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Industrywide Studies Report Of An In-Depth Industrial Hygiene Survey Of The ~~Texaco~~ Texaco Chemical Company, Port Neches, Texas

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16. Abstract (Limit: 200 words)

Environmental and breathing zone samples were analyzed for 1,3-butadiene (106990) at the Texaco Chemical Company (SIC-2869), Port Neches, Texas in April, 1985. Company Industrial hygiene monitoring data was reviewed. Engineering controls and work practices were observed. Breathing zone 1,3-butadiene concentrations ranged up to 125 parts per million (ppm). The highest exposures occurred for laboratory technicians cleaning sample cylinders. The OSHA standard for 1,3-butadiene is 1,000ppm. Mean environmental 1,3-butadiene exposures were generally below 2ppm, except in the chromatography laboratory where a concentration of 5.1ppm was measured. Company data showed geometric mean time weighted average exposures to be below 2ppm. Engineering controls consisted of single and dual mechanical seals on 1,3-butadiene pumps. Quality control sampling involved on line gas chromatographs and open loop systems. The open loop systems were in the process of being replaced by closed loop systems. All personnel were required to wear hard hats, safety glasses, and safety shoes. Half or full face respirators were also used. The authors conclude that the NIOSH data generally agrees with the company's air monitoring data. Control programs at the facility appear to control adequate protection. Recommendations include converting to closed loop quality control sampling systems and training employees to use respirators properly.

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DISCLAIMER

PURPOSE OF SURVEY:	To conduct an in-depth survey of a 1,3-butadiene monomer producing plant to assess the extent of worker exposure, the status and nature of existing engineering controls, and current industrial hygiene programs.
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EMPLOYEE REPRESENTATIVES CONTACTED:	David Hutto, Technician Control Union Cecil Oubre, Carpenters Local 610 Ronald Robinson, Pipefitters Local 195 John Tuohy, IBEW, Local 390 D. Williams, Boilermakers Local 305 Dennis Wills, OCAW Local 4-228
STANDARD INDUSTRIAL CLASSIFICATION OF PLANT:	2869 - Industrial Organic Chemicals, not elsewhere classified.

ABSTRACT

An in-depth survey was conducted at Texaco Chemical Company's Neches Butane Products Plant in Port Neches, Texas on April 9-12, 1985. The purpose of the survey was to assess the extent of worker exposure at a 1,3-butadiene monomer production facility and to determine the status and nature of existing engineering controls and industrial hygiene programs. The impetus for this investigation came from recent toxicological studies that have identified 1,3-butadiene as an animal and potential human carcinogen.

The Neches Butane Products Plant, which opened in 1944, began producing 1,3-butadiene by dehydrogenation of a butane/butylene feed. In March 1980, the dehydrogenation process was shut down and the plant began recovering 1,3-butadiene from crude ethylene unit byproduct feedstreams purchased from outside producers.

During the survey, descriptive information was collected on the company's control technology, work force, past employee exposures, recordkeeping, and medical, safety, and industrial hygiene programs. A detailed industrial hygiene survey was conducted to characterize employee exposures to 1,3-butadiene.

Personal and area monitoring were performed using a new sampling and analytical method developed by NIOSH. Personal exposures were characterized for five job descriptions, and area concentrations were determined for three work environments. Employee 8-hour time-weighted average (TWA) exposures varied greatly across different job categories. Laboratory technicians performing sample cylinder cleaning have the highest mean exposure (125 ppm) of any job category; process technicians in the loading area have the second highest mean exposure (64 ppm). Other job categories monitored showed mean TWA exposures at or below 12 ppm (approximately). Mean area concentrations in those work environments measured during normal operating conditions were found to be below 2 ppm, with the exception of the laboratory area used to conduct "dry" analyses which had a mean concentration of 5.1 ppm. These data appear to be in general agreement with historical monitoring data reported by Texaco.

Recommendations were made pertaining to the use of additional engineering controls to reduce worker exposures below existing levels.

ACKNOWLEDGEMENTS

This report was prepared in cooperation with PEI Associates, Incorporated (formerly PEDCo Environmental, Incorporated). The principal PEI author was Leslie J. Ungers, C.I.H. His responsibilities during this investigation were completed under the scope of work of Contract No. 68-02-3976, Task 24 with the U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, D.C.

INTRODUCTION

Inhalation exposure of rats and mice to 1,3-butadiene induced a carcinogenic response at multiple sites. Mammary fibroadenomas/carcinomas, uterine sarcomas, Leydig cell adenomas of the testes, thyroid follicular cell adenomas, exocrine tumors of the pancreas, and Zymbal gland carcinomas were identified in rats exposed at concentrations of 1,000 or 8,000 ppm of 1,3-butadiene. Mice exposed to 625 or 1,250 ppm of 1,3-butadiene developed a high incidence of malignant lymphomas; an increased incidence of other tumors, including hemangiosarcoma; and testicular and ovarian atrophy.[1,2]

The offspring of pregnant rats exposed to 1,3-butadiene at 8,000 ppm had major skeletal defects. In addition, fetal toxicity was observed when pregnant dams were exposed at 200 ppm, 1,000 ppm, and 8,000 ppm.[3]

Epidemiological studies of workers employed in facilities producing styrene-butadiene rubber (SBR) have indicated an increased, but not statistically significant, risk of mortality from leukemia and from neoplasms of the lymphatic and hematopoietic tissues.[4,5]

Based on these data, the National Institute for Occupational Safety and Health (NIOSH) recommends that 1,3-butadiene be regarded as a potential occupational carcinogen and teratogen and as a possible reproductive hazard.[6] Because of the number of workers potentially exposed to 1,3-butadiene and the resulting potential health risk, NIOSH researchers are conducting an extent-of-exposure study of the 1,3-butadiene monomer production industry.

The NIOSH study of the monomer industry is divided into three phases. The first phase consisted of a literature review, a definition of the 1,3-butadiene industry, and the development of a study design. The second phase involved conducting a series of walk-through surveys at each of the 11 companies producing 1,3-butadiene monomer, and then selecting facilities for in-depth industrial hygiene surveys. The nature of the process, the process controls, the worker exposures, and the company's industrial hygiene, safety, and medical programs are discussed in a walk-through report written for each of the facilities visited. The final phase involved conducting in-depth industrial hygiene surveys at four selected facilities. The site selection criteria for the in-depth surveys were type of pump seals, method of transporting 1,3-butadiene, sole producer status, and the method of quality control cylinder sampling. As part of the final phase, an in-depth survey report has been written for each of the companies visited.

EXPOSURE EVALUATION CRITERIA

The current Permissible Exposure Limit (PEL) enforced by the Occupational Safety and Health Administration (OSHA) for 1,3-butadiene is 1000 ppm for an 8-hour time-weighted average (TWA).[7] The American Conference of Governmental Industrial Hygienists (ACGIH) has included 1,3-butadiene in their Notice of Intended Changes for the 1985-1986 Threshold Limit Values

(TLVs) based upon reported animal carcinogenicity data.[8] The intended change identified 1,3-butadiene as an "A2" industrial substance suspected of carcinogenic potential in man. A numerical TLV of 10 ppm was proposed in connection with the notice.

NIOSH in their Current Intelligence Bulletin recommends that 1,3-butadiene be regarded as a potential occupational carcinogen and teratogen and as a possible reproductive hazard.[6]

HISTORY AND DESCRIPTION OF THE PLANT

The Neches Butane Products Company began production of 1,3-butadiene in 1944 by the dehydrogenation of butane and butylene feedstocks. The facility in Port Neches was one of the plants developed by the Reconstruction Finance Corporation during World War II. The company received management and engineering assistance from area refineries: Socony-Vacuum Oil Company, Atlantic Refinery Company, Texaco, Gulf, and Pure Oil. Texaco, Gulf, U.S. Rubber Company, and B. F. Goodrich Chemical Company later bought the company as a partnership. By January 1981, Texaco had bought out all other partners.

In March 1980, the dehydrogenation process was shut down and the plant began recovering 1,3-butadiene from crude ethylene unit byproduct (C4) feedstocks purchased from outside producers. The nameplate capacity of the plant is 360 million pounds per year of 1,3-butadiene. The production rate at the time of the survey was 300 million pounds per year of 1,3-butadiene. Methyl tertiary butyl ether (MTBE) is also produced in a separate unit. No other major products are produced at the facility. The 1,3-butadiene facility covers 10 acres of the 200-acre plant.

PROCESS DESCRIPTION

The crude ethylene unit byproduct (C4 feed) is a blend of four-carbon chain hydrocarbons. The C4 crude feedstock is received from other producers by pipeline, marine vessel, rail and truck. The majority is received via ship or barge.

Chemical Process

The crude ethylene unit byproduct feed used at Texaco Chemical is a blend from several suppliers. The extraction solvent used at Texaco is beta-methoxy propionitrile (BMOP) and furfural. The process includes on-line gas chromatographs for quality control determinations. Figure 1 is a simplified flow diagram of the 1,3-butadiene production process. The finished 1,3-butadiene has a purity greater than 99 percent and is stored in pressurized storage tanks. Texaco Chemical's on-site storage capacity for 1,3-butadiene is 106,000 barrels. The 1,3-butadiene monomer product is shipped primarily by pipeline to other plants in Orange and Port Neches, Texas. Small quantities are shipped by barge and rail.

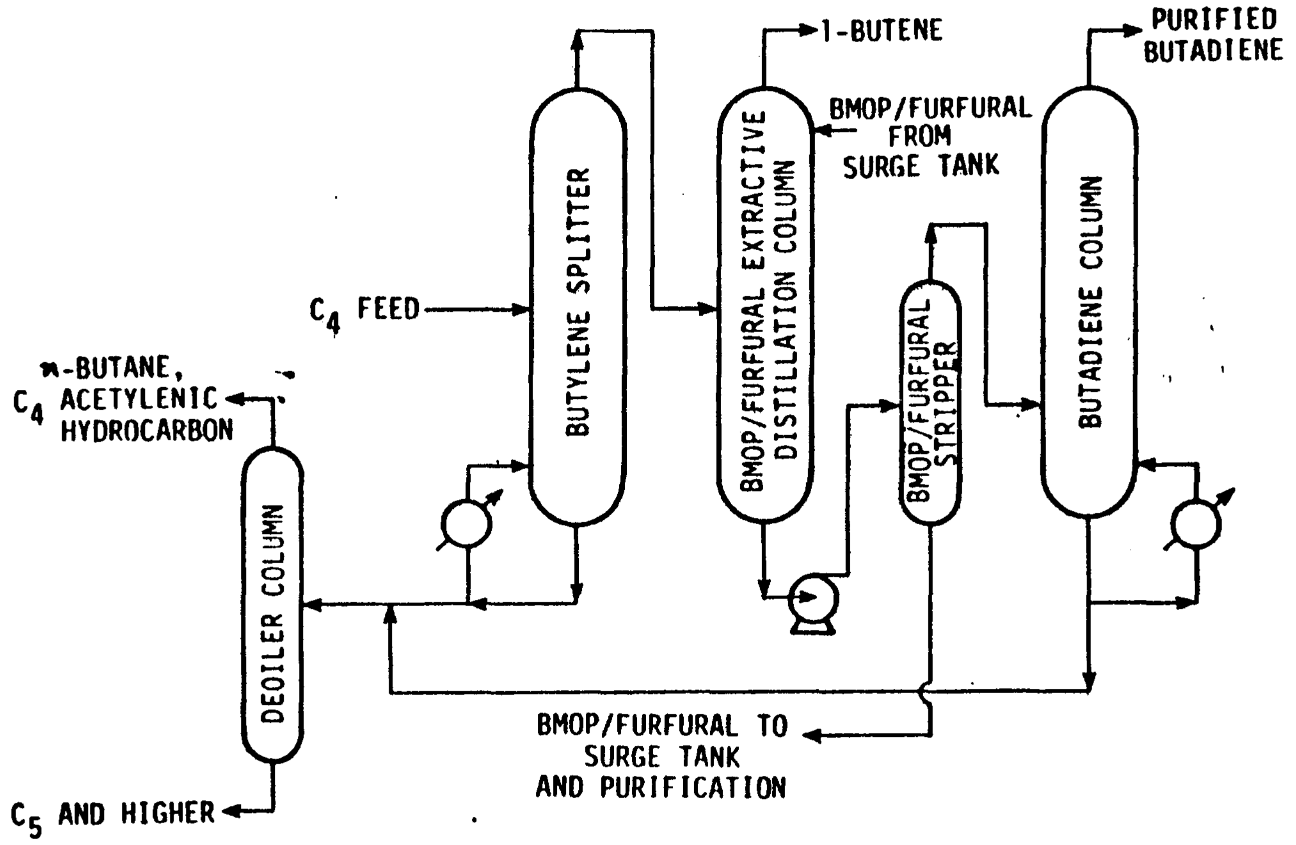

Figure 1. Simplified flow diagram for production of 1,3-butadiene monomer by ethylene coproduct process at Texaco's Port Neches, Texas plant.

Chemical Handling

As previously mentioned, the ethylene unit byproduct is received from several suppliers. The crude is tested for 1,3-butadiene content before entering the process. During the production process, workers collect samples of the ethylene unit byproduct in various stages of refinement, and also collect samples of the finished 1,3-butadiene. These samples, obtained for quality control purposes, are collected from the process stream (at pressures greater than atmospheric), in a sample cylinder. The collected samples are then transported to an on-site control laboratory for analysis.

None of the 1,3-butadiene monomer is consumed at the plant.

CONTROL DESCRIPTION

Large chemical process operations such as those at the Texaco Chemical facility incorporate a number of controls designated to prevent the release of chemical intermediates and products into the environment. Many of these controls are an integral part of the process equipment, whereas others have been added for a specific purpose. Some controls are designed to reduce occupational exposures, which can arise from inhalation or skin contact whereas others are intended to abate environmental releases. Frequently, the environmental controls also function indirectly to reduce the level of toxic contaminants in the workplace air.

NIOSH examined Texaco Chemical's monomer production facility to identify those controls that directly or indirectly reduce workplace exposures. Controls identified during the survey are presented by the process operation or work task they are designed to control.

Engineering Controls

Several engineering controls are in place at the Texaco facility that directly or indirectly control the release of 1,3-butadiene to the work environment. Engineering control techniques are implemented in three operational categories:

A. Process Flow
All but one of the process pumps located in the 1,3-butadiene recovery area (pump alley) are equipped with single mechanical seals. The odd pump was equipped with a tandem (or dual) mechanical seal, but was not operating during the survey. A discussion of both control measures is provided below:

1. Single Mechanical Seals
Figure 2 is a schematic diagram of single mechanical seal. The rotating seal rings and stationary elements are lapped to a high degree of flatness to maintain contact throughout their mutual surface area. The faces are held together by a combination of pressures: pressure exerted by a mechanical spring and pump pressure transmitted through the liquid being pumped. Single mechanical seal represent an improvement over packed seals and are in general use throughout the 1,3-butadiene monomer industry.

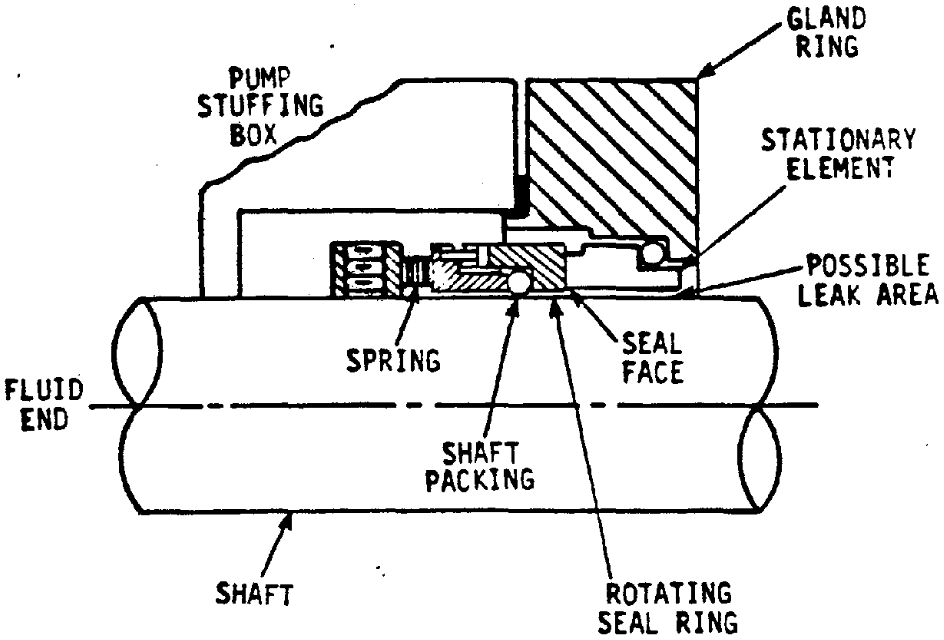

Figure 2. Diagram of a single mechanical seal.

2. Tandem (Dual) Mechanical Seals

Figure 3 is a schematic diagram of a tandem seal. The tandem seal consists of two single mechanical seals mounted in such a way as to produce a space between the two seals. A seal liquid, usually oil, is circulated through the cavity in the pump casing at a somewhat higher pressure than the product being moved; however, in the case of 1,3-butadiene processing, the pump oil is at a lower pressure than the process stream. The loss of 1,3-butadiene into the cavity and the resulting displacement of oil to the work environment is used as an indication of seal failure. This warning property gives the tandem seal arrangement an advantage over the single seal design.

B. Quality Control (QC) Samples

The QC program at Texaco Chemical requires workers to perform three major tasks: the collection of the 1,3-butadiene, a laboratory analysis of the sample, and purge/cleaning of the sample cylinders. Each task has individual controls associated with it.

1. Sample Collection

Two control options were in use at Texaco: on-line gas chromatographs and the replacement of manual "open-loop" cylinder samples with "closed-loop" systems.* The use of on-line gas chromatographs eliminated the need for some manual sampling. When manual sampling was needed, Texaco Chemical employed the use of open-loop cylinder samplers. At the time of the survey Texaco Chemical was planning to convert their existing sample locations to a closed-loop system. Figure 4 presents a schematic of Texaco's proposed closed-loop system.

2. Laboratory Analyses

Laboratory analyses were performed in a facility with 60 percent makeup air. Subsequently, a system utilizing 100% makeup air was installed. Transfer of 1,3-butadiene samples from sample cylinders to laboratory glassware were conducted under laboratory hoods; however, GC injections were conducted in the open laboratory using a closed sample injection system.

(During this survey NIOSH researchers made face velocity measurements of the laboratory hoods. Results of these measurements were as follows: The mean face velocity of laboratory hoods in the facility used to conduct the wet (chemical) analyses was 61 lfpm with a range of 20 to 102 lfpm. The laboratory used to conduct the chromatograph analyses was equipped with a single hood having a mean face velocity of 138 lfpm.)

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* At the time of the survey only a few QC sampling locations had been converted to closed loop systems. The survey results represent a facility that is essentially an open-loop process.

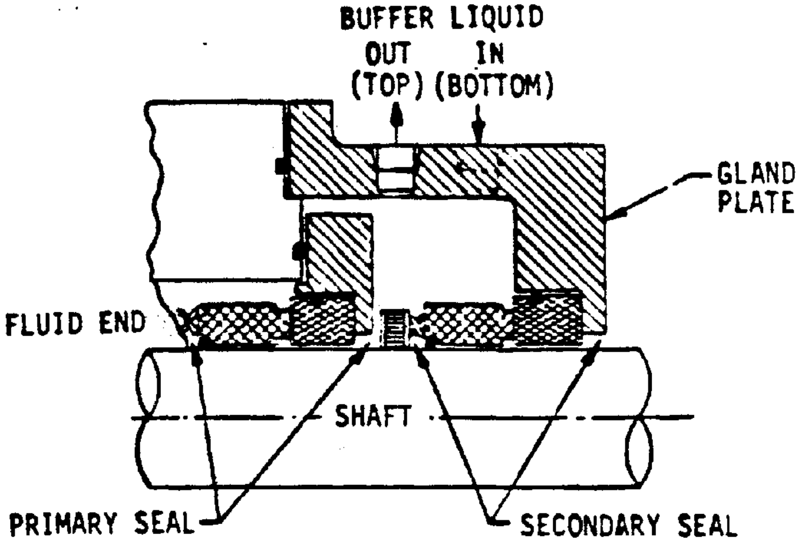

Figure 3. Diagram of a dual mechanical seal. (tandem arrangement)

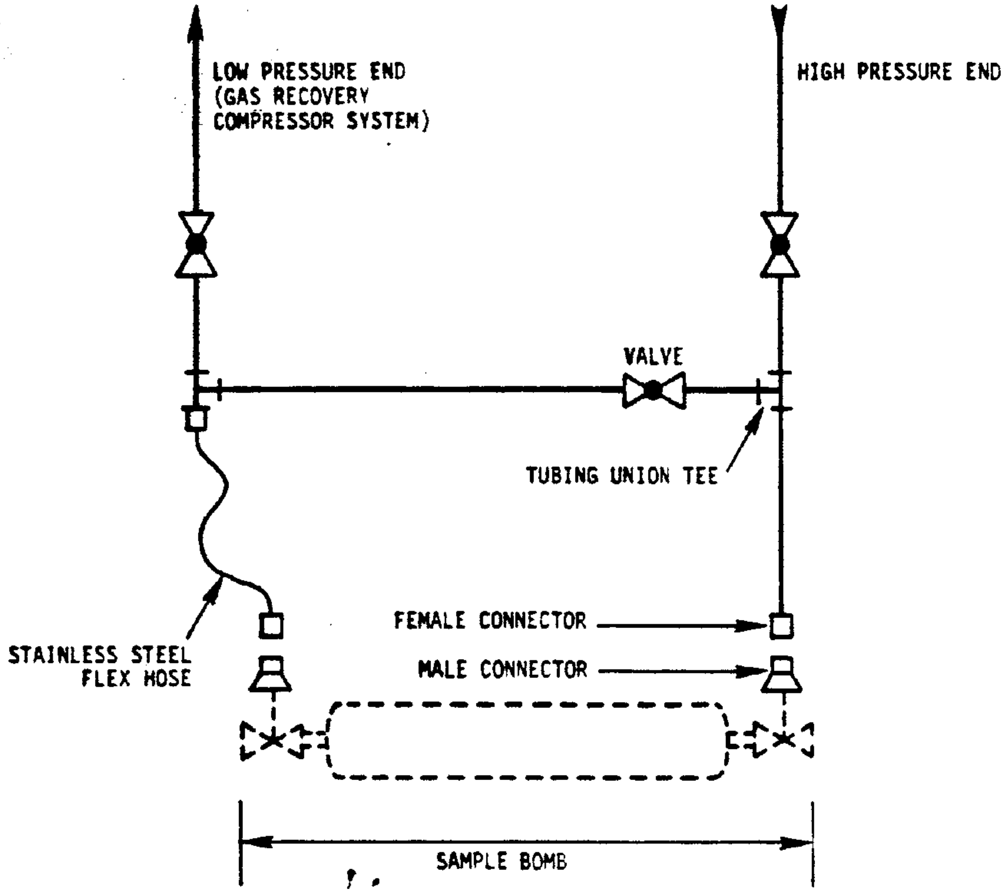

Figure 4. Texaco's proposed closed-loop sampling system.

3. Cylinder Purge/Cleaning
   After a sufficient quantity of 1,3-butadiene has been removed for analysis, the cylinders are removed from the laboratory to an outside steam manifold for purging of the remaining sample and steam-cleaning. Excess 1,3-butadiene is exhausted to a plant compressor through an enclosed system.

C. Transportation
   The loading of 1,3-butadiene into rail tank cars is monitored with two types of "fill" gauges: slip tube and magnetic. Both gauges monitor the filling operation by measuring the level of 1,3-butadiene in the tank car. At Texaco Chemical both types of gauges were used during the loading of rail tank cars.

1. The slip-tube gauge achieves this task by releasing a small plume of 1,3-butadiene vapor to the ambient air. The vapor acts as a visual signal to the loading area technician that the 1,3-butadiene in the tank car (or vessel) has reached a predetermined level. This type of gauge can be considered an engineering control to the extent that it negates the need for the process technician to be in close proximity to the tank port.

2. The magnetic gauge, which operates without the release of vapor into the air, can be considered an improvement over the slip-tube design. A magnetic ring or "doughnut" located inside the tank car floats on the surface of the 1,3-butadiene. As the tank car fills, the ring rises over an enclosed shaft. Inside the shaft is a metered rod which projects out over the top of the car. The extent of this projection is monitored by the loading area technician and provides an accurate measure of the level of 1,3-butadiene in the tank car.

Administrative Controls

Texaco Chemical requires that certain decontamination procedures be followed during the repair, maintenance, or cleaning of process equipment. These precautions are designed to assure that maintenance workers are not overexposed to 1,3-butadiene during the performance of their tasks. One such procedure is to have process technicians "blind," decommission, steam, and nitrogen purge process equipment before maintenance workers enter the area. Often hydroblasting or water cleaning is also performed. The decontamination procedures produce two effects, the latter of which can be classified as an administrative control:

1. The most qualified personnel (process technicians) shut down and clean the equipment.

2. Exposures to maintenance workers are limited to the time it takes to repair the equipment, not to the full decontamination/repair task.

PERSONAL PROTECTIVE EQUIPMENT

Texaco Chemical requires all workers in the process areas to wear hard hats and safety glasses. Workers are also required to carry half-face cartridge respirators while working in the plant. Process technicians taking bomb samples or decontaminating faulty equipment (e.g., process pumps with leaking seals) are required to wear the respirators and use PVC/neoprene gloves. Air-line respirators with full-face pieces are required during maintenance operations in poorly ventilated or enclosed spaces. Laboratory technicians are required to wear safety glasses, PVC/neoprene gloves, and protective aprons when conducting analyses. In addition, they are required to wear half face organic vapor cartridge respirators when handling butadiene sample cylinders when charging GC.

DESCRIPTION OF THE WORKFORCE

A number of job descriptions are found at Texaco Chemical among 1,3-butadiene workers. These descriptions can be grouped into the following classifications:

Process technician/process area (including tank farms) (A and B operators):	Responsible for the outdoor activities in the process area. Takes QC samples and decontaminates the pumps and equipment prior to maintenance. Also responsible for monitoring the process.
Process technician/loading area:	Loads rail cars, intercoastal barges, and marine vessels. The number of rail cars, barges, and vessels loaded per day varies with customer demand for 1,3-butadiene. Rail cars are loaded daily during the day shift, while the barges and vessels are loaded as they are received, night or day.
Process technician/control room:	Operates the computerized control room and is responsible for monitoring the process conditions.
Maintenance technician:	Conducts maintenance and repair on equipment decontaminated by the process technician.
Laboratory technician:	Conducts analysis of 1,3-butadiene QC samples for both purity (chromatographic analysis) and impurities (wet chemical analysis).

DESCRIPTION OF PAST WORKER EXPOSURES

Industrial hygiene data on 1,3-butadiene is available for the period 1981 through 1984. Table 1 summarizes personal monitoring data as reported by Texaco Chemical for 1,3-butadiene exposures. Geometric mean 8-hour TWAs for all job descriptions are below 2 ppm. Arithmetic mean 8-hour TWAs above 5 ppm for maintenance technicians (pipefitters, machinists) would appear to be due to a few very high measurements.

All personal samples were reported to have been collected on charcoal tubes with low-flow pumps and analyzed by gas chromatography techniques similar to NIOSH Method S-91.[9]

PERSONNEL RECORDS SYSTEM

Texaco Chemical maintains personnel records on terminated as well as current employees. The records date back to 1962. Five of the six unions which represent workers at the plant have death insurance and maintain records on the death of members. Death certificates are filed at the company with a copy of each certificate sent to the insurance company. The personnel records are maintained on standard forms for each employee and provide the following information:

1) name
2) social security number
3) date of birth
4) date of employment
5) date of termination
6) department
7) pay classification.

The records do not detail specific job classifications for each employee.

MEDICAL, SAFETY, AND INDUSTRIAL HYGIENE PROGRAMS

Texaco Chemical maintains medical, safety, and industrial hygiene programs at the Port Neches facility.

Medical Program

The company conducts pre-employment physicals on all employees. Periodic physical examinations are available to all employees but are not mandatory, the sole exception being annual hearing tests which are required. The medical examination includes:

1) physical examination
2) hearing test
3) vision test
4) pulmonary function test
5) blood analysis
6) urinalysis
7) electrocardiogram (EKG).

TABLE 1. SUMMARY OF TEXACO'S MONITORING RESULTS FOR 1,3-BUTADIENE, 1981-1984

Job title	No. of samples	8-hour TWA*, ppm		
		Range	Geometric mean	Arithmetic mean
Maintenance technician				
Pipefitter	44	0.01 - 606.56	1.70	47.44
Machinist	7	0.12 - 159.63	0.71	23.19
Boilermaker	52	0.01 - 16.46	0.17	1.54
Laborer	4	0.01 - 3.69	0.32	1.48
Process technician/ process area				
Operator	77	0.01 - 159.49	1.06	5.06
Operator helper	13	0.16 - 34.40	0.71	3.89
HD operator	41	0.13 - 22.00	1.26	3.65
Foreman	11	0.14 - 7.23	0.43	1.01
Instruments	2	1.67 - 2.32	1.97	2.00
Electric instruments	7	0.14 - 1.90	0.47	0.78
Laboratory technician				
Technical lab	14	0.01 - 6.30	0.23	1.18
Non-technical lab (includes yard)	40	0.16 - 22.49	1.80	4.24

* Time-weighted average.

The plant has one part-time physician on site for half-days, five days a week. Two licensed full-time registered nurses and one part-time nurse are also on duty at the plant. At least one employee in each shift is trained in emergency care. The plant has an agreement for emergency care with a local hospital.

Safety Program

The company maintains an organized safety program. The program is periodically reviewed by the Occupational Safety and Health Administration (OSHA). The company has an established safety committee with union and management representatives. The chairman of the Safety Committee reports directly to the plant manager. Safety meetings are held monthly.

The safety program requires that hard hats, safety glasses (goggles), and safety shoes be worn in the process areas. PVC/neoprene rubber gloves are required for decontamination, maintenance, QC sampling, and laboratory personnel.

Laboratory personnel are also required to wear protective aprons during chemical handling operations. 3M half-face organic vapor respirators are carried by each employee working in the process area. Scott full-face respirators are available to employees for protection during decontamination, maintenance, and QC sampling activities. Showers and a central clothing/changing area is provided. Smoking is not permitted in the production area because of the explosion hazard of 1,3-butadiene.

Industrial Hygiene Program

The industrial hygiene program maintains up-to-date toxicity information on the chemicals handled in the plant. Personal sampling for 1,3-butadiene began in 1981. Texaco Chemical has adopted an internal exposure standard of 10 ppm (TWA) for 1,3-butadiene, which is substantially lower than the present OSHA PEL. Other sampling has included various C_4's, total hydrocarbons, styrene, acrylonitrile, and furfural.

SAMPLING AND ANALYTICAL METHODS

A new sampling and analytical method for 1,3-butadiene was used by NIOSH during the Texaco Chemical in-depth survey. The new method is similar to the old NIOSH Method S-91 for 1,3-butadiene.[9] The new method includes changes in both sampling apparatus and analytical procedure. A brief summary of the method is presented here; more detailed information is provided in Appendix A.

Sampling, Transport, and Storage

During the in-depth survey of the Texaco Chemical plant, both personal and area sampling were performed. The samples were collected with SKC Model 224 and Gillian Model HFS-113A-UT portable low-flow air-sampling pumps. The charcoal tubes were connected to the pumps with plastic Tygon tubing.

Sampling pumps used during the survey were checked for significant air-flow deviation (greater than 5 percent) after each sampling period. To assure the quality of results, sample blanks and quality assurance spikes were generated, analyzed, and reported in accordance with NIOSH Quality Assurance/Quality Control procedures.

The sample was collected with separable solid sorbent tubes. The forward tube contains 400 mg of coconut charcoal and acts as the primary collection medium. The backup tube contains 200 mg of charcoal and acts to quantify the level of breakthrough.

For this method, samples are collected with low-flow pumps at a flow rate of 0.02 to 0.5 lpm. Sample air volumes are limited to a minimum of 1 liter and a maximum of 25 liters. During full-period sampling, the working range of the new method is 0.17 to 220 mg/m^3, or 0.07 to 100 ppm. For short-term 15-minute samples taken at 0.5 lpm, the working range is 0.33 to 730 mg/m^3, or 0.13 to 330 ppm.

Field samples are refrigerated during shipment and storage. Samples are considered to remain stable for at least 28 days when kept at 4°C.

Desorption and Analysis

The sample charcoal is desorbed in 4 ml of methylene chloride for 30 minutes. Analysis is performed by gas chromatography with a flame ionization detector. At the lower range of an analytical method, it may not be possible to confidently attribute an instrument response to the substance in question. The point at which instrument response can confidently be attributed to the contaminant being measured is called the "limit of detection" (LOD). If an instrument response is attributed to the contaminant, it may be present at such low levels that the confidence interval for the results reported may be excessive. The point at which the range of possible values are within acceptable limits is called the "limit of quantitation" (LOQ). The estimated limit of quantitation (LOQ) was 11 ug per sample. The limit of detection was 3 ug per sample. These limits were calculated from the statistics of the calibration curve.

Media standards were run along with the field samples. These were 400 mg beds of coconut charcoal loaded with aliquots of pure 1,3-butadiene gas as air was drawn through each tube. Solution standards corresponding to the same levels were also run to determine desorption efficiency. A separate correction for desorption efficiency was unnecessary since media standards were used for the calibration curve. The desorption efficiency ranged from 65.2 to 104.6% for levels from 2.26 to 1018 ug per sample.

Pentane and methyl acetylene are the only substances found to interfere with chromatography when present at concentrations greater than 100 times the 1,3-butadiene concentration.

RESULTS

Personal Sampling

A total of 35 personal samples were collected during the in-depth survey. These samples represented five job descriptions:

1) process technicians/process area
2) process technicians/loading area
3) process technicians/control room
4) process technicians/storage area
5) laboratory technician.

Table 2 presents a summary of the personal samples collected at Texaco. The number of samples taken, the range of measurements, the arithmetic mean, the geometric mean, and the geometric standard deviation are presented by job description. The raw data on personal samples (including date, sample ID, air volume, duration, and concentration) are presented by job description in Appendix B, Table B-1.

Area Sampling

A total of 11 area samples were collected during the in-depth survey. These samples characterized three work environments:

1) process area/pump alley
2) process area/control room
3) laboratory/wet and dry analysis and bomb voiding.

Table 3 summarizes the area samples collected at Texaco Chemical. The number of samples taken, the range of measurements, the arithmetic mean, the geometric mean, and the geometric standard deviation are presented by work environment. The raw data on area samples (including data, sample ID, air volume, duration, and concentration) are presented by work environment in Appendix B, Table B-2.

DISCUSSION

The industrial hygiene survey of the Texaco Chemical 1,3-butadiene production facility indicates that the workers' exposures to 1,3-butadiene are below the TLV cited in the ACGIH Notice of Intended Changes for the 1984-85 TLVs[2] and the OSHA Permissible Exposure Limit (PEL).[1] However, during the NIOSH survey there were no maintenance activities in the 1,3-butadiene production area. Maintenance work in the production area reportedly can have an overall upward influence on the potential for exposure to other employees in the production unit because it usually is related to a faulty piece of equipment that is leaking 1,3-butadiene.

The arithmetic mean, full-shift, time-weighted exposures vary greatly across job descriptions. Laboratory technicians performing sample cylinder voiding

TABLE 2. SUMMARY OF PERSONAL SAMPLES (ppm)

Job description	Number of samples	Arithmetic mean	Min.	Max.	Geometric mean	Geometric standard deviation
Process technician/ process area						
° Rover/operator	8	6.76	0.27	34.9	1.13	4.86
° Instrumentation	5	0.75	<0.07[a]	2.55	0.28	4.96
° Maintenance	1	<0.21[b]	-	-	-	-
Process technician/loading area	2	63.77	3.97	123.57	-	-
Process technician/control room	2	1.79	1.70	1.87	-	-
Process technician/storage area	5	0.45	<0.04[a]	1.53	0.22	3.73
Laboratory technician						
Wet Chemical	3	1.68	0.76	2.55	1.50	1.86
Chromotograph	4	4.14	0.56	6.31	3.02	3.10
Cylinder voiding						
- full period	3	125.52	0.42	373.54	7.43	33.58
- short term	3	44.27	1.53	108.44	15.59	8.64
Cylinder sampling - short term (4-17 min.)	3	50.42	<0.65[a]	146.60	7.26	15.76

[a] Laboratory analysis of analyte was below limit of detection (3μg/sample).

[b] Laboratory analysis of analyte was below limit of quantitation (11μg/sample).

TABLE 3. SUMMARY OF AREA SAMPLES (ppm)

Work environment	Number of samples	Arithmetic mean	Min.	Max.	Geometric mean	Geometric standard deviation
Process/pump alley	4	0.20	0.10	0.33	0.18	1.65
Process/control room	1	2.13	-	-	-	-
Laboratory						
Wet-chemical	2	0.81	0.75	0.86	0.80	-
Chromatograph	3	5.10	3.93	5.88	5.02	1.24
Cylinder voiding	1	1.91	-	-	-	-

have the highest mean exposure (125.52 ppm) of any job category. A contract laboratory technician (janitor) voiding sample bombs received the highest individual TWA exposure (373.54 ppm) of any worker monitored. As a job description process technicians have the second highest arithmetic mean exposure (63.77 ppm for technicians in the loading area and 6.76 ppm for technicians in the process area).

Area samples collected in the production area during the in-depth survey indicated that under normal operating conditions arithmetic mean airborne concentration of 1,3-butadiene in all work environments measured was less than 2 ppm. However, the highest arithmetic mean concentrations (5.10 ppm) was found in the laboratory area used to conduct "chromatograph" analyses for purity of the 1,3-butadiene samples. The highest individual 8-hour airborne concentration (5.88 ppm) was also detected in the "chromatograph" laboratory.

CONCLUSIONS

Based on an evaluation of data supplied by Texaco Chemical and on the results of the survey, several observations can be made:

1) The historical exposure data supplied by Texaco Chemical (Table 1) for process technicians are in general agreement with the NIOSH survey results for the job title (Tables 2).

2) Texaco Chemical monitored pipefitters (maintenance), a job category which appears to experience very high exposure levels. No employees in this job category were working in the 1,3-butadiene production area during the NIOSH in-depth survey.

3) High exposures were measured during the NIOSH survey for the laboratory contract janitor performing cylinder voiding tasks. This exposure data cannot be identified in the Texaco data.

4) High short-term exposures were also measured during several instances of quality control sampling. These short-term exposures may not, however, be indicative of routine quality control sampling. Texaco Chemical reports that 8-TWAs for routine quality control sampling may be even higher. It should be noted that Texaco employees wear respirators during quality control sampling.

5) The current exposure control programs at Texaco Chemical (see section on Control Description) serve to maintain most workers' 8-hour exposures to less than 10 ppm (proposed TLV) of 1,3-butadiene, with the exception of these employee voiding sample cylinders. The rover/operator and process technician/loading area also had some exposures that exceeded 10 ppm.

RECOMMENDATIONS

In the context of the OSHA PEL for 1,3-butadiene (1000 ppm) the control programs at Texaco Chemical appear to provide adequate protection. However, because of certain job-related exposure excursions and the concern that 1,3-butadiene may present both a carcinogenic and teratogenic risk, additional exposure control measures should be considered by Texaco:

1) Texaco's proposed conversion to a "closed-loop" sampling system should be implemented. This conversion should serve to lower the mean exposure of process technicians working in the process area.

2) As evident from the sampling results for cylinder voiding and sampling (short-term sampling), employees assigned to these tasks are being exposed to relatively high levels of 1,3-butadiene. Based on the observed work practices of the cylinder voiding procedures, consideration should be given to training the contract employee in the proper use of a respirator. Modification in the design of the building (shed) could significantly reduce the potential for exposure.

3) Texaco Chemical presently uses both slip-tube and magnetic gauges during the loading of railcars with 1,3-butadiene. Because magnetic gauges are known to limit the release of 1,3-butadiene during loading, a program to convert to 100 percent magnetic gauges should be considered.

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APPENDIX A

SAMPLING AND ANALYTICAL METHODS FOR 1,3-BUTADIENE

FORMULA: C_4H_6, $CH_2=CHCH=CH_2$

M.W.: 54.09

1,3-BUTADIENE

METHOD: ####
ISSUED: DRAFT

OSHA: 1000 ppm
NIOSH: potential carcinogen [1]
ACGIH: suspect carcinogen
(1 ppm = 2.21 mg/m^3 @ NTP)

PROPERTIES: gas; vapor density 1.9 (air = 1); explosive range 2.0 to 11.5% v/v in air; compressibility factor 0.972 @ NTP; BP -4.4 °C; VP 280 kPa (26 psig) @ 25 °C

SYNONYMS: CAS #106-99-0

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut charcoal, 400- and 200-mg in separate tubes)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 3 L
-MAX: 25 L (@ 100 ppm)

SHIPMENT: separate front and back tubes, chill below -4 °C

SAMPLE STABILITY: insignificant loss after 21 days below -4 °C

BLANKS: 10% (≥2) of samples

ACCURACY

RANGE STUDIED: 0.19 to 19 mg/m^3 (25-L samples)

BIAS: see EVALUATION OF METHOD

OVERALL PRECISION (s_r): 0.060

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: 1,3-butadiene

DESORPTION: 4 mL methylene chloride; 30 min

INJECTION: 1 µL

TEMPERATURE-INJECTION: 200 °C
-DETECTOR: 200 °C
-COLUMN: see APPENDIX A

CARRIER GAS: Helium

COLUMNS: fused silica, 10-m x 0.50-mm ID 1.8-µm CP WAX 57 CB (backflushable), and 50-m x 0.32-mm ID Al_2O_3/KCl PLOT (see APPENDIX A)

CALIBRATION: vapor-spiked sampling media

RANGE: 1.1 to 440 µg per sample

ESTIMATED LOD: 0.2 µg per sample

PRECISION (s_r): 0.025

APPLICABILITY: The upper limit of the sampler is 220 mg/m^3 (100 ppm) for a 25-L sample. Above 22 mg/m^3 (10 ppm), desorbed samples should be diluted. Below 1.1 mg/m^3 (0.5 ppm), the desorption efficiency may be less than 80%.

INTERFERENCES: Pentane, methyl acetylene, and vinylidene chloride are potential chromatographic interferences. Other hydrocarbons present at permissible levels may significantly decrease the sampler's capacity for 1,3-butadiene.

OTHER METHODS: This method supercedes S91 [2].

REAGENTS:

1. Methylene chloride,* chromatographic quality (containing cyclohexene as stabilizer).
2. 1,3-Butadiene,* 99.5%, in cylinder equipped for gas withdrawal, with needle valve.
3. Helium, purified.
4. Hydrogen, purified.
5. Air, filtered.
6. Water, distilled.

*See Special Precautions.

EQUIPMENT:

1. Sampler: Two charcoal tubes in series, each tube glass, 8.5 cm long, 8 mm OD, 6 mm ID, ends flame-sealed, containing activated coconut shell charcoal, such as SKC Lot 120, 400 mg in front tube, 200 mg in back tube. In both tubes, the charcoal section is preceded by a silylated glass wool plug and followed by a 3-mm urethane foam plug.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator, and column (see APPENDIX A).
4. Ice, wet.
5. Vials, 5-mL, 2-mL, and other convenient sizes, with PTFE-lined caps.
6. Pipettes, TD, 4-, 2-, and 1-mL.
7. Syringes, gas-tight, 250-, 100-, 25-, and 10-µL.
8. Beaker, 150-mL.
9. Gas drying tube with serum cap to fit stem and 2-cm piece of plastic tubing to fit over serum cap.

SPECIAL PRECAUTIONS: 1,3-Butadiene is a potential occupational carcinogen, teratogen, and reproductive hazard [1]. Methylene chloride is toxic and very volatile. Work should be performed in a well-ventilated fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of sampler tubes immediately before sampling. Connect smaller tube to personal sampling pump with flexible tubing and to larger tube with a short piece of plastic tubing.
3. Sample at an accurately known flow rate of 0.01 to 0.2 L/min for a sample size of 3 to 25 L.
4. Separate the tubes, cap with plastic (not rubber) caps, and pack securely for shipment. Chill below -4 °C during shipment and storage.

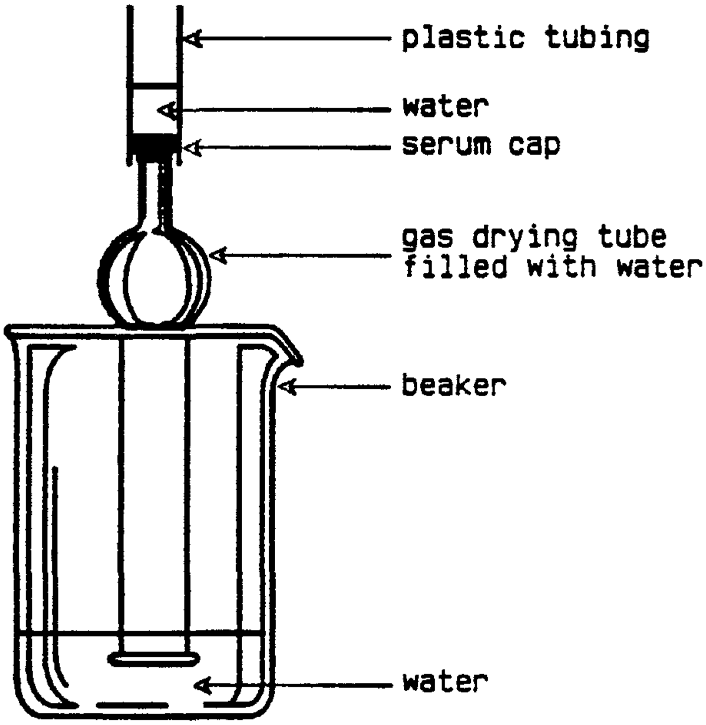
SAMPLE PREPARATION:

5. Add 4.0 mL methylene chloride to 5-mL vials and 2.0 mL to 2-mL vials. Loosely cap vials and thoroughly chill in ice.
6. Place front sorbent sections in 5-mL vials and back sections in 2-mL vials. Discard glass wool and foam plugs. Immediately attach crimp cap to each vial.
7. Remove from ice and allow to stand 30 min with occasional agitation.
8. Transfer sample solution to appropriate vial and cap if using an autosampler. Thoroughly chill solution and vial before making transfer.

CALIBRATION AND QUALITY CONTROL:

NOTE: The accurate measurement of pure 1,3-butadiene gas by gas-tight syringe is a critical step in the calibration. Flakes of PTFE from the plunger tip can obstruct the needle or act like a one-way valve, letting gas enter the syringe, but hindering its exit. Even a slight obstruction can cause 1,3-butadiene to be liquified as the plunger is depressed, making delivery incomplete. Bracketing gas samples with water, as described below, allows the volume taken to be approximately verified, and assures complete delivery. The precision of the analysis of multiple independent standards is another indicator of the accuracy of the volumes taken.

9. Make up stock solutions in triplicate at three concentration levels, e.g., 200 ~~m~~μL of 1,3-butadiene gas in 1 mL solution, and both 200 and 50 ~~m~~μL of gas in 4 mL solution:
   a. Prepare a beaker and drying tube assembly as shown below. Bubble 1,3-butadiene under the lower edge of the drying tube so that water is displaced and the gas is trapped in the tube.



   b. Pipet methylene chloride into a vial, attach cap, and thoroughly chill in ice.
   c. Take a known amount of 1,3-butadiene from the drying tube with a 100- or 250-~~m~~μL gas-tight syringe. Bracket the gas in the syringe with small amounts of water taken from the area above the serum cap before and after withdrawing the gas. Do not take water from inside the drying tube, since it may contain a significant amount of dissolved 1,3-butadiene.
   d. Slowly inject the 1,3-butadiene and water below the surface of the methylene chloride.
   e. Agitate and continue to chill the vial to complete dissolution.

10. Calibrate daily with media blanks and triplicate independent media standards of at least five levels ranging from, e.g., 0.5 to 200 ~~m~~μL 1,3-butadiene gas per sample:
   a. Break ends of larger sampler and attach to personal sampling pump with flexible tubing.
   b. Take pure gas (as in step 9.c) for the higher levels or up to 40 ~~m~~μL of a stock solution for lower levels.
   c. Inject the gas and surrounding water plugs or the stock solution at a point inside the sampler near the glass wool plug while drawing clean air through tube at 0.05 L/min. Continue to draw air through the tube for 5 min or just until the stock solution evaporates.
   d. Seal tube with plastic caps.
   e. Store at temperature below -4 °C overnight, then desorb (steps 5 through 8).
   f. Analyze media standards and blanks together with samples (steps 13 and 14).
   g. Convert gas volumes to masses, correcting for compressibility and water vapor (see APPENDIX B), and prepare a calibration graph (peak areas or heights vs. concentration of 1,3-butadiene taken in ~~m~~μg/mL).

11. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in calibration range (step 10).
    a. Dilute the stock solutions (step 9) to extend the range of standards down to 0.1 µL 1,3-butadiene gas per 4 mL solution. Avoid including water in the portions diluted.
    b. Transfer solutions as in step 8 if using an autosampler, and analyze together with media standards (steps 13 and 14).
    c. Convert gas volumes to masses, correcting for compressibility and water vapor (see APPENDIX B), and prepare DE calibration graph of peak area or height vs. µg/mL 1,3-butadiene.
    d. Read the concentrations, µg/mL, in media standards and blanks from DE calibration graph and multiply by the desorption volume to calculate the masses recovered.
    e. Prepare a graph of DE vs. µg taken. DE = (mass found - blank mass)/(mass taken).
12. Analyze three quality control blind spikes to insure that calibration graph (step 10) is in control.

MEASUREMENT:

13. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page ####-1. Inject sample aliquot manually using solvent flush technique or with autosampler.

    NOTE: If detector response is above range of working standards, dilute with methylene chloride, reanalyze, and apply appropriate dilution factor in calculations.
14. Measure peak area or height.

CALCULATIONS:

15. Determine the concentration, µg/mL, of 1,3-butadiene found in each sample front (W_f) and back (W_b) sorbent section from calibration graph (step 10), and multiply by desorption volume and dilution factor, if any, to calculate the mass, µg, found.

    NOTE 1: This calibration method corrects for media blank and DE. Do not duplicate corrections.

    NOTE 2: For any sampler with $W_b > W_f/10$, report breakthrough and possible sample loss.

16. Calculate concentration of analyte in the volume of air sampled, V (L):

$$C = \frac{(W_f + W_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

The detector response to standard solutions was linear over the range 0.07 to 110 µg/mL. The pooled s_r was 0.038. (Higher concentrations overloaded the analytical column.) The estimated limit of detection for the analytical method was 0.02 µg/mL or 6 picograms on the analytical column.

The capacity of a 400-mg charcoal sorbent section was 31 L for a sample at 80% RH and approximately 100 ppm 1,3-butadiene. When exposed to pure 1,3-butadiene followed by 80% RH air, breakthrough occurred after 35 L for 0.7 mL 1,3-butadiene, and 28.5 L for 2.5 mL. The corresponding average concentrations were 20 and 88 ppm respectively. Adding water to media standards just after spiking or during desorption had no significant effect on desorption efficiencies. For the analysis of media standards at levels of 1.1, 4.4, 18, 125, and 480 µg per sample, the pooled s_r was 0.025, and the desorption efficiencies were 67%, 68%, 75%, 102%, and 97%, respectively.

In a study of temperature effects on storage stability, 400-mg charcoal tubes were spiked with 26 µg 1,3-butadiene and stored either at ambient temperature or in a freezer below -4 °C. Recoveries were measured relative to media standards stored overnight in the freezer. The recoveries (and days stored) were 94% (7), 93% (14), and 98% (21) for the chilled samples, and 95% (1), 76% (7), 61% (14), and 65% (21) for the ambient samples.

In a preliminary evaluation of precision and accuracy, charcoal tubes were spiked with 125 µg via calibrated sampling valve. The recovery was 102.2% versus media standards and 96.8% versus standard solutions; the s_r was 0.016. Subsequently, charcoal tubes were exposed to known volumes of approximately 10% 1,3-butadiene in helium, followed by 25 L of air at 80% RH. The 1,3-butadiene concentration was independently determined by packed column gas chromatography and thermal conductivity detection. Media standards were prepared via calibrated sampling valves at all levels. At 463 µg, the recovery was 101.6% versus media standards and 91.3% versus standard solutions; the s_r was 0.047. At 45.3 µg, the recovery was 112.3% versus media standards and 102.9% versus standard solutions; the s_r was 0.048. At 4.64 µg, the recovery was 80.3% versus media standards and 103.8% versus standard solutions; the s_r was 0.011. The two lowest levels of media standards appeared to be high, possibly due to absorption of 1,3-butadiene by internal parts of the sampling valve. The study was repeated at 4.71 µg, with media standards prepared as in step 10. The recovery was 129.5% versus media standards and 91.2% versus standard solutions; the s_r was 0.023. The s_r pooled for all levels was 0.033. Assuming a sampling pump error of 0.05, the precision of the total sampling and analytical method was 0.060. For levels at and above 45 µg (0.8 ppm in 25 L), the apparent bias could be attributed to experimental errors in the preparation and analysis of standards and samples rather than a true bias in the method. At lower levels, a primary source of error appeared to be the preparation and analysis of media standards.

REFERENCES:

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[3] MacCallum, R. N., and J. J. McKetta. "Low Pressure Z_S of C_4 Hydrocarbons," Hydrocarbon Process. Petrol. Refiner, V. 42, No. 5, 191-4 (May 1963).

METHOD WRITTEN BY: R. Alan Lunsford, Ph.D., and Yvonne T. Gagnon, NIOSH/DPSE.

APPENDIX A. GAS CHROMATOGRAPH COLUMN SELECTION, INSTALLATION, AND OPERATION:

The column specified in NIOSH Method S91 [2] was 6-m x 3-mm OD stainless steel, packed with 10% FFAP on 80/100 Chromosorb W AW-DMCS. This column provides a convenient separation of 1,3-butadiene from the desorbing solvent. However, if other light hydrocarbons are present, interferences are likely. Any column which separates 1,3-butadiene from the other substances present, and which otherwise provides satisfactory chromatographic performance, is acceptable. For the development of this method, a 50-m x 0.32-mm ID fused silica porous layer open tubular (PLOT) column coated with Al_2O_3/KCl (Chrompack #7515 or equivalent) was chosen because it provides excellent separation of the C_4 hydrocarbons at temperatures above ambient. However, it also presents some disadvantages. High boiling or polar substances may accumulate on the column and irreversibly change the retention behavior. Also, water in samples reversibly changes the surface activity and causes retention time variability. These problems can be eliminated by using a polar, backflushable pre-column, e.g., a 10-m x 0.5-mm ID fused silica column coated with a

1.8-μm film of cross-linked Carbowax (Chrompack #7648 or equivalent). The pre-column allows light hydrocarbons to pass through, but water, methylene chloride, and polar or high boiling components are retained and can be backflushed. Eliminating the solvent peak significantly reduces the time required to complete the analysis.

Figures 1 and 2 schematically illustrate the installation and operation of the recommended columns in a HP 5880 gas chromatograph equipped with the dual multimode capillary inlet system. Connect the solenoid valves as shown, forming the flush inlet and vent from the spare inlet's flow controller and split vent lines. Join the columns and the lines to the solenoid valve and back pressure regulator with a zero-dead-volume cross. Set the conditions as shown in Figure 1 and adjust the oven temperature to 50 °C. Measure the flow from the split vent. Turn off the solenoid valves and adjust the flush vent back pressure regulator so that the split vent flow approximates the value previously determined. In other words, turning the solenoid valves off or on should only slightly change the split vent flow, though there may be a fluctuation as pressures equalize.

Set the chromatograph to hold the initial oven temperature at 50 °C for 2 min. At 1.3 min turn off the solenoid valves. (Determine the optimum time to switch the valves by starting with a longer time, e.g., 2 min, and decreasing it until the methylene chloride peak is eliminated.) Then program the temperature to 120 °C at 20 °C/min and hold 6 min. Finally, clear the column, if necessary, by programming to 200 °C at 30 °C/min and holding 5 min. At the end of the run, turn on the valves to prepare for the next injection.

APPENDIX B. CONVERSION OF 1,3-BUTADIENE VOLUME TO MASS:

MacCallum and McKetta [3] determined the compressibility factor, Z, which corrects for non-ideal behavior, for 1,3-butadiene at temperatures, T, ranging from 10 to 75 °C, and pressures, P, from approximately 420 to 1050 mm Hg. Multiple regression of the observed values against P, PT, and PT^2, yields the following equation (standard error of the estimated Z is 0.000635 for 13 degrees of freedom):

$$Z = a + bP + cPT + dPT^2$$

where: $a = 1.00095$
$b = -4.84089 \times 10^{-5}$
$c = 4.44816 \times 10^{-7}$
$d = -1.15744 \times 10^{-9}$

The mass, M (μg), of 1,3-butadiene, corrected for compressibility and the presence of water vapor (when the gas is stored above water), may be calculated by the following equation:

$$M = \frac{(P - P_v)\cdot V\cdot 54.09}{Z\cdot 62.36\cdot (T + 273.2)}$$

where: P_v = vapor pressure of water @ T °C (mm Hg)
V = volume of 1,3-butadiene (μL)
54.09 = molecular weight of 1,3-butadiene ($g\cdot mol^{-1}$)
62.36 = gas constant ($mm\ Hg\cdot L\cdot mol^{-1}\cdot K^{-1}$)
273.2 = absolute temperature of 0 °C (K)

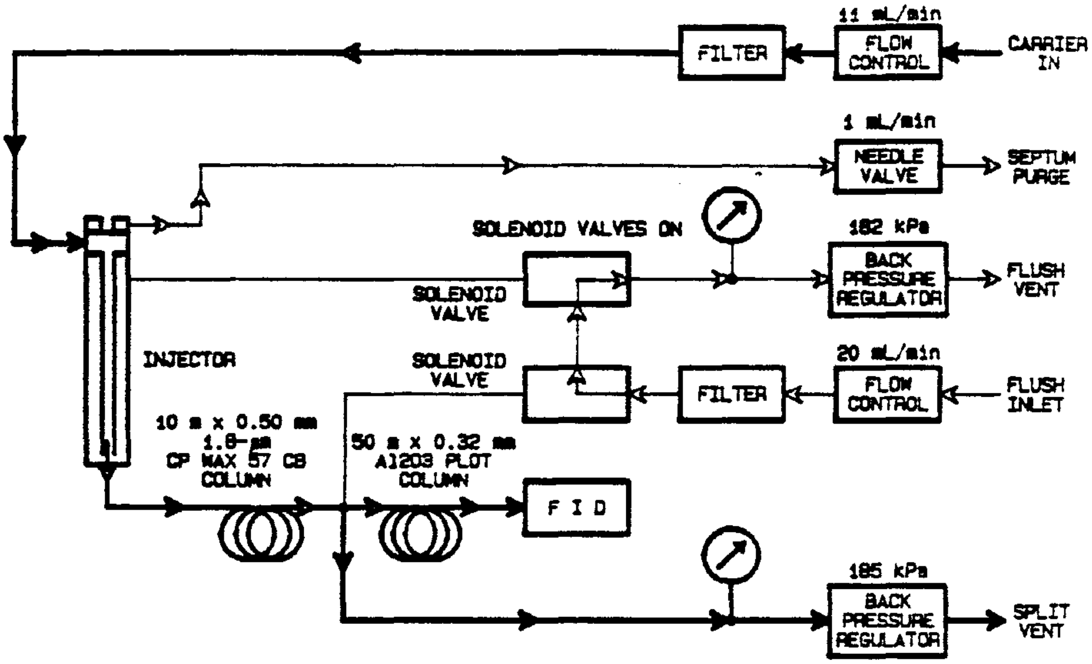

Figure 1. Flow diagram for pre-column system in inject mode.

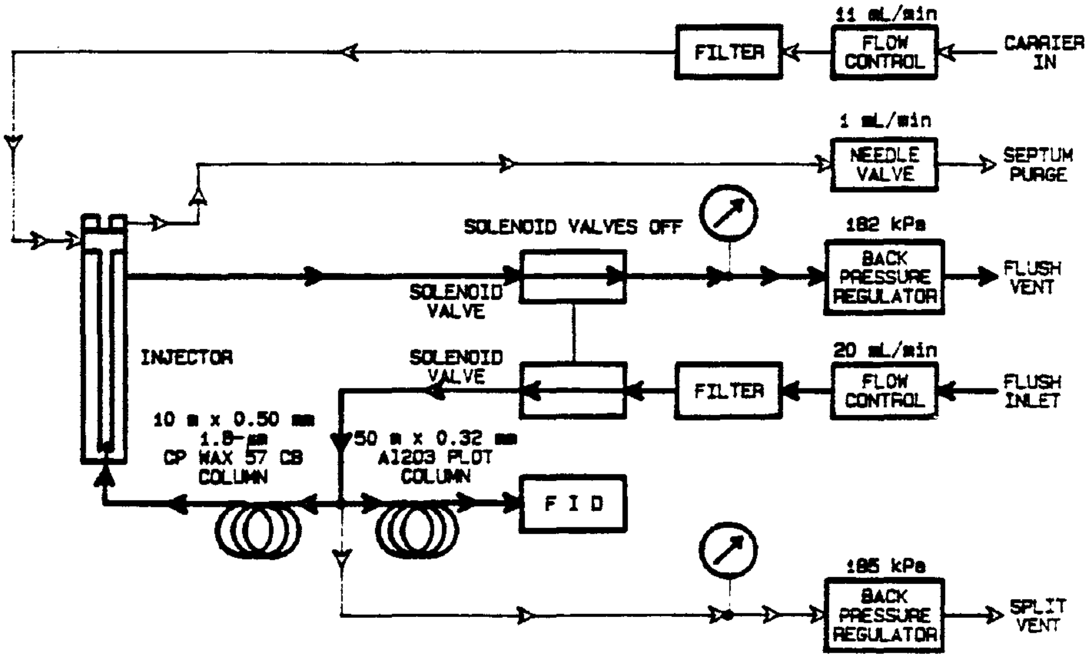

Figure 2. Flow diagram for pre-column system in backflush (normal) mode.

FORMULA: $H_2C=CHCH=CH_2$; C_4H_6
M.W.: 54.09

BUTADIENE

METHOD: No. to be assigned
ISSUED: [illegible]

OSHA: 1,000 ppm
NIOSH: Potential carcinogen [1]
ACGIH: Suspect carcinogen [2]
(10 ppm = 22.1 mg/m³ @ NTP)

PROPERTIES: Gas; vapor density 1.9 (air = 1); explosive range 2.0 to 11.5% v/v in air; BP -4.4°C; VP 250 kPa (21 psig) @ 21°C

SYNONYMS: Biethylene, bivinyl, divinyl, erythrene, pyrrolylene, vinylethylene, CAS No. 106-99-0

Sampling

SAMPLER: Miniature solid sorbent tube containing 5 mg of charcoal ("Grob Trap") [3]

FLOW RATE: 0.02 L/min to 0.05 L/min

VOL.-MINIMUM: 5 L at 0.01 ppm
VOL.-MAXIMUM: To be determined

SHIPMENT: Sealed in air tight containers and refrigerated

SAMPLE STABILITY: To be determined

BLANKS: 2 or more field blanks per set

ACCURACY

RANGE STUDIED: 30 to 0.01 ppm

BIAS: To be determined

OVERALL PRECISION (S_r): To be determined

Measurement

TECHNIQUE: Gas chromatography, FID

ANALYTE: Butadiene

DESORPTION: 50 µL of cold methylene chloride

INJECTION VOLUME: 2 µL

TEMPERATURES:
Injection - 140°C
Detector - 250
Column - 50°C for 3 min, then 10°C/min to 80°, hold 5 min.

CARRIER GAS: Nitrogen, 20 mL/min

COLUMN: 20 ft x 1/8 in. st. steel, 10% SP-1000 on 80/100 mesh Supelcoport

CALIBRATION: Butadiene in methylene chloride

RANGE: 0.05 µg to 50 µg

ESTIMATED LOD: 0.05 µg

PRECISION: To be determined

APPLICABILITY: Applicable for butadiene concentrations 1 to 0.01 ppm (2.21 mg/m³ to 0.022 mg/m³) for 5 to 10 L air sample.

INTERFERENCES: None identified. The chromatographic column or separation conditions may be changed to provide confirmation of identity. Alternate chromatographic columns are: (1) GP 80/100 Carbopak C/0.19% picric acid, 2 m x 1/8 in. OD SS or (2) 23% SP-1700 on 80/100 Chromosorb P AW, 30 ft x 1/8 in. OD SS.

OTHER METHODS: This method is a modification of NIOSH Method No. S 91 [4] which can be used but which provides a higher limit of detection because of the larger volume of solvent.

REAGENTS:

1. 1,3-Butadiene, 99.5% purity.
2. Methylene chloride, pesticide quality.
3. Calibration stock solution, 221 ng/μL. Dissolve 0.1 mL of gaseous butadiene in 1 mL of methylene chloride by slowly injecting the gas into 1 mL of methylene chloride in a 2-mL vial through a septum in the cap. Make dilutions as needed.

EQUIPMENT:

1. Sampler: Glass tube, 62 mm long, 6 mm OD, 2 mm ID, containing 5 mg of charcoal sealed between gold-plated st. steel filters [1]. Pressure drop may become significant at flow rates greater than 0.1 L/min. The average pressure drop for samples was determined to be 1.1 PSI at a flow rate of 100 mL/min of nitrogen. Pressure drop does vary from one sample to another.
2. Plastic caps for samplers.
3. Personal sampling pump with flexible connecting tubing. The pumps must have electronically controlled flow rates <u>not</u> dependent on critical orifice or back pressure of samples. The air sample must not pass through any tubing before it passes through the charcoal trap.
4. Gas chromatograph, FID detector, integrator and column (see above).
5. Microliter syringes for liquids (gas-tight), 10 μL, readable to 0.1 μL, several 50 μL, readable to 1 μL and other sizes convenient for making standards.
6. Gas tight syringes with valve closure, 1 or 2 mL, readable to 0.1 mL for transferring gaseous butadiene.
7. Gas sampling bulb (glass) or bag (aluminum layered polyester), with septum access, for containing the butadiene gas used to make standards.
8. Cone-bottom sample vials, 100 μL size, with septum caps. Septum-cap vial, 2 mL size for standards.

SPECIAL PRECAUTIONS: 1,3-Butadiene is a potential occupational carcinogen, teratogen, and reproductive hazard [1,2]. Methylene chloride is toxic and very volatile. Work should be performed in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a personal sampler in line. Set to 20 mL/min (or 50 mL/min).
2. Remove the adsorption tubes from the storage container just before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Re-check the pump-sampler flow rate. Either re-adjust flow to 20 mL/min (or 50 mL/min) OR record the actual flow rate.
4. Field blanks - Open and expose to ambient air for 5 min. Cap and treat as samples.
5. Sample at 20 or 50 mL per minute for a total sample size of 10 L.
6. Cap the samplers with plastic, <u>not rubber</u>, caps and pack securely in an insulated container with ice packs for shipment.

SAMPLE PREPARATION:

Note: Store the capped samplers refrigerated in tightly sealed glass jars until preparation begins.

5. Cool methylene chloride, 100 μL sample vials and the syringes to be used for handling solvent and extracts in refrigerator.
6. Holding the sampler upright, syringe inject 50 μL of [illegible] methylene chloride into the smaller (shorter) end of the sampler tube. Let the methylene chloride gravity flow downward until it has (apparently) all passed through the charcoal bed. Cover the upper (shorter) end of the sampler with teflon tape or other soft teflon material and hold in place. Almost invert the sampler with the liquid-containing end up and withdraw the extract into a 50-μL syringe. Observe and record the volume. Dispense the extract into a 100-μL sample vial, cap tightly, and store refrigerated. Carry out the gas chromatography analysis as soon as possible and absolutely within 1 hour.

CALIBRATION AND QUALITY CONTROL:

7. Calibrate daily with at least five working standards over the range 50 ng to 5 mg of butadiene per sample (2 ng/μL to 100 μg/μL).
   a. Add measured amounts of calibration stock solution to methylene chloride in volumetric flasks and dilute to mark. Mix and transfer to vials with teflon-lined septum caps. Prepare fresh working standards every 48 hours.
   b. Analyze standards together with blank and sample extracts (steps 9 and 10).
   c. Prepare calibration graph (peak area of butadiene versus quantity injected).
8. Protocols for preparing spiked samplers: Slowly inject gaseous standard onto charcoal filter in closed system as air is drawn through.

MEASUREMENT:

9. Set gas chromatograph according to manufacturers recommendations and to the conditions given above. Inject sample aliquot manually using solvent flush technique. Analyze each sample extract in duplicate with no delay between duplicate injections. The retention time of butadiene under these conditions is 2.7 min. Note: If peak area is above the linear range of the working standards, dilute the sample extract with methylene chloride, re-analyze, and apply appropriate dilution factor in calculations.
10. Measure peak areas with electronic integrator.

CALCULATIONS:

Note: At the present time, external standards are used for determining the sample concentrations of butadiene.

11a. The mass, μg, of butadiene in the sample extract is determined by:

$$\mu g = \frac{A_e}{A_{std}} \times C_{std} \times V_e$$

where
A_e = area of butadiene GC peak in sample extract.
A_{std} = area of butadiene GC peak in standard.
C_{std} = concentration of butadiene in standard, μg/mL.
V_e = volume of sample extract, mL.

11b. The concentration of butadiene in the air sampled (C) is

$$C = \frac{\mu g}{V_a}, \frac{mg}{m^3}$$

where: C = concentration of butadiene in air.

V_a = volume of air sampled, liters.

EVALUATION OF METHOD:

The method for analysis of butadiene is being evaluated using Grob charcoal samplers. Recoveries are being determined for concentrations of 10 ppb - 1 ppm using 2-hour sampling at 0.05 L/min (6 L of air) and 4-hour sampling at 0.02 L/min (4.8 L of air).

Breakthrough: With a 10 µg spike on a primary trap with a backup trap, 1.4% of the dose was found on the backup trap. The capacity of the Grob samplers under simulated sampling conditions is still to be determined.

REFERENCES:

[1] NIOSH Current Intelligence Bulletin 41, "1,3-Butadiene," U.S. Department of Health and Human Services, Publ. (NIOSH) 84-105 (1984).

[2] "TLVs - Threshold Limit Values for Chemical Substances and Physical Agents in the Work Environment with Intended Changes for 1984-85," ACGIH, Cincinnati, OH (1984).

[3] Available from Tekmar Company, P.O. Box 371856, Cincinnati, Ohio 45222.

[4] NIOSH Manual of Analytical Methods, 2nd ed., V. 2, S 91, U.S. Dept. Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

APPENDIX B

NIOSH SAMPLING DATA

TABLE B-1. PERSONAL SAMPLING DATA

Job description	Date	Sampling ID	Air volume, liters	Duration, min.	Concentration ppm
Process technician/Process area	4/11	T56	22.70	465	0.27
	4/11	T52	22.15	441	0.49
° Rover/ operator	4/11	T50	22.31	473	1.00
	4/11	T49	23.01	471	0.55
	4/9	T15	23.19	461	1.76
	4/9	T22	28.09	459	2.11
	4/9	T19	22.6	448	34.9
	4/9	T24	22.15	456	0.29
° Instrumentation	4/11	T54	21.81	430	2.55
	4/11	T53	18.85	424	<0.07[b]
	4/10	T27	21.51	420	<0.14[b]
	4/10	T32	25.07	496	0.92
	4/9	T12	21.60	434	0.08[a]
° Maintenance	4/9	T11	8.60	176	0.21[a]
Process technician/loading area	4/11	T61	18.79	459	3.97
	4/9	T21	21.82	443	123.57
Process technician/control room	4/10	T36	21.34	453	1.87
	4/10	T34	22.64	449	1.70
Process technician/storage area	4/11	T57	25.98	485	0.20
	4/11	T58	23.99	491	0.15[a]
	4/10	T28	19.42	476	1.53
	4/10	T26	24.96	502	<0.04[b]
	4/10	T20	4.30	210	0.31[a]
Laboratory technician					
Wet chemical	4/11	T51	20.33	410	0.76
	4/10	T30	23.10	474	2.55
	4/9	T6	18.40	449	1.73
Chromatograph	4/11	T47	22.81	467	6.31
	4/10	T38	23.08	472	4.82
	4/9	T18	25.78	515	4.88
	4/9	T4	24.43	454	0.56

Table B-1 (continued)

Job description	Date	Sampling ID	Air volume, liters	Duration, min.	Concentration ppm
Cylinder voiding	4/11	T72	12.59	26	22.84
	4/11	T60	22.78	482	2.61
	4/10	T39	6.94	14	1.53
	4/10	T35	20.18	400	0.42
	4/9	T5	22.14	452	373.54
	4/9	T23	23.70	23	108.44
Cylinder sampling	4/12	T68	2.03	4	<0.65[b]
	4/12	T67	8.14	17	146.60
	4/11	T45	2.73	5	4.02

[a] Laboratory analysis of analyte was below limit of quantitation (11µg/sample).

[b] Laboratory analysis of analyte was below limit of detection (3µg/sample).

[c] Analysis of back section of charcoal indicates that breakthrough has occurred.

TABLE B-2. AREA SAMPLING DATA

Work environment	Date	Sample ID	Air volume, liters	Duration min.	Concentration, ppm
Process/ pump alley	4/11	T55	22.88	455	0.33
	4/10	T33	22.02	444	0.10
	4/10	T31	21.73	439	0.16[a]
	4/9	T13	21.48	456	0.21
Process/ control room	4/10	T37	20.21	447	2.13
Laboratory					
Wet chemical	4/10	T17	25.22	466	0.86
	4/9	T3	21.85	490	0.75
Chromotograph	4/11	T48	23.31	470	5.49
	4/10	T25	23.32	469	3.93
	4/9	T2	24.33	490	5.88
Cylinder voiding	4/10	T40	6.71	13	1.91

[a] Laboratory analysis of analyte was below limit of quantitation (11μg/sample).