ESTABLISHED 1935

COO-4748-1
Distribution Category UC-901

INDUSTRIAL HEALTH FOUNDATION, INC.

A NONPROFIT ORGANIZATION FOR THE ADVANCEMENT OF HEALTHFUL WORKING CONDITIONS IN INDUSTRY

A RESEARCH AMBIENT AIR INDUSTRIAL HYGIENE SURVEY OF THE PITTSBURGH ENERGY TECHNOLOGY CENTER

at

Bruceton, Pennsylvania

FINAL REPORT
For Period April 15, 1978 - August 30, 1978

by

H. Wilbur Speicher
Certified Industrial Hygiene
Engineer/Health Physicist

and

Kenneth W. Kretchman
Industrial Hygienist

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MASTER

Daniel C. Braun, M.D.
President

Prepared for

THE UNITED STATES DEPARTMENT OF ENERGY
PITTSBURGH ENERGY TECHNOLOGY CENTER
UNDER CONTRACT NO. EW-78-S-02-4748

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ABSTRACT

This ambient air industrial hygiene evaluation was made in six selected process areas at the Pittsburgh Energy Technology Center and was performed by Industrial Health Foundation on April 15-August 30, 1978.

Personal and area sampling for predetermined dusts, vapors, gases and fumes was conducted with NIOSH approved equipment and procedures.

The sample analyses were performed at the Industrial Health Foundation's AIHA accredited Analytical Laboratory.

The results, reported as time-weighted average concentrations during the sampling period, indicate compliance with the present OSHA permissible values except for benzene concentrations in both laboratory areas.

The present benzene TLV was exceeded on one occasion in each of the laboratory areas. These results indicate a need for periodic monitoring of both areas. It is recommended that:

1. Chemical adjustable hood windows in each of the laboratory areas be positioned and used as marked to assure an adequate face velocity of at least 100 feet per minute. The hood in the solvent analysis laboratory could have its effectiveness improved by modifying the sides, top and bottom with a design similar to the new airflow hoods in the solvent separation laboratory. This modification can be easily made by mounting 6-8" wide flanges at 45° to the horizontal on the two sides and top. The bottom of the hood should have a "rolled" edge.
2. Future air sampling be conducted in the laboratory areas to assure benzene concentrations are maintained at levels below the OSHA permissible values.

3. The tube cleaning operation in the centrifuge area be provided with local exhaust ventilation.
4. Local exhaust ventilation at the top of the centrifuge be improved to capture the heated vapors when the cap is removed to obtain the tubes for cleaning.

INTRODUCTION

This evaluation of selected materials in the coal gasification and liquefaction processes at PETC was conducted by Industrial Health Foundation at the request of Mr. John Sourbeer, Safety Specialist for the Pittsburgh Energy Center at Bruceton, Pa.

Sampling was conducted from April 15, 1978 to August 30, 1978 by H. Wilbur Speicher, Certified Industrial Hygiene Engineer/Health Physicist and Kenneth W. Kretchman, Industrial Hygienist, on the staff of the Industrial Health Foundation.

METHODS AND PROCEDURES

Personal and area sampling was conducted in six (6) work areas where coal research is conducted at PETC. Sampling was conducted in two to three days in each area. Sampling location and tests conducted are listed in Table I.

TABLE I

LOCATION	TESTS CONDUCTED
1. Centrifuge area	Total hydrocarbons-benzene solubles. Benzene-naphtha
2. Coal-Oil Slurry	Total hydrocarbons-benzene solubles. Respirable dust (silica)
3. Water Treatment area	Phenol, Ammonia, Cresol Total hydrocarbons-Benzene Solubles
4. Flame Spray Area	Nitrogen dioxide Nickel
5. Solvent Analysis Lab	Benzene-Pentane Total hydrocarbons-Benzene Solubles
6. Solvent Separation Lab	Benzene-Pentane Total Hydrocarbons-Benzene Solubles

Information regarding the number of employees monitored and a sample description (personal or area sample) is provided in the Tables under the Results section of this report.

Sampling and analytical procedures used during this evaluation were in accordance with NIOSH recommended methods.

Table II lists the analytical methods used for this study. These procedures are detailed in Appendix A.

TABLE II

<u>ANALYSES</u>	<u>ANALYTICAL METHOD REF.</u>	<u>VARIATION</u>
Nickel (Ni)*	NIOSH P & CAM 173	None
Nitrogen Dioxide*	NIOSH P & CAM 108	None
Phenol*	NIOSH S330	Column used- Dexil 300
Cresol*	NIOSH S167	Column used- 10% FFAP
Pentane*	NIOSH S379	None
Coal tar pitch volatile	NIOSH P & CAM 217	None
Silica*	NIOSH P & CAM 109	None
Benzene*	NIOSH P & CAM 311	Column used- 10% FFAP
Ammonia	Criteria for a recommended standard... Occupational Exposure to Ammonia, U.S. Dept. H.E.W., Public Health Service, Center of Disease Control, NIOSH, 9496 (1974)	None

*All analytical methods were taken from the NIOSH Manual of Analytical Methods, U.S. Dept. of H.E.W., April 1977, Volumes 1-3.

Sampling equipment used for this evaluation was calibrated by the standard soap film method. This technique involves drawing air through the appropriate collection media while pump flow adjustments are made to obtain a desired air flow rate.

After collection, the air samples were packed and hand carried to the Industrial Health Foundation's AIHA accredited Laboratory for analysis. This transfer process meets OSHA regulations. Instrumentation used for sample analyses was calibrated by recognized standards. See Appendix C for analytical equipment calibration procedures. The AIHA certification for the IHF Analytical Laboratory is maintained by participation in the PAT (Proficiency Analytical Testing) program which includes analyses of known concentrations of various samples periodically with the results reported to NIOSH.

A brief description of the sampling procedures, specific for each of the substances tested, are on the following pages:

Benzene

Exposure to benzene vapors in the laboratory operations was evaluated by means of personal and area sampling using SKC 222-41 low volume pumps and charcoal tubes in series.

Full work shift personal and area samples were collected in the Solvent Analysis and the Solvent Separation Laboratories.

Prior to sampling, the pumps were calibrated by the standard soap film method, with a charcoal tube in series, with a flow rate of 50 ml per minute.

Sampling was conducted over four days in the Solvent Separation Laboratory. During two days, (6/9/78 and 7/11/78), one charcoal tube sample was collected each day in the breathing zone of the worker (chemist) for the entire workshift to determine his personal exposure to benzene vapors. An area sample was collected approximately 5 feet from the chemical hood in each laboratory to determine ambient laboratory concentrations. The same procedure was used during three sampling days in the Solvent Analyses Laboratory.

During two days, (8/13/78 and 8/18/78) of sampling in the Solvent Separation Laboratory, sequential sampling was conducted. One charcoal tube was worn during the forenoon and a new tube was worn during the afternoon to more accurately determine when the maximum exposure might occur. Sequential area samples were collected at the face area of the solvent storage hood, as well as the hood being used for chemical analyses, to determine the source of possible benzene exposure.

Gas chromatography analysis was performed at the IHF Analytical Laboratory by means of a Perkin-Elmer gas chromatograph equipped with a flame ionization detector.

Total Hydrocarbons and Benzene Soluble Material

Sampling was conducted for total hydrocarbons and benzene soluble material in the Solvent Analysis and the Solvent Separation Laboratories, the Centrifuge and Coal-Oil Slurry Areas, and the Water Treatment Area.

MSA Model G pumps were used to draw air through silver membrane filters with an 0.8 micron pore size and preceded by glass fiber filters, both of which were held in two-piece cassettes.

Each pump was calibrated with a representative filter in series for flow rates of approximately 1.5 liters per minute.

Full work shift personal and area samples were collected. The samples were delivered to the IHF Analytical Laboratory where total hydrocarbons were determined by total weight and ultrasonic extraction used to determine the benzene soluble portion of the material collected on the filters.

Duplicate samples were collected in the Water Treatment Area and submitted to PETC for research purposes.

It was originally intended to collect duplicate samples in all areas. However, due to process shutdowns and a time limitation for collection of the samples, it was agreed by the Technical Project Officer and contractor that collection of duplicate samples in the other areas would not be necessary.

Phenol

Sampling for phenol in the Water Treatment Area was performed by means of MSA Model S pumps and midget glass bubblers.

Each pump, with a bubbler containing 15 ml of 0.1 normal sodium hydroxide solution as the absorbing reagent, in series, was calibrated for flow rates ranging from 0.6l to 1.25 liters per minute by the standard soap film method.

Full work shift area samples were collected in the vicinity of the biological reactors during each of the three days when samples were collected. One sample was collected at the south end of the Water Treatment Area during the second day of sampling.

Phenol was evaluated by a colormetric analysis at the IHF Analytical Laboratory.

Ammonia

Determination of ammonia concentrations in the Water Treatment Area was performed by means of MSA Model S personal pumps in series with a midget all glass impinger containing 10 ml. of sulfuric acid as the absorbing solution.

Each pump, with an impinger in series, was calibrated to a flow rate of 1.0 liter per minute by the standard soap film method.

Full work shift area samples were collected in the biological reactor section and at the ammonia stripping facility in the Water Treatment Area.

All samples were analyzed by gas chromatography at the IHF Analytical Laboratory.

Cresol

Full work shift sampling for cresol vapors in the Water Treatment Area was performed by means of SKC 222-41 low volume pumps used in series with silica gel (1000 mg) tubes.

Each pump, in series with a silica gel tube, was calibrated prior to sampling by the standard soap film method for a flow rate of approximately 50 ml/min.

Two personal samples and one area sample were collected in the Water Treatment Area. The area sampler was placed in the vicinity of the biological reactors. Full work shift samples were always collected.

All samples were analyzed by gas chromatography at the IHF Analytical Laboratory.

Nickel

Area sampling for nickel was conducted in the enclosed Flame Spray Area utilizing MSA Model G pumps and 37 millimeter cellulose acetate Type AA Millipore filters with 0.8 micron pore sizes. Flow rates ranged from 1.49 to 1.72 liters per minute.

Six area samples were collected in the enclosed spraying area on three different days. On each of the three days, a sample was collected near the metal spray gun located a few inches inside the exhaust hood face area. Another sample was collected within 3 feet of the face area.

Forty to sixty minute samples were collected because of the short duration of the metal spraying operation.

All samples were analyzed by atomic absorption spectrophotometry at the IHF Analytical Laboratory.

Nitrogen Dioxide (NO₂)

Since nitrogen dioxide gas may be generated during metal spraying of nickel alloy with an oxy-acetylene torch, four area samples of 40 to 60 minutes each were collected at the same locations where the nickel fume samples were collected. MSA Model S pumps and all-glass midget bubblers containing a solution of acetic and sulfanilic acids for the absorbing reagent were used for collecting the gas samples. Each pump was calibrated prior to sampling for flow rates ranging from 0.30 to 0.36 liters per minute.

A colorimetric analysis was used to determine NO₂ concentrations.

Silica

Respirable dust samples for silica were collected in the Coal-Oil Slurry Area to determine the amount of silica contained in the dust generated from the coal screening operation.

MSA Model G pumps were used in series with PVC filters having a 5.0 micron pore size. The filter was held in a two-piece cassette which was placed in a Dorr-Oliver cyclonic separator and located near the worker's breathing zone. The function of the cyclone was to collect only the respirable fraction of the dust on the PVC filter.

Each pump was calibrated with the filter mounted in the cyclone and in series by the standard soap film method. Flow rates ranging from 1.6 to 1.7 liters per minute. The filters were desiccated and weighed before and after sampling to avoid a weight error from moisture absorption by the filter.

Personal and Area samples were collected for full work shift exposures. Compliance with OSHA standards was determined from a knowledge of the percent of quartz and cristobalite, if any, in the samples, and by using the following formulae to calculate the OSHA permissible values:

$$\text{Calculated TLV quartz} = \frac{10}{\% \text{ quartz} + 2} \text{ mg/m}^3$$

$$\text{Calculated TLV cristobalite} = \frac{5}{\% \text{ cristobalite} + 2} \text{ mg/m}^3$$

RESULTS

The results of repeated sampling are compiled according to sampling location, and listed in the following tables. A brief summary of the values obtained in each area, as related to OSHA regulations and ACGIH (American Conference of Governmental Industrial Hygienists) recommended limits, precedes the results listed for each sampled area. One exposure (benzene) exceeded the OSHA permissible levels. It was collected in the Solvent Separation Laboratory (Sample #2440 on 6/9/78).

A full description of the analytical methods used for analyses of the samples appears in Appendix A.

A complete listing of analytical results, the corresponding sampling location, and dates when samples were collected appears in Appendix B.

A description of the calibration procedures for the analytical equipment appears in Appendix C.

WATER TREATMENT AREA

All results obtained from evaluations made on three different days for phenol, ammonia, cresol, total hydrocarbons, and benzene soluble material in this area were well below the OSHA permissible values.

WATER TREATMENT AREA
Building 84 Room 120

PHENOL

Date	Sample I.D.	Location	Results (ppm)
5/9/78	Area 1972	Bio reactor area	< 0.01
	Area 1973	Bio reactor area	< 0.02
	Area 1974	At ammonia stripping	< 0.02
5/17/78	Area 2010	Bio reactor area	< 0.03
	Area 2011	Bio reactor area	< 0.02
	Area 2012	South end of WT area	< 0.02
6/9/78	Area 2295	Bio reactor area	< 0.13
	Area 2296	Bio reactor area	< 0.17
<p style="text-align: center;">TLV's</p> <p>OSHA 5 ppm</p> <p>ACGIH 5 ppm</p>			

WATER TREATMENT AREA
Building 84 Room 120

AMMONIA

Date	Sample I.D.	Location	Results (ppm)
5/9/78	Area 1975	At ammonia stripping	0.22
	Area 1976	Bio reactor area	0.08
	Area 1977	Bio reactor area	0.05
5/17/78	Area 2007	South end of WT area	0.07
	Area 2008	Bio reactor area	0.08
	Area 2009	Bio reactor area	0.05
6/9/78	Area 2297	Bio reactor area	0.06
	Area 2298	South end of WT area	0.08
	Area 2299	Bio reactor area	0.06
TLV's			
OSHA	50 ppm		
ACGIH	25 ppm		

WATER TREATMENT AREA
Building 84 Room 120

CRESOL

Date	Sample I.D.	Location	Results (ppm)
5/9/78	Pers 1961	Varies	< 0.29
	Pers 1963	Varies	< 0.30
	Area 1962	Bio reactor area	0.30
5/17/78	Pers 2002	Varies	0.30
	Pers 2003	Varies	< 0.76
	Area 2001	Bio reactor area	< 0.28
6/9/78	Pers 2304	Varies	< 0.38
	Pers 2305	Varies	< 0.57
	Area 2306	Bio reactor area	< 0.27
<p style="text-align: center;">TLV's</p> <p>OSHA 5 ppm</p> <p>ACGIH 5 ppm</p>			

WATER TREATMENT AREA
Building 84 Room 120

TOTAL HYDROCARBONS/BENZENE SOLUBLES

Date	Sample I.D.	Location	Results (mg/m ³)	
			*BS	*TH
4/25/78	Pers 1654	Varies	< 0.10	0.16
	Pers 1655	Varies	< 0.08	0.36
	Area 1656	Bio reactor area	< 0.07	0.20
5/9/78	Pers 1969	Varies	< 0.08	0.42
	Pers 1971	Varies	< 0.08	0.57
	Area 1970	South end of WT area	< 0.07	0.44
5/17/78	Pers 1995	Varies	< 0.08	0.51
	Pers 1996	Varies	< 0.12	1.36
	Area 1997	South end of WT area	< 0.07	0.51
<p style="text-align: center;">TLV's</p> <p>OSHA 0.15 mg/m³</p> <p>ACGIH 0.20 mg/m³ Benzene Solubles</p>				

*BS - Benzene Solubles

*TH - Total Hydrocarbons

SOLVENT ANALYSIS LABORATORY

Values obtained from personal sampling for benzene, benzene soluble material and pentane were all below the OSHA permissible values.

SOLVENT ANALYSIS LABORATORY
Building 83 Room 336

BENZENE

Date	Sample I.D.	Location	Results (ppm)
4/25/78	Pers 1662	At hood	0.79
	Area 1663	5 ft. from hood	0.28
5/9/78	Pers 1958	At hood	0.91
	Area 1959	5 ft. from hood	* 4.92 0.14 * 0.15
5/17/78	Pers 2004	At hood	4.02
	Area 2005	5 ft. from hood	0.27
<p style="text-align: center;">TLV's</p> <p>OSHA 1.0 ppm Benzene 1000 ppm Pentane</p> <p>ACGIH 10.0 ppm 600 ppm</p>			

*Pentane results

SOLVENT ANALYSIS LABORATORY
Building 83 Room 336

TOTAL HYDROCARBONS/BENZENE SOLUBLES

Date	Sample I.D.	Location	Results (mg/m ³)	
			*BS	*TH
4/25/78	Pers 1652	By hood	< 0.07	0.16
	Area 1653	5 ft. from hood	< 0.07	0.11
5/9/78	Pers 1968	By hood	< 0.08	0.18
	Area 1967	5 ft. from hood	< 0.08	0.14
5/17/78	Pers 1998	By hood	< 0.07	0.48
	Area 1999	5 ft. from hood	< 0.07	0.47
<p style="text-align: center;">TLV's</p> <p>OSHA 0.15 mg/m³ Benzene Solubles</p> <p>ACGIH 0.20 mg/m³</p>				

*BS - Benzene Solubles

*TH - Total Hydrocarbons

SOLVENT SEPARATION LABORATORY

Values obtained from personal sampling for benzene showed result slightly above the OSHA TLV on 6/9/78 and below the TLV on 7/11/78. Both area sample results were well below the 1.0 ppm limit permitted by OSHA.

Pentane and hydrocarbon-benzene soluble results were well below OSHA and ACGIH limits.

Additional sampling for benzene conducted in this area on 5/18/78 and 8/30/78 showed all results to be below the OSHA TLV.

SOLVENT SEPARATION LABORATORY

BENZENE

Date	Sample I.D.	Location	Results (ppm)
6/9/78	Pers 2308	At hood	1.19 * 0.37
	Area 2309	5 ft. from hood	0.16 * 0.18
7/11/78	Pers 2769	At hood	0.31
	Area 2770	5 ft. from hood	0.17
<div>TLV's</div> <div> <div>OSHA</div> <div>1.0 ppm</div> <div>1000 ppm</div> </div> <div> <div>ACGIH</div> <div>10.0 ppm</div> <div>600 ppm</div> </div> <div> <div>Benzene</div> <div>Pentane</div> </div>			

* Pentane results

SOLVENT SEPARATION LAB
Building 83

BENZENE

Date	Sample I.D.	Location	Results		TWA
			AM	PM	
8/18	Pers	Varies - Hood area	0.32	1.38	0.85
	Area	At Working hood	<0.32	<0.46	<0.78
	Area	At Solvent hood Storage	-	1.43	
8/30	Pers	Varies - Hood area	0.32	0.76	0.4
	Area	At Working hood	<0.34	<0.42	<0.76
	Area	At Solvent hood Storage	<0.38	<0.47	<0.85
<p style="text-align: center;">TLV's</p> <p>OSHA 1.0 ppm</p> <p>ACGIH 10.0 ppm</p>					

SOLVENT SEPARATION LABORATORY

TOTAL HYDROCARBONS/BENZENE SOLUBLES

Date	Sample I.D.	Location	Results (mg/m ³)	
			*BS	*TH
6/9/78	Pers 2301	At hood	< 0.09	0.18
	Area 2302	5 ft. from hood	< 0.09	0.19
7/11/78	Pers 2773	At hood	< 0.09	0.02
	Area 2774	5 ft. from hood	< 0.09	0.02
<div>TLV's</div> <div> <div>OSHA 0.15 mg/m³</div> <div>ACGIH 0.20 mg/m³</div> </div> <div>Benzene Solubles</div>				

*BS - Benzene Solubles

*TH - Total Hydrocarbons

FLAME SPRAY AREA

Results of the nickel fume samples collected inside the Flame Spray exhaust hood enclosure at the face area were far below the current OSHA recommended value of 1.0 mg/m^3 .

Results obtained from nitrogen dioxide sampling in this area were also well below the OSHA permissible values.

The values for both nickel and nitrogen dioxide at a distance of three feet from the face area of the exhaust hood were lower than at the hood face area.

FLAME SPRAY OPERATION
BUILDING 87

NITROGEN DIOXIDE

Date	Sample I.D.	Location	Results (ppm)
6/29/78	Area 2528	1 ft. from hood	0.005
	Area 2529	3 ft. from hood	0.004
7/11/78	Area 2771	3 ft. from hood	0.003
	Area 2772	At hood face	0.008
<p style="text-align: center;">TLV's</p> <p>CSHA 5 ppm</p> <p>ACGIH 5 ppm</p>			

FLAME SPRAY OPERATION
Building 87

* Nickel

Date	Sample I.D.	Location	Results (mg/m ³)
6/7/78	Area 2372	3 ft. from hood face	0.04
	Area 2373	At hood face	0.43
	Area 2374	1 ft. from hood face	0.89
6/29/78	Area 2662	3 ft. from hood face	N.D.
	Area 2663	1 ft. from hood face	N.D.
7/11/78	Area 2780	At hood face	0.09
	Area 2781	At hood face	0.22
<p style="text-align: center;">TLV's</p> <p>OSHA 1.0 mg/m³</p> <p>ACGIH 1.0 mg/m³</p>			

N.D. - Not detected

* All values listed represent average concentrations determined from a one-hour sampling period.

CENTRIFUGE AREA

Results obtained from evaluations made on three different days for total hydrocarbons and benzene soluble material in Personal and Area samples showed all values to be below permissible OSHA and ACGIH values, with the exception of three benzene soluble samples collected on 5/11/78. This excess result may be due to a short sampling period at that time. (See Discusssion for further explanation.)

CENTRIFUGE AREA
PROCESS DEVELOPMENT UNIT (PDU) 1/2 TON PER DAY

TOTAL HYDROCARBONS/BENZENE SOLUBLES

Date	Sample I.D.	Location	Results (mg/m ³)	
			*BS	*TH
4/27/78	Pers 1722	At Centrifuge	<0.01	-
	Pers 1723	At Centrifuge	<0.01	0.36
	Area 1724	10 ft. North of Centrifuge	<0.01	0.37
5/11/78	Pers 1979	At Centrifuge	<0.30	1.15
	Pers 1980	At Centrifuge	<0.32	1.34
	Area 1981	10 ft. North of Centrifuge	0.32	0.89
6/29/78	Area 2665 (Background)	10 ft. North of Centrifuge	<0.06	0.19
<p style="text-align: center;">TLV's</p> <p>OSHA 0.15 mg/m³ Benzene, Solubles</p> <p>ACGIH 0.20 mg/m³</p>				

* BS - Benzene Solubles

* TH - Total Hydrocarbons

- Uncertainty on this weighing

CENTRIFUGE OPERATION
PROCESS DEVELOPMENT UNIT (PDU) 1/2 TON PER DAY

BENZENE (FROM NAPHTHA)

Date	Sample I.D.	Location	Results (ppm)
5/11/78	Pers 1983	At Centrifuge	< 0.33
	Pers 1984	At Centrifuge	< 0.56
	Area 1985	10 ft. North of centrifuge	< 0.72
6/29/78	Area 2661 (Background)	10 ft. North of centrifuge	0.13
<p style="text-align: center;">TLV's</p> <p>OSHA 1.0 ppm</p> <p>ACGIH 10.0 ppm</p>			

CENTRIFUGE OPERATION
PROCESS DEVELOPMENT UNIT (PDU) 1/2 TON PER DAY

NAPHTHA

Date	Sample I.D.	Location	Results (mg/m ³)
4/27/78	Pers 1729	At Centrifuge	41.18
	Pers 1730	At Centrifuge	140.33
	Area 1731	10 ft. North of Centrifuge	26.66
<p style="text-align: center;">TLV's</p> <p>OSHA 400 mg/m³</p> <p>ACGIH -</p>			

COAL-OIL SLURRY AREA

All results for samples containing total hydrocarbons, benzene soluble material, and respirable silica dust indicated compliance with the present OSHA permissible values.

The respirable dust samples were analyzed for silica by the x-ray diffraction method. Neither quartz nor cristobalite was detected in any of the samples.

COAL-OIL SLURRY MIXING OPERATION
 Building 83 Room 116

TOTAL HYDROCARBONS/BENZENE SOLUBLES

Date	Sample I.D.	Location	Results (mg/m ³)	
			*BS	*TH
4/27/78	Pers 1725	Slurry Area (varies)	<0.01	3.79
	Area 1726	20 ft. North of Unit	<0.01	0.55
	Area 1727	10ft. North of Unit	<0.01	0.27
6/7/78	Area 2370 (Background)	20 ft. North of unit	<0.07	0.28
6/29/78	Area 2665 (Background)	10 ft. North of unit	0.12	0.27
<p style="text-align: center;">TLV's</p> <p>OSHA 0.15 mg/m³</p> <p>ACGIH 0.20 mg/m³</p> <p style="text-align: center;">Benzene Solubles</p>				

* BS - Benzene Solubles

* TH - Total Hydrocarbons

COAL-OIL SLURRY MIXING OPERATION
Building 83 Room 116

FREE SILICA (PERCENT)*

Date	Sample I.D.	Location	Results (%)
4/27/78	Pers 1718	Slurry Area (varies)	N.D.
	Area 1719	20 ft. North of unit	N.D.
	Area 1720	10 ft. North of unit	N.D.
4/25/78	Pers 1658	Slurry Area (varies)	N.D.
	Area 1659	20 ft. North of unit	N.D.
	Area 1660	10 ft. North of unit	N.D.
6/7/78	Area 2368 (background)	10 ft. North of unit	N.D.
<p style="text-align: center;">TLV's</p> <p>OSHA</p> <p>ACGIH</p>			

* Free silica was not detected in any of the samples.

DISCUSSION

It should be emphasized that values listed in the Results Section of this report represent average concentrations obtained during the sampling period. These values, for most samples, represent a minimum seven-hour sampling period. Compliance with OSHA standards is based on a comparison of eight-hour time-weighted average (TWA) exposures with existing threshold limit values (TLV's). The TWA is determined by use of the following formula:

$$TWA = \frac{C_1 T_1 + C_2 T_2 + C_N T_N}{\text{Total sampling time or eight hours}}$$

Where: T = Sampling time (hours)
 C = Average concentration during T

For purposes of this evaluation, the actual sampling time in hours was used as the denominator in the formulae. It was felt that results expressed as average concentrations would provide more useful information than an eight-hour TWA for purposes of this evaluation.

Sampling conducted in the Flame Spray Area for determination of nickel fume and nitrogen dioxide concentrations covered a period of only 40-60 minutes because of the normal short-term nature of this process.

Two samples (No. 1978 and 1980) for total hydrocarbon and for benzene soluble material collected on 5/11/78 in the Centrifuge Area were not large enough to be above the lower sensitivity of the analytical equipment because of the short sampling period. One sample (No. 1981) resulted in a concentration in excess of the

existing OSHA TLV. This value may represent a maximum concentration due to the short sampling period, during maximum exposure conditions.

It should also be noted that due to the fact that maintenance work was being carried out in the Centrifuge Area during the day shift, production during the evening work shifts, (4/27/78 and 5/11/78), represented about twice the normal.

Values for benzene concentrations in the Solvent Analysis Laboratory and the Solvent Separation Laboratory were well below the current permissible OSHA value of 1.0 ppm, but results from personal samples indicate that exposures could at times exceed this permissible value. Continued maintenance of the ventilation system in this area, along with more emphasis on handling materials under the chemical hoods, should maintain benzene concentrations to the minimum possible levels.

The Centrifuge and Coal-Oil Slurry operations were discontinued before three full sampling periods could be completed but background samples were collected in these areas to fulfill sampling requirements. This change in working conditions, along with the increased workload in the Centrifuge Area, resulted in unusual conditions for sampling. Normal conditions were obtained during the sampling periods in the other process areas.

All operations in Building 83 were under temporary ventilation during sampling. Extensive ventilation system changes were being made in the Centrifuge Area during this evaluation.

RECOMMENDATIONS

Following are recommendations that were observed during the environmental survey and the air sample results:

A greater effort should be made to limit the use of benzene to shorter work periods. Use of benzene should be used, if at all possible, inside a satisfactory ventilated and designed chemical hood.

Good natural ventilation existed in the Centrifuge, Coal-Oil Slurry, and Water Treatment Areas during this evaluation, but consideration should be given to additional air sampling during the winter months when the buildings are closed.

Although the results for naphtha and benzene exposures in the Centrifuge Area are within OSHA permissible values, it is recommended that the tube cleaning operation be provided with adequate local exhaust ventilation.

Rags used for cleaning centrifuge tubes and solvent spillage should be immediately placed in closed containers.

The local exhaust ventilation on the platform where the tubes are moved from the centrifuges does not appear to be adequate. It should be improved to capture the toxic vapors when the centrifuges are opened.

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APPENDIX A

Benzene

Analyte:	Benzene	Method No.:	S311
Matrix:	Air	Range:	13-51.8 ppm
OSHA Standard:	Ceiling - 25 ppm Peak - 50 ppm 8-hr. T.W.A. - 10 ppm	Precision ($\overline{CV}_T$):	0.059
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	4/23/76

1. Principle of the Method (Reference 11.1)

- 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.
- 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 for standards.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 13-51.8 ppm at an atmospheric temperature and pressure of 24°C and 762 mm Hg, using a 2-liter sample. Under the conditions of sample size (2 liters) the probable useful range of this method is 2.5-100 ppm. 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 benzene and other substances in the air. The first section of the charcoal tube was found to hold at least 6.8 mg of benzene when a test atmosphere containing 149.1 mg/cu m of benzene in air was sampled at 0.19 liter per minute for 240 minutes; breakthrough was not observed at this time since no benzene was detected in the backup section of the charcoal tube.

(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. 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 efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.
- 3.2 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.
- 3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered 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 13-51.8 ppm was 0.059. This value corresponds to a 1.5 ppm standard deviation at the OSHA ceiling standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.
- 4.2 On the average the concentrations obtained at the OSHA ceiling standard level using the overall sampling and analytical method were 0.8% higher than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result in Section 10.5.

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 may also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample.

- 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 within $\pm 5\%$ 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 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 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 (3-ft x 1.8-in. O.D. stainless steel) packed with 50/80 mesh Porapak, Type Q.
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.
- 6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.
- 6.8 Pipets: 1.0-ml delivery pipets.
- 6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

- 7.1 Chromatographic quality carbon disulfide.
- 7.2 Benzene, reagent grade.
- 7.3 Hexane, reagent grade.
- 7.4 Purified nitrogen.
- 7.5 Prepurified hydrogen.
- 7.6 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 nearer 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 At the ceiling concentration, a sample size of 2 liters is recommended. Sample for 10 minutes at a flow rate of 0.20 liter per minute.

8.3.6 At the 8-hour time weighted average concentration, a sample size of 12 liters is recommended. Sample at a flow rate of 0.20 liter per minute.

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

- 8.3.8 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.
- 8.3.9 With each batch of ten samples submit one tube from the same lot of tubes which was used for sample collection and which is subjected to exactly the same handling as the samples except that no air is drawn through it. Label this as a blank.
- 8.3.10 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.3.11 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample 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. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.
- 8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (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. If an automatic sample injector is used, 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. 50 ml/min (60 psig) nitrogen carrier gas flow
 2. 65 ml/min (24 psig) hydrogen gas flow to detector
 3. 500 ml/min (50 psig) air flow to detector
 4. 200°C injector temperature
 5. 265°C manifold temperature (detector)
 6. 115°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 evaporation of solvent

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter 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 microliter 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-microliter 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 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters 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 method.

- 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, provided 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 64 mm, 4-mm I.D. glass tube, flame sealed at one end. 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 a hexane solution of benzene containing 43.9 $\mu\text{g}/\text{ml}$ is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample vials, capped with Teflon-faced septa, may be used in place of the glass tubes. The amount injected is equivalent to that present in a 2-liter air sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X of the OSHA ceiling 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 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 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples. These standards are used to confirm the calibration of the gas chromatograph.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

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

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus 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/1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert 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/1.0 ml versus peak area. Note: Since no internal standard is used in this 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 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/1.0 ml carbon disulfide, and the volume of sample injected is identical to the volume of the standard injected.

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

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

$$\text{mg sample} = \text{mg found in front section of sample tube}$$

$$\text{mg blank} = \text{mg found in front section of blank tube}$$

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount 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 the analyte in the air sampled can be expressed in mg/cu m.

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

10.6 Another method of expressing concentration is ppm.

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

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
M.W. = 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, NIOSH Contract CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

BENZENE-SOLUBLE COMPOUNDS IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte: Benzene Solubles	Method No.: P&CAM 217
Matrix: Air particulates trapped on silver membrane and glass fiber filters	Range: 20 μg /sample
Procedure: Ultrasonic extraction with benzene, aliquot evaporated to dryness and weighed	Precision (CV): 0.02 (analytical) for 1 mg; 0.23 (analytical) for 20 μg
Date Issued: 1/29/76	Classification: D (Operational)
Date Revised:	

1. Principle of the Method

Particulate matter suspended in air is collected on a filter. The filter is extracted with benzene with ultrasonic agitation. An aliquot of the extract is evaporated to dryness and the residue is weighed.

2. Range and Sensitivity

The limit of detection is estimated to be 20 μg of benzene-soluble material in a filter sample; this value is two times the standard deviation of values determined for six blank filters. For a 300-liter air sample the limit of detection is, therefore, 0.067 mg/m^3 . The range of the method extends upward to any weighable amount greater than 20 μg per sample.

3. Interferences

By definition, the method is inherently free of interferences that could occur in the particulate material collected on a filter. Errors may be caused by extraneous dust picked up in handling the filter or by changes in humidity or temperature during weighing. These errors may be avoided if the sample is properly protected and if temperature and humidity are controlled.

4. Precision and Accuracy

- 4.1 The analytical precision is dependent upon the amount of residue remaining to be weighed after evaporation of the solvent, as illustrated by the following example. Several benzene extracts of samples of aluminum reduction plant emissions were combined to give a solution containing the equivalent of 1.350 mg of benzene-soluble material per sample; nine aliquots of this solution gave residue weights with a coefficient of variation of 0.02. Benzene extracts of six blank filters gave residue weights with a coefficient of variation of 0.23.
- 4.2 The accuracy of this method has not been determined.

5. Advantages and Disadvantages

- 5.1 Ultrasonic agitation has been reported to be more efficient than Soxhlet extraction for dissolving organic materials in particulate samples. For example, the recovery of polycyclic arenes is higher with ultrasonic extraction than with Soxhlet extraction. (Reference 11.3).
- 5.2 A major advantage of the method is that it is simple and direct. The analysis can be made by a technician with minimum training. An experienced technician should be able to analyze a set of 12 samples in 4 hr. If the extraction, evaporation, and weighing are staggered, it should be possible to analyze three sets of 12 samples in an 8-hr day.
- 5.3 The method is free of interference if temperature and humidity are constant during weighing and if the laboratory atmosphere is dust-free.
- 5.4 The method is empirical and nonspecific, and measures all substances in a sample that are soluble in benzene. It yields no information on the composition of the benzene-soluble material.

6. Apparatus

6.1 Air Sampling Equipment

- 6.1.1 Glass fiber filters, 37 mm, free of organic binder, with an efficiency of at least 99% as determined by the DOP penetration test.
- 6.1.2 Silver membrane filters, 37 mm, 0.8 μ m pore size, Sela Corporation of America, No. FM-37-(0.8), or equivalent.
- 6.1.3 Disposable plastic filter holder (cassette) for 37-mm filters, Millipore M000 037 PO, or equivalent. In order to accommodate the two filters, the cassette must be held together with tape or a shrinkable band.

6.1.4 **Personal sampling pump** capable of operating for 4 hr at 1.5 ℓ /min. The pump should be calibrated with a representative filter assembly in the line. A wet or dry test meter or a glass rotameter capable of measuring the flow rate of 1.5 ℓ /min to within $\pm 5\%$ may be used for the calibration.

6.2 **Electrobalance.** Cahn Instruments, Model G-2, or equivalent.

6.3 **Vacuum oven.** Thelco Model 19, GCA Precision Scientific, or equivalent.

6.4 **Ultrasonic bath.** Dynasonics Corporation, Model NT-201, 90 kHz, 60 W, or equivalent. An ultrasonic bath operating at a lower frequency and having a higher power output may improve extraction efficiency. (See Reference 11.4.). A test tube support is needed for use in the ultrasonic bath.

6.5 **Test tubes,** 100 mm by 16 mm, with Teflon-lined screw caps

6.6 **Teflon weighing cups,** Cahn Instruments No. 2034, or equivalent, approximate tare weight, 60 mg.

6.7 **Allihn tubes,** fine-porosity fritted glass, 30 mL.

6.8 **Small glass vials** with Teflon-lined screw caps.

6.9 **Volumetric pipettes,** 1 and 5 mL.

6.10 **Wood applicator sticks,** 6 in. long and 1/16 in. diameter.

6.11 **Weighing paper,** 3.5 by 4.5 in.

6.12 **Tweezers.**

7. **Reagents**

7.1 **Benzene,** ACS reagent grade.

7.2 **Nitrogen,** prepurified.

8. **Procedure**

8.1 **Cleaning of Equipment.** Wash the glassware with detergent solution and rinse with tap water and distilled water. Wash the Teflon weighing cups with reagent grade acetone and allow them to dry.

8.2 Collection and Shipping of Samples

8.2.1 Assemble the filters in the filter holder so that the air being sampled passes first through a glass fiber filter and then through a silver membrane filter. Remove the small plugs from the filter holder and connect the filter holder to the sampling pump by means of an adaptor and a length of tubing. Sample at least 300 liters of air at 1.5 L/min. The optimum sample volume will depend on the type of workroom environment being sampled. Since high concentrations of particulate material or certain types of mists may plug the filters, the flow rate should be checked about once every hour. On completion of sampling, reinsert the small plugs in the inlet and outlet of the filter holder.

8.2.2 With each group of samples prepare at least three blanks consisting of a filter holder with representative filters that have been handled in the same manner as the sample filters, except that no air is drawn through them. The samples and the blanks should be shipped promptly in a light-proof container to prevent photooxidation or damage during transit.

8.3 **Analysis of Samples** The glass fiber and silver membrane filters are extracted together in the same test tube. At least three sets of blank filters are extracted along with each group of samples.

8.3.1 Extraction

1. Remove the top portion of the filter holder. Hold the bottom portion containing the filters over a piece of weighing paper to catch any particulate material that may fall out. Remove the small plug from the bottom portion of the filter holder and insert an applicator stick through the hole. Gently raise the filters and grasp the unexposed edge with tweezers. Fold the filters in half and then lengthwise so that they can be inserted into a test tube. Push the folded filters to the bottom of the test tube with the applicator stick. Add to the test tube any particulate material remaining in the filter holder or collected on the weighing paper.
2. Pipette 5.0 mL of benzene into the test tube. This amount of solvent should completely cover the filters. Be careful during the subsequent extraction and filtering procedures to avoid significant loss of benzene by evaporation.
3. Place the test tubes in the test tube support in the ultrasonic bath so that the level of water in the bath is above the level of the solvent. Turn on the ultrasonic bath and sonicate the sample for 5 min.

4. Decant the solvent into an Allihn tube and collect the filtrate in a small vial. Force the solvent through the Allihn filter under positive nitrogen pressure. This may be accomplished by connecting the nitrogen cylinder to a glass "T," leaving one arm of the "T" open and connecting the other arm to a No. 4 one-hole rubber stopper, which is pressed against the top of the Allihn tube; pressure is controlled with a finger placed against the open arm of the "T." When the filtration has been completed, close the vial tightly with a Teflon-lined screw cap.

8.3.2 Gravimetric Determination

1. Transfer 1.0 ml of the benzene solution to a tared Teflon cup. Evaporate the solvent in a preheated vacuum oven at 40°C and 200 torr and continue drying for a total of 2 hr. The residue should be visibly dry in about 1 hr and in 2 hr all of the benzene will have been removed.
2. Equilibrate the sample for at least 30 min in a weighing room where the temperature and humidity are kept constant. Determine the weight of the residue to the nearest microgram. Because of the small weight difference being measured, it is critical that the temperature and humidity be the same when the residue is weighed as when the empty Teflon cup is weighed.

9 Calibration and Standards

No calibration or standards are required for this method.

10 Calculations

The result of this analysis is expressed as the weight (in mg) of benzene-soluble material in a filter sample. The weight of the residue from a 1.0-ml aliquot of sample extract is corrected by subtracting the average weight of the residue from aliquots of the blank-filter extracts. This corrected weight is multiplied by 5 to obtain the total amount of benzene-soluble material in the sample.

11. References

- 11.1 Bolden, C., and E. Sawicki, *Int. J. Environ. Anal. Chem.*, **4**, 9 (1975).
- 11.2 Seim, H.J., W.W. Hanneman, L. R. Barsotti, and T.J. Walker, "A Combined Gravimetric and Gas Chromatographic Determination of Airborne Particulate Polycyclic Organic Matter (PROM)," American Industrial Hygiene Conference, Minneapolis, Minn., June 1975.
- 11.3 Chatot, G., M. Castegnaro, J.L. Roche, and R. Fontanges, *Anal. Chim. Acta*, **53**, 259 (1971).
- 11.4 Alliger, H., *Am. Lab.*, **7** (10), 75 (1975).
- 11.5 Richards, R.T., D.T. Donovan, and J.R. Hall, *Am. Ind. Hyg. Ass. J.*, **28**, 590 (1967).

Phenol

Analyte:	Phenol	Method No.: S330
Matrix:	Air	Range: 9.46-37.8 mg/cu m
OSHA Standard:	5 ppm (19 mg/cu m)-skin	Precision ($\overline{CV}_T$): 0.068
Procedures:	Bubbler collection in dilute sodium hydroxide; GC analysis of the collected samples after acidification with sulfuric acid	Validation Date: 8/1/75

1. Principle of the Method

- 1.1 A known volume of air is drawn through a midjet bubbler containing 15 ml of 0.1 N sodium hydroxide to trap the phenol vapors present.
- 1.2 The resulting solution is acidified with sulfuric acid.
- 1.3 An aliquot of the collected sample is injected into a gas chromatograph.
- 1.4 The area of the resulting peak is determined and compared with the areas for standards.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 9.46-37.8 mg/cu m at an atmospheric temperature and pressure of 22°C and 760 mm Hg, using a 100-liter sample. Under the conditions of sample size (100 liters) the probable useful range of this method is 5-60 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 6-mg sample. The method is capable of measuring much smaller amounts if the analytical method recovery is adequate.

3. Interference

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

- 3.2 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 9.46-37.8 mg/cu m was 0.068. This value corresponds to a 1.3 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.1.
- 4.2 A collection efficiency of 1.00 ± 0.01 was determined for the collecting medium. On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 2.6% lower than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result in paragraph 10.3.

5. Advantages and Disadvantages of the Method

- 5.1 The samples collected in bubblers are analyzed by means of a quick, instrumental method.

6. Apparatus

- 6.1 Sampling Equipment. The sampling unit for the bubbler collection method consists of the following components:
- 6.1.1 A standard glass midget bubbler containing the collection medium (Section 7.4).
 - 6.1.2 A pump suitable for delivering at least 1 liter per minute for 100 minutes. The sampling pump is protected from splashover or solvent condensation by a 5-cm long by 6-mm I.D. glass tube loosely packed with a plug of glass wool and inserted between the exit arm of the bubbler and the pump.
 - 6.1.3 An integrating volume meter such as a dry gas or wet test meter.
 - 6.1.4 Thermometer.
 - 6.1.5 Manometer.
 - 6.1.6 Stopwatch.

- 6.2 Gas chromatograph equipped with a flame ionization detector.
- 6.3 Column (4-ft long x 1/4-in O.D. stainless steel) packed with 35/60 mesh Tenax.
- 6.4 An electronic integrator or some other suitable method for measuring peak areas.
- 6.5 Microliter syringes: 10-microliter, and other convenient sizes for making standards and injecting samples into the GC.
- 6.6 Volumetric flasks: convenient sizes for making solutions.
- 6.7 Pipets: 15 ml or other convenient sizes.

7. Reagents

- 7.1 Distilled water.
- 7.2 Phenol, reagent grade.
- 7.3 Sulfuric acid, reagent grade.
- 7.4 Collection medium, 0.1 N sodium hydroxide. Dissolve 4.0 g of sodium hydroxide in distilled water and dilute to a final volume of 1 liter.
- 7.5 Purified nitrogen.
- 7.6 Purified 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 Sampling Pumps. Each pump should be calibrated by using an integrating volume meter (Section 6.1.3) or other means.
- 8.3 Collection and Shipping of Samples.
 - 8.3.1 Pour 15 ml of the collection medium (Section 7.4) into each midget bubbler.
 - 8.3.2 Connect the midget bubbler with a 5-cm glass adsorption tube (6-mm I.D. and 8-mm O.D.) containing the glass wool plug, then to the personal sampling pump using short pieces of flexible tubing. The air being sampled should not pass through any tubing or other equipment before entering the bubbler.

- 8.3.3 Turn the pump on to begin sample collection. Care should be taken to measure the flow rate, the time and/or the volume as accurately as possible. Record the atmospheric pressure and the temperature. If the pressure reading is not available, record the elevation. The sample should be taken at a flow rate of 1 liter per minute. A sample size of 100 liters is recommended.
- 8.3.4 After sampling, the bubbler stem may be removed and cleaned. Tap the stem gently against the inside wall of the bubbler bottle to recover as much of the sampling solution as possible. Wash the stem with 1 ml of distilled water, adding the wash to the bubbler. The bubblers are sealed with a hard, non-reactive stopper (preferably Teflon or glass). Do not seal with rubber. The stoppers on the bubblers should be tightly sealed to prevent leakage during shipping.
- 8.3.5 Care should be taken to minimize spillage or loss by evaporation.
- 8.3.6 Whenever possible, hand delivery of the samples is recommended. Otherwise, special bubbler shipping cases designed by NIOSH should be used to ship the samples.
- 8.3.7 A "blank" bubbler should be handled in the same manner as the bubblers containing samples (fill, seal, and transport) except that no air is sampled through this bubbler.

8.4 Analysis of Samples

- 8.4.1 The sample in each bubbler is analyzed separately.
- 8.4.2 Transfer the solution to a 25-ml volumetric flask.
- 8.4.3 Rinse the bubbler twice with 1 ml of distilled water and add the rinses to the flask.
- 8.4.4 Add 0.1 ml of concentrated sulfuric acid to the flask and mix. Check with pH paper to make sure that the pH is less than 4.
- 8.4.5 Dilute to mark with distilled water and mix.
- 8.4.6 GC Conditions. The typical operating conditions for the gas chromatograph are:
1. 50 ml/min (60 psig) nitrogen carrier gas flow
 2. 65 ml/min (24 psig) hydrogen gas flow to detector

3. 500 ml/min (50 psig) air flow to detector
4. 215°C injector temperature
5. 225°C manifold temperature (detector)
6. 200°C column temperature

The glass inlet on the GC should be cleaned at the end of each day with water and acetone rinses. Reinsert the glass inlet into the injection port and let it bake out overnight.

8.4.7 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-microliter 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 microliter 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-microliter 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 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters 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 method.

8.4.8 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable means of area measurement, and preliminary results are read from a standard curve prepared as discussed below in paragraph 9.

8.5 Standard Solutions

8.5.1 Procedure for preparing standard solutions. Six standards at each of the three levels (0.5X, 1X, and 2X the OSHA standard) are prepared by introducing a known amount of analyte into 15 ml of 0.1 N sodium hydroxide in a 25-ml volumetric flask. The amount introduced is equivalent to that present in a 1-liter air sample. The standards are acidified with 0.1 ml of concentrated sulfuric acid and made up to volume with distilled water. The solution should be checked with pH paper to make sure that its pH is less than 3. A parallel blank is prepared in the same manner, except that no analyte is added. The standards and blank are analyzed in exactly the same manner as the samples in Section 8.4.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/sample. A series of standards, varying in concentration over the range of interest, are prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting mg/sample 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 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed because the standard curve is based on mg/sample 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.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

$$\text{mg sample} = \text{mg found in sample bubbler}$$

$$\text{mg blank} = \text{mg found in blank bubbler}$$

10.3 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{corrected mg (Section 10.3)} \times 1000 \text{ (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.4 Another method of expressing concentration is ppm.

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

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

M.W. = molecular weight (g/mole) of analyte

760 = standard pressure (mm Hg)

298 = standard temperature (°K)

11. Reference

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

AMMONIA

METHOD FOR ANALYSIS OF AIR SAMPLES

Equipment

- (a) Spectrophotometer
- (b) 50-ml beakers
- (c) 1 each 1-, 2-, 5-, 10-, 20-ml pipets
- (d) 1-cm cuvettes
- (e) 1-liter volumetric flasks

Reagents

- (a) Nessler Reagent

Dissolve 100 g of mercury (II) iodide and 70 g of potassium iodide in a small quantity of water, and add this mixture slowly, with stirring, to a cool solution (15-20 C) of 160 g sodium hydroxide in 500 ml water. Dilute to 1 liter. Store in rubber-stoppered borosilicate glassware and out of sunlight to maintain reagent stability for periods up to a year under normal laboratory conditions.

- (b) Ammonium chloride, stock solution (1.0 ml = 1.0 mg ammonia)

Dissolve 3.141 g of ammonium chloride in water and dilute to 1 liter with distilled, ammonia-free water.

- (c) Ammonium chloride, standard solution (1.0 ml = 10.0 μ g ammonia)

Dilute 10.0 ml of 1.0 mg ammonia/ml stock solution to 1000 ml with distilled, ammonia-free water.

Preparation of Standard Curve

To a series of 50-ml beakers add 25.0, 23.0, 20.0, 17.0, and 13.0 ml of absorbing solution (Appendix I). To these beakers in the same order add 0.0, 2.0, 5.0, 8.0, and 12.0 ml of ammonium chloride standard solution, so that the final volume is 25 ml. Add 2.0 ml of Nessler reagent, mix well, and cover beakers. After 20 minutes the color intensity is measured spectrophotometrically in a 1-cm cell at 425 nm against the reagent blank.

Analysis of Samples

Samples should be analyzed within a week of collection. Transfer an aliquot of the blank and sample solutions to 50-ml beakers. Add absorbing solution to adjust the final volume to 25 ml in each beaker. Add 2.0 ml of Nessler reagent, mix well, and cover beakers. After 20 minutes the color intensity is determined by the same procedure as the standards.

Calculations

From the standard curve determine the micrograms of ammonia in the sample solution aliquot. Calculate the concentration of ammonia in the air as ppm:

$$\text{ppm ammonia} = \frac{1.44 \mu\text{l NH}_3}{\mu\text{g NH}_3} \times \frac{\text{AB}}{\text{CDE}}$$

$$\text{Where } \frac{1.44 \mu\text{l NH}_3}{\mu\text{g NH}_3} = \frac{\mu\text{mole}}{17 \mu\text{g NH}_3} \times \frac{22.4 \mu\text{l}}{\mu\text{mole}} \times \frac{298 \text{ K}}{273 \text{ K}}$$

- A = Sample solution volume in milliliters = 20 ml
(10 ml scrubber solution plus 10 ml rinse)
- B = μg of ammonia in aliquot analyzed
- C = Volume of aliquot in milliliters
- D = Time of sampling period in minutes
- E = Sampling impinger flow rate in liters/min.

Cresol, All Isomers

Analyte:	Cresol, all isomers	Method No.: S167
Matrix:	Air	Range: 10.54-42.2 mg/cu m
OSHA Standard:	5 ppm (22 mg/cu m)-skin	Precision ($\overline{CV}_T$): 0.068
Procedure:	Adsorption on silica gel, desorption with acetone, GC	Validation Date: 8/1/75

1. Principle of the Method (Reference 11.1)

- 1.1 A known volume of air is drawn through a silica gel tube to trap the organic vapors present.
- 1.2 The silica gel in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with acetone.
- 1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.
- 1.4 The combined areas of the resulting two peaks are determined and compared with areas obtained for standards.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 10.54-42.2 mg/cu m at an atmospheric temperature and pressure of 22°C and 760 mm Hg, using a 20-liter sample. Under the conditions of sample size (20 liters) the probable useful range of this method is 5-60 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 1-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 silica gel tube. This capacity varies with the concentrations of the analyte and other substances in the air. The first section of the silica gel tube was found to hold at least 1.87 mg of analyte when a test atmosphere containing

42.2 mg/cu m of analyte in air was sampled at 0.185 liter per minute for 240 minutes. (The silica gel tube consists of two sections of silica gel 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. Interferences

- 3.1 Silica gel has a high affinity for water, so organic vapors will not be trapped efficiently in the presence of a high relative humidity. This effect may be important even though there is no visual evidence of condensed water in the silica gel tube.
- 3.2 When compounds other than the isomers of cresol are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample. Since acetone is used to desorb the analyte from the silica gel, it is not possible to measure acetone in the sample.
- 3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered 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 10.54-42.2 mg/cu m was 0.068. This value corresponds to a 1.5 mg/cu m standard deviation 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 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 4.2% lower than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result from paragraph 10.5.

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 substances 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 silica gel 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 within $\pm 5\%$ at the recommended flow rate. (Reference 11.3)
- 6.2 Silica gel 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 silica gel separated by a 2-mm portion of urethane foam. The adsorbing section contains approximately 150 mg of silica gel, the backup section, approximately 75 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 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 mesh, acid washed DMCS Chromosorb W.
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

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

6.8 Pipets: 1.0-ml delivery pipets.

6.9 Volumetric flasks: convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality acetone.

7.2 Cresol (all isomers) - prepare a standard mixture of the isomers by adding together 20 g of the ortho, 40 g of the meta, and 30 g of the para isomers and mix.

7.3 Prepurified hydrogen.

7.4 Filtered compressed air.

7.5 Purified nitrogen.

7.6 n-Hexane, reagent grade.

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 silica gel 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 silica gel is used as a back-up and should be positioned nearest the sampling pump.

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

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

8.3.5 A sample size of 20 liters is recommended. Sample at a flow of 0.20 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm 5\%$.

- 8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.
- 8.3.7 The silica gel 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 bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the silica gel tubes.

8.4 Analysis of Samples

- 8.4.1 Preparation of Samples. In preparation for analysis, each silica gel tube is scored with a file in front of the first section of silica gel and broken open. The glass wool and the silica gel in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.
- 8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of acetone is pipetted into each sample container. Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, 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. 50 ml/min (60 psig) nitrogen carrier gas flow
 2. .65 ml/min (24 psig) hydrogen gas flow to detector
 3. 500 ml/min (50 psig) air flow to detector
 4. 230°C injector temperature
 5. 250°C manifold temperature (detector)
 6. 200°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-microliter 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 microliter 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-microliter 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 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters 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 method.

8.4.5 Measurement of area. Although there are three isomers of cresol, there are only two peaks on the gas chromatogram, because the meta and para isomers have the same retention time. The total area of the two sample peaks 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 silica gel 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 the same batch of silica gel is used.

8.5.2 Procedure for determining desorption efficiency. Silica gel equivalent to the amount in the first section of the sampling tube (approximately 150 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This silica gel must be from the same batch as that used in obtaining the samples and can be obtained from unused silica gel tubes. The open end is capped with Parafilm.

A standard solution is prepared by placing 1100 mg of the mixture of the isomers of cresol in a 10-ml volumetric flask and making it up to volume with n-hexane. A known amount of the standard solution is injected directly into the silica gel with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

The amount injected is equivalent to that present in a 20-liter air sample at the selected level. Six tubes at each of the three levels are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the silica gel. These 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 1.0 ml of acetone with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) is dependent on the amount of analyte collected on the silica gel. The desorption efficiency equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

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

The desorption efficiency is dependent on the amount of analyte collected on the silica gel. Plot the desorption efficiency versus 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/1.0 ml acetone, because samples are desorbed in this amount of acetone. A series of standards, varying in concentration over the range of interest, are 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/1.0 ml versus total 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 Read the weight, in mg, corresponding to each combined peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/1.0 ml acetone 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.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

$$\text{mg sample} = \text{mg found in front section of sample tube}$$

$$\text{mg blank} = \text{mg found in front section of blank tube}$$

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (See Section 8.5.2) for the amount 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 the analyte in the air sampled can be expressed in mg/cu m.

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

10.6 Another method of expressing concentration is ppm.

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

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
M.W.	= 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, NIOSH Contract No. CDC-99-74-45.
- 11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

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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 $\mu\text{g}/\text{ml}$ 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- μ m 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 ($1000\ \mu\text{g}/\text{ml}$) for each metal in Table 1, commercially prepared or prepared per instrument manufacturer's recommendations.
- 7.4 Lanthanum nitrate [$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$].
- 7.5 Cesium nitrate (CsNO_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 $0.2 \times \text{TLV}$.

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 ($>2 \text{ mg}$) 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 $\text{HNO}_3\text{:H}_2\text{SO}_4$. 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 [$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$] 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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NITROGEN DIOXIDE IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Nitrogen Dioxide	Method No.:	P&CAM 108
Matrix:	Air	Range:	.01 to 10 µg/liter
Procedure:	Colorimetric	Precision:	< 5% RSD
Date Issued:	12/11/72		
Date Revised:	January 10, 1974	Classification:	C (Tentative)

1. Principle of the Method

The nitrogen dioxide is absorbed in an azo dye forming reagent (Reference 1). A stable pink color is produced within 15 minutes which may be read visually or in an appropriate instrument at 550 nm.

2. Range and Sensitivity

2.1 This method is intended for the manual determination of nitrogen dioxide in the atmosphere in the range of 0.005 to about 5 parts per million (ppm) by volume or 0.01 to 10 µg/liter, when sampling is conducted in fritted bubblers. The method is preferred when high sensitivity is needed.

2.2 Concentrations of 5 to 100 ppm in industrial atmospheres and in gas burner stacks also may be sampled by employing evacuated bottles or glass syringes. For higher concentrations, for automotive exhaust, and/or for samples relatively high in sulfur dioxide content, other methods should be applied.

3. Interferences

3.1 A tenfold ratio of sulfur dioxide to nitrogen dioxide produces no effect. A 30-fold ratio slowly bleaches the color to a slight extent. The addition of 1 percent acetone to the reagent before use retards the fading by forming another temporary product with sulfur dioxide. This permits reading within 4 to 5 hours (instead of the 45 minutes required when acetone is not added) without appreciable interferences. Interference from sulfur dioxide may be a problem in some stack gas samples (Section 2.2).

3.2 A fivefold ratio of ozone to nitrogen dioxide will cause a small interference, the maximal effect occurring in 3 hours. The reagent assumes a slightly orange tint.

3.3 Peroxyacynitrate (PAN) can give a response of approximately 15 to 35 percent of an equivalent molar concentration of nitrogen dioxide (Reference 2). In ordinary ambient air the concentrations of PAN are too low to cause any significant error.

3.4 The interferences from other nitrogen oxides and other gases which might be found in polluted air are negligible. However, if the evacuated bottle or syringe method is used to sample concentrations above 5 ppm, interference from NO (due to oxidation to NO₂) is possible (Section 8.2.3).

3.5 If strong oxidizing or reducing agents are present, the colors should be determined within 1 hour, if possible, to minimize any loss.

4 Precision and Accuracy

4.1 A precision of 1 percent of the mean can be achieved with careful work (Reference 3); the limiting factors are the measurements of the volume of the sample and of the absorbance of the color.

4.2 At present, accuracy data are not available.

5 Advantages and Disadvantages of the Method

This is a simple method with direct coloration of absorbing reagent, which can be put directly into cuvettes and read, or diluted with absorbing reagent and read.

6 Apparatus

6.1 **Absorber.** The sample is absorbed in an all-glass bubbler with a 60 μ maximum pore diameter frit.

6.1.1 The porosity of the fritted bubbler, as well as the sampling flow rate, affect absorption efficiency. An efficiency of over 95 percent may be expected with a flow rate of 0.4 liter/minute or less and a maximum pore diameter of 60 μ . Frits having a maximum pore diameter less than 60 μ will have a higher efficiency but will require an inconvenient pressure drop for sampling (see formula in Section 6.1.2). Considerably lower efficiencies are obtained with coarser frits, but these may be utilized if the flow rate is reduced.

- 6.1.2 Since the quality control by some manufacturers is rather poor, it is desirable to measure periodically the porosity of an absorber as follows: Carefully clean the apparatus with dichromate-concentrated sulfuric acid solution and then rinse it thoroughly with distilled water. Assemble the bubbler, add sufficient distilled water to barely cover the fritted portion, and measure the vacuum required to draw the first perceptible stream of air bubbles through the frit. Then calculate the maximum pore diameter as follows:

$$\text{Maximum pore diameter } (\mu) = \frac{30 s}{P}$$

where:

s = surface tension of water at the test temperature in dynes/cm
(73 at 18°C, 72 at 25°C, and 71 at 31°C),

P = measured vacuum, mm Hg.

- 6.1.3 Rinse the bubbler thoroughly with water and allow to dry before using. A rinsed and reproducibly drained bubbler may be used if the volume (r) of retained water is added to that of the absorbing reagent for the calculation of results. This correction may be determined as follows: Pipet into a drained bubbler exactly 10 ml of a colored solution (such as previously exposed absorbing reagent) of absorbance A_1 . Assemble the bubbler and rotate to rinse the inside with the solution. Rinse the fritted portion by pumping gently with a rubber bulb. Read the new absorbance, A_2 , of the solution. Then:

$$10A_1 = (10 + r) A_2$$

or:

$$r = 10 \frac{A_1}{A_2} - 1$$

- 6.2 **Air Metering Device.** A glass rotameter capable of accurately measuring a flow of 0.4 liter/minute is suitable. A wet test meter is convenient to check the calibration.
- 6.3 **Sampling Probe.** A glass or stainless steel tube 6 to 10 mm in diameter provided with a downward-facing intake (funnel or tip) is suitable. A small loosely fitting plug of glass wool may be inserted, when desirable, in the probe to exclude water droplets and particulate matter. The dead volume of the system should be kept minimal to permit rapid flushing during sampling to avoid losses of nitrogen dioxide on the surfaces.

- 6.4 **Grab-Sample Bottles.** Ordinary glass-stoppered borosilicate glass bottles of 30 to 250 mL sizes are suitable if provided with a mating ground joint attached to a stopcock for evacuation. Calibrate the volume by weighing with connecting piece, first empty, then filled to the stopcock with distilled water.
- 6.5 **Glass Syringes.** 50 or 100 mL syringes are convenient (although less accurate than bottles) for sampling.
- 6.6 **Air Pump.** A vacuum pump capable of drawing the required sample flow for intervals of up to 30 minutes is suitable. A tee connection at the intake is desirable. The inlet connected to the sampling train should have an appropriate trap and needle valve, preferably of stainless steel. The second inlet should have a valve for bleeding in a large excess flow of clean air to prevent condensation of acetic acid vapors from the absorbing reagent, with consequent corrosion of the pump. Alternatively, soda lime may be used in the trap. A filter and critical orifice may be substituted for the needle valve (Reference 4).
- 6.7 **Spectrophotometer or Colorimeter.** A laboratory instrument suitable for measuring the pink color at 550 nm, with stoppered tubes or cuvettes. The wavelength band width is not critical for this determination.
- 6.8 Assorted laboratory glassware.

7 Reagents

All chemicals used should be analytical reagent grade (Reference 5).

- 7.1 **Nitrite-Free Water.** All solutions are made in nitrite-free water. If available distilled or deionized water contains nitrite impurities (produces a pink color when added to absorbing reagent), redistill it in an all-glass still after adding a crystal each of potassium permanganate and of barium hydroxide.
- 7.2 **N-(1-Naphthyl) -Ethylenediamine Dihydrochloride, Stock Solution (0.1%).** Dissolve 0.4 g of the reagent in 100 mL of water. Solution is stable for several months if kept well stoppered in a brown bottle in the refrigerator. (Alternatively, weighed small amounts of the solid reagent may be stored.)
- 7.3 **Absorbing Reagent.** Dissolve 5 g of anhydrous sulfanilic acid (or 5.5 g of $\text{NH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$) in almost a liter of water containing 140 mL of glacial acetic acid. Gentle heating is permissible to speed up the process. To the cooled mixture, add 20 mL of the 0.1% stock solution of N-(1-naphthyl) -ethylenediamine dihydrochloride, and dilute to 1 liter. Avoid lengthy contact with air during both preparation and use, since discoloration of reagent will result because of absorption of nitrogen dioxide. The solution is stable for several months if kept

well-stoppered in a brown bottle in the refrigerator. The absorbing reagent should be allowed to warm to room temperature before use.

- 7.4 **Standard Sodium Nitrite Solution** (0.0203 g/liter). One ml of this working solution of sodium nitrite (NaNO_2) produces a color equivalent to that of $10\ \mu\text{l}$ of nitrogen dioxide (10 ppm in 1 liter of air at 760 mm of mercury and 25°C ; see Section 10.2.1). Prepare fresh just before use by dilution from a stronger stock solution containing 2.03 g of the reagent grade granular solid (calculated as 100 percent) per liter. It is desirable to assay (Reference 5), the solid reagent, especially if it is old. The stock solution is stable for 90 days at room temperature, and for a year in a brown bottle under refrigeration.

8. Procedure

- 8.1 **Cleaning of Glassware.** All washed glassware should be allowed to stand awhile in chromic acid solution, and then thoroughly rinsed with single and then double distilled water.
- 8.2 **Collection and Storage of Samples.** Three methods are described below. Concentrations below 5 ppm are sampled by the bubbler method. Higher concentrations may be sampled by the evacuated bottle method, or more conveniently (but less accurately) by the glass syringe method. The latter method is more useful when appreciable concentrations (e.g., 20 ppm) of nitric oxide are expected.

8.2.1 Bubbler Method

- 1 Assemble, *in order*, a sampling probe (optional), a glass rotameter, fritted absorber, and pump. Use ground-glass connections upstream from the absorber. Butt-to-butt glass connections with slightly greased vinyl or pure gum rubber tubing also may be used for connections without losses if lengths are kept minimal. The sampling rotameter may be used upstream from the bubbler provided occasional checks are made to show that no nitrogen dioxide is lost. The rotameter must be kept free from spray or dust.
- 2 Pipet 10.0 ml of absorbing reagent into a dry fritted bubbler (Section 6.1.3).
- 3 Draw an air sample through it at the rate of 0.4 liter/minute (or less) long enough to develop sufficient final color (about 10 to 30 minutes). Note the total volume of air sampled.
- 4 Measure and record the sample air temperature and pressure.

8.2.2 Evacuated Bottle Method

1. Sample in bottles of appropriate size containing 10.0 mL (or other convenient volume) of absorbing reagent. For 1 cm spectrophotometer cells, a 5:1 ratio of air sample volume to reagent volume will cover a concentration range up to 100 ppm; a 25:1 ratio suffices to measure down to 2 ppm.
2. Wrap a wire screen or glass-fiber-reinforced tape around the bottle for safety purposes.
3. Grease the joint lightly with silicone or fluorocarbon grease.
4. If a source of vacuum is available at the place of sampling, it is best to evacuate just before sampling to eliminate any uncertainty about loss of vacuum. A three-way Y stopcock connection is convenient. Connect one leg to the sample source, one to the vacuum pump, and the third to a tee attached to the bottle and to a mercury manometer or accurate gauge. In the first position of the Y stopcock, the bottle is evacuated to the vapor pressure of the absorbing reagent. In the second position of the Y stopcock the vacuum pump draws air through the sampling line to flush it thoroughly. The actual vacuum in the sample bottle is read on the manometer. In the third position of the Y stopcock the sampling line is connected to the evacuated bottle and the sample is collected.
5. The stopcock on the bottle is then closed. Allow 15 minutes with occasional shaking for complete absorption and color development.
6. For calculation of the standard volume of the sample, record the temperature and the pressure. The pressure is the difference between the filled and evacuated conditions. The uncorrected volume is that of the bottle plus that of the connection up to the stopcock minus the volume of absorbing reagent.

8.2.3 Glass Syringe Method

1. Ten mL of absorbing reagent is kept in a capped 50 (or 100) mL glass syringe, and 40 (or 90) mL of air is drawn in at the time of sampling.
2. The absorption of nitrogen dioxide is completed by capping and shaking vigorously for 1 minute, after which the air is expelled (When appreciable concentrations, e.g., 20 ppm, of nitric oxide are suspected, interference caused by the oxidation of nitric oxide to nitrogen dioxide is minimized by expelling the air sample immediately after the absorption period.)

3. Additional air may be drawn in and the process repeated several times, if necessary, to develop sufficient final color.

8.2.4 Effects of Storage. Colors may be preserved, if well stoppered, with only 3 to 4% loss in absorbance per day; however, if strong oxidizing or reducing gases are present in the sample in concentrations considerably exceeding that of the nitrogen dioxide, the colors should be determined as soon as possible to minimize any loss. (See Section 3 for effects of interfering gases.)

8.3 Analysis of Samples

8.3.1 After collection or absorption of the sample, a red-violet color appears. Color development is complete within 15 minutes at room temperature.

8.3.2 Compare with standards visually or transfer to stoppered cuvettes and read in a spectrophotometer at 550 mμ, using unexposed reagent as a reference. Alternatively, distilled water may be used as a reference and the absorbance of the reagent blank deducted from that of the sample.

8.3.3 Colors too dark to read may be quantitatively diluted with unexposed absorbing reagent. The measured absorbance is then multiplied by the dilution factor.

Calibration and Standards

Either of two methods of calibration may be employed. The most convenient is standardizing with nitrite solution. Greater accuracy is achieved by standardizing with accurately known gas samples in a precision flow dilution system (References 3,6,7). The recently developed permeation tube technique (Reference 8) appears promising. If the gaseous method is used, the stoichiometric factor is eliminated from the calculations. Concentrations of the standards should cover the expected range of sample concentrations.

9.1 Nitrite Solution Method

9.1.1 Add graduated amounts of the NaNO_2 solution up to 1 ml (measured accurately in a graduated pipet or small buret) to a series of 25 ml volumetric flasks, and dilute to the mark with absorbing reagent.

9.1.2 Mix, allow 15 minutes for complete color development and read the colors (Section 8.3).

9.1.3 Good results can be obtained with these small volumes of standard solution if they are carefully measured. Making the calibration solutions up to 25 ml total volume, rather than the 10 ml volume used for samples, facilitates accuracy. If preferred, even larger volumes may be used with correspondingly larger volumetric flasks.

9.1.4 Plot the absorbances of the standard colors against the μl of nitrogen dioxide per ml of absorbing reagent. The latter values are equal to the corresponding ml of standard nitrite solution times 0.4 (Section 10.2.2). If preferred, transmittance may be plotted instead of absorbance, using semilogarithmic graph paper. The plot follows Beer's law. Draw the straight line through the origin giving the best fit, and determine the slope, K, which is μl of NO_2 intercepted at absorbance of exactly 1.0 or at 10 percent transmittance. For 1 cm cells, the value of K is about 0.73.

9.2 Gaseous Standard Methods. Two techniques are outlined below. Consult the original references for complete details, and Section 10.3 for calculations.

9.2.1 Method 1 (Reference 3) for gaseous standardization is as follows.

1. About 5 ml of pure liquid nitrogen dioxide is placed in a small glass bubbler (10 mm in diameter and 100 mm in length) provided with ground glass stopcocks and spherical joints on both intake and outlet tubes.
2. The bubbler is immersed in a thermos bottle ice bath and connected to an air line. A small pump with flowmeter delivers a steady stream of a few ml/min of air to the bubbler, thence through two flowmeters which permit the discarding of up to 90 percent of the NO_2 and finally to a large stream of carbon filtered air (1000 to 1500 liters/min) from a small blower. All this air passes through a 10 cm Biram anemometer mounted on the end of a pipe 10 cm in diameter. It has been found empirically with this arrangement that the anemometer reading in ft/min times 1.64 is equivalent to liters/min.
3. The bubbler is weighed to 0.1 mg at the beginning and end of an accurately measured time period. The stopcocks are closed each time before the bubbler is removed from the ice bath and wiped dry for weighing.

9.2.2 Method 2 (References 6,7) for preparing known dilutions of nitrogen dioxide consists in making a preliminary dilution (about 0.4%) of nitrogen dioxide in air in a stainless steel tank at 1000 lbs pressure. Subsequent dilution, by air in a flow system at atmospheric pressure, of the analyzed

tank mixture controlled by an asbestos plug and manometer yields concentrations of 0.1 to 10 ppm NO₂

- 9.2.3 Sample the gas mixtures by the bubbler method (Section 8.2.1), and read the colors (Section 8.3). Select concentrations and sample volumes to produce colors covering the accurate absorbance range of the spectrophotometer.
- 9.2.4 Standardization by gaseous samples can be based either upon a weight-volume relationship if the source of nitrogen dioxide is weighed, or a volume-volume relationship if the source is an analyzed tank mixture.
- 9.2.5 Calculate the concentration of the sample air stream, C, in ppm by volume (μℓ NO₂/ℓ of air).

$$C = \frac{10^6 (W_1 - W_2)}{t} \times \frac{0.532}{F_1} \times \frac{F_2}{F_3}$$

or: $C = C_t \times \frac{F_2}{F_3}$

where:

C = concentration of sample air stream in ppm.

(W₁ - W₂) = difference between initial and final weights, in grams, of nitrogen dioxide bubbler (or of permeation tube); weight loss is usually 0.01 to 0.05 g.

t = time interval in minutes, between the weighings.

0.532 = (24.47/46.0), ideal volume in ℓ at 25°C and 760 mm Hg of 1.0 g of nitrogen dioxide.

F₁ = flow rate, in ℓpm, of air passed through nitrogen dioxide bubbler (or over permeation tube), corrected to 25°C and 760 mm Hg.

F₂ = flow rate, in ℓpm, of concentrated gas mixture injected into sample air stream.

F₃ = total flow rate, in ℓpm, of sample air stream

C_t = analyzed concentration of the tank mixture, in ppm by volume on an ideal gas basis.

- 9.2.6 For each standard color, calculate the μℓ of nitrogen dioxide/ml of absorbing reagent:

$$\mu\ell \text{ NO}_2/\text{m}\ell = C V$$

where:

C = ppm concentration (Section 9.2.5)

V = volume of air sample at 25°C and 760 mm Hg, in $\ell/\text{m}\ell$ of absorbing reagent.

9.2.7 Plot the absorbances of the colors against the $\mu\ell$ of gaseous nitrogen dioxide/ $\text{m}\ell$ of absorbing reagent. Draw the straight line through the origin giving the best fit, and determine the slope, K (the value of $\mu\ell/\text{m}\ell$ intercepted at absorbance of exactly 1.0).

10. Calculations

10.1 For convenience, standard conditions are taken as 760 mm Hg and 25°C, at which the molar gas volume is 24.47 liters. (This is identical with standard conditions for Threshold Limit Values of the American Conference of Governmental Industrial Hygienists; it is very close to the standard conditions used (Reference 9) for air-handling equipment, of 29.92 in. Hg, 70°F, and 50 percent relative humidity, at which the molar gas volume is 24.76 liters, of 1.2 percent greater.)

Ordinarily the correction of the sample volume to these standard conditions is slight and may be omitted; however, for greater accuracy, it may be made by means of the perfect gas equation.

10.2 Standardization by nitrite solution is based upon the empirical observation (References 1,6) that 0.72 mole of sodium nitrite produces the same color as 1 mole of nitrogen dioxide.

10.2.1 This factor is applied to calculate the equivalence of the nitrite solution to the volume of NO_2 absorbed as follows: One $\text{m}\ell$ of the working standard solution contains 2.03×10^{-5} g NaNO_2 . Since the molecular weight of NaNO_2 is 69.00, this is equivalent to:

$$\frac{2.03 \times 10^{-5}}{69.00} \times \frac{24.47}{0.72} = 1 \times 10^{-5} \ell \text{ of NO}_2, \text{ or}$$

$$= 10 \mu\ell \text{ of NO}_2$$

10.2.2 In Section 9.1, the calibration standard containing 1 $\text{m}\ell$ of nitrite solution ($10 \mu\ell \text{ NO}_2$) per 25 $\text{m}\ell$ total volume is equivalent to 10/25 or 0.4 $\mu\ell$ of NO_2 per $\text{m}\ell$.

10.3 Compute the concentration of nitrogen dioxide in the sample as follows:

$$\text{Nitrogen dioxide, ppm} = AK/V$$

where:

A = measured absorbance

K = standardization factor from Section 9.1.4 or 9.2.7

V = volume of air sample, at 25°C and 760 mm Hg, in liters/ml of absorbing reagent.

10.4 If preferred, the graph from Section 9.1.4 or 9.2.7 may be used instead as follows:

$$\text{Nitrogen dioxide, ppm} = \mu\text{l NO}_2 \text{ per ml/V}$$

10.4.1 If V is a simple multiple of K, calculations are simplified. Thus, for the K value of 0.73 previously cited, if exactly 7.3 liters of air are sampled through a bubbler containing 10 ml of absorbing reagent, $K/V = 1$, and the absorbance is also ppm directly.

10.4.2 For exact work, an allowance may be made in the calculations for sampling efficiency and for fading of the color using the following equation:

$$\text{Nitrogen dioxide, ppm} = A_c K/VE$$

where:

A_c = corrected absorbance; the absorbance is corrected for fading of the color as indicated in Section 8.2.4 when there is a prolonged interval between sampling and measurement of the absorbance.

E = sampling efficiency; for a bubbler, E is estimated from prior tests using two absorbers in series (Reference 7 and Section 6.1.1); for a bottle or syringe, $E = 1.0$.

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FREE SILICA (QUARTZ, CRISTOBALITE, TRIDYMITE) IN ATMOSPHERIC DUST

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Quartz, Cristobalite, Tridymite	Method No.:	P&CAM 109
Matrix:	Atmospheric Dust	Range:	5 – 200 $\mu\text{g}/\text{cm}^2$
Procedure:	X-ray Diffraction		
Date Issued:	4/7/72	Precision:	$\pm 5 \mu\text{g}$
Date Revised:	1/15/74	Classification:	D (Operational)

1. Principle of Method

- 1.1 Atmospheric dust samples are collected on membrane filters.
- 1.2 The filters are ashed and the residues along with an internal calibration standard are redistributed onto silver membrane filters.
- 1.3 Each sample is scanned by X-ray diffraction to determine the presence of free silica (quartz, cristobalite, and/or tridymite).
- 1.4 If present, the mass of each free silica species is determined by measuring the ratio of the diffraction peak intensities of the free silica species and the internal standard (fluorite) and comparing this ratio to a calibration curve.

2. Range and Sensitivity

- 2.1 The analytical range extends from 5 $\mu\text{g}/\text{cm}^2$ to 200 $\mu\text{g}/\text{cm}^2$ for each free silica species; the total atmospheric dust loading on the filter must not exceed 1 mg/cm^2
- 2.2 The sensitivity is 5 μg for each free silica species.

3. Interferences

- 3.1 Several minerals have diffraction peaks that correspond in position to the major peak for quartz; these include micas (biotite, muscovite), potash, feldspars (microcline, plagioclase), sillimanite, graphite, iron carbide (FeC), and zircon. The

presence of these interferences is usually encountered in specific, recognizable situations and can be verified by X-ray diffraction analysis. Analytical measurements can be carried out at a secondary quartz peak with a commensurate decrease in sensitivity.

- 3.2 Comparable interference may occur for cristobalite and tridymite. This can be determined by X-ray diffraction analysis. If interference occurs, secondary cristobalite and tridymite peaks must be used.
- 3.3 Diffraction peak interference may also occur for the fluorite (CaF_2) internal calibration standard. Compensation must be made for increased peak intensity from the interfering species or an alternate standard must be employed.
- 3.4 The presence of specific elements in the sample (iron, in particular) may result in appreciable X-ray fluorescence, leading to high background intensity. This situation may be circumvented by employing a diffracted beam monochromator.

4. Precision and Accuracy

- 4.1 Bumstead (Reference 11.1) has reported eleven replicate measurements of quartz in 2 mg of coal dust as having an average of 0.63% (12.6 μg), a range of 0.51-0.91% and a standard deviation of 0.114% (2.3 μg); he reports an accuracy of $\pm 30\%$ (3.8 μg) of the quartz present in the sample.
- 4.2 No information is available regarding the accuracy for cristobalite or tridymite.

5. Advantages and Disadvantages

- 5.1 The X-ray diffraction method offers sensitivity equivalent to or greater than other methods (infrared or colorimetric), is non-destructive to the sample, is rapidly performed and may be automated.
- 5.2 The X-ray diffraction method is limited to a sample size of a few milligrams. Application of the method requires a rather high degree of technical skill and expensive equipment.

6. Apparatus

- 6.1 **Sampling Equipment.** The sampling unit for the filter-collection method has the following components:
 - 6.1.1 The filter unit consisting of the filter media (Section 6.1.4) and a two-piece filter cassette holder.

- 6.1.2 A personal sampling pump. This pump must be properly calibrated (with a representative filter unit in the line) so the volume of air sampled can be measured accurately.
- 6.1.3 Ten-mm nylon cyclone.
- 6.1.4 Polyvinyl chloride membrane filters (or equivalent), 37 mm and 5.0 μ m pore size. (Gelman VM-1 filters are unacceptable because of the high background produced by the ash.)
- 6.2 X-ray diffraction equipment, including copper and/or molybdenum target X-ray tubes.
- 6.3 Low temperature radiofrequency asher: Tracerlab Model LTA 600 or equivalent, or muffle furnace.
- 6.4 Ultrasonic bath.
- 6.5 Filtration apparatus.
- 6.6 Silver membrane filters, 25 mm diameter having an 0.45 μ m pore size: Sela Flotronics.
- 6.7 Aluminum weighing pans.
- 6.8 Porcelain crucibles with covers.
- 6.9 100 ml Pyrex beakers.
- 6.10 Glass microscope slides.
- 6.11 Non-serrated, non-magnetic forceps.
- 6.12 Metal spatula

Reagents

- 1 Quartz, cristobalite and tridymite powders: Acid-washed and wet-sieved through 10 μ m sieve.
- 2 Fluorite (CaF_2) 400 mesh powder, Analytical Grade.
- 3 Wetting agent Aerosol OT.

7.4 Petroleum jelly.

7.5 Standard Solutions of fluorite, quartz, cristobalite and tridymite. (Refer to Section 9.1.)

8. Procedure

8.1 Cleaning of Equipment. It is important that all equipment be kept as free of contaminant dust as possible.

8.1.1 The spatula, forceps, etc., may be satisfactorily cleaned using ethyl alcohol and disposable non-linting tissues.

8.1.2 The aluminum weighing pans are cleaned by rinsing twice with distilled water and twice with ethyl alcohol, and allowing to dry in a dust-free environment.

8.2 Collection and Shipping of Samples

8.2.1 Samples are collected on 5.0 μ m pore size, PVC (or equivalent) membrane filters. The quantity of dust collected on the filter should be 2 mg or less. The filters are held in plastic cassettes that permit the attachment of a 10 mm nylon cyclone to the inlet side of the cassette to collect a respirable sample. The filter is kept in the cassette for shipment.

8.2.2 Whenever an air sample or series of air samples is collected, a bulk sample of the suspected parent material of the atmospheric contaminant should be obtained and shipped back to the laboratory with the air samples.

8.3 Analysis of Samples

8.3.1 Either of these two described methods may be used to ash the sample.

1. Using forceps and spatula, place the filter samples in aluminum weighing pans and situate within the sample compartments of the low-temperature asher so that the sample exposure to the radiofrequency-excited oxygen plasma is optimized. The samples are ashed for one hour at 100 watts RF power and at an oxygen flow rate of 75 mL/min., using the techniques recommended in the instrument manual.
2. Using forceps and spatula, place the filter samples in porcelain crucibles, loosely cover and place in muffle furnace. Hold for two hours at 600°C (800°C if graphite is present in the sample).

- 8.3.2 Carefully scrape the ash residue into a 100 mL beaker. Rinse the weighing pan (or crucible) several times with about 5 mL of water and pour the rinse water into the beaker. Add 1 mL of the CaF_2 standard solution, a few drops of wetting agent, and distilled water to bring volume up to about 50 mL.
- 8.3.3 Ultrasonically agitate the beaker and its contents for 30 minutes at maximum setting.
- 8.3.4 Filter solution through a 25 mm diameter, 0.45 μm pore size silver membrane filter under suction. Thoroughly wash down the filter holder with distilled water to ensure that all dust particles have been transferred to the filter.
- 8.3.5 Using forceps, remove the filter, place in a Petri dish and dry at 105°C for 15 minutes.
- 8.3.6 The silver filter is then attached to a glass microscope slide with petroleum jelly, and inserted into the X-ray diffractometer. A portion of the filter should be inserted beneath the clamping surface of the diffractometer.
- 8.3.7 The diffractometer is then scanned over the 2θ -range corresponding to $d = 4.5$ to $2.3\text{\AA}$ (For a copper tube, $2\theta = 18^\circ$ to 39° and for a molybdenum tube, $2\theta = 9^\circ$ to 18°). The presence of crystalline forms of silica is determined by the occurrence of diffraction peak, as follows:

<u>Mineral</u>	<u>d (Most Intense)</u>	<u>d (Second Most Intense)</u>
Quartz	3.34 $\text{\AA}$	4.26
Cristobalite	4.05	2.49
Tridymite	4.11	4.33
Fluorite Standard	3.15	

The presence of interfering compounds can be determined by the presence and identification of other X-ray diffraction peaks.

- 8.3.8 The intensity of the most intense diffraction peak for quartz, cristobalite and tridymite (as given in Section 8.3.7) is determined by measuring peak height or peak area from the diffraction scan or by scaler (fixed time or fixed count) measurement at peak position. All measurements must be corrected for background. Comparable measurements are made for the fluorite standard at $d = 3.15\text{\AA}$. If diffraction peaks from other compounds interfere with the most intense quartz, cristobalite or tridymite peak, the second most intense peak for these silica compounds must be employed.

- 8.3.9 The free silica to fluorite intensity ratios are determined, and the mass of quartz, cristobalite and/or tridymite is determined from the appropriate calibration curve.

9. Calibration and Standards

9.1 Standards

- 9.1.1 A standard solution of fluorite is prepared by adding 20 mg of fluorite to 100 ml of distilled water containing a few drops of wetting agent and agitation.
- 9.1.2 Known amounts of quartz, cristobalite and tridymite are weighed to the nearest 0.1 mg and are added to 100 ml distilled water containing a few drops of wetting agent to provide five standard solutions of each mineral covering a concentration range of 0.01 – 0.3 mg/ml.

9.2 Standard Curve

- 9.2.1 One ml each of the standard fluorite solution (Section 9.1.1) and one of the crystalline free silica solutions (Section 9.1.2) are added to 50 ml distilled water and are analyzed according to steps 8.3.4 through 8.3.8. Similar data are collected for each of the free silica solutions (Section 9.1.2).
- 9.2.2 Standard curves are prepared for quartz, cristobalite and tridymite in which the intensity ratio of the free silica standard to fluorite is plotted against free silica mass in mg. This plot should give a nearly straight line that passes through the origin.

10. Calculations

The concentration of free silica in air can be expressed as milligrams silica per cubic meter of air sampled.

$$\text{mg SiO}_2/\text{m}^3 = \frac{\text{mg Q} + \text{mg C} + \text{mg T}}{V_s}$$

where:

$\text{mg SiO}_2/\text{m}^3$ = total milligrams of free silica per cubic meter of air sampled.

$\left. \begin{array}{l} \text{mg Q} \\ \text{mg C} \\ \text{mg T} \end{array} \right\}$ = milligrams of quartz, cristobalite and tridymite, respectively, determined from the appropriate calibration curve.

V_s = volume of air sampled in cubic meters ($1000\text{l} = 1\text{m}^3$) at standard conditions of 25°C and 760 mm Hg.

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Pentane

Analyte:	Pentane	Method No.:	S379
Matrix:	Air	Range:	1476-6190 mg/cu m
OSHA Standard:	1000 ppm (2950 mg/cu)	Precision ($\overline{CV}_T$):	0.055
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	3/14/75

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.
- 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 injection of standards.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 1476-6190 mg/cu m at an atmospheric temperature and pressure of 24°C and 769 mm Hg, using a 2-liter sample. Under the conditions of sample size (2 liters) the probable useful range of this method is 300-8850 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for an 18-mg sample. This 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 analyte and other substances in the air. The first section of the charcoal tube was found to hold 18 mg of analyte when a test atmosphere containing 5640 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 16.5 minutes; breakthrough was observed at this time, i.e., the concentration of analyte in the effluent was 5% 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 using 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 analyte 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 1476-6190 mg/cu m was 0.055. This value corresponds to a 160 mg/cu m standard deviation 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 On the average the values obtained using the overall sampling and analytical method were 9.7% lower than the "true" value at the OSHA standard level.

These data are based on validation experiments using the internal standard method.

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 substances 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 within $\pm 5\%$ 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 (20-ft x 1/8-in stainless steel) packed with 10% FFAP on 80/100 mesh Chromosorb W AW-DMCS.
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.
- 6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.
- 6.8 Pipets: 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 Chromatographic quality carbon disulfide
- 7.2 Pentane, reagent grade
- 7.3 Nonane, or other suitable internal standard
- 7.4 Purified helium
- 7.5 Prepurified hydrogen
- 7.6 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 2 liters is recommended. Sample at a rate of 0.05 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm 5\%$.
- 8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

- 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 charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample 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. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.
- 8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (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. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.
- 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:
1. 30 ml/min (60 psig) Helium carrier gas flow
 2. 35 ml/min (25 psig) Hydrogen gas flow to detector
 3. 400 ml/min (60 psig) Air flow to detector
 4. 225°C injector temperature
 5. 250°C manifold temperature (detector)
 6. 52°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-microliter 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 microliter 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-microliter 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 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters 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.

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, provided 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 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. 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 analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

Six tubes at each of three concentration levels (0.5X, 1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 2-liter sample at the selected level. The tubes are allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These 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 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

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

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus 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 per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert 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 sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide 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.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

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 amounts 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 (see Section 8.5.2) for the amount 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 the analyte in the air sampled can be expressed in mg per cu m.

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

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

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

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. 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, NIOSH Contract No. CDC-99-74-45.
- 11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

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APPENDIX B

INDUSTRIAL HEALTH FOUNDATION

5231 Centre Ave., Pittsburgh, Pa. 15232

ANALYTICAL RESULTSCompany/Plant: Department of Energy
Bruceton, Pa.

Assay: Coal Tar Pitch Volatiles and Total Hydrocarbons

Analytical Method: Ultrasonic Extraction with Benzene and Gravimetric

IHF No.	Sample No.	Dust Wt.	CTPV mg	Volume of Air Sampled m ³	Dust mg	CTPV mg/m ³
1652-78	Ag 75	0.12	<0.05	0.73	0.16	<0.07
1653-78	Ag 77	0.08	<0.05	0.72	0.11	<0.07
1654-78	Ag 72	0.08	<0.05	0.49	0.16	<0.10
1655-78	Ag 71	0.22	<0.05	0.61	0.36	<0.08
1656-78	Ag 74	0.14	<0.05	0.69	0.20	<0.07

David R. Fussaro
David R. Fussaro, Ph.D., Supervisor
Analytical Laboratory

INDUSTRIAL HEALTH FOUNDATION
5231 Centre Avenue, Pittsburgh, Pa. 15232

ANALYTICAL LABORATORY

G.C. Analysis

Company/Plant: Department of Energy
Bruceton, Pa.

Assay: Benzene

IHF No.	Sample No.	Compound				Volume of Air Sampled	ppm	Comments
			Sampling Section mg	Back-up Section mg	Total mg			
1662-78	5	Benzene	0.06	0.00	0.06	23.7	0.79	
1663-78	6	Benzene	0.02	0.00	0.02	22.5	0.28	

David R. Fussaro
David R. Fussaro, Ph.D., Supervisor
Analytical Laboratory

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ANALYTICAL LABORATORY

Company/Plant: Department of Energy
Bruceton, Pa.

Assay: Free Silica

Analytical Method: X-ray Diffraction

IHF No.	Filter No.	Dust Wt. mg	Quartz %	Cristobalite %	Sampling Data			Dust mg/m ³	Calculated TLV mg/m ³ Quartz	Calculated TLV ₃ mg/m ³ Cristobalite
					lpm	min	m ³			
1658-78	PV 2879	0.30	N.D.	N.D.	1.69	328	0.55	0.55	----	----
1659-78	PV 2870	0.13	N.D.	N.D.	1.71	455	0.78	0.17	----	----
1660-78	PV 2878	0.06	N.D.	N.D.	1.50	450	0.67	0.09	----	----

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David R. Fussaro, Ph.D., Supervisor
Analytical Laboratory

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5231 Centre Ave., Pittsburgh, Pa. 15232

ANALYTICAL LABORATORY

Company/Plant: Department of Energy
 Bruceton, Pa

Assay: Free Silica

Analytical Method: x-ray diffraction

IHF No.	Filter No.	Dust Wt. mg	Quartz %	Cristobalite %	Sampling Data			Dust mg/m ³	Calculated TLV mg/m ³ Quartz	Calculated TLV ³ mg/m ³ Cristobalite
					lpm	min	m ³			
1718-78	PV-2868	0.26	N.D.	N.D.	1.70	330	.561	0.46	—	—
1719-78	PV-2877	0.09	N.D.	N.D.	1.71	352	.602	0.15	—	—
1720-78	PV-2881	0.06	N.D.	N.D.	1.71	345	.590	0.10	—	—

David R. Fussaro
 David R. Fussaro, Ph.D., Supervisor
 Analytical Laboratory

INDUSTRIAL HEALTH FOUNDATION
5231 Centre Avenue, Pittsburgh, Pa. 15232

ANALYTICAL LABORATORY

G.C. Analysis

Company/Plant: Department of Energy
Bruceton, Pa.

Assay: High Flash Naptha

IHF No.	Sample No.	Compound				Volume of Air Sampled	ppm	Comments
			Sampling Section mg	Back-up Section mg	Total mg			
1729-78	2	Naptha	0.70	0.00	0.70	16.97		
1730-78	3	Naptha	4.21	0.00	4.21	29.56		
1731-78	4	Naptha	0.48	0.00	0.48	17.99		

David R. Fussaro
David R. Fussaro, Ph.D., Supervisor
Analytical Laboratory

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ANALYTICAL RESULTS

Company/Plant: Department of Energy
Bruceton, Pa.

Assay: Coal Tar Pitch Volatiles and Total Hydrocarbons

Analytical Method: Ultrasonic Extraction with Benzene and Gravimetric

IHF No.	Sample No.	Dust Wt. mg	CTPV Wt. mg	Volume of Air Sampled m ³	Dust mg/m ³	CTPV mg/m ³
1722-78	Ag 90	*	<0.05	0.603	--	<0.01
1723-78	Ag 84	0.22	<0.05	0.603	0.36	<0.01
1724-78	Ag 98	0.23	<0.05	0.620	0.37	<0.01
1725-78	Ag 83	2.08	<0.05	0.549	3.79	<0.01
1726-78	Ag 96	0.33	<0.05	0.598	0.55	<0.01
1727-78	Ag 89	0.16	<0.05	0.590	0.27	<0.01

* Accurate weight could not be obtained because of uncertainty in this weighing.

David R. Fussaro
David R. Fussaro, Ph.D., Supervisor
Analytical Laboratory

5231 Centre Ave., Pittsburgh, Pa. 15232

Company/Plant: Department of Energy
Bruceton, Pa.

Analytical Method: Colorimetric

David R. Fussaro
David R. Fussaro, Ph.D., Supervisor
Analytical Laboratory

5231 Centre Ave., Pittsburgh, Pa. 15232

Company/Plant: Department of Energy
Bruceton, Pa.

Analytical Method: Ultrasonic Extraction with Benzene and Gravimetric

[illegible]

David R. Fussaro

David R. Fussaro, Ph.D., Supervisor
Analytical Laboratory

INDUSTRIAL HEALTH FOUNDATION
5231 Centre Avenue, Pittsburgh, Pa. 15232

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G.C. Analysis

Company/Plant: Department of Energy
Bruceton, Pa.

Assay: Benzene and Pentane

IHF No.	Sample No.	Compound				Volume of Air Sampled Liters	ppm	Comments
			Sampling Section mg	Back-up Section mg	Total mg			
1958-78	1	Pentane	0.30	0.00	0.30	20.76	4.92	
		Benzene	0.06	0.00	0.06	20.76	0.91	
1959-78	2	Pentane	0.01	0.00	0.01	21.98	0.15	
		Benzene	0.01	0.00	0.01	21.98	0.14	

David R. Fussaro
David R. Fussaro, Ph.D., Supervisor
Analytical Laboratory

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G.C. Analysis

Company/Plant: Department of Energy
Bruceton, Pa.

Assay: Cresol

IHF No.	Sample No.	Compound				Volume of Air Sampled	ppm	Comments
			Sampling Section mg	Back-up Section mg	Total mg			
1961-78	3	Cresol	<0.03	0.00	<0.03	23.35	<0.29	
1962-78	4	Cresol	0.03	0.00	0.03	22.29	0.30	
1963-78	5	Cresol	<0.03	0.00	<0.03	20.27	<0.34	

David R. Fussaro
David R. Fussaro, Ph.D., Supervisor
Analytical Laboratory

INDUSTRIAL HEALTH FOUNDATION
5231 Centre Avenue, Pittsburgh, Pa. 15232

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G.C. Analysis

Company/Plant: Department of Energy

Assay: Benzene

IHF No.	Sample No.	Compound				Volume of Air Sampled liters	ppm	Comments
			Sampling Section mg	Back-up Section mg	Total mg			
1983-78	8	Benzene	<0.01	0.00	<0.01	9.50	<0.33	
1984-78	9	Benzene	<0.01	0.00	<0.01	5.57	<0.56	
1985-78	10	Benzene	<0.01	0.00	<0.01	4.38	<0.72	

David R. Fussaro
David R. Fussaro, Ph.D., Supervisor
Analytical Laboratory

INDUSTRIAL HEALTH FOUNDATION
5231 Centre Avenue, Pittsburgh, Pa. 15232

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G.C. Analysis

Company/Plant: Department of Energy

Assay: Phenol

IHF No.	Sample No.	Compound				Volume of Air Sampled liters	ppm	Comments
			Sampling Section mg	Back-up Section mg	Total mg			
1972-78	11	Phenol	<0.03	0.00	<0.03	560.4	<0.01	
1973-78	12	Phenol	<0.03	0.00	<0.03	445.0	<0.02	
1974-78	13	Phenol	<0.03	0.00	<0.03	455.0	<0.02

David R. Fussaro, Ph.D., Supervisor
Analytical Laboratory

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5231 Centre Avenue, Pittsburgh, Pa. 15232

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Bruceton, Pa.

Assay: Cresol

IHF No.	Sample No.	Compound				Volume of Air Sampled	ppm	Comments
			Sampling Section	Back-up Section	Total			
2002-78	21	Cresol	0.03	0.00	0.03	22.9	0.30	
2001-78	23	Cresol	<0.03	0.00	<0.03	24.5	<0.28	
2003-78	24	Cresol	<0.03	0.00	<0.03	8.9	<0.76

David R. Fussaro, Ph.D., Supervisor
Analytical Laboratory

INDUSTRIAL HEALTH FOUNDATION
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Company/Plant: Department of Energy
Bruceton, Pa.

Assay: Benzene

IHF No.	Sample No.	Compound				Volume of Air Sampled Liters	ppm	Comments
			Sampling Section mg	Back-up Section mg	Total mg			
2004-78	25	Benzene	0.29	0.00	0.29	22.60	4.02	A significant
2005-78	26	Benzene	0.02	0.00	0.02	23.50	0.27	amount of pentane
								was found in
								sample 25, and a
								smaller amount in
								sample 26.

David R. Fussaro
David R. Fussaro, Ph.D., Supervisor
Analytical Laboratory

INDUSTRIAL HEALTH FOUNDATION
5231 Centre Avenue, Pittsburgh, Pa. 15232

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Company/Plant: Department of Energy

Assay: Phenol

IHF No.	Sample No.	Compound				Volume of Air Sampled liters	ppm	Comments
			Sampling Section mg	Back-up Section mg	Total mg			
2010-78	14A	Phenol	<0.03	0.00	<0.03	301.9	<0.03	
2011-78	13A	Phenol	<0.03	0.00	<0.03	500.0	<0.02	
2012-78	12A	Phenol	<0.03	0.00	<0.03	480.0	<0.02	

David R. Fussaro
David R. Fussaro, Ph.D., Supervisor
Analytical Laboratory

5231 Centre Ave., Pittsburgh, Pa. 15232

Company/Plant: Dept. of Energy

Assay: Coal Tar Pitch Volatiles and Total Hydrocarbons

Analytical Method: Ultrasonic Extraction with Benzene and Gravimetric

[illegible]

David R. Fussaro
David R. Fussaro, Ph.D., Supervisor
Analytical Laboratory

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Company/Plant: Department of Energy
Bruceton, Pa.

Assay: Nitrogen Dioxide (NO₂)

Analytical Method: Spectrophotometric

David R. Fussaro
David R. Fussaro, Ph.D., Supervisor
Analytical Laboratory

INDUSTRIAL HEALTH FOUNDATION
5231 Centre Avenue, Pittsburgh, Pa. 15232

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G.C. Analysis

Company/Plant: Department of Energy
Bruceton, Pa.

Assay: Benzene and Pentane

IHF No.	Sample No.	Compound	Sampling Section	Back-up Section	Total	Volume of Air Sampled Liters	ppm	Comments
			mg	mg	mg			
2308-78	6	Benzene	0.07	0.00	0.07	18.38	1.19	
		Pentane	0.02	0.00	0.02	18.38	0.37	
2309-78	7	Benzene	0.01	0.00	0.01	19.08	0.16	
		Pentane	0.01	0.00	0.01	19.08	0.18	

David R. Fussaro
David R. Fussaro, Ph.D., Supervisor
Analytical Laboratory

5231 Centre Ave., Pittsburgh, Pa. 15232

Company/Plant: Department of Energy
Bruceton, Pa.

Analytical Method: Ultrasonic Extraction with Benzene

[illegible]

David R. Fussaro
David R. Fussaro, Ph.D., Supervisor
Analytical Laboratory

5231 Centre Ave., Pittsburgh, Pa. 15232

Analytical Method: Colorimetric

[illegible]

David R. Fussaro
David R. Fussaro, Ph.D., Supervisor
Analytical Laboratory

INDUSTRIAL HEALTH FOUNDATION
5231 Centre Avenue, Pittsburgh, Pa. 15232

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G.C. Analysis

Company/Plant: Department of Energy

Assay: Phenol

IHF No.	Sample No.	Compound				Volume of Air Sampled liters	ppm	Comments
			Sampling Section mg	Back-up Section mg	Total mg			
2295-78	138	Phenol	<0.23			474.0	<0.13	
2296-78	148	Phenol	<0.23			350.8	<0.17	

David R. Fussaro
David R. Fussaro, Ph.D., Supervisor
Analytical Laboratory

INDUSTRIAL HEALTH FOUNDATION
5231 Centre Avenue, Pittsburgh, Pa. 15232

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G.C. Analysis

Company/Plant: Department of Energy
Bruceton, Pa.

Assay: Cresol

IHF No.	Sample No.	Compound				Volume of Air Sampled liters	ppm	Comments
			Sampling Section mg	Back-up Section mg	Total mg			
2304-78	3	Cresol	<0.03	0.00	<0.03	18.12	<0.38	
2305-78	4	Cresol	<0.03	0.00	<0.03	11.82	<0.57	
2306-78	5	Cresol	<0.03	0.00	<0.03	25.23	<0.27	

David R. Fussaro
David R. Fussaro, Ph.D., Supervisor
Analytical Laboratory

INDUSTRIAL HEALTH FOUNDATION

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ANALYTICAL RESULTS

Company/Plant: Department of Energy
Bruceton, Pa.

Assay: Coal Tar Pitch Volatiles (CTPV)

Analytical Method: Ultrasonic Extraction with Benzene

IHF No.	Sample No.	Weight of Dust mg	CTPV mg	Volume of Air Sampled m ³	Dust mg/m ³	CTPV mg/m ³
2370-78	107	0.19	<0.05	0.683	0.28	<0.07

David R. Fussaro

David R. Fussaro, Ph.D., Supervisor
Analytical Laboratory

5231 Centre Ave., Pittsburgh, Pa. 15232

Company/Plant: Department of Energy
Bruceton, Pa.

Assay: Nickel in Air

Analytical Method: Atomic Absorption

[illegible]

David R. Fussaro
David R. Fussaro, Ph.D., Supervisor
Analytical Laboratory

INDUSTRIAL HEALTH FOUNDATION

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ANALYTICAL LABORATORY

Company/Plant: Department of Energy
Bruceton, Pa.

Assay: Free Silica

Analytical Method: x-ray Diffraction

IHF No.	Filter No.	Dust Wt. mg	Quartz %	Cristobalite %	Sampling Data			Dust mg/m ³	Calculated TLV mg/m ³ Quartz	Calculated TLV ₃ mg/m ³ Cristobalite
					lpm	min	m ³			
2368-78	PV 2931	<0.01	N.D.	N.D.	1.71	450	0.770	<0.01	--	--

N.D. = Not Detected

David R. Fussaro
David R. Fussaro, Ph.D., Supervisor
Analytical Laboratory

INDUSTRIAL HEALTH FOUNDATION

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ANALYTICAL RESULTS

Company/Plant: Department of Energy
 Bruceton, Pa.

Assay: Nitrogen Dioxide (NO₂)

Analytical Method: Spectrophotometric

IHF No.	Sample No.		$\mu\text{l NO}_2/\text{ml}$	Volume of Air Sampled Liters	ppm
2528-78	1		0.085	18.0	0.005
2529-78	13		0.089	21.6	0.004

David R. Fussaro
David R. Fussaro, Ph.D., Supervisor
Analytical Laboratory

INDUSTRIAL HEALTH FOUNDATION
5231 Centre Avenue, Pittsburgh, Pa. 15232

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G.C. Analysis

Company/Plant: Department of Energy
Bruceton, Pa.

Assay: Benzene

IHF No.	Sample No.	Compound				Volume of Air Sampled Liters	ppm	Comments
			Sampling Section mg	Back-up Section mg	Total mg			
2661-78	1	Benzene	0.01	0.00	0.01	24.49	0.13	

David R. Fussaro
David R. Fussaro, Ph.D., Supervisor
Analytical Laboratory

5231 Centre Ave., Pittsburgh, Pa. 15232

Company/Plant: Department of Energy
Bruceton, Pa.

Analytical Method: Ultrasonic Extraction with Benzene

[illegible]

David R. Fussaro
David R. Fussaro, Ph.D., Supervisor
Analytical Laboratory

5231 Centre Ave., Pittsburgh, Pa. 15232

Company/Plant: Department of Energy
Bruceton, Pa.

Analytical Method: Atomic Absorption

[illegible]

David R. Fussaro
David R. Fussaro, Ph.D., Supervisor
Analytical Laboratory

5231 Centre Ave., Pittsburgh, Pa. 15232

Company/Plant: Department of Energy
Bruceton, Pa.

Analytical Method: Atomic Absorption

David R. Fussaro
David R. Fussaro, Ph.D., Supervisor
Analytical Laboratory

5231 Centre Ave., Pittsburgh, Pa. 15232

Company/Plant: Department of Energy
Bruceton, Pa.

Analytical Method: Ultrasonic Extraction with Benzene

David R. Fussaro
David R. Fussaro, Ph.D., Supervisor
Analytical Laboratory

INDUSTRIAL HEALTH FOUNDATION
5231 Centre Avenue, Pittsburgh, Pa. 15232

ANALYTICAL LABORATORY

G.C. Analysis

Company/Plant: Department of Energy
Bruceton, Pa.

Assay: Benzene

IHF No.	Sample No.	Compound	Sampling Section	Back-up Section	Total	Volume of Air Sampled Liters	ppm	Comments
			mg	mg	mg			
2769-78	1	Benzene	0.02	0.00	0.02	20.16	0.31	
2770-78	2	Benzene	0.01	0.00	0.01	18.82	0.17	

David R. Fussaro
David R. Fussaro, Ph.D., Supervisor
Analytical Laboratory

5231 Centre Ave., Pittsburgh, Pa. 15232

Company/Plant: Department of Energy
Bruceton, Pa.

Analytical Method: Spectrophotometric

[illegible]

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ANALYTICAL LABORATORY

G.C. Analysis

Company/Plant: Department of Energy
Bruceton, Pa.

Assay: Benzene

IHF No.	Sample No.	Compound				Volume of Air Sampled liters	ppm	Comments
			Sampling Section mg	Back-up Section mg	Total mg			
3181-78	1	Benzene	<0.01	0.00	<0.01	9.70	<0.32	
3182-78	2	Benzene	0.01	0.00	0.01	9.66	0.32	
3183-78	3	Benzene	<0.01	0.00	<0.01	6.76	<0.46	
3184-78	4	Benzene	0.03	0.00	0.03	6.81	1.38	
3185-78	5	Benzene	0.03	0.00	0.03	6.58	1.43	

David R. Fussaro
David R. Fussaro, Ph.D., Supervisor
Analytical Laboratory

INDUSTRIAL HEALTH FOUNDATION
5231 Centre Avenue, Pittsburgh, Pa. 15232

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G.C. Analysis

Company/Plant: Department of Energy
Bruceton, Pa.

Assay: Benzene

IHF No.	Sample No.	Compound				Volume of Air Sampled liters	ppm	Comments
			Sampling Section mg	Back-up Section mg	Total mg			
3328-78	1	Benzene	0.01	0.00	0.01	9.95	0.32	
3329-78	2	Benzene	0.02	0.00	0.02	8.25	0.76	
3330-78	3	Benzene	<0.01	0.00	<0.01	9.33	<0.34	
3331-78	4	Benzene	<0.01	0.00	<0.01	7.46	<0.42	
3332-78	5	Benzene	<0.01	0.00	<0.01	8.23	<0.38	
3333-78	6	Benzene	<0.01	0.00	<0.01	6.72	<0.47	

David R. Fussaro
David R. Fussaro, Ph.D., Supervisor
Analytical Laboratory

Sample Date: 4/25/78
 Sample Type: Total hydrocarbons/benzene solubles (filter)
 Analytical Method: Benzene extraction
 Calibration Date: 4/24/78
 Date Shipped: 4/26/78
 Date Analyzed: 5/1/78
 Sampling Conducted By: Speicher & Kretchman

Sample No.	Area/Description	Pump	Flow Rate (l/min.)	Start Time	Finish Time	(mg/m ³) Results	
						*BS	*TH
1652	Solvent Analysis Lab Pers -	3	1.50	7:55 a.m.	4:02 p.m.	< 0.07	0.16
1653	Solvent Analysis Lab Area - 5 ft. from hood	7	1.50	8:00	4:02	< 0.07	0.11
1654	Water Treatment Pers -	8	1.50	8:10	3:04	< 0.10	0.16
1655	Water Treatment Pers -	9	1.50	8:10	3:58	< 0.08	0.36
1656	Water Treatment Area - Bio reactor area	10	1.49	8:15	3:58	< 0.07	0.20

* BS - Benzene Solubles
 * TH - Total Hydrocarbons

Sample Date: 4/25/78
 Sample Type: Respirable Silica Dust (filter)
 Analytical Method: X-ray diffraction - weight
 Calibration Date: 4/24/78
 Date Shipped: 4/26/78
 Date Analyzed: 5/3/78
 Sampling Conducted By: Speicher & Kretchman

Sample No.	Area/Description	Pump	Flow Rate (l/m)	Start Time	Finish Time	Results (mg/m ³)
1658	Coal-oil slurry Pers -	6	1.69	8:25 a.m.	1:53 p.m.	0.55
1659	Coal-oil slurry Area - 20 ft. from unit	5	1.71	8:30	4:05	0.17
1660	Coal-oil slurry Area - 10 ft. from unit	11	1.50	8:35	4:05	0.09

Sample Date: 4/25/78
 Sample Type: Benzene (charcoal tube - lot 107)
 Analytical Method: GC
 Calibration Date: 4/24/78
 Date Shipped: 4/26/78
 Date Analyzed: 5/1/78
 Sampling Conducted By: Speicher & Kretchman

Sample No.	Area/Description	Pump	Flow Rate (ml/min)	Start Time	Finish Time	Results ppm
1662	Solvent Analysis Lab Pers -	5	50 ml/min	7:55 a.m.	4:02 p.m.	0.79
1663	Solvent Analysis Lab Area - 5 ft. from hood	6	50 ml/min	8:00	4:02	0.28

Sample Date: 4/27/78
 Sample Type: Respirable silica dust (filter)
 Analytical Method: X-ray diffraction - weight
 Calibration Date: 3/27 & 4/24/78
 Date Shipped: 4/28/78
 Date Analyzed: 5/3/78
 Sampling Conducted By: Speicher

Sample No.	Area/Description	Pump	Flow Rate (l/min)	Start Time	Finish Time	Results (mg/m ³)
1718	Coal-oil slurry Pers -	8	1.70	4:25 p.m.	9:55 p.m.	0.46
1719	Coal-oil slurry Area - 20 ft. from unit	7	1.71	4:33	10:25	0.15
1720	Coal-oil slurry Area - 10 ft. from unit	3	1.71	4:35	10.20	0.10

Sample Date: 4/27/78
 Sample Type: Total hydrocarbons/benzene solubles (filter)
 Analytical Method: Benzene extraction
 Calibration Date: 4/24/78
 Date Shipped: 4/28/78
 Date Analyzed: 5/3/78
 Sampling Conducted By: Speicher

Sample No.	Area/Description	Pump	Flow Rate (l/min.)	Start Time	Finish Time	(mg/m ³) Results	
						*BS	*TH
1722	Centrifuge Pers -	10	1.70	4:10 p.m.	10:05 p.m.	< 0.01	---
1723	Centrifuge Pers -	9	1.70	4:10	10:05	< 0.01	0.36
1724	Centrifuge Area - 10 ft. North of Centrifuge	11	1.70	4:10	10:05	< 0.01	0.37
1725	Coal-oil Slurry Pers -	6	1.69	4:30	9:55	< 0.01	3.79
1726	Coal-oil Slurry Area - 20 ft. from WT	2	1.71	4:35	10:25	< 0.01	0.55
1727	Coal-oil Slurry Area - 10 ft. from unit	4	1.71	4:35	10:20	< 0.01	0.27

* BS - Benzene Solubles

* TH - Total Hydrocarbons

--- Uncertainty on this weighing

Sample Date: 4/27/78
 Sample Type: Naptha (charcoal - lot 107)
 Analytical Method: GC
 Calibration Date: 4/24/78
 Date Shipped: 4/28/78
 Date Analyzed: 5/12/78
 Sampling Conducted By: Speicher

Sample No.	Area/Description	Pump	Flow Rate (ml/min.)	Start Time	Finish Time	Results (mg/m ³)
1729	Centrifuge Pers -	6	50	4:10 p.m.	10:05 p.m.	41.18
1730	Centrifuge Pers -	2	50	4:10	10:05	140.33
1731	Centrifuge Area (10 ft. N. of Centrifuge)	5	50	4:10	10:15	26.66

Sample Date: 5/9/78
 Sample Type: Benzene - Pentane (charcoal - Lot 107)
 Analytical Method: GC
 Calibration Date: 4/24/78
 Date Shipped: 5/16/78
 Date Analyzed: 6/9/78
 Sampling Conducted By: Speicher & Kretchman

Sample No.	Area/Description	Pump	Flow Rate (ml/min)	Start Time	Finish Time	Results (ppm)
1958	Solvent Analysis Lab Pers -	6	50	8:34 a.m.	3:53 p.m.	*B 0.91 *P 4.92
1959	Solvent Analysis Lab area 5 ft. from hood	5	50	8:30	3:53	*B 0.14 *P 0.15

*B - Benzene
 *P - Pentane

Sample Date: 5/9/78
 Sample Type: Cresol (Silica gel)
 Analytical Method: GC
 Calibration Date: 5/8/78
 Date Shipped: 5/16/78
 Date Analyzed: 6/13 & 14/78
 Sampling Conducted By: Speicher & Kretchman

Sample No.	Area/Description	Pump	Flow Rate (ml/min)	Start Time	Finish Time	Results (ppm)
1961	Water Treatment Pers -	1	50	8:10 a.m.	3:55 p.m.	< 0.29
1962	Water Treatment Area - Bio reactor area	3	50	8:05	3:55	0.30
1963	Water Treatment Pers -	4	50	8:05	3:55	< 0.34

Sample Date: 5/9/78
 Sample Type: Total hydrocarbons/benzene solubles (filter)
 Analytical Method: Benzene extraction
 Calibration Date: 4/24/78
 Date Shipped: 5/16/78
 Date Analyzed: 5/22/78
 Sampling Conducted By: Speicher & Kretchman

Sample No.	Area/Description	Pump	Flow Rate (l/min.)	Start Time	Finish Time	(mg/m ³) Results	
						*BS	*TH
1969	Water Treatment Pers -	9	1.50	8:05 a.m.	4:00 p.m.	< 0.08	0.42
1970	Water Treatment Area -, South end of WT area	10	1.49	8:05	3:45	< 0.07	0.44
1971	Water Treatment Pers -	8	1.50	8:05	3:55	< 0.08	0.57
1967	Solvent Analysis Lab Area - 5 ft. from hood	6	1.50	8:30	3:53	< 0.08	0.14
1968	Solvent Analysis Lab Pers -	7	1.50	8:30	3:53	< 0.08	0.18

* BS - Benzene Solubles
 * TH - Total Hydrocarbons

Sample Date: 5/09/78
 Sample Type: Phenol (bubbler)
 Analytical Method: GC
 Calibration Date: 5/08/78
 Date Shipped: 5/16/78
 Date Analyzed: 6/21/78
 Sampling Conducted By: Speicher & Kretchman

Sample No.	Area/Description	Pump	Flow Rate (l/min)	Start Time	Finish Time	Results (ppm)
1972	Water Treatment Area - Bio reactor area	11	1.25	8:20 a.m.	3:50 p.m.	< 0.01
1973	Water Treatment Area - Bio reactor area	12	1.0	8:20	3:45	< 0.02
1974	Water Treatment Area - At ammonia stripping	13	1.0	8:15	3:50	< 0.02

Sample Date: 5/9/78
 Sample Type: Ammonia (impinger)
 Analytical Method: Colorimetric
 Calibration Date: 5/8/78
 Date Shipped: 5/16/78
 Date Analyzed: 5/23/78
 Sampling Conducted By: Speicher & Kretchman

Sample No.	Area/Description	Pump	Flow Rate (l/min)	Start Time	Finish Time	Results (ppm)
1975	Water Treatment Area - At ammonia stripping	3	1.0	8:15 a.m.	3:50 p.m.	0.22
1976	Water Treatment Area - Bio reactor area	15	1.0	8:15	3:45	0.08
1977	Water Treatment Area - Bio reactor area	16	1.0	8:15	3:50	0.05

Sample Date: 5/11/78
 Sample Type: Total hydrocarbons/benzene solubles (filter)
 Analytical Method: Benzene extraction
 Calibration Date: 4/24/78
 Date Shipped: 5/16/78
 Date Analyzed: 5/22/78
 Sampling Conducted By: Speicher

Sample No.	Area/Description	Pump	Flow Rate (l/min.)	Start Time	Finish Time	(mg/m ³) Results	
						*BS	*TH
1979	Centrifuge Pers -	9	1.50	4:10 p.m.	6:00 p.m.	< 0.30	1.15
1980	Centrifuge Pres -	3	1.50	4:15	6:00	< 0.32	1.34
1981	Centrifuge Area - 10 ft. North of Centrifuge	6	1.50	4:15	6:00	0.32	0.89

* BS - Benzene Solubles
 * TH - Total Hydrocarbons

Sample Date: 5/11/78
 Sample Type: Benzene (charcoal - Lot 107)
 Analytical Method: GC
 Calibration Date: 4/24/78
 Date Shipped: 5/16/78
 Date Analyzed: 6/9/78
 Sampling Conducted By: Speicher

Sample No.	Area/Description	Pump	Flow Rate (ml/min.)	Start Time	Finish Time	Results (ppm)
1983	Centrifuge Pers -	2	50	4:15 p.m.	6:00 p.m.	< 0.33
1984	Centrifuge Pers -	5	50	4:10	6:00	< 0.56
1985	Centrifuge Area - 10 ft. N. of Centrifuge	6	50	4:30	6:00	< 0.72

Sample Date: 5/17/78
 Sample Type: Total hydrocarbons/benzene solubles (filter)
 Analytical Method: Benzene extraction
 Calibration Date: 5/16/78
 Date Shipped: 5/18/78
 Date Analyzed: 5/26/78
 Sampling Conducted By: Speicher & Kretchman

Sample No.	Area/Description	Pump	Flow Rate (l/min.)	Start Time	Finish Time	(mg/m ³) Results	
						*BS	*TH
1995	Water Treatment Pers -	8	1.50	8:00 a.m.	4:00 p.m.	< 0.08	0.51
1996	Water Treatment Pers -	10	1.49	8:30	1:06	< 0.12	1.36
1997	Water Treatment Area - South end of WT area	11	1.50	7:50	4:10	< 0.07	0.51
1998	Solvent Analysis Lab Pers -	7	1.50	8:20	3:55	< 0.07	0.48
1999	Solvent Analysis Lab Area - 5 ft. from hood	9	1.50	8:22	3:55	< 0.07	0.47

* BS - Benzene Solubles
 * TH - Total Hydrocarbons

Sample Date: 5/17/78
 Sample Type: Cresol (Silica gel)
 Analytical Method: GC
 Calibration Date: 5/8/78
 Date Shipped: 5/18/78
 Date Analyzed: 6/13 & 14/78
 Sampling Conducted By: Speicher & Kretchman

Sample No.	Area/Description	Pump	Flow Rate (ml/min)	Start Time	Finish Time	Results (ppm)
2002	Water Treatment Pers -	1	50)	8:00 a.m.	4:10 p.m.	0.30
2001	Water Treatment Area - Bio reactor area	3	50	7:50	4:18	< 0.28
2003	Water Treatment Pers -	4	50	8:30	11:40	< 0.76

Sample Date: 5/17/78
 Sample Type: Benzene (charcoal - Lot 107)
 Analytical Method: GC
 Calibration Date: 4/24/78
 Date Shipped: 5/18/78
 Date Analyzed: 6/9/78
 Sampling Conducted By: Speicher & Kretchman

Sample No.	Area/Description	Pump	Flow Rate (ml/min.)	Start Time	Finish Time	Results (ppm)
2004	Solvent Analysis Lab Pers -	5	50	8:20 a.m.	3:55 p.m.	4.02
2005	Solvent Analysis Lab Area - 5 ft. from hood	6	50	8:20	3:55	0.27

Sample Date: 5/17/78
 Sample Type: Ammonia (impinger)
 Analytical Method: Colorimetric
 Calibration Date: 5/16/78
 Date Shipped: 5/18/78
 Date Analyzed: 5/23/78
 Sampling Conducted By: Speicher & Kretchman

Sample No.	Area/Description	Pump	Flow Rate (l/min)	Start Time	Finish Time	Results (ppm)
2007	Water Treatment Area - South end of WT area	3	1.00	7:50 a.m.	4:10 p.m.	0.07
2008	Water Treatment Area - Bio reactor area	15	0.99	7:55	3:05	0.08
2009	Water Treatment Area - Bio reactor area	16	1.00	7:50	4:10	0.05

Sample Date: 5/17/78
 Sample Type: Phenol (bubbler)
 Analytical Method: GC
 Calibration Date: 5/16/78
 Date Shipped: 5/18/78
 Date Analyzed: 6/21/78
 Sampling Conducted By: Speicher & Kretchman

Sample No.	Area/Description	Pump	Flow Rate (l/min.)	Start Time	Finish Time	Results (ppm)
2010	Water Treatment Area - Bio reactor area	14	0.61	7:50 a.m.	4:05 p.m.	< 0.03
2011	Water Treatment Area - Bio reactor area	13	1.00	7:50	4:10	< 0.02
2012	Water Treatment Area - Bio reactor area	12	1.00	7:50	3:50	< 0.02

Sample Date: 6/7/78
 Sample Type: Respirable dust silica (filter)
 Analytical Method: X-ray diffraction & weight
 Calibration Date: 5/16/78
 Date Shipped: 6/13/78
 Date Analyzed: 6/26/78
 Sampling Conducted By: Speicher

Sample No.	Area/Description	Pump	Flow Rate (l/min.)	Start Time	Finish Time	Results (mg/m ³)
2368	Coal-Oil Slurry Area - 10 ft. North of Unit	4	1.71	7:55 a.m.	3:25 p.m.	< 0.01

Sample Date: 6/7/78
 Sample Type: Total hydrocarbons/benzene solubles (filter)
 Analytical Method: Benzene Extraction
 Calibration Date: 5/16/78
 Date Shipped: 6/13/78
 Date Analyzed: 6/26/78
 Sampling Conducted By: Speicher

Sample No.	Area/Description	Pump	Flow Rate (l/min.)	Start Time	Finish Time	Results (mg/m ³)	
						*BS	*TH
2370	Coal-Oil Slurry Area- 20 ft. North of Unit (background)	3	1.50	7:53 a.m.	3:30 p.m.	< 0.07	0.28

* BS - Benzene Solubles
 * TH - Total Hydrocarbons

Sample Date: 6/7/78
 Sample Type: Nickel (filter)
 Analytical Method: AA
 Calibration Date: 5/16/78
 Date Shipped: 6/13/78
 Date Analyzed: 7/5/78
 Sampling Conducted By: Speicher

Sample No.	Area/Description	Pump	Flow Rate (l/min.)	Start Time	Finish Time	Results (mg/m ³)
2372	Flame Spray Area - 3 ft. from hood	6	1.50	9:35 a.m.	12:10 p.m.	0.04
2373	Flame Spray Area - At hood	8	1.49	9:35	10:35	0.48
2374	Flame Spray Area - 1 ft from hood	8	1.49	11:00	12:10	0.89

Sample Date: 6/9/78
 Sample Type: Phenol (bubbler)
 Analytical Method: GC
 Calibration Date: 6/8/78
 Date Shipped: 6/13/78
 Date Analyzed: 6/21/78
 Sampling Conducted By: Kretchman

Sample No.	Area/Description	Pump	Flow Rate (l/min.)	Start Time	Finish Time	Results (ppm)
2295	Water Treatment Area - Bio reactor area	13	1.00	8:06 a.m.	4:00 p.m.	< 0.13
2296	Water Treatment Area - Bio reactor area	14	0.74	8:06	4:00	< 0.17

Sample Date: 6/9/78
 Sample Type: Ammonia (Impinger)
 Analytical Method: Colorimetric
 Calibration Date: 6/8/78
 Date Shipped: 6/13/78
 Date Analyzed: 6/21/78
 Sampling Conducted By: Kretchman

Sample No.	Area/Description	Pump	Flow Rate (l/min.)	Start Time	Finish Time	Results (ppm)
2297	Water Treatment Area - Bio reactor area	3	0.99	8:07 a.m.	4:00 p.m.	0.06
2298	Water Treatment Area - South end of WT Area	15	0.99	8:07	4:00	0.08
2299	Water Treatment Area - Bio reactor area	16	0.93	8:07	4:00	0.06

Sample Date: 6/9/78
 Sample Type: Total hydrocarbons/benzene solubles (filter)
 Analytical Method: Benzene extraction
 Calibration Date: 5/30/78
 Date Shipped: 6/13/78
 Date Analyzed: 6/26/78
 Sampling Conducted By: Kretchman

Sample No.	Area/Description	Pump	Flow Rate (l/min.)	Start Time	Finish Time	(mg/m ³) Results	
						*BS	*TH
2301	Solvent Separation Lab Pers -	8	1.50	8:37 a.m.	3:57 p.m.	<0.09	0.18
2302	Solvent Separation Lab Area - 5 ft. from hood	9	1.50	8:42	4:02	<0.09	0.19

* BS - Benzene Solubles
 * TH - Total Hydrocarbons

Sample Date: 6/9/78
 Sample Type: Cresol (Silica Gel)
 Analytical Method: GC
 Calibration Date: 5/8/78
 Date Shipped: 6/13/78
 Date Analyzed: 7/3/78
 Sampling Conducted By: Kretchman

Sample No.	Area/Description	Pump	Flow Rate (ml/min.)	Start Time	Finish Time	Results (ppm)
2304	Water Treatment Pers -	4	50	8:08 a.m.	3:46 p.m.	< 0.38
2305	Water Treatment Pers -	3	50	8:25	3:48	< 0.57
2306	Water Treatment Area - Bio reactor area	1	50	8:15	3:56	< 0.27

Sample Date: 6/9/78
 Sample Type: Benzene-Pentane (charcoal Lot 107)
 Analytical Method: GC
 Calibration Date: 4/24/78
 Date Shipped: 6/13/78
 Date Analyzed: 6/26/78
 Sampling Conducted By: Kretchman

Sample No.	Area/Description	Pump	Flow Rate (ml/min.)	Start Time	Finish Time	Results (ppm)
2308	Solvent Separation Lab Pers -	5	50	8:37 a.m.	3:57 p.m.	*B 1.19 P 0.37
2309	Solvent Separation Lab Area - 5 ft. from hood	6	50	8:42	4:02	*B 0.16 P 0.18

*B - Benzene
 P - Pentane

Sample Date: 6/29/78
 Sample Type: Nickel (filter)
 Analytical Method: AA
 Calibration Date: 6/27/78
 Date Shipped: 7/10/78
 Date Analyzed: 7/17/78
 Sampling Conducted By: Speicher

Sample No.	Area/Description	Pump	Flow Rate (l/min.)	Start Time	Finish Time	Results (mg/m ³)
2262	Flame Spray Area - 3 ft. from hood	6	1.72	9:40 a.m.	10:40 p.m.	N. D.
2263	Flame Spray Area - Hood face	8	1.70	9:40	10:40	N. D.

N. D. - Not detected.

Sample Date: 6/29/78
 Sample Type: NO₂ (bubbler)
 Analytical Method: Colorimetric
 Calibration Date: 6/28/78
 Date Shipped: 6/30/78
 Date Analyzed: 6/30/78
 Sampling Conducted By: Speicher

Sample No.	Area/Description	Pump	Flow Rate (l/min.)	Start Time	Finish Time	Results (ppm)
2528	Flame Spray Area - Hood face	1	0.30	9:40 a.m.	10:40 p.m.	0.005
2529	Flame Spray Area - 3 ft. from hood face	13	0.36	9:40	10:40	0.004

Sample Date: 6/29/78
 Sample Type: Benzene (Charcoal - Lot 107)
 Analytical Method: GC
 Calibration Date: 4/24/78
 Date Shipped: 7/10/78
 Date Analyzed: 7/14/78
 Sampling Conducted By: Speicher

Sample No.	Area/Description	Pump	Flow Rate (ml/min.)	Start Time	Finish Time	Results (ppm)
2661	Centrifuge Area - 10 ft. North of Centrifuge	6	50	7:35 a.m.	3:22 p.m.	0.13

Sample Date: 6/29/78
 Sample Type: Total hydrocarbon/benzene solubles (filter)
 Analytical Method: Benzene extraction
 Calibration Date: 6/27/78
 Date Shipped: 7/10/78
 Date Analyzed: 7/14/78
 Sampling Conducted By: Speicher

Sample No.	Area/Description	Pump	Flow Rate (l/min.)	Start Time	Finish Time	(mg/m ³) Results	
						*BS	*TH
2666	Coal-oil Slurry Area - 10 ft. North of unit	9	1.70	7:23 a.m.	3:30 p.m.	0.12	0.27
2665	Centrifuge Area - 10 ft. North of Centrifuge	11	1.71	7:30	3:20	< 0.06	0.19

* BS - Benzene Solubles
 * TH - Total Hydrocarbons

Sample Date: 7/11/78
 Sample Type: Benzene (Charcoal - Lot 107)
 Analytical Method: GC
 Calibration Date: 4/24/78 and 5/8/78
 Date Shipped: 7/13/78
 Date Analyzed: 7/14/78
 Sampling Conducted By: Kretchman

Sample No.	Area/Description	Pump	Flow Rate (ml/min.)	Start Time	Finish Time	Results (ppm)
2769	Solvent Separation Lab Pers -	6	50	8:16 a.m.	3:34 p.m.	0.31
2770	Solvent Separation Lab Area - 5 ft. from hood	3	50	8:16	3:34	0.17

Sample Date: 7/11/78
 Sample Type: NO₂ (bubbler)
 Analytical Method: Colorimetric
 Calibration Date: 7/10/78
 Date Shipped: 7/12/78
 Date Analyzed: 7/13/78
 Sampling Conducted By: Kretchman

Sample No.	Area/Description	Pump	Flow Rate (l/min.)	Start Time	Finish Time	Results (ppm)
2771	Flame Spray Area - 3 ft. from hood	1	0.30	10:28 a.m.	11:08 a.m.	0.003
2772	Flame Spray Area - Hood face	13	0.36	10:28	11:08	0.008

Sample Date: 7/11/78
 Sample Type: Total hydrocarbons/benzene solubles (filter)
 Analytical Method: Benzene extraction
 Calibration Date: 6/27/78
 Date Shipped: 7/13/78
 Date Analyzed: 7/14/78
 Sampling Conducted By: Kretchman

Sample No.	Area/Description	Pump	Flow Rate (l/min.)	Start Time	Finish Time	(mg/m ³) Results	
						*BS	*TH
2773	Solvent Separation Lab Pers -	8	1.49	8:16 a.m.	3:34 p.m.	< 0.09	< 0.02
2774	Solvent Separation Lab Area - 5 ft. from hood	9	1.54	8:13	3:34	< 0.09	0.02

* BS - Benzene Solubles
 * TH - Total Hydrocarbons

Sample Date: 7/11/78
 Sample Type: Nickel (filter)
 Analytical Method: AA
 Calibration Date: 6/27/78
 Date Shipped: 7/13/78
 Date Analyzed: 7/17/78
 Sampling Conducted By: Kretchman

Sample No.	Area/Description	Pump	Flow Rate (l/min.)	Start Time	Finish Time	Results (mg/m ³)
2780	Flame Spray Area - Hood face	11	1.71	10:28 a.m.	11:08 a.m.	0.09
2781	Flame Spray Area - Hood face	7	1.70	10:28	11:08	0.22

Sample Date: 8/18/78
 Sample Type: Benzene (Charcoal tube - lot 107)
 Analytical Method: GC
 Calibration Date: 8/17/78
 Date Shipped: 8/21/78
 Date Analyzed: 9/15/78
 Sampling Conducted By: Kretchman

Sample No.	Job/Category/ Area	Pump	Flow Rate ml/min	Start Time	Finish Time	Results ppm
3181-78	Solvent Separation Lab Area - bath hood	1	50	8:25 a.m.	11:30 a.m.	<0.32
3182-78	Solvent Separation Lab Personal	6	50	8:15	11:25	0.32
3183-78	Solvent Separation Lab Area - bath hood	1	50	12:35 p.m.	2:47 p.m.	<0.46
3184-78	Solvent Separation Lab Personal	6	50	12:35	2:46	1.38
3185-78	Solvent Separation Lab Area - solvent hood	5	50	12:35	2:47	1.43

Sample Date: 8/30/78
 Sample Type: Benzene (Charcoal tube - lot 107)
 Analytical Method: GC
 Calibration Date: 8/17/78
 Date Shipped: 8/31/78
 Date Analyzed: 9/15/78
 Sampling Conducted By: Kretchman

Sample No.	Job/Category/ Area	Pump	Flow Rate	Start Time	Finish Time	Results
3328-78	Solvent Separation Lab Personal	6	50	8:11 a.m.	11:22 p.m.	0.32
3329-78	Solvent Separation Lab Personal	6	50	11:01	3:33	0.76
3330-78	Solvent Separation Lab Area - Solvent Storage hood	5	50	8:15	11:23	<0.34
3331-78	Solvent Separation Lab Area - Solvent Storage hood	5	50	11:00	3:33	<0.42
3332-78	Solvent Separation Lab Area - Working hood	2	50	8:20	11:23	<0.38
3333-78	Solvent Separation Lab Area - Working hood	2	50	1:00	3:33	<0.47

APPENDIX C

ANALYTICAL EQUIPMENT CALIBRATION PROCEDURES

1. Spectrophotometer (Beckman DB - GT)

The wave length to be used for the analysis is calibrated at seven reference points during alternate months with a Holmium Oxide filter. A linearity check for absorbency is made at 510 millimicrons with 2% and 4% solutions of cobalt sulfate for reference values.

2. Gas Chromatograph (Perkin-Elmer 3920)

Chromatograms of two or three known standard concentrations are made before each series of unknown samples are evaluated. All standards must not differ from each other by more than $\pm 10\%$ of the expected instrument response.

3. Atomic absorption Spectrophotometer (Perkin-Elmer 603)

Two different solution concentrations of a known metal content for each metal to be evaluated are prepared from dilutions of a commercially high purity stock solution standard. These solutions are used to produce specific instrument responses before unknown samples for any metal is evaluated. Then, known concentrations of each metal to be evaluated are added to new sample collection media ("controls") for analysis. The metal content is removed from this media and treated by a similar method to that used for the preparation of the unknown samples for evaluation.

4. X-ray diffraction

A known silica standard is analysed daily or prior to the analysis of a series of unknown dust samples. Known concentrations of silica in dust samples are also analyzed on a periodic basis.