective aprons (bib type), face shields and half-mask chemical respirators. Use of protective equipment is at the employee's option. However, employees are advised of the preferred protective equipment for each job and strongly encouraged to adhere to accepted work and safety practices. The laboratory does not presently have a written program on respiratory protection.

All injuries that occur on the job, no matter how minor, are reported promptly to an employee's immediate supervisor. Emergency treatment of serious injuries is obtained at the local county hospital.

The laboratory's approach to health and safety for laboratory F-S operations over the past five years has been consistent. The company has emphasized employee training (use of appropriate work practices) and the use of appropriate personal protective equipment as important means for limiting potential worker exposure to chemical solvents and other work hazards.

FACILITY 5: DESCRIPTION OF FACILITY AND FLOAT-SINK OPERATIONS

GENERAL INFORMATION

Facility 5, which is located in Clarksburg, West Virginia, is a full service commercial laboratory that performs a full range of coal analyses routinely required by the coal industry, including tests such as:

- ash
- moisture
- volatile matter
- Btu value
- fixed carbon
- fusion
- free swelling index
- sulfur
- sulfur forms

and most important, in terms of the scope of this Task Order:

- coal washabilities or laboratory float-sink testing

Although the company has been in business in the Clarksburg area since 1957, it has only been located in its present address since June, 1981.

The laboratory is housed in an L-shaped, split-level, facility that provides approximately 6500 square feet of usable floor space for four departments. These are: coal preparation, wet-sizing (float-sink), analytical testing and administrative support. Coal preparation and wet-sizing are set up in one wing of the facility (the two story wing) and analytical testing and administrative support are set up in the other (the single story wing). The facility is constructed essentially of cement block and prefabricated steel (See Figure 1).

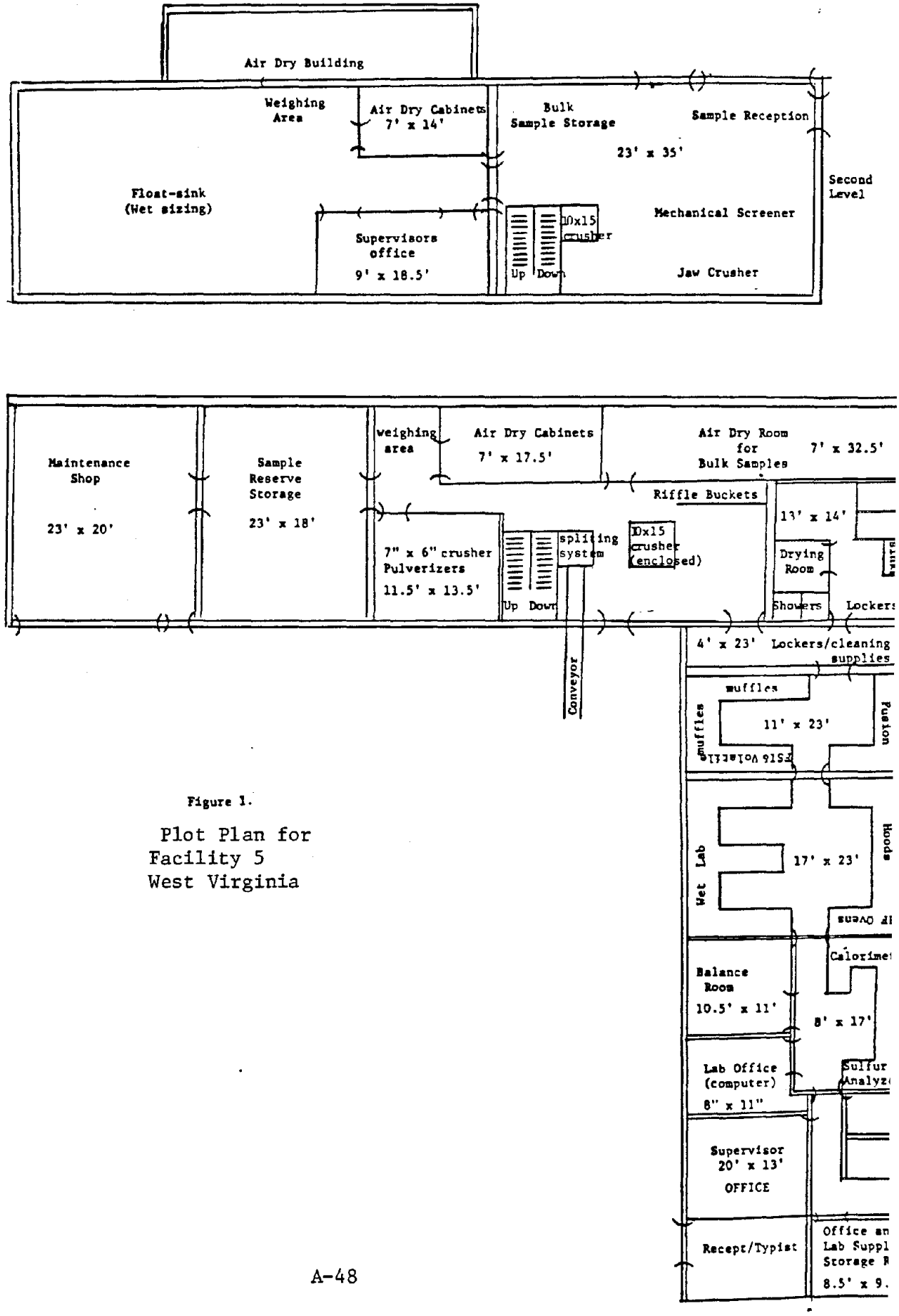


Figure 1.

Plot Plan for
Facility 5
West Virginia

LABORATORY FLOAT-SINK OPERATIONS

Float-sink operations are carried out in the "wet-sizing" work area, which covers about 900 square feet of floor space (See Figure 2). Operations are set up at three work stations. Separations are carried out in cabinet-like enclosures equipped with floor level, down-draft exhaust ventilation. Basically the three work stations are separated into float-sink operations for coarse, intermediate and fine coal samples.

The testing methods involved at each operation are similar and basically involve: sample immersion, float-coal recovery, reimmersion of the sink material and repetition of the procedure until the required sample fractions have been obtained. At each step recovered fractions must be carefully drained of excess liquid and set aside for drying and subsequent analysis. Separations are usually carried out by a single technician at individual work stations.

Sample drying is carried out in two areas set off from the main work area. Bulk or coarse coal samples are dried in the Air Dry Building, a room about 32 feet x 7-1/2 feet in area. The Air Dry Building is constructed of pre-fabricated steel paneling. It is heated by passive solar energy and auxiliary gas heaters. It is also equipped with general mechanical exhaust ventilation. Small or fine coal samples are dried in air-drying cabinets in a room about 14 feet x 7-1/2 feet in size. Like the large sample drying area, this room is also equipped with general mechanical exhaust ventilation. However, unlike the large sample drying area, this room lacks make up air inlets which would improve both air exchange and exhaust efficiency.

Prior to 1981, the float-sink operations were quite different than those described above. Downdraft tables were used for fine and intermediate operations, while ventilated cabinets were used for bulk wash operations. While the actual work procedures and solvents were similar, it was the impression of employees questioned during the survey that the amount of float-sink work in the past was greater than the current workload.

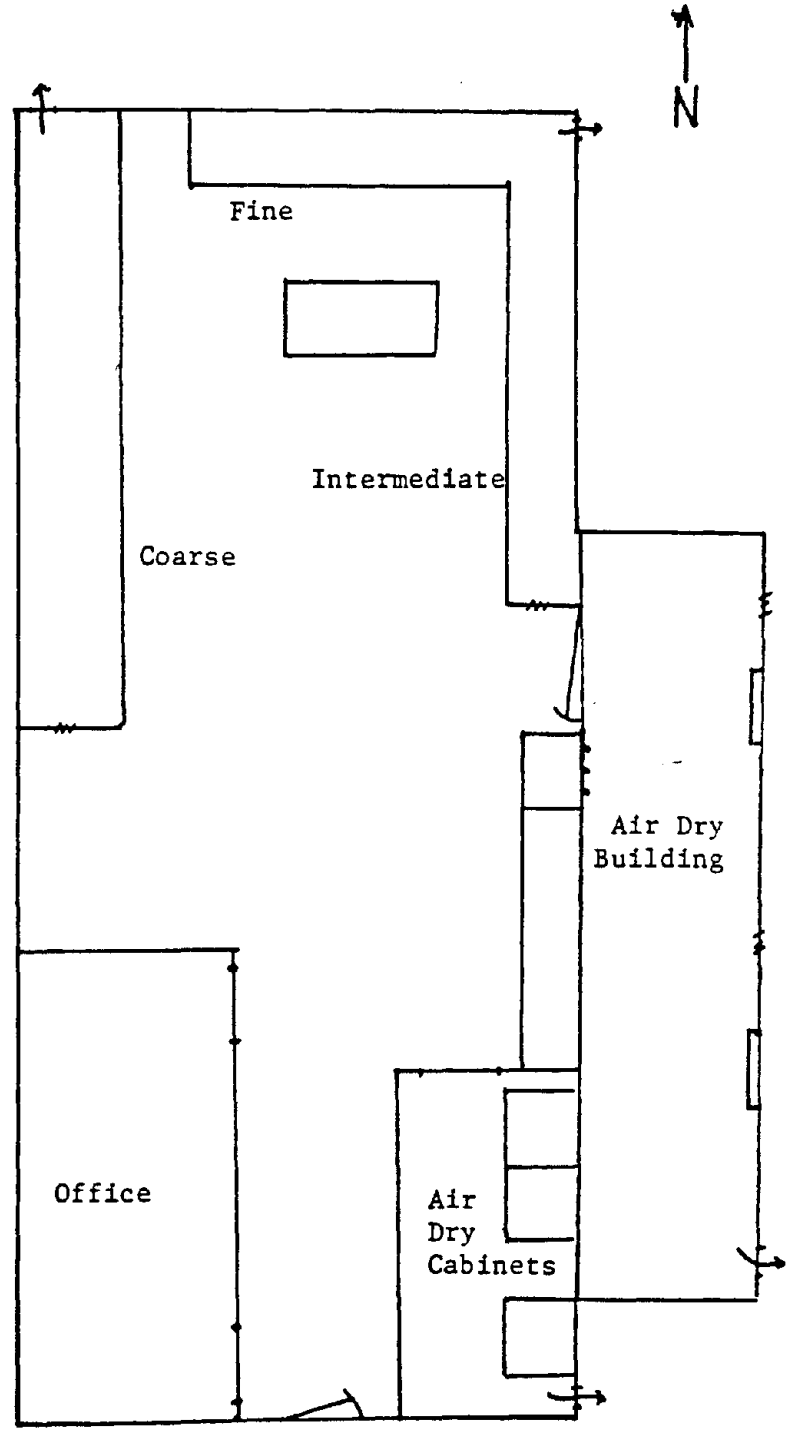


Figure 2.

Washability Laboratory
Float-Sink (Wet-Sizing)

CHEMICALS USED IN LABORATORY FLOAT-SINK OPERATIONS

Three chemicals are used to make up the necessary test solutions for coal fractionation; these are:

- Perchloroethylene
- Ethylene dibromide (EDB)
- VM&P naphtha

Test solutions at pre-made specific gravities, over the normal range of float-sink separations (i.e., 1.40, 1.45, 1.50, 1.55, 1.60 and 1.70) are stored in covered containers in the bulk coarse and intermediate float-sink enclosures. At the time of the survey, there were about 10 to 12 5-gallon containers of test solution on-hand for fine and intermediate float-sink operations and about 5 to 6 6-gallon containers of test solution on-hand for bulk coarse coal operations.

Bulk quantities (55-gallon drums) of each solvent are stored in a chemical repository about 16-1/2 feet x 8 feet in area, located beneath the Air Dry Building. Each chemical is dispensed to the work area above by means of a closed-line pumping system. The dispensing area is situated in the Air Dry Building where it is isolated from the general washability work area but accessible. Additionally, it is in an area equipped with mechanical exhaust ventilation to minimize environmental exposure concentrations of solvents in the room.

EXPOSURE HAZARDS

Both chemical toxicity and degree of exposure (e.g., amount used) have to be evaluated when considering exposure hazards for this operation. Table 1 shows the Federal OSHA Permissible Exposure Limits (PELs) for the three solvents of concern and other relevant exposure information.

In terms of quantity used, perchloroethylene, with a specific gravity of about 1.60, is the most significant. Although the current Federal OSHA standard for perchloroethylene is 100 ppm (TWA), NIOSH has published in the 1976 Criteria Document on perchloroethylene a recommended permissible exposure level of 50 ppm averaged over a workshift of up to 10 hours, with a ceiling of 100 ppm averaged over a 15-minute period. In 1978, NIOSH further recommended that it is prudent to handle perchloroethylene as if it were a human carcinogen. This recommendation was based on the results of a National Cancer Institute study that indicated perchloroethylene causes liver cancer in laboratory mice.

Ethylene dibromide (EDB) and naphtha are probably used in about the same quantities over a period of time. They are not used as frequently or in as large quantities as perchloroethylene.

Although OSHA's current standard for work exposure to EDB is 20 ppm as a TWA concentration with an acceptable ceiling concentration of 30 ppm, since 1977 NIOSH has recommended in a Criteria Document that occupational exposure be limited to a ceiling concentration of 0.13 ppm as determined over any 15-minute sampling period. NIOSH concluded that chronic occupational exposure to EDB poses a serious hazard that may result in an increased risk of adverse reproductive, carcinogenic and other effects (liver, kidneys, heart and other internal organs and systems). In California, EDB has been regulated as a carcinogen since 1981 with a PEL of 0.13 ppm as a TWA and ceiling concentration.

VM&P naphtha is regarded principally as a sensory irritant capable of affecting the eyes and throat. VM&P naphtha produces olfactory fatigue in airborne concentrations ranging from 140-880 ppm. Few studies in the literature report effects from dermal exposure to VM&P raphtha. However, since it

TABLE 1. EXPOSURE INFORMATION FOR FLOAT-SINK SOLVENTS

	EDB	PERCHLOROETHYLENE	VM&P NAPHTHA
Vapor Pressure (mmHg) @ 20°C	11	14	2-20
Dermal Hazard	yes	yes	yes
Potential Carcinogen	yes	yes	no
Exposure Guidelines (ppm)			
A) OSHA Standard			
TWA	20	100	500* (2000
Ceiling	30	200	----
Peak	50 (5 minutes)	300 (5 min/3-hr period)	----
B) NIOSH Recommended Limits			
TWA	---	50	**(350 m
Ceiling	0.13	100	---
C) ACGIH Threshold Limit Values			
TWA	A2***	50	300
STEL	A2***	---	400

*Petroleum distillates (naphtha)

**ppm varies from 75-100 ppm according to the mean molecular weight of the VM&P naphtha mixture (typically from 87 to 114).

***A2 Classification. "Industrial Substance Suspect of Carcinogenic Potential For Man. Chemical substance or substances associated with industrial processes, which are suspect of inducing cancer hazard on either (1) limi epidemiological evidence, exclusive of clinical reports of single cases, (2) demonstration of carcinogenesis in one or more animal species by approx. methods."

is a refined petroleum product similar to stoddard solvent and mineral spirits, which are considered primary irritants, VM&P naphtha is also considered a dermal irritant.

The current Federal occupational health standard for VM&P naphtha is defined under petroleum distillates (naphtha) as 500 ppm (2000 mg/m^3) determined as an 8-hour TWA concentration. NIOSH has recommended an identical limit for all common petroleum solvents, which is defined on a weight basis, of 350 mg/m^3. For VM&P naphtha, which has a mean molecular weight range of from 87 to 114, the NIOSH recommended TWA ranges in ppm from about 75 to 100 ppm. The NIOSH limit is designed for up to a 10-hour workshift, 40-hour workweek. The NIOSH limit is believed to be sufficiently low to prevent sensory irritation (eye and throat) and long-term toxicity. The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned VM&P naphtha a TLV-TWA of 300 ppm and a TLV-STEL (short-term exposure limit) of 400 ppm. The STEL is the maximum allowable concentration, or ceiling, which should not be exceeded at any time during the 15-minute excursion period. As many as four excursions up to the STEL are permissible in a day provided there are at least 60 minutes between each exposure and the daily TLV-TWA is not exceeded.

WORK FORCE

While overall there are 27 employees who work on-site,

- 1 Division Manager
- 1 Assistant Division Manager
- 1 Branch Manager
- 3 Office Personnel
- 14 Workers in sampling and preparation
- 4 Laboratory Technicians
- 3 Float-Sink Technicians

27

at the time of the detailed survey, there were actually only three employees assigned to the Coal Washability Department. Those assigned included a departmental supervisor or foreman and two laboratory float-sink or coal washability technicians. Following is a brief description of the activities of these full-time shift personnel.

- Washability Supervisor (1) is responsible for overall departmental production activities, including production scheduling, man-power allocation and other supervisory functions. Occasionally, he will also assist with some production tasks such as sample weigh-in, sample tagging and clean coal preparation. The current supervisor has been with the company and involved with laboratory float-sink for six years.

- Laboratory Float-Sink or Coal Washability Technicians (2) are responsible for production output. Their job responsibilities primarily involve coal screening, laboratory float-sink and clean coal sample preparation. For a typical work week the amount of time a technician spends among each of these functions is estimated as:

  - 15 percent for screening
  - 65 percent for laboratory float-sink (coal washing)
  - 20 percent for clean coal sample preparation

The two technicians involved with float-sink at the time of the survey had been with the company and involved with coal fractionation for 8 years and less than 1 year, respectively.

The current work schedule in coal washabilities is a 5-day, 40-hour work week. The shift schedule is from 8:00 A.M. to 4:00 P.M. A thirty-minute lunch break is taken around noon depending on work in progress.

ENGINEERING CONTROL MEASURES

Engineering controls are emphasized as the primary means for limiting worker exposure to the chemical solvents used in float-sink operations. Figure 3 provides an illustration of this. Each operation is carried out in a cabinet-like enclosure that is equipped with either floor level or downdraft exhaust ventilation. Additionally, each enclosure is designed with a fresh air supply system that provides both make up air to the exhaust system and enhanced directional air flow into the enclosure away from the breathing zone of the worker.

There are two units which provide exhaust ventilation to the various float-sink enclosures in use. One unit provides exhaust ventilation for the bulk or coarse coal float-sink set-up; the second unit provides ventilation exhaust for both the fine and intermediate float-sink enclosures. The exhaust ventilation blowers in use for each of these two system are:

Dayton Non-Overloading Blowers Model No. 6K-272-F
with an:
- 18-1/4" wheel
- 1-1/2 H.P. motor
- 1310 Blower RPM

the exhaust air discharge rating is:
- 4910 CFM

There are also two separate blower units which provide supply air to the bulk or coarse coal operation and the fine and intermediate set-ups. These blowers bring in outside air in conjunction with the operation of two identical 100,000 BTU furnace units and have been utilized to deliver

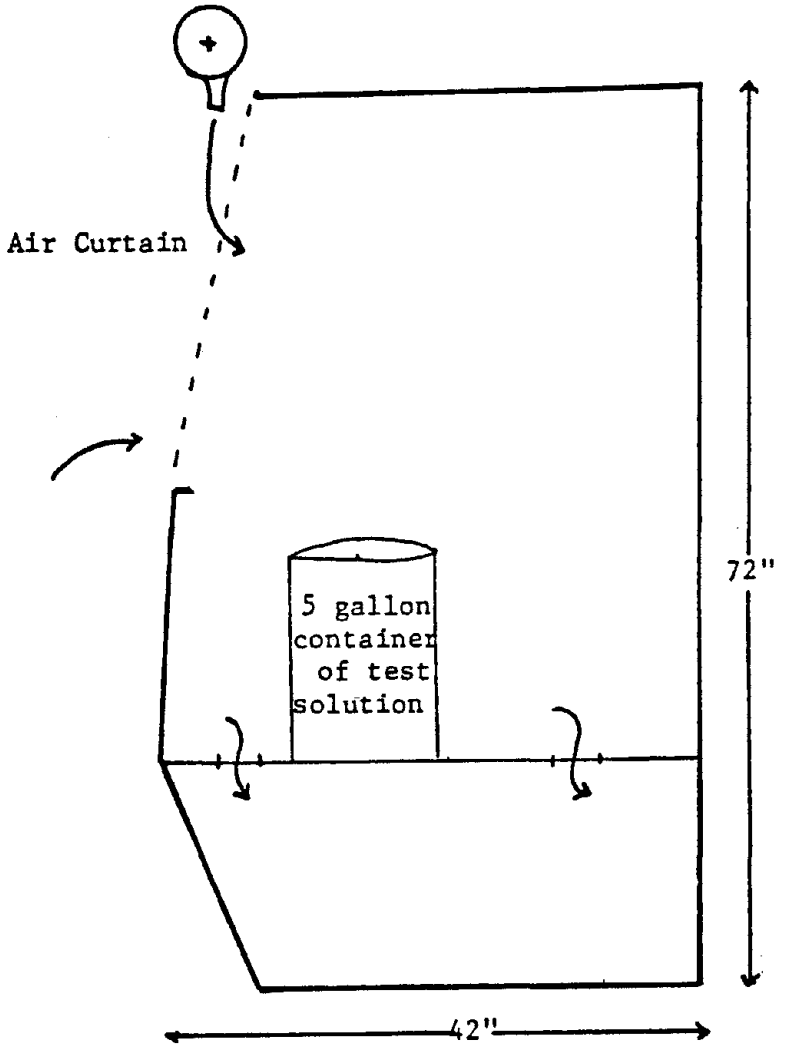


Figure 3

Fine and Intermediate
Float-Sink Enclosure
Design (sideview)

make-up air to the face of each float-sink enclosure. The air flow for each system is estimated at approximately 1300 cfm.

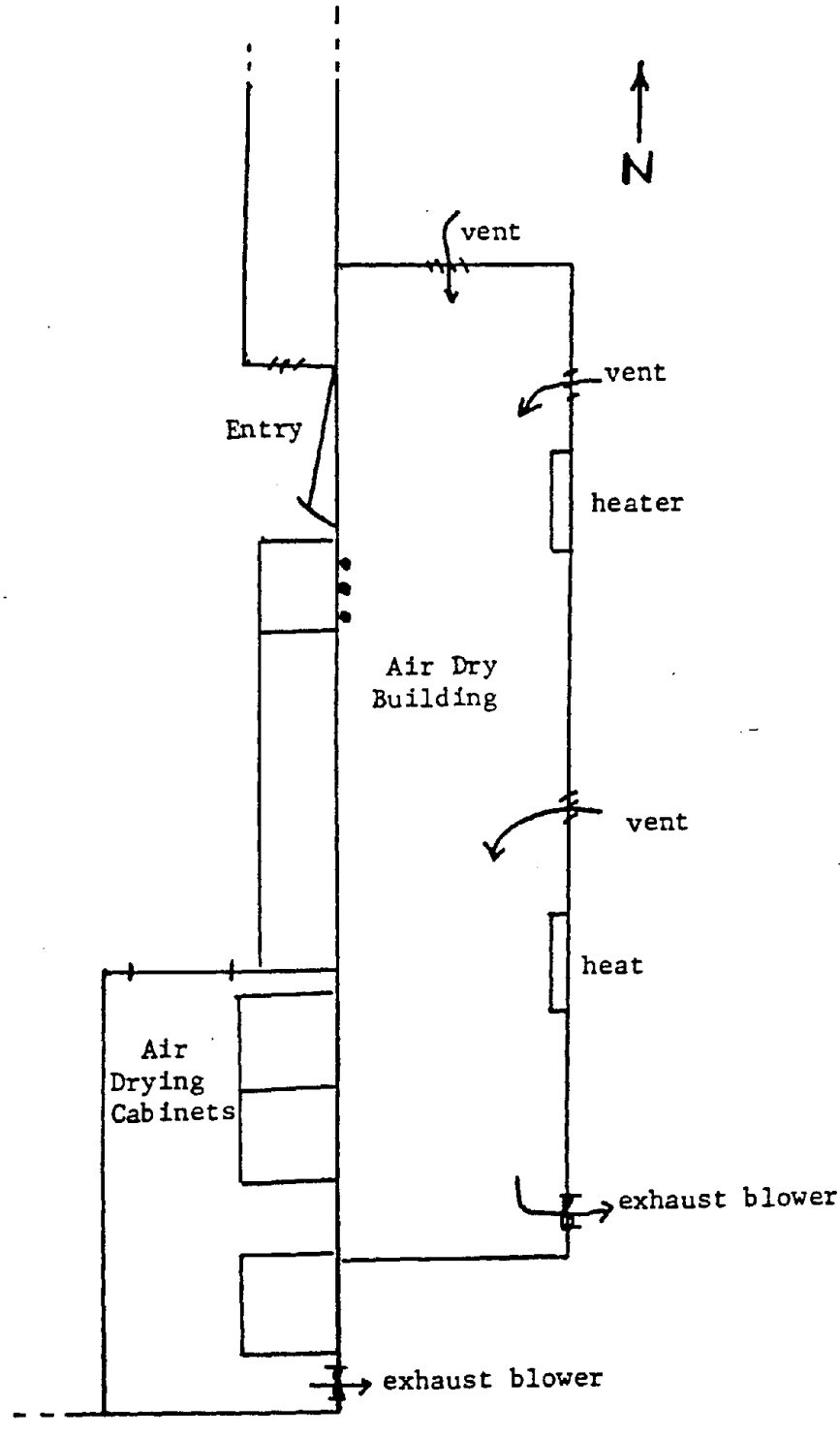
To minimize occupational exposure to solvent vapors during sample drying and solvent dispensing, the laboratory has set up two isolation areas: one for bulk or coarse coal samples, another for small or fine coal samples. The Air Dry Building (for bulk or coarse coal samples) is about 32 feet x 7-1/2 feet in area. It is constructed of prefabricated steel siding and is heated by passive solar energy and two auxiliary gas heaters. Make up air to the room is provided by three strategically placed air inlets. With the location of an 8-inch floor level exhaust in the southeast corner of the drying area, the general room air flow is away from the room entry (See Figure 4). The approximate discharge rate for the exhaust is 1150 cfm.

The air drying cabinet room is about 14 feet x 7-1/2 feet in size. It houses three air drying cabinets for drying fine coal samples. These cabinets are not equipped with local exhaust ventilation controls. To reduce the airborne concentration of solvent vapors, Commercial Testing and Engineering has installed an 8" floor level exhaust blower similar to the one used for the Air Dry Building. However, unlike the Air Dry Building, this room lacks a suitable inlet for make up air. The measured exhaust discharge on the 8" blower reflected this, with a discharge of only about 350 cfm as compared to 1150 cfm for the Air Dry Building.

MEDICAL, INDUSTRIAL HYGIENE AND SAFETY PROGRAMS

There is currently no medical surveillance program in effect for those Facility 5 employees involved with laboratory float-sink operations. While workers do submit responses to a routine medical questionnaire upon employment, employees are not presently given either pre-employment or periodic physical exams for work-related reasons. The medical assistance available on-site is limited to first-aid administered by supervisors. Emergency medical care is available at a nearby city hospital.

Figure 4 Airflow Through Air Dry Building



Industrial hygiene monitoring is carried out infrequently at these operations. Previous monitoring has involved qualitative use of detector tubes for solvent vapors. However, historical monitoring data on the results of these tests was unavailable.

The safety program in effect is carried out by departmental supervisors and a laboratory safety supervisor (part-time). Employees are provided with a written Safety Practices Manual, which covers general on the job safety practices as well as safety rules for coal preparation and laboratory float-sink operations. The program emphasizes hazard awareness and the use of personal protective equipment. Administrative measures were noted which restricted the use of ethylene dibromide in test solutions below 1.60 and required that float-sink operations be performed only when at least two employees ("buddy-system") are present in the work area.

Use of personal protective equipment is also emphasized. Current use includes safety shoes, safety glasses, face-shields, protective gloves and aprons, protective rubber boots and chemical cartridge organic vapor respirators. Equipment sets are issued to each employee and are stored in individual equipment lockers. As part of the safety program, employees are provided appropriate instruction in the proper use, maintenance and sanitation of respiratory protection. Training emphasizes how to obtain a correct fit with equipment and how to recognize expiration of the organic vapor cartridges.

As part of an effective occupational safety and health program, the laboratory has an established program of sanitation and housekeeping. Routine work area cleaning is a daily activity. Floors and walkways are kept dry and clean; exits are kept clear. Spills are cleaned up promptly. Inspection of facilities to identify unsanitary conditions is the responsibility of individual departmental supervisors and a laboratory housekeeping supervisor.

APPENDIX B

SAMPLING AND ANALYTICAL METHODS

B1. TRACE METALS (MODIFIED FOR ICPAES)
NIOSH METHOD NO. P&CAM 173

B2. METHYLISOBUTYL CARBINOL (MIBC)
NIOSH METHOD NO. S60

B3. DOWFROTH M-222, PERCHLOROETHYLENE, VM&P NAPHTHA AND XYLENE
NIOSH METHOD NO. P&CAM 127

B4. ETHYLENE DIBROMIDE (1,2-DIBROMOETHANE)
NIOSH METHOD NO. 260

APPENDIX B1

GENERAL PROCEDURE FOR METALS

Measurements Research Branch

Analytical Method

Analyte:	Trace Metals (Tables 1 and 2)	**Method No.:**	P&CAM 173
Matrix:	Air	**Range:**	Varies with analyte (Table 2)
Procedure:	Filter collection, atomic absorption analysis	**Precision:**	3% RSD (Analytical)
Date Issued:	9/17/73		
Date Revised:	3/11/77	**Classification:**	D (Operational)

1. Principle of the Method

1.1 This procedure describes a general method for the collection, dissolution and determination of trace metals in industrial and ambient airborne material. The samples are collected on membrane filters and treated with nitric acid to ash the organic matrix and to dissolve the metals present in the sample. The analysis is subsequently made by atomic absorption spectrophotometry (AAS).

1.2 Samples and standards are aspirated into the appropriate AAS flame. A source of characteristic radiation energy is necessary for each metal. The absorption of this characteristic energy by the atoms of interest in the flame is related to the concentration of the metal in the aspirated sample. The flames and operating conditions for each element are listed in Table 1.

2. Range and Sensitivity

The sensitivity, detection limit, and optimum working range for each metal are given in Table 2. The sensitivity is defined as that concentration of a given element which will absorb 1% of the incident radiation (0.0044 absorbance units) when aspirated into the flame. The detection limit is defined as that concentration of a given element which produces a signal equivalent to two times the standard deviation of the blank signal for aqueous solutions. Detection limits and blank values for real samples may be greater than those given in Table 2 since the blanks resulting from the reagents and the filter material have not been taken into account. The working range for an analytical precision better than 3% is generally defined as those sample concentrations which will absorb greater than 10% of the incident radiation and are in the linear region of the calibration curve. The values for the sensitivity and detection limits are instrument dependent and may vary from instrument to instrument.

3. Interferences

3.1 In atomic absorption spectrophotometry, the occurrence of interference is less common than in many other analytical determination methods. Interferences can occur, however, and when encountered are corrected for as indicated in the following sections. The known interfer-

ences and correction methods for each metal are indicated in Table 1. The methods of standard additions and background monitoring and correction (11.1-11.4) are used to identify the presence of an interference problem. Insofar as possible, the matrix of the samples and standards are matched to minimize the possible interference problems.

3.1.1 Background or non-specific absorption can occur from particles produced in the flame which can scatter the incident radiation causing an apparent absorption signal. Light scattering problems may be encountered when solutions of high salt content are being analyzed. Light scattering problems are most severe when measurements are made at the lower wavelengths (i.e., below about 250 nm). Background absorption may also occur as the result of the formation of various molecular species which can absorb light. The background absorption should be accounted for by the use of background correction techniques (use of D_2 or H_2 continuum or a nearby non-absorbing wavelength) (11.1, 11.6).

3.1.2 Spectral interferences are those interferences which occur as the result of an atom different from that being measured absorbing a portion of the incident radiation. Such interferences are extremely rare in atomic absorption. In some cases, multi-element hollow cathode lamps may cause a spectral interference by having closely adjacent radiation lines from two different elements. In such instances, multi-element hollow cathode lamps should not be used, or the use of more narrow spectral slits or alternate wavelengths may be used to alleviate the problem.

3.1.3 Ionization interferences can occur when easily ionized atoms are being measured. The degree to which such atoms are ionized is dependent upon the atomic concentration and presence of other easily ionized atoms in the sample. Ionization interferences can be controlled by the addition to the sample of a high concentration of another easily ionized element which will buffer the electron concentration in the flame. Typically, 1000 to 2000 μg/ml of an alkali metal (K, Na, Cs) salt is added to sample and standard solutions.

3.1.4 Chemical interferences occur in atomic absorption spectrophotometry when species present in the sample cause variations in the degree to which atoms are formed in the flame. Such interferences may be corrected for by controlling the sample and standard matrix, by using the method of standard additions, or by use of a higher temperature flame (11.2, 11.6).

3.1.5 Physical interferences may result if the physical properties of the samples vary significantly. Changes in viscosity and surface tension can affect the sample aspiration rate and thus cause erroneous results. Sample dilution and/or the method of standard additions are used to correct such interferences. High concentrations of silicates in the sample can cause an interference for many of the elements and may cause aspiration problems. No matter what elements are being measured, if large amounts of silicates are extracted from the samples, the samples should be allowed to stand for several hours and centrifuged or filtered to remove the silicates.

3.2 This procedure describes a generalized method for sample preparation which is applicable to the majority of samples of interest. There are, however, some relatively rare chemical forms of a few of the elements listed in Table 1 which will not be dissolved by this procedure. If such chemical forms are suspected, results obtained using this procedure should be compared with those obtained using an appropriately altered dissolution procedure. Alternatively, the results may be compared with values obtained utilizing a non-destructive technique which does not require sample dissolution (e.g., X-ray fluorescence, activation analysis).

4. Precision and Accuracy

4.1 The relative standard deviation of the analytical measurement is approximately 3% when measurements are made in the ranges listed in Table 2. The overall relative standard deviation will be somewhat larger than this value due to errors associated with the sample collection and preparation steps.

4.2 No data are presently available on the accuracy of this method for actual air samples.

5. Advantages and Disadvantages of the Method

5.1 The sensitivity is adequate for all metals in air samples provided an adequate volume of air is sampled.

5.2 A disadvantage of the method is that approximately 2 ml of solution is necessary for each metal determination. Also, the necessary dilution limits the detection of small quantities of analyte or replicate analysis of several elements per sample.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the collection of personal air samples has the following components:

6.1.1 The filter unit, consisting of the filter media (6.2) and appropriate cassette filter holder, either a 2- or 3-piece filter cassette (Millipore Filter Corporation, Bedford, Mass., or equivalent).

6.1.2 A personal sampling pump of sufficient capacity to maintain a face velocity of 2.6 cm/sec (1-2 lpm using a 37-mm filter). This pump must be calibrated so the volume of air sampled can be measured to an accuracy of $\pm$ 5%. The pump must be calibrated with a representative filter unit in the line.

6.1.3 Thermometer.

6.1.4 Manometer.

6.1.5 Stopwatch.

6.1.6 Various clips, tubing, spring connectors, and belt for connecting sampling apparatus to worker being sampled.

6.2 Cellulose ester membrane filter, 0.8-μm pore size, 37-mm (Millipore Type AA or equivalent).

6.3 Glassware, borosilicate. Before use, all glassware must be cleaned in 1:1 diluted nitric acid and rinsed several times with distilled water.

6.3.1 125-ml Phillips or Griffin beakers with watch glass covers.

6.3.2 15-ml graduated centrifuge tubes.

6.3.3 10-ml volumetric flasks.

6.3.4 100-ml volumetric flasks.

6.3.5 1-liter volumetric flasks.

6.3.6 125-ml polyethylene bottles.

6.3.7 Additional auxiliary glassware such as pipettes and different size volumetric glassware will be required depending on the elements being determined and the dilutions required to have sample concentrations above the detection limit and in the linear response range (i.e., see Table 2). All pipettes and volumetric flasks required in this procedure should be calibrated class A volumetric glassware.

6.4 Hotplate (suitable for operation at 140°C).

6.5 Equipment for Analysis

6.5.1 Atomic absorption spectrophotometer, with burner heads for air-acetylene and nitrous oxide-acetylene flames.

6.5.2 Hollow cathode or electrodeless discharge lamps, for each metal and a continuum lamp (D_2 or H_2).

6.5.3 Two stage regulators, for air, acetylene, and nitrous oxide.

6.5.4 Heating tape and rheostat, for nitrous oxide regulator (second regulator stage and connecting hose to the instrument should be heated to approximately 60°C to prevent freeze-up).

6.6 Supplies

6.6.1 Acetylene gas (cylinder), of a grade specified by the manufacturer of the instrument employed. (Replace cylinder when pressure decreases below 100 psi.)

6.6.2 Nitrous oxide gas (cylinder).

6.6.3 Air supply, with a minimum pressure of 40 psi, filtered to remove oil and water.

7. Reagents

7.1 Purity. ACS analytical reagent grade chemicals or equivalent shall be used in all tests. References to water shall be understood to mean double distilled water or equivalent. Care in selection of reagents and in following the listed precautions is essential if low blank values are to be obtained.

7.2 Concentrated nitric acid (68-71%), redistilled, specific gravity 1.42.

7.3 Standard stock solutions (1000 μg/ml) for each metal in Table 1, commercially prepared or prepared per instrument manufacturer's recommendations.

7.4 Lanthanum nitrate [$La(NO_3)_3 \cdot 6H_20$].

7.5 Cesium nitrate ($CsN0_3$).

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Before initial use, glassware is cleaned with a saturated solution of sodium dichromate in concentrated sulfuric acid (Note: Do not use for chromium analysis) and then rinsed thoroughly with warm tap water, concentrated nitric acid, tap water, and deionized water, in that order, and then dried.

8.1.2 All glassware is soaked in a mild detergent solution immediately after use to remove any residual grease or chemicals.

8.1.3 For glassware which has previously been subjected to the entire cleaning procedure, it is not necessary to use the chromic acid cleaning solution.

8.2 Collection and Shipping of Samples

8.2.1 Ambient atmospheric particulate matter and industrial dusts and fumes are sampled with cellulose membrane filters. Sample flow rate is monitored with a calibrated rotameter (11.5) or the equivalent. The flow rate, ambient temperature, and barometric pressure are recorded at the beginning and the end of the sample collection period.

8.2.2 For personal sampling, 37-mm diameter filters in holders are used. The personal sampling pumps for this application are operated at 1.5 lpm. In general, a 2-hour

sample at 1.5 lpm will provide enough sample to detect the elements sought at air concentrations of 0.2 × TLV.

8.2.3 After sample collection is complete, plug the openings of the cassette and submit the sampling unit to the laboratory. Losses of sample due to overloading (>2 mg) of the filter must be avoided.

8.2.4 Filter samples should be sealed in individual plastic filter holders for storage and shipment.

8.3 Preparation of Samples

8.3.1 The samples and blanks (minimum of 1 filter blank for every 10 filter samples) are transferred to clean 125-ml Phillips or Griffin beakers and 6.0 ml HNO_3 is added. Antimony samples are ashed in 6.0 ml of a 5:1 mixture of HNO_3:H_2SO_4. Each beaker is covered with a watch glass and heated on a hot plate (140°C) in a fume hood until the sample dissolves and a slightly yellow solution is produced. Approximately 4 hours of heating will be sufficient for most air samples. However, subsequent additions of HNO_3 may be needed to completely ash and destroy high concentrations of organic material, and under these conditions longer ashing times will be needed. Once the ashing is complete as indicated by a clear solution in the beaker, the watch glass is removed and the sample is allowed to evaporate to near dryness (approximately 0.5 ml).

8.3.2 Remove the beaker from the hot plate, cool, and add 1 ml HNO_3 and 2-3 ml of distilled H_2O. For lead samples, concentrated HCl is used instead of HNO_3. The solution is quantitatively transferred with distilled water to a 10-ml volumetric flask. If any elements are being determined which require the ionization buffer, 0.2 ml of 50 mg/ml Cs is added to the volumetric flask (see Table 1, footnote d). If any elements requiring the releasing agent are being determined, 0.2 ml of 50 mg/ml La is added to each volumetric flask (see Table 1, footnote 3). The samples are then diluted to volume with water.

8.3.3 The 10-ml solution may be analyzed directly for any element of very low concentration in the sample. Aliquots of this solution may then be diluted to an appropriate volume for the other elements of interest present at higher concentrations. (Note: Approximately 2 ml of solution are required for each element being analyzed.) The dilution factor will depend upon the concentration of elements in the sample and the number of elements being determined by this procedure.

8.4 Analysis of Samples

8.4.1 Set the instrument operating conditions as recommended by the manufacturer. The instrument should be set at the radiation intensity maximum for the wavelength listed in Table 1 for the element being determined.

8.4.2 Standard solutions should match the sample matrix as closely as possible and should be run in duplicate. Working standard solutions, prepared fresh daily, are aspirated into the flame and the absorbance recorded. Prepare a calibration graph as described in Section 9.2.3. (Note: All combustion products from the AA flame must be removed by direct exhaustion through the use of a good separate flame ventilation system.)

8.4.3 Blank filters must be carried through the entire procedure each time samples are analyzed.

8.4.4 Aspirate the appropriately diluted samples directly into the instrument and record the absorbance for comparison with standards. Should the absorbance be above the calibration range, dilute an appropriate aliquot to 10 ml. Aspirate water between each sample. A mid-range standard must be aspirated with sufficient frequency (i.e.,

once every 5 samples) to assure the accuracy of the sample determinations. To the extent possible, all determinations are to be based on replicate analysis.

9. Calibration and Standards

9.1 Ionization and chemical interference suppressants

9.1.1 Lanthanum solution (50 mg/ml). Dissolve 156.32 g of lanthanum nitrate [$La(NO_3)_3 \cdot 6H_2O$] in 2% (v/v) HNO_3. Dilute to volume in a 1-liter volumetric flask with 2% (v/v) HNO_3. When stored in a polyethylene bottle, this solution is stable for at least one year.

9.1.2 Cesium solution (50 mg/ml). Dissolve 73.40 g of cesium nitrate ($CsNO_3$) in distilled water. Dilute to volume in a 1-liter volumetric flask with distilled water. When stored in a polyethylene bottle this solution is stable for at least one year.

9.2 Standard metal solutions

9.2.1 Dilute standards (100 μg metal/ml). Pipet 10 ml of the stock (1000 μg metal/ml; Section 7.3) into a 100-ml volumetric flask, add 10 ml HNO_3 and dilute to volume with distilled water. For antimony standards, 5 ml H_2SO_4 is added with the HNO_3. Lead standards require 10 ml HCl instead of 10 ml HNO_3. Prepare these standards fresh weekly. (Note: Silver standards must be stored in amber bottles away from direct light.)

9.2.2 Working standards. Working standards for each metal of interest are prepared by dilution of the dilute standards (9.2.1) or the stock standards (7.3) such that the final acid concentration is the same for the samples and standards (i.e., 10% v/v HNO_3 in most cases). Lanthanum or cesium is added to samples and standards as indicated in Table 1 such that the final concentration is 1000 μg La or Cs/ml. Concentrations of the working standards should cover the range for the metal of interest (Table 2). Prepare these solutions fresh daily.

9.2.3 The standard solutions are aspirated into the flame and the absorbance (or concentration) recorded. If the instrument used displays transmittance, these values must be converted to absorbance. A calibration curve is prepared by plotting absorbance (units) versus metal concentration. The best fit curve (calculated by linear least square regression analysis) is fitted to the data points. This line or the equation describing the line is used to obtain the metal concentration in the samples being analyzed.

9.2.4 To insure that the preparation procedure is being properly followed, clean membrane filters are spiked with known amounts of the elements being determined by adding appropriate amounts of the previously described standards and carried through the entire procedure. The amount of metal is determined and the per cent recovery calculated. These tests will provide recovery and precision data for the procedure as it is carried out in the laboratory for the soluble compounds of the elements being determined.

9.2.5 Analysis by the method of standard additions. In order to check for interferences, samples are initially and periodically analyzed by the method of standard additions and the results compared to those obtained by the conventional analytical determination. For this method the sample is divided into three 2-ml aliquots. To one of the aliquots an amount of metal approximately equal to that in the sample is added. To another aliquot twice this amount is added. (Note: Additions should be made by micropipetting techniques such that the volume does not exceed 1% of the original aliquot volume, i.e., 10 μl and 20 μl additions to a 2-ml aliquot.) The solutions are then analyzed and the absorbance readings are plotted against metal added to the

original sample. The line obtained from such a plot is extrapolated to 0 absorbance and the intercept on the concentration axis is taken as the amount of metal in the original sample (11.2). If the result of this determination does not agree to within 10% of the values obtained with the procedure described in section 9.2.3, an interference is indicated and standard addition techniques should be utilized for sample analysis.

10. Calculations

10.1 The uncorrected volume collected by the filter is calculated by averaging the beginning and ending sample flow rates, converting to cubic meters and multiplying by the sample collection time. The formula for this calculation is

$$V = \frac{(F_B + F_E)\, t}{2000}$$

where:

V = sample volume (m^3)

F_B = sample flow rate at beginning of sample collection (lpm)

F_E = sample flow rate at end of sample collection (lpm)

t = sample collection time (minutes)

10.2 After any necessary correction for the blank has been made, metal concentrations are calculated by multiplying the micrograms of metal per ml in the sample aliquot by the aliquot volume and dividing by the fraction which the aliquot represents of the total sample and the volume of air collected by the filter:

$$\mu g \text{ metal}/m^3 = \frac{(C \times V_A) - B}{V \times F}$$

where:

C = concentration (μg metal/ml) in the aliquot

V_A = volume of aliquot (ml)

B = total μg of metal in the blank

F = fraction of total sample in the aliquot used for measurement (dimensionless)

V = volume of air sampled (m^3)

11. References

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11.10 Analytical Data for Elements Determined by Atomic Absorption Spectroscopy, Varian Techtron, Walnut Creek, California, 1971.

11.11 Detection Limits for Model AA-5 Atomic Absorption Spectrophotometer, Varian Techtron, Walnut Creek, California, 1971.

Table 1. Instrument Parameters

Element	Type of Flame o = oxidizing r = reducing	Analytical Wavelength (nm)	Interferences[b]	Remedy[b]	References
Ag	Air-C_2H_2(o)	328.1	IO_3^-, WO_4^{-2}, Mn_4^{-2}	c	(5)
Al[a]	N_2O-C_2H_2(r)	309.3	Ionization, SO_4^{-2}, V, Fe, HCl, H_2SO_4	c,d,e	(4,6)
As	Air-C_2H_2(o)	193.7	Background absorption	g	(6)
Ba	N_2O-C_2H_2(r)	553.6	Ionization, large conc. of Ca	d,f	(1,4)
Be[a]	N_2O-C_2H_2(r)	234.9	Al, Si, Mn	c,g	(4)
Bi	Air-C_2H_2(o)	223.1		g	
Ca	Air-C_2H_2(r) N_2O-C_2H_2(r)	422.7	Ionization & chemical	d,e	(1,4)
Cd	Air-C_2H_2(o)	228.8		g	
Co[a]	Air-C_2H_2(o)	240.7		g	
Cr[a]	Air-C_2H_2(r)	357.9	Fe, Ni	c	(4)
Cu	Air-C_2H_2(o)	324.8			
Fe	Air-C_2H_2(o)	248.3	High Ni conc., Si	c,g	(1,4)
In	Air-C_2H_2(o)	303.9	Al, Mg, Cu, Zn, $H_3PO_4^{-3}$	c	(10)
K	Air-C_2H_2(o)	766.5	Ionization	d	(1,4)
Li	Air-C_2H_2(o)	670.8	Ionization	d	(11)
Mg	Air-C_2H_2(o) N_2O-C_2H_2(o)	285.2	Chemical Ionization	e d	(1,4)
Mn	Air-C_2H_2(o)	279.5			
Mo	N_2O-C_2H_2(r)	313.3	Ca and other ions	h	(6)
Na	Air-C_2H_2(o)	589.6	Ionization	e	(1,4)
Ni	Air-C_2H_2(o)	232.0		g	
Pb	Air-C_2H_2(o)	217.0 283.3	Ca, High conc. $SO_4^{=}$	c,g	(7)
Pd	Air-C_2H_2(o)	247.6	Al, Co, Ni, Pt, Rh, Ru	e	(6)
Rb	Air-C_2H_2(o)	780.0	Ionization	d	(1,8)
Sb	Air-C_2H_2(o)	217.6	Pb	i,g	(6)
Si	N_2O-C_2H_2(r)	251.6	Avoided by not using multi-element lamp containing Fe		
Sr	Air-C_2H_2(r) N_2O-C_2H_2(r)	460.7	Ionization & chemical	d,e	(1,8)
Te	Air-C_2H_2(o)	214.3		g	(6)
Tl	Air-C_2H_2(o)	276.8			
V[a]	N_2O-C_2H_2(r)	318.4			
Zn	Air-C_2H_2(o)	213.9		g	

a. Some compounds of these elements will not be dissolved by the procedure described here. When determining these elements one should verify that the types of compounds suspected in the sample will dissolve using this procedure. (See Section 3.2)

b. High concentrations of silicates in the sample can cause an interference for many of the elements in this table and may cause aspiration problems. No matter what elements are being measured, if large amounts of silicates are extracted from the samples, the samples should be allowed to stand for several hours and centrifuged or filtered to remove the silicates.

c. Samples are periodically analyzed by the method of additions to check for chemical interferences. If interferences are encountered, determinations must be made by the standard additions method or, if the interferent is identified, it may be added to the standards.

d. Ionization interferences are controlled by bringing all solutions to 1000 μg/ml Cs (samples and standards).

e. 1000 μg/ml solution of La as a releasing agent is added to all samples and standards.

f. In the presence of very large Ca concentrations (greater than 0.1%) a molecular absorption from $Ca(OH)_2$ may be observed. This interference may be overcome by using background correction when analyzing for Ba.

g. Use D_2 or H_2 continuum for background correction.

h. Add 1000 μg/ml Al to both standards and samples.

i. Use alternate Sb line (231.2 nm).

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APPENDIX B2

Methyl Isobutyl Carbinol

Analyte:	Methyl Isobutyl Carbinol	Method No.: S60
Matrix:	Air	Range: 45-175 mg/cu m
OSHA Standard:	25 ppm (105 mg/cu m)	Precision ($\overline{CV_T}$): 0.080
Procedure:	Adsorption on charcoal, desorption with eluent, GC	Validation Date: 1/17/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide containing 5% 2-propanol.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 45-175 mg/cu m at an atmospheric temperature and pressure of 25 C and 743 mm Hg, using a 10-liter sample. Under the conditions of sample size (10 liters) the probable range of this method is 10-300 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 2.5-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of the analyte and other substances in the air. The first section of the charcoal tube was found to hold at least 11.3 mg of the analyte when a test atmosphere of 237 mg/cu m of the analyte in dry air was sampled at 0.2 liters per minute for 4 hours. At that time the concentration of the

analyte in the effluent was less than 1% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2.) If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments with toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 45 to 175 mg/cu m was 0.080. This value corresponds to a standard deviation of 28.4 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 The average values obtained using the overall sampling and analytical method were 1.8% higher than the "true" value at the OSHA standard level.

4.3 The above data are based on validation experiments using the internal standard method. (Reference 11.2)

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more compounds suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined accurately (±5%) at the recommended flow rate, (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600 C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in. stainless steel) packed with 10% FFAP on 80/100 Chromosorb W-AW.

6.5 An electronic integrator or some other suitable method for determining peak size areas.

6.6 Two-milliliter glass sample containers with glass stoppers or Teflon®-lined caps. If an automatic sample injector is used, the sample injector vials can be used.

6.7 Microliter syringes: 10-µl, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery type.

6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Eluent: Carbon disulfide (chromatographic grade) containing 5% 2-propanol (reagent grade).

7.2 4-Methyl-2-pentanol (reagent grade).

7.3 Internal Standard: n-Tetradecane (99+%) or other suitable standard.

7.4 n-Heptane (reagent grade).

7.5 Purified nitrogen.

7.6 Prepurified hydrogen.

7.7 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a flow of 0.20 liters per minute or less. The flow rate should be known with an accuracy of at least ±5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available the elevation should be recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the suspected compound should be submitted to the laboratory in glass containers with Teflon®-lined caps. These liquid bulk samples should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container or automatic sample injector vial. The separating section of foam is removed and discarded; the second section is transferred to another sample container or vial. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of the eluent is pipetted into each sample container. For the internal standard method a 0.1 percent solution of internal standard in the eluent is used. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the solvent is added to minimize volatilization.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (80 psig) nitrogen carrier gas flow.
2. 30 ml/min (50 psig) hydrogen gas flow to detector.
3. 300 ml/min (50 psig) air flow to detector.
4. 200 C injector temperature.
5. 300 C manifold temperature (detector).
6. 120 C column temperature.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-µl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 µl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 µl to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 µl in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique. In this case 2-µl injections are satisfactory.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below (see Section 9).

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided that the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.0-ml sample container. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. A

250 mg/ml stock solution of the analyte in n-heptane is prepared. A known amount of this solution is injected directly intthe activated charcoal with a 10-µl syringe, and the container is capped. The amount injected is equivalent to that present in a 10-liter sample at the selected level. It is not practical to inject the neat liquid directly because the amounts to be added would be too small to measure accurately.

At least six tubes at each of three levels (0.5X, 1X, and 2X the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These six tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

The weight of analyte found in each tube is determined from the standard curve (Section 9). Desorption efficiency is determined by the following equation:

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus the weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/ml of eluent. To minimize error due to the volatility of the eluent, one can add 10 times the weight to 10 ml of the eluent. (For the internal standard method use eluent containing 0.1 percent of the internal standard.) A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentrations in mg/ml versus peak area. In the case of the internal standard method plot the concentration versus the ratio of peak area of analyte to peak area of internal standard.

Note: Whether the absolute area or internal standard method is used standard solutions should be analyzed at the same time that the sample analysis is done. This will minimize the effect variations of FID response.

10. Calculations

10.1 Read the weights, in mg, corresponding to each peak area (area ratio in case of the internal standard method) from the standard curve. No volume corrections are needed, because the standard curve is based on mg/ml eluent and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (Section 8.5.2) for the amount of analyte found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

10.5 The concentration of analyte in the air sampled can be expressed in mg per cu m, which is numerically equal to ug per liter of air

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm:

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (C) of air sampled
24.45 = molar volume (liter/mole) at 25 C and 760 mm Hg
MW = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (K)

11. References

11.1 White L. D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 "Documentation of NIOSH Validation Tests", Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract No. HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes, September 15, 1972".

ORGANIC SOLVENTS IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Organic Solvents (See Table 1)	**Method No.:**	P&CAM 127
Matrix:	Air	**Range:**	For the specific compound, refer to Table 1
Procedure:	Adsorption on charcoal desorption with carbon disulfide, GC		
Date Issued:	9/15/72	**Precision:**	10.5% RSD
Date Revised:	2/15/77	**Classification:**	See Table 1

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, graduated test tube and desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

The lower limit in mg/sample for the specific compound at 16 × 1 attenuation on a gas chromatograph fitted with a 10:1 splitter is shown in Table 1. This value can be lowered by reducing the attenuation or by eliminating the 10:1 splitter.

3. Interferences

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped. Preliminary experiments indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more solvents are known or suspected to be present in the air, such information (including their suspected identities), should be transmitted with the sample, since with differences in polarity, one may displace another from the charcoal.

3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Hence, retention time data on a single column, or even on a number of columns, cannot be considered as proof of chemical identity. For this reason it is important that a sample of the bulk solvent(s) be submitted at the same time so that identity(ies) can be established by other means.

3.4 If the possibility of interference exists, separation conditions (column packing, temperatures, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The mean relative standard deviation of the analytical method is 8% (11.4).

4.2 The mean relative standard deviation of the analytical method plus field sampling using an approved personal sampling pump is 10% (11.4). Part of the error associated with the method is related to uncertainties in the sample volume collected. If a more powerful vacuum pump with associated gas-volume integrating equipment is used, sampling precision can be improved.

4.3 The accuracy of the overall sampling and analytical method is 10% (NIOSH–unpublished data) when the personal sampling pump is calibrated with a charcoal tube in the line.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more solvents suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists. During sample storage, the more volatile compounds will migrate throughout the tube until equilibrium is reached (33% of the sample on the backup section).

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 An approved and calibrated personal sampling pump for personal samples. For an area sample, any vacuum pump whose flow can be determined accurately at 1 liter per minute or less.

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 lpm.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (20 ft × ⅛ in) with 10% FFAP stationary phase on 80/100 mesh, acid-washed DMCS Chromosorb W solid support. Other columns capable of performing the required separations may be used.

6.5 A mechanical or electronic integrator or a recorder and some method for determining peak area.

6.6 Microcentrifuge tubes, 2.5 ml, graduated.

6.7 Hamilton syringes: 10 μl, and convenient sizes for making standards.

6.8 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Spectroquality carbon disulfide (Matheson Coleman and Bell).

7.2 Sample of the specific compound under study, preferably chromatoquality grade.

7.3 Bureau of Mines Grade A helium.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 **Cleaning of Equipment:** All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 **Calibration of Personal Pumps.** Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 **Collection and Shipping of Samples**

8.3.1 Immediately before sampling, the ends of the tube should be broken to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The small section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be vertical during sampling to reduce channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 The flow, time, and/or volume must be measured as accurately as possible. The sample should be taken at a flow rate of 1 lpm or less to attain the total sample volume required. The minimum and maximum sample volumes that should be collected for each solvent are shown in Table 1. The minimum volume quoted must be collected if the desired sensitivity is to be achieved.

8.3.6 The temperature and pressure of the atmosphere being sampled should be measured and recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly before they are shipped to minimize tube breakage during shipping.

8.3.10 Samples of the suspected solvent(s) should be submitted to the laboratory for qualitative characterization. These liquid bulk samples should not be transported in the same container as the samples or blank tube. If possible, a bulk air sample (at least 50 l air drawn through tube) should be shipped for qualitative identification purposes.

8.4 **Analysis of Samples**

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a small stoppered test tube. The separating section of foam is removed and discarded; the second section is transferred to another test tube. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, one-half ml of carbon disulfide is pipetted into each test tube. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 85 cc/min. (70 psig) helium carrier gas flow.
2. 65 cc/min. (24 psig) hydrogen gas flow to detector.
3. 500 cc/min. (50 psig) air flow to detector.
4. 200°C injector temperature.
5. 200°C manifold temperature (detector).
6. Isothermal oven or column temperature — refer to Table 1 for specific compounds.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blowback or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10 μl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume.. The needle is removed from the solvent, and the plunger is pulled back about 0.2 μl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-μl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back a short distance to minimize evaporation of the sample from the tip of the needle. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 **Determination of Desorption Efficiency**

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process for a given compound, provided the same batch of charcoal is used. NIOSH has found that the desorption efficiencies for the compounds in Table 1 are between 81% and 100% and vary with each batch of charcoal.

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8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 5-cm, 4-mm I.D. glass tube, flame-sealed at one end (similar to commercially available culture tubes). This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the compound is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. The amount injected is usually equivalent to that present in a 10-liter sample at a concentration equal to the federal standard.

At least five tubes are prepared in this manner and allowed to stand for at least overnight to assure complete absorption of the specific compound onto the charcoal. These five tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of CS_2 with the same syringe used in the preparation of the sample. These are analyzed with the samples.

The desorption efficiency equals the difference between the average peak area of the samples and the peak area of the blank divided by the average peak area of the standards, or

$$\text{desorption efficiency} = \frac{\text{Area sample} - \text{Area blank}}{\text{Area standard}}$$

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml CS_2 because samples are desorbed in this amount of CS_2. To minimize error due to the volatility of carbon disulfide, one can inject 20 times the weight into 10 ml of CS_2. For example, to prepare a 0.3 mg/0.5 ml standard, one would inject 6.0 mg into exactly 10 ml of CS_2 in a glass-stoppered flask. The density of the specific compound is used to convert 6.0 mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5 ml versus peak area.

NOTE: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 The weight, in mg, corresponding to each peak area is read from the standard curve for the particular compound. No volume corrections are needed, because the standard curve is based on mg/0.5 ml CS_2 and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{Correct mg} = \text{mg}_s - \text{mg}_b$$

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where:

mg_s = mg found in front section of sample tube

mg_b = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 The corrected amounts present in the front and backup sections of the same sample tube are added to determine the total measured amount in the sample.

10.4 This total weight is divided by the determined desorption efficiency to obtain the corrected mg per sample.

10.5 The concentration of the analyte in the air sampled can be expressed in mg per m^3.

$$mg/m^3 = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liters/m}^3\text{)}}{\text{Air volume sampled (liters)}}$$

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$ppm = mg/m^3 \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L. D., D. G. Taylor, P. A. Mauer, and R. E. Kupel, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere", Am Ind Hyg Assoc J 31:225, 1970.

11.2 Young, D. M. and A. D. Crowell, Physical Adsorption of Gases, pp. 137-146, Butterworths, London, 1962.

11.3 Federal Register, 37:202:22139-22142, October 18, 1972.

11.4 NIOSH Contract HSM-99-72-98, Scott Research Laboratories, Inc., "Collaborative Testing of Activated Charcoal Sampling Tubes for Seven Organic Solvents", pp. 4-22, 4-27, 1973.

TABLE 1

Parameters Associated With P&CAB Analytical Method No. 127

Organic Solvent	Method Classification	Detection limit (mg/sample)	Sample Volume (liters) Minimum(a)	Maximum(b)	GC Column Temp.(°C)	Molecular Weight
Acetone	D	—	0.5	7.7	60	58.1
Benzene	A	0.01	0.5	55	90	78.1
Carbon tetrachloride	A	0.20	10	60	60	154.0
Chloroform	A	0.10	0.5	13	80	119
Dichloromethane	D	0.05	0.5	3.8	85	84.9
p-Dioxane	A	0.05	1	18	100	88.1
Ethylene dichloride	D	0.05	1	12	90	99.0
Methyl ethyl ketone	B	0.01	0.5	13	80	72.1
Styrene	D	0.10	1.5	34	150	104
Tetrachloroethylene	B	0.06	1	25	130	166
1,1,2-trichloroethane	B	0.05	10	97	150	133
1,1,1-trichloroethane (methyl chloroform)	B	0.05	0.5	13	150	133
Trichloroethylene	A	0.05	1	17	90	131
Toluene	B	0.01	0.5	22	120	92.1
Xylene	A	0.02	0.5	31	100	106

(a) Minimum volume, in liters, required to measure 0.1 times the OSHA standard

(b) These are breakthrough volumes calculated with data derived from a potential plot (11.2) for activated coconut charcoal. Concentrations of vapor in air at 5 times the OSHA standard (11.3) or 500 ppm, whichever is lower, 25°C, and 760 torr were assumed. These values will be as much as 50% lower for atmospheres of high humidity. The effects of multiple contaminants have not been investigated, but it is suspected that less volatile compounds may displace more volatile compounds (See 3.1 and 3.2)

APPENDIX B4

1,2-DIBROMOETHANE

Measurements Research Branch

Analytical Method

Analyte:	1,2-Dibromoethane	Method No.:	P&CAM 260
Matrix:	Air	Range:	0.002 to 8.0 mg/m^3 for a 25-liter air sample
Procedure:	Charcoal adsorption, benzene-methanol desorption, GC-ECD analysis	Precision:	0.079 at 40 ng per sample (Analytical)
Date Issued:	8/1/78	Classification:	E (Proposed)
Date Revised:			

1. Synopsis

   1.1 A known volume of air is drawn through a charcoal tube to trap the 1,2-dibromoethane vapor present.

   1.2 The charcoal in the tube is transferred to a 10-ml volumetric flask and the analyte is desorbed with 10.0 ml of 99:1 benzene-methanol (v/v).

   1.3 An aliquot of the desorbed sample is subjected to gas chromatographic analysis using an electron-capture detector.

2. Working Range, Sensitivity, and Detection Limit

   2.1 The range of an electron-capture detector most useful for the quantitation of 1,2-dibromoethane depends upon the type of detector and chromatograph used. For a non-linearized ^{63}Ni electron-capture detector in a Tracor MT 220 Gas Chromatograph, the most useful range for quantitation was 20 to 400 pg of 1,2-dibromoethane per aliquot injected. This range corresponds to 40 to 80 ng of 1,2-dibromoethane per sample solution.

   For a 25-liter air sample, this method is applicable to air concentrations which range from 0.002 to 8.0 mg/m^3. The upper limit of the method depends upon the capacity of the charcoal tube and involves dilution of the sample solution.

2.2 The detection limit was approximately 4 pg per injection or 8 ng per sample solution.

3. Interferences

3.1 Compounds which are detected by the electron-capture detector and have retention times approximating that of 1,2-dibromoethane will interfere with the analysis.

3.2 When the amount of water in the air is so great that condensation actually occurs in the charcoal tube, vapors of 1,2-dibromoethane may not be trapped efficiently.

3.3 When interfering compounds are known or suspected to be present in the air, such information including their suspected identities should be transmitted with the sample.

4. Precision and Accuracy

4.1 The precision in relative standard deviation (RSD) versus the sample size for the analytical method is presented in the following table.

Precision (RSD)	Sample Size (ng)
0.032	2400
0.062	200
0.079	40

4.2 The precision and accuracy are affected by drift in detector response. Satisfactory precision can be realized by use of an appropriate internal standard.

4.3 Recoveries of analyte through desorption decrease with increasing storage times at room temperature. These decreases are more pronounced at lower levels of analyte. Storage of the charcoal tube samples at -25 °C permits satisfactory recoveries.

4.4 Dilution of the sample solution is a potential source of error. Solutions containing 1,2-dibromoethane in concentrations above the useful range of the detector must be diluted.

4.5 The capacity of the charcoal tube with respect to 1,2-dibromoethane is limited. When the sample loading in the backup section of the tube exceeds 10% of that found in the front section, the possibility of sample loss exists.

4.6 The precision of the method is dependent upon the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise because the pump is usually calibrated for one tube only.

5. Advantages and Disadvantages

5.1 The sampling device is small, portable, and involves no liquids.

5.2 The highly selective nature of an electron-capture detector dramatically reduces the potential number of interferences.

5.3 The use of an internal standard is required in order to attain good precision.

5.4 Recoveries of 1,2-dibromoethane from charcoal are decreased upon storage of the charcoal tube samples at room temperature, particularly at lower levels of analyte (See Section 4.3).

6. Apparatus

6.1 Personal sampling pump, the flow rate of which can be accurately determined at 200 ml per minute or less with the charcoal tube in line.

6.2 Charcoal tubes: Glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I. D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600 °C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than 25 torr at a flow rate of 200 ml/min.

6.3 Gas chromatograph equipped with an electron-capture detector. A glass tube filled with 20/40 mesh activated charcoal should be attached to the exit port in order to trap the 1,2-dibromoethane in the effluent gas stream. A glass tube with a 2-cm I.D. and a length of 25 cm was found to have little or no effect upon the retention time of 1,2-dibromoethane.

6.4 Gas chromatography column, 1.8 m x 4 mm I.D., constructed from borosilicate glass and packed with 3% OV-210 on 80/100 Gas Chrom Q.

6.5 Syringes, 10-µl and other convenient sizes for preparing standard solutions.

6.6 Glass vials, 2-ml.

6.7 Pipets, 10.0-ml and 1.0-ml.

6.8 Volumetric flasks, 10.0-ml.

6.9 Parafilm.

7. Reagents

7.1 Benzene, pesticide quality

7.2 Methanol, pesticide quality.

7.3 99:1 Benzene-methanol (v/v).

7.4 1,2-Dibromoethane of known purity.

7.5 An appropriate internal standard, such as 1,1,2,2-tetrachloroethane or 1,2-dibromopropane. See Section 8.3.8.

7.6 A solution of internal standard in 99:1 benzene-methanol (v/v).

8. Procedure

8.1 Cleaning of Equipment

8.1.1 The syringes are rinsed well, first with methanol and then with benzene.

8.1.2 All other glassware should be cleaned with soap and water, then rinsed with the following in sequence: distilled water, pesticide quality methanol, pesticide quality benzene.

8.2 Collection and Shipping of Samples

8.2.1 Immediately before sampling, the ends of the charcoal tubes are broken to provide an opening of at least one-half the internal diameter of the tube.

8.2.2 The smaller section of charcoal is used as a backup and should be positioned nearest the sampling pump.

8.2.3 The charcoal tube is placed in a vertical position during sampling in order to minimize channeling through the charcoal.

8.2.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.2.5 The sampling time, volume and flow rate are measured. The sample is taken at a flow rate of 200 ml per minute or less. The total volume sampled should be no more than 25 liters.

8.2.6 The temperature, pressure and relative humidity of the atmosphere being sampled are recorded.

8.2.7 To obtain a blank sample, a charcoal tube is handled in exactly the same manner as each sample tube except that no air is drawn through it.

8.2.8 The charcoal tubes are capped with the supplied plastic caps immediately after sampling.

8.2.9 Low levels of 1,2-dibromoethane can not be stored on charcoal at ambient temperatures for long periods of time. Therefore, if the analysis can not be performed within 16-24 hours after sampling has been completed, the samples must be stored at -25 °C or below. Refrigerated samples may be stored for two weeks.

8.2.10 For shipment to the laboratory, the samples are packed firmly in an insulated container cooled with dry ice.

8.2.11 If appropriate, a sample of the bulk material in a glass container with a Teflon-lined cap is prepared and shipped to the laboratory in a separate container.

8.3 Analysis of Samples

8.3.1 Preparation of Samples. Each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 10-ml volumetric flask. The separating section of polyurethane foam is removed and discarded. The charcoal in the second (smaller) section is transferred to a separate 10-ml volumetric flask. These two sections are analyzed separately.

8.3.2 Desorption of Samples. Prior to analysis, 10.0-ml of 99:1 benzene-methanol (v/v) is added to each 10-ml volumetric flask containing a section of charcoal. Each flask is stoppered and allowed to stand with occasional agitation over a 1-hour period.

8.3.3 GC conditions

nitrogen carrier gas flow:	35 ml/min
inlet temperature:	175 °C
detector temperature:	315 °C
column temperature:	50 °C
^{63}Ni detector operating mode:	DC at 90 to 95% standing current

8.3.4 Injection. By means of the solvent-flush injection technique, 5-µl aliquots of sample solutions are injected into the gas chromatograph.

8.3.5 After each injection, the syringe is rinsed thoroughly, first with methanol and then with benzene. Otherwise, traces of 1,2-dibromoethane will remain in the syringe and contaminate the solvent-flush solution. Periodically, an injection of solvent-flush solution only [99:1 benzene-methanol (v/v)] should be made to check the cleanliness of the syringe and the purity of the solvent-flush solution.

8.3.6 A preliminary analysis of the samples is run in order to determine: (a) whether the sample solutions are too concentrated for the useful range of the detector, and (b) which region of the chromatogram may be a suitable location for an internal standard peak.

8.3.7 If necessary, an appropriate volume of each original sample solution is diluted to 10.0 ml with 99:1 benzene-methanol (v/v). These diluted solutions should be reanalyzed in order to: (a) test whether the amount of 1,2-dibromoethane injected is now within the useful range of the detector and (b) aid in the selection of a suitable internal standard.

8.3.8 The use of an internal standard is required in order to compensate for changes in detector sensitivity with time. The approximate retention times of 1,2-dibromoethane and two potential internal standards [under the GC conditions described in this method] are:

Compound	Retention Time (min)	B.P. (°C)
1,2-Dibromoethane	2.2	131
1,2-Dibromopropane	2.9	140
1,1,2,2-Tetrachloroethane	4.1	146

The selection of an internal standard is based on three criteria:

8.4.8.1 Absence of components in the sample which would interfere with the internal standard.

8.4.8.2 Absence of adsorption of the internal standard by the charcoal while in 99:1 benzene-methanol (v/v) solution. If the internal standard is one other than 1,2-dibromopropane or 1,1,2,2-tetrachloroethane, then it must be tested.

8.4.8.3 Proximity of the internal standard peak to the 1,2-dibromoethane peak.

8.3.9 A stock solution of the selected internal standard in 99:1 benzene-methanol (v/v) is prepared such that 5.0 µl of this stock solution contains approximately 400 ng of internal standard. To each diluted sample solution and each standard solution, 5.0 µl of this internal standard stock solution is added.

8.3.10 Aliquots (5-µl) of these solutions are injected into the gas chromatograph for quantitative analysis.

8.4 Determination of Recovery

8.4.1 Activated charcoal equivalent to the amount in the front (larger) section of the sampling tube is poured into a 2-ml glass vial. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. A known amount of 1,2-dibromoethane in a 5-µl aliquot of benzene solution is added directly to the charcoal with a microliter syringe. The vial is sealed immediately with Parafilm.

8.4.2 Six samples at each of three different levels are prepared in the above manner and allowed to stand 16-24 hours in order to assure complete adsorption of the 1,2-dibromoethane onto the charcoal. A parallel blank vial is treated in exactly the same manner except that no sample is added to it. The samples and the blank are treated with 10.0 ml of 99:1 benzene-methanol (v/v) in the manner described in Section 8.3.2.

8.4.3 Three control solutions are prepared by injecting the same quantity of 1,2-dibromoethane into 10.0-ml portions of 99:1 benzene-methanol (v/v) with the same syringe used in the preparation of the samples.

8.4.4 The samples, the blank, and the control solutions are analyzed on the same day in accordance with Section 8.3.

8.4.5 Recovery (R) is equal to the difference between the average quantity of 1,2-dibromoethane recovered from the samples and the quantity recovered from the blank divided by the average quantity of 1,2-dibromoethane measured in the control solutions.

8.4.6 The desorption efficiency obtained is dependent upon the amount of analyte collected on the charcoal. Therefore, a plot of "desorption efficiency" versus "quantity of analyte measured" is constructed. This curve is used in Section 10.2 to correct for adsorption losses.

9. Calibration and Standardization

9.1 A series of standards varying in concentration over the range of interest is prepared. The range of interest may be in the vicinity of 40 to 800 ng per 10.0 ml of 99:1 benzene-methanol (v/v). These standards are analyzed during the same time period as the samples.

9.2 In view of the low concentrations involved, the volume of a solution prepared from X number of ng of 1,2-dibromoethane and 10.0 ml of solvent is very nearly 10.0 ml and can be assumed to be 10.0 ml for the purpose of this analytical method.

9.3 A calibration curve is constructed daily by plotting quantity of 1,2-dibromoethane per 10.0 ml of solution versus the ratio of 1,2-dibromoethane peak area to internal standard peak area.

10. Calculations

10.1 Determine the quantity of 1,2-dibromoethane, W (ng), in 10.0 ml of diluted sample solution from the calibration curve.

10.2 Determine the total quantity of 1,2-dibromoethane, Q, in the air sample:

$$Q = \left(\frac{W \cdot F}{R}\right)_A + \left(\frac{W \cdot F}{R}\right)_B$$

where:

F -- Dilution factor. The dilution factor is equal to 10.0 ml divided by the volume of original sample solution which was diluted to 10.0 ml.

R -- Recovery (Section 8.4.5).

A -- Reference to the front section of the sampling tube.

B -- Reference to the back section of the sampling tube.

10.3 In the event the blank gives rise to a peak with the same retention time as that of 1,2-dibromoethane, the analyst must determine or compensate for it.

10.4 Determine the concentration, C ($\mu g/m^3$), of 1,2-dibromoethane in air.

$$C = \frac{Q}{V}$$

where: V is the volume of air sampled in liters.

11. Reference

Method S104, "Ethylene Dibromide," NIOSH Manual of Analytical Methods, Second Edition, Volume 2, 1977, U. S. Government Printing Office, Washington, D.C.

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Samuel P. Tucker
Organic Methods Development Section

APPENDIX C

MATERIAL SAFETY DATA SHEET

Dow Chemical U.S.A. Midland, Michigan 48640 Emergency Phone: 517-636-4400
Dowell Division Tulsa, Oklahoma 74102 Emergency Phone: 918-582-0104

Product Name: DOWFROTH (R) M222 FLOTATION FROTHER

Ingredients: Nonionic surfactant

Section 1 Physical Data

Boiling point: decomposes
VAP Press: low
VAP Density (Air=1): --
Sol. in water: highly soluble
SP. Grav: 1.02@ 74 F
% volatile by vol: --
Appearance and Odor: dark brown liquid, no odor.

Section 2 Fire and Explosion Hazard Data

Flash Point: 310 F
Method used: SETA Closed Cup
Extinguishing media: Water fog, alcohol foam, CO_2, Dry chemical
Special Fire Fighting Equipment and Hazards: None Required
Flammable limits (STP in air)
LFL: not deter. UFL: not deter.

Section 3 Reactivity Data

Stability: stable
Incompatibility: oxidizing material
Hazardous decomposition: carbon dioxide, carbon monoxide, and formaldehyde may form on burning
Hazardous polymerization: will not occur

Section 4 Spill, Leak and Disposal Procedures

Action to take for spills (use appropriate safety equipment):
Contain and recover as much free material as possible.
Clean or remove contaminated area affected by the spill.

Disposal Method: incineration is preferred, material must be disposed of in accordance with Federal, State and Local Regulation.

Section 5 Health Hazard Data

Solubility: soluble in water
Descr.: nonionic surfactant, dark brown liquid

Ingestion: Low acute oral toxicity; single dose oral LD_{50} (female rats) > 5000 mg/kg

Eye contact: slight discomfort, transient slight conjunctival redness and very slight corneal injury.

Skin contact: Prolonged and repeated - slight redness and slight scaling.

Skin absorption: not likely to be absorbed in acutely toxic amounts.

Inhalation: not likely to be a problem.

Effects of Overexposure: effects not established.

Section 6 First Aid -- Note to Physician

First Aid Procedures:

Eyes: *Irrigate with flowing water immediately and continuously for 15 minutes. Refer to medical personnel.*

Skin: *Contact will probably cause no more than irritation. Wash off in flowing water or shower. Wash clothing before reuse.*

Inhalation: *Remove to fresh air if effects occur. Consult medical personnel.*

Ingestion: *Low in toxicity. Induce vomiting if large amounts are ingested.*

Note to physician:

Eyes: *May cause slight corneral injury or burn. Stain for evidence of corneal injury. If cornea is burned, instill antibiotic steroid preparation frequently. Consult Ophthalmologist.*

Skin: *May cause mild irritation. If rash is present, treat as any contact dermatitis. Not likely to be absorbed in acutely toxic amounts.*

Respiratory: *No toxic data*

Oral: *Low in toxicity*

Systemic: *Human effects not established. No specific antidote. Treatment based on sound judgement of physician and the individual reactions of the patient.*

Section 7 Special Handling Information

Ventilation: *Good ventilation usually adequate for most operations.*

Respiratory Protection: *None normally needed. For emergencies, a self-contained breathing apparatus or full face respirator with an approved organic vapor canister is recommended.*

Protective Clothing: *Clean, body-covering clothing. In addition, gloves, boots, depending upon the extent and severity of exposure likely.*

Eye Protection: *Chemical workers goggles*

Section 8 Special Precautions and Additional Information

Precautions to be taken in handling and storage: Practice caution and personal cleanliness.

(R) indicates a registered trademark name of the Dow Chemical Company.