

EXTENT-OF-EXPOSURE STUDY:
1,3-BUTADIENE MONOMER PRODUCTION INDUSTRY

E. Radha Krishnan, P.E.
Leslie J. Ungers, C.I.H.
Paula A. Morelli-Schroth

PEI Associates, Inc.
11499 Chester Road
P.O. Box 46100
Cincinnati, Ohio 45246

John M. Fajen
National Institute for Occupational Safety and Health
4676 Columbia Parkway
Cincinnati, Ohio 45226

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Surveillance, Hazard Evaluations, and Field Studies
Cincinnati, Ohio 45226

June 1987

DISCLAIMER

Mention of company or product name in this report does not constitute endorsement by the National Institute for Occupational Safety and Health (NIOSH).

NIOSH Project Officer: John M. Fajen

PEI Associates, Inc., Principal Investigators: E. Radha Krishnan, P.E.
Leslie J. Ungers, C.I.H.

ACKNOWLEDGMENTS

The NIOSH Project Officer for this study was John M. Fajen. Other participants from NIOSH included Dennis R. Roberts, R. Alan Lunsford, and Yvonne T. Gagnon. The study was conducted under an Interagency Agreement with the U.S. Environmental Protection Agency (EPA), Office of Toxic Substances, Washington, D.C. This report was prepared for NIOSH by PEI Associates, Inc. (PEI). PEI was contracted by EPA on this study to conduct an occupational exposure analysis and control technology assessment for 1,3-butadiene (Contract No. 68-02-4248).

The cooperation of the companies that participated in the study is greatly appreciated. The review and comments provided by the companies were very helpful for this extent-of-exposure study.

PREFACE

The National Institute for Occupational Safety and Health (NIOSH) has been granted the authority and responsibility under the Occupational Safety and Health Act of 1970 to conduct field research studies in industry, evaluate findings, and report on these findings. Section 20(a)7 of this Act states that NIOSH shall conduct and publish industrywide studies of the effects of chronic or low-level exposure to industrial materials, processes, and stresses on the potential for illness, disease, or loss of functional capacity in aging adults. Section 22(e) provides the authority to enter into contracts, agreements, or other arrangements with appropriate public agencies or private organizations for the purpose of conducting studies relating to responsibilities under the Act. Under an Interagency Agreement with EPA, NIOSH and the EPA contractor, PEI Associates, Inc., performed an extent-of-exposure study of 1,3-butadiene for the 1,3-butadiene monomer production industry.

The predominant uses of 1,3-butadiene (C_4H_6) are in the manufacture of synthetic rubbers, plastics, and resins. Of the synthetic rubbers, styrene-butadiene rubber and polybutadiene rubber make up more than half the demand for 1,3-butadiene. Recent chronic oncology studies have indicated that 1,3-butadiene is carcinogenic to mice and rats at levels near the current Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL) of 1000 parts per million (ppm). At the time of this report, OSHA had initiated new rulemaking action with respect to reducing worker exposures to 1,3-butadiene. Based upon reported animal carcinogenicity data, the American Conference of Governmental Industrial Hygienists (ACGIH) has included 1,3-butadiene as an "A2" industrial substance suspected of carcinogenic potential in man. A Threshold Limit Value (TLV) of 10 ppm has been assigned to 1,3-butadiene.

NIOSH recommends in its Current Intelligence Bulletin that 1,3-butadiene be regarded as a potential occupational carcinogen and teratogen and as a possible reproductive hazard. NIOSH has estimated that approximately 65,000 workers in the United States are potentially exposed to 1,3-butadiene during its manufacture, processing, and use. Historical industrial hygiene data on the extent of worker exposure to 1,3-butadiene suffer from the drawbacks of the sampling and analytical methods used in that the analytical procedures are susceptible to interference from C_4 compounds other than 1,3-butadiene and were developed for a standard of 1000 ppm.

This extent-of-exposure study of the 1,3-butadiene monomer industry was undertaken to determine the size of the exposed workforce, evaluate control technologies and personal protective equipment programs, and assess occupational exposures to 1,3-butadiene using a new sampling and analytical method for 1,3-butadiene developed by NIOSH. The new NIOSH method has a lower limit of quantitation of 0.02 ppm for an 8-hour sample; moreover, it is not susceptible to interference from other C_4 compounds. This report contains a discussion of the sampling and analytical method, brief descriptions of the facilities surveyed, a discussion of the results, and recommendations based on the results.

The study was conducted in three phases: 1) a literature evaluation, 2) walk-through industrial hygiene surveys at ten selected facilities, and 3) comprehensive in-depth industrial hygiene monitoring surveys at four facilities. After each phase, the information and data collected were reviewed and evaluated prior to progressing to the next phase. The new NIOSH analytical method for 1,3-butadiene was used to collect the field industrial hygiene samples.

ABSTRACT

Following preliminary, walk-through, industrial hygiene surveys of ten U.S. plants in which 1,3-butadiene monomer is produced, four facilities were selected for detailed evaluation of occupational exposures to the chemical. Exposures were assessed using a new sampling and analytical method developed by NIOSH that is sensitive to low concentrations of 1,3-butadiene and not susceptible to interferences from other C₄ compounds. A total of 111 personal samples (comprised of 88 full-shift and 23 short-term samples) for 5 job categories, and 100 area samples (comprised of 97 full-shift and 3 short-term samples) for 5 work environments and points along the plant perimeter at the four 1,3-butadiene monomer production facilities were collected and analyzed. The findings were reported separately for the four plants. This report consolidates the findings from the individual plant surveys.

In addition to background information on production and uses, toxicity and occupational exposure standards, and production processes, this report includes descriptions of operations and jobs, types of controls, past worker exposures, health and safety programs, air sampling data collected, summary tables of worker exposure levels to 1,3-butadiene, sampling and analytical procedures and methods, evaluation of findings, and recommendations.

The monitoring results from the present NIOSH study for the 1,3-butadiene monomer industry show that full-shift exposures for all job categories are well below the current OSHA PEL of 1000 ppm. Geometric mean full-shift exposures for all job categories are also below the ACGIH TLV of 10 ppm. A few individual exposures exceed 10 ppm for three job categories comprised of process technicians in the process area, process technicians in the rail car loading area, and laboratory technicians responsible for cylinder voiding. These high exposures are associated with either inadequate engineering controls or poor work practices. Recommendations on additional control measures are presented for further reducing worker exposures to 1,3-butadiene.

CONTENTS

	<u>Page</u>
Disclaimer	ii
Acknowledgments	iii
Preface	iv
Abstract	vi
Tables	ix
Figures	xi
Introduction	1
Study goals	1
Study objectives and scope	1
Study limitations	2
Background	2
Chemical and physical properties	2
Toxicology and epidemiology studies	3
Applicable standards and recommended limits	4
Production and use	5
Manufacturing processes	5
Study Design	10
Site selection criteria	10
Sampling and analytical methods	11
Sampling strategy	13
Facilities Surveyed	13
Site description	12
Process description	14
Workforce characterization	17
Controls	21
Past worker exposures	32
Medical, safety, and industrial hygiene programs	35
Personnel recordkeeping	42
NIOSH Industrial Hygiene Results	44

CONTENTS (continued)

	<u>Page</u>
Discussion	55
Personal monitoring data	57
Area monitoring data	61
Conclusions	61
Recommendations	64
References	65
Appendices	
A New NIOSH sampling and analytical method for 1,3-butadiene	A-1
B NIOSH personal and area monitoring data collected at Plants A, B, C, and D	B-1

TABLES

<u>Number</u>		<u>Page</u>
1	Chemical and physical properties of 1,3-butadiene	3
2	Usage profile for 1,3-butadiene	5
3	Workforce distribution at 1,3-butadiene monomer production facilities	17
4	Summary of Plant A's personal monitoring results for 1,3-butadiene in process, loading, and laboratory areas, 1982-1984	33
5	Summary of Plant B's personal monitoring results for 1,3-butadiene, 1981-1984	34
6	Summary of Plant C's personal monitoring results for 1,3-butadiene, 1979-1983	36
7	Summary of Plant D's personal monitoring results for 1,3-butadiene, 1981	37
8	Summary of Plant D's personal monitoring results for 1,3-butadiene, 1984	38
9	Summary of NIOSH's personal samples collected at Plant A, 1985 (ppm)	45
10	Summary of NIOSH's area samples collected at Plant A, 1985 (ppm)	47
11	Summary of NIOSH's personal samples collected at Plant B, 1985 (ppm)	48
12	Summary of NIOSH's area samples collected at Plant B, 1985 (ppm)	50
13	Summary of NIOSH's personal samples collected at Plant C, 1985 (ppm)	51
14	Summary of NIOSH's area samples collected at Plant C, 1985 (ppm)	53

(continued)

TABLES (continued)

<u>Number</u>		<u>Page</u>
15	Summary of NIOSH's personal samples collected at Plant D, 1985 (ppm)	54
16	Summary of NIOSH's area samples collected at Plant D, 1985 (ppm)	56
17	Summary of full-shift personal samples collected at 1,3-butadiene monomer production facilities	59
18	Summary of short-term personal samples collected at 1,3-butadiene monomer production facilities	60
19	Summary of full-shift area samples collected at 1,3-butadiene monomer production facilities	63

FIGURES

<u>Number</u>		<u>Page</u>
1	Flow diagram for production of 1,3-butadiene by the Ethylene Coproduct Process	7
2	Flow diagram for recovery of 1,3-butadiene from C ₄ streams	9
3	Diagram of a single mechanical seal	23
4	Diagram of a dual mechanical seal (back-to-back arrangement)	24
5	Diagram of a dual mechanical seal (tandem arrangement)	24
6	A closed-loop sampling system	25
7	Diagram of vacuum vented enclosure at Plant C for voiding of sample bombs	31
8	Probability plot of full-shift 1,3-butadiene personal exposures	58
9	Probability plot of full-shift 1,3-butadiene area concentrations	62

INTRODUCTION

Under the terms of the authority and responsibility given to the National Institute for Occupational Safety and Health (NIOSH) to develop needed information regarding potentially toxic substances in industry, NIOSH under an Interagency Agreement with the U.S. Environmental Protection Agency (EPA) initiated an industrial hygiene study of the extent-of-exposure to 1,3-butadiene in the 1,3-butadiene monomer producing industry. PEI Associates, Inc. (PEI) was a contractor to EPA on this study, concurrently conducting a control technology assessment for minimizing occupational exposures to 1,3-butadiene, including control costs and estimates of control effectiveness. Because of NIOSH's and EPA's common interest in determining the extent of occupational exposure to 1,3-butadiene in the monomer industry, NIOSH and PEI coordinated their efforts in this study. 1,3-Butadiene was selected for study because recent chronic oncology studies have shown that 1,3-butadiene is carcinogenic in rats and mice at levels near the current Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL) of 1000 ppm. Epidemiological studies of workers employed in facilities producing 1,3-butadiene monomer and styrene-butadiene rubber, however, have not indicated a statistically significant increase in mortality from malignant neoplasms of any specific site, although non-significant increases have been observed for mortality of lymphatic and hematopoietic tissues.¹⁻³ At the time of this report, OSHA had initiated a new rulemaking process to reduce occupational exposures to 1,3-butadiene.

Limited published data exist on the extent of worker exposure to 1,3-butadiene. The data are highly suspect because they are based on analytical methods that do not adequately separate 1,3-butadiene from other C₄ hydrocarbons and were developed for a standard of 1000 ppm. It is believed that the historical monitoring results tend to overestimate exposure to 1,3-butadiene. The use of the existing exposure data is of questionable value in any risk assessment.

STUDY GOALS

The primary goal of this industrial hygiene study was to identify and document the potential for 1,3-butadiene exposure in the monomer production industry as it relates to various job descriptions of potentially exposed workers. A secondary goal was to identify individuals exposed to 1,3-butadiene who might be suitable for inclusion in other occupational health-related studies (e.g., genotoxicity study, epidemiology study).

STUDY OBJECTIVES AND SCOPE

To meet the study goals, the following objectives were established for this study:

- ° Identify job categories and describe specific tasks where exposures may occur at 1,3-butadiene monomer facilities.

- ° Describe current industrial hygiene and safety practices, including engineering controls, work practices, and administrative controls.
- ° Develop and validate a new NIOSH sampling and analytical method for 1,3-butadiene that is not susceptible to interference from other C₄ compounds, and is sensitive at lower concentrations.

The 1,3-butadiene study was separated into three industry categories: the 1,3-butadiene monomer production industry, the 1,3-butadiene-based polymer (or chemical) production industry, and the polymer end-use industry. This report pertains to the 1,3-butadiene monomer production industry.

The study of the monomer industry was conducted using a three-phased approach. The first phase consisted of a literature review (e.g., toxicity, previous sampling and analytical methods, process descriptions, historical monitoring data) pertaining to 1,3-butadiene; this was completed in early 1984. The second phase consisted of industrial hygiene walk-through surveys at ten (10) 1,3-butadiene monomer production plants. These visits, which were made in conjunction with PEI, were conducted from May to December 1984. The third phase of the study consisted of in-depth industrial hygiene exposure monitoring surveys (employing the new NIOSH sampling and analytical method) at four (4) representative facilities. These surveys were conducted during the period of March to May 1985 in conjunction with PEI and Midwest Research Institute (MRI), a second EPA contractor. MRI evaluated for EPA another new sampling and analytical method (Grob Trap) for 1,3-butadiene that is sensitive at concentrations below 1 ppm. The results from Grob Trap monitoring are not included in this report.

STUDY LIMITATIONS

The industrial hygiene data collected during the study represent evaluations of worker exposures to 1,3-butadiene at the facilities selected for the study. The site selection criteria for the study was designed to be representative of the variations in industry. However, exposures evaluated in this study may not necessarily reflect possible variations in exposure due to seasonal or operational changes. An attempt was made to evaluate exposures for each job category and associated work environment encountered during the surveys. No abnormal exposure situations were encountered; the reported exposure measurements are, therefore, considered to represent only those exposures associated with normal operating conditions.

BACKGROUND

CHEMICAL AND PHYSICAL PROPERTIES

1,3-Butadiene (C₄H₆) is a colorless gas at room temperature and atmospheric pressure. It is highly flammable and possesses a mild aromatic odor.⁴ It is only slightly soluble in water, but readily soluble in organic solvents such as benzene, toluene, and cyclohexane. 1,3-Butadiene is stored in the liquid state, requiring pressurized or refrigerated vessels. Additional chemical and physical properties are listed in Table 1.

Table 1. Chemical and physical properties of 1,3-butadiene⁴⁻⁶

Chemical identity	1,3-Butadiene
CAS Registry No.	106-99-0
Synonyms	Biethylene, bivinyl, butadiene, buta-1,3-diene, alpha-gamma-butadiene, divinyl, erythrene, NCI-C50602, pyrrolyene, vinylethylene
Molecular weight	54.10
Molecular formula	C ₄ H ₆
Structural formula	CH ₂ :CHCH:CH ₂
Boiling point	-4.41°C (at 760 mm Hg)
Freezing point	-108.9°C
Heat of vaporization, J/g (cal/g), 25°C	389 (93)
Explosive limits, vol % 1,3-butadiene in air	
Lower	2.0
Upper	11.5
Vapor pressure	2 atm at 15.3°C 5 atm at 47.0°C
Recognition (odor) threshold	1.3 ppm

TOXICOLOGY AND EPIDEMIOLOGY STUDIES

Recent inhalation exposure studies of rats and mice to 1,3-butadiene reported induction of 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 adenomas were identified in rats exposed at concentrations of 1000 or 8000 ppm of 1,3-butadiene.⁷ Mice exposed to 625 or 1250 ppm of 1,3-butadiene developed a high incidence of malignant lymphomas and an increased incidence of other tumors, including hemangiosarcomas of the heart. Testicular and ovarian atrophy were also observed in mice.⁸

The offspring of pregnant rats exposed to 1,3-butadiene at 8000 ppm had major skeletal defects. Pregnant rats exposed at 200, 1000, or 8000 ppm of 1,3-butadiene exhibited depressed body weight gain at all concentrations. In

addition, fetal growth was significantly retarded among rats exposed at 8000 ppm.⁹

Occupational exposure at 2000, 4000, or 8000 ppm concentrations of 1,3-butadiene is reported to cause irritation of the skin, eyes, nose, and throat. Coughing, drowsiness, and fatigue have also been reported at higher, but unspecified, exposure concentrations. These physiological responses dissipated upon removal of the workers from the area where 1,3-butadiene had accumulated.¹⁰⁻¹² Dermatitis and frostbite may result from exposure to liquid and evaporating 1,3-butadiene.¹¹

In the late 1970's, a retrospective cohort study was conducted at two styrene-butadiene rubber production facilities in the U.S. The combined cohorts consisted of 2756 white males who had an average length of employment of approximately 10 years. No historical exposure data were available. Environmental sampling conducted at the time of the study characterized the most likely chemical exposures to be 1,3-butadiene, styrene, and benzene. Average exposure concentrations of 1,3-butadiene in the two facilities were 1.24 ppm (range of 0.11 to 4.17 ppm) and 13.5 ppm (range of 0.34 to 174 ppm). No statistically significant excesses in total or cause-specific mortality were observed for the total worker populations of either facility. However, a subgroup of workers from one had a non-statistically significant excess mortality rate for cause-specific categories of the lymphatic and hematopoietic tissues.³

A 1985 report of a cohort study at a 1,3-butadiene production plant showed an increased standardized mortality ratio (using U.S. population rates for comparison) for lymphosarcoma and reticulum cell sarcoma in the total cohort, and an increased standardized mortality ratio (using Texas Gulf Coast rates for comparison) for stroke in the non-routinely exposed group. Neither the corresponding local standardized mortality ratio nor the national standardized mortality ratio was statistically significant. In addition, consistently elevated, though nonsignificant, increases in other lymphohematopoietic cancer were noted in each of the eight subcohorts examined.²

APPLICABLE STANDARDS AND RECOMMENDED LIMITS

Based on the 1968 Threshold Limit Value (TLV) of the American Conference of Governmental Industrial Hygienists (ACGIH),¹³ OSHA promulgated a standard for occupational exposure to 1,3-butadiene of 1000 ppm (2200 mg/m³) determined as an 8-hour time-weighted average (TWA) concentration.¹⁴ The TLV of 1000 ppm was based on the absence of significant progressive injury to rats and guinea pigs exposed at 600, 2300, or 6700 ppm of 1,3-butadiene during an 8-month daily exposure period and on the occurrence of only mild irritation experienced by human subjects exposed at 8000 ppm.¹³ At the time of this report, OSHA had initiated new rulemaking action with respect to reducing worker exposures to 1,3-butadiene.

Based upon reported animal carcinogenicity data, the ACGIH has included 1,3-butadiene as an "A2" industrial substance suspected of carcinogenic potential in man.¹⁵ A numerical TLV of 10 ppm has been assigned to 1,3-butadiene.

NIOSH, in its Current Intelligence Bulletin, recommends that 1,3-butadiene be regarded as a potential occupational carcinogen and teratogen and as a possible reproductive hazard.¹⁶

PRODUCTION AND USE

The total U.S. demand for 1,3-butadiene in 1985 was 3.25 billion pounds, of which about 2.45 billion pounds was domestically produced.¹⁷ The predominant uses of 1,3-butadiene are in the manufacture of synthetic rubbers, plastics, and resins. It is also used to a lesser degree as a chemical intermediate in the manufacture of various other products such as fungicides and industrial solvents. Of the synthetic rubbers, styrene-butadiene rubber and polybutadiene rubber make up more than half of the demand for 1,3-butadiene; these rubbers are used primarily in the tire industry.^{18,19}

The use of 1,3-butadiene is thus primarily affected by rubber and tire demand. Table 2 shows the present domestic usage profile for 1,3-butadiene. There has been a significant decline in demand in recent years, with domestic production dropping from 3.6 billion pounds in 1979 to 2.5 billion pounds in 1984.^{20,21} This decline in demand has been accompanied by only a slight decrease in industry capacity.

Table 2. Usage profile for 1,3-butadiene¹⁷

<u>Product</u>	<u>Percentage of total consumption</u>
Styrene-butadiene rubber (SBR)	37
Polybutadiene rubber (PBR)	22
Adiponitrile	13
Styrene-butadiene copolymer latexes	9
Neoprene	7
Acrylonitrile-butadiene-styrene (ABS) resins	6
Nitrile rubber (NBR)	3
Miscellaneous (pesticides, solvents, etc.)	<u>3</u>
Total	100

1,3-Butadiene is currently produced in the U.S. by 10 companies at 12 locations. The current domestic capacity of the 1,3-butadiene monomer plants is approximately 4 billion pounds per year.²² The construction of approximately half of these facilities dates back to World War II, when the chemical was first used in the production of styrene-butadiene rubber. All 12 facilities presently recover 1,3-butadiene from a coproduct generated during ethylene production.

MANUFACTURING PROCESSES

There are three processes by which 1,3-butadiene has been commercially produced: 1) catalytic dehydrogenation of n-butene and n-butane (the Houdry process), 2) oxidative dehydrogenation of n-butene (the Oxo-D or O-X-D

process), and 3) recovery from a C₄ coproduct stream generated in the cracking of hydrocarbons to produce ethylene (the ethylene coproduct process). All three processes involve the production of 1,3-butadiene from a C₄ hydrocarbon stream. All three processes use solvent extraction and extractive distillation to further concentrate the 1,3-butadiene. Based on the similar nature of the process operations, worker exposures are estimated to be similar for all three processes.

The ethylene coproduct process is currently the only method being used to produce 1,3-butadiene in the U.S. Ethylene is the largest volume industrial organic chemical and is used to produce plastics, resins, fibers, elastomers, solvents, surfactants, coatings, elasticizers and antifreeze.²³ From an economic viewpoint, there has been a shift to the use of cheaper, heavier feedstocks for ethylene production resulting in an increase in the 1,3-butadiene content of the coproduct.²⁴ Coupled with the increased demand for ethylene and other olefins, this has resulted in the ethylene coproduct process being the preferred method for 1,3-butadiene production. It should be noted, however, that since the facilities are still in place at many 1,3-butadiene manufacturing locations to produce 1,3-butadiene by catalytic or oxidative dehydrogenation, changes in feedstock economics or increases in 1,3-butadiene demand could cause the dehydrogenation units to be activated.

Ethylene Coproduct Process

The production of 1,3-butadiene by the ethylene coproduct method is a two-stage process: 1) production of a C₄ coproduct during the ethylene manufacturing step, and 2) recovery of 1,3-butadiene from the coproduct.²³ The ethylene manufacturing process consists of the cracking of hydrocarbons (e.g., naphtha, gas oil, ethane, propane) to produce ethylene as the primary product. A coproduct stream composed primarily of C₄ hydrocarbons is also produced. The amount of 1,3-butadiene in the coproduct is dependent on the feedstock and the severity of the cracking process. The heavier the feedstock and the more severe the cracking, the more 1,3-butadiene is produced. Average C₄ coproduct yields from naphtha and gas oil feedstocks are 16 weight percent and 22 weight percent, respectively, of the ethylene product.²⁵ The 1,3-butadiene content of the C₄ coproduct may range from 20 to 70 percent.

Modern ethylene plants are normally designed for near maximum cracking severity.²³ Extraction solvents typically used in the process include acetonitrile, dimethyl formamide, furfural, or cuprous ammonium acetate. The conventional extraction solvents produce a 1,3-butadiene stream that must also be treated to eliminate acetylenes. Acetylenes are particularly undesirable because they can polymerize, contributing to equipment fouling and foaming problems.³

Figure 1 is a flow diagram for the commercial production of 1,3-butadiene by the ethylene coproduct process using a naphtha feedstock. 1,3-Butadiene constitutes approximately 5 percent of the naphtha feed. The naphtha is fed to pyrolysis heaters, a fuel oil stripper, and a quench tower to separate fuel oil and some of the gasoline fraction. The vapor stream then proceeds to a caustic scrubber and dryer. Methane and ethane are removed while acetylene is hydrogenated to ethylene. Products then removed from the vapor

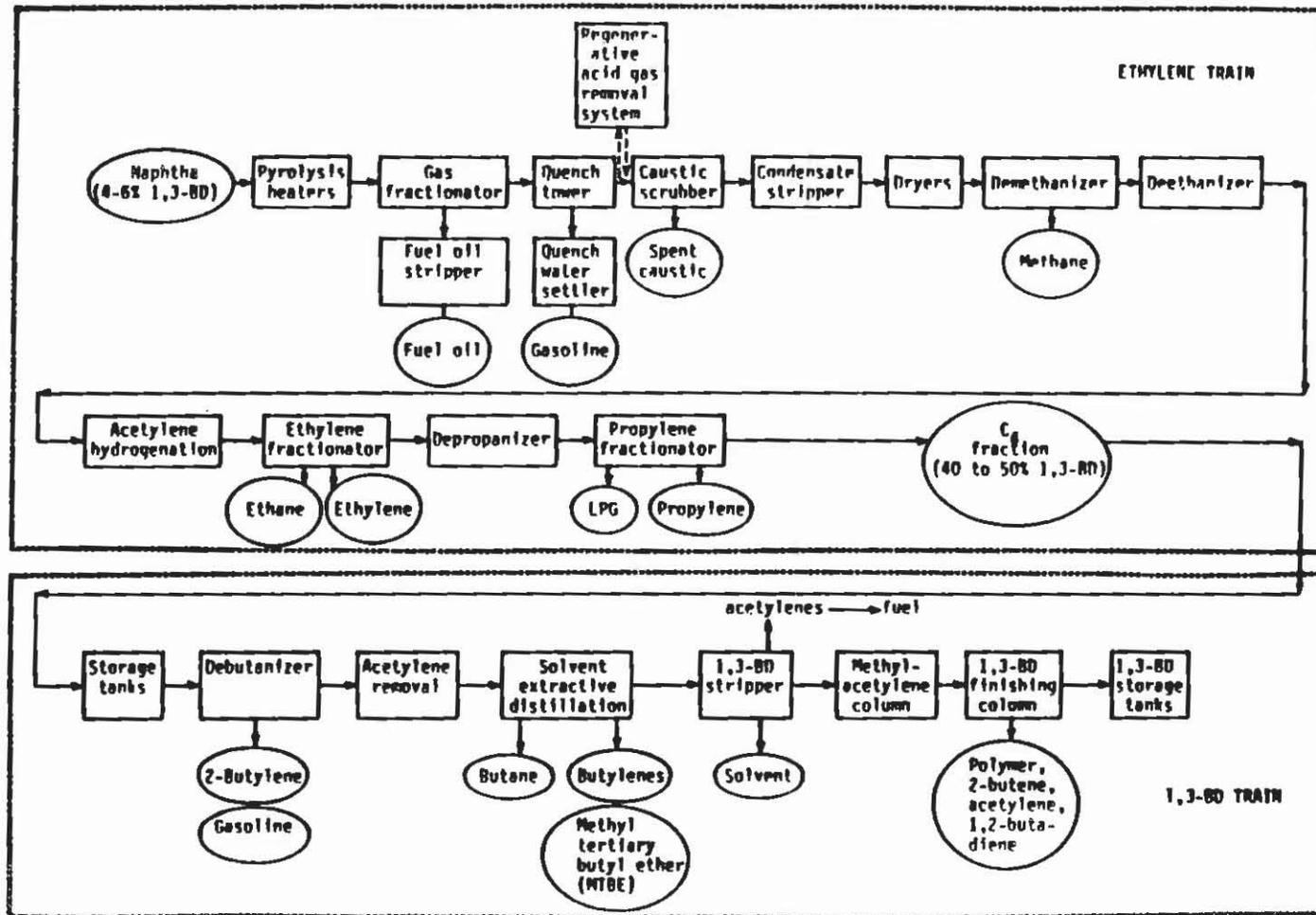


Figure 1. Flow diagram for production of 1,3-Butadiene by the Ethylene Coproduct Process.

stream include ethane, ethylene, liquid petroleum gas (LPG), and propylene.²⁵ This leaves a C₄ stream containing approximately 40 percent 1,3-butadiene, which is fed to the 1,3-butadiene recovery plant. Isobutene is the other major constituent in the C₄ stream.²⁶

Figure 2 shows a detailed flow diagram of the 1,3-butadiene monomer production (recovery) process. This type of process flow is used irrespective of the source of crude feedstock (i.e., ethylene coproduct or dehydrogenation process). Individual plants employ variations to this basic process flow diagram. Some 1,3-butadiene recovery plants obtain C₄ crude streams from different suppliers and blend them to a feed stream containing 40 to 50 percent 1,3-butadiene for processing. The C₄ feed streams and the finished 1,3-butadiene product are stored in pressurized or refrigerated spheres.

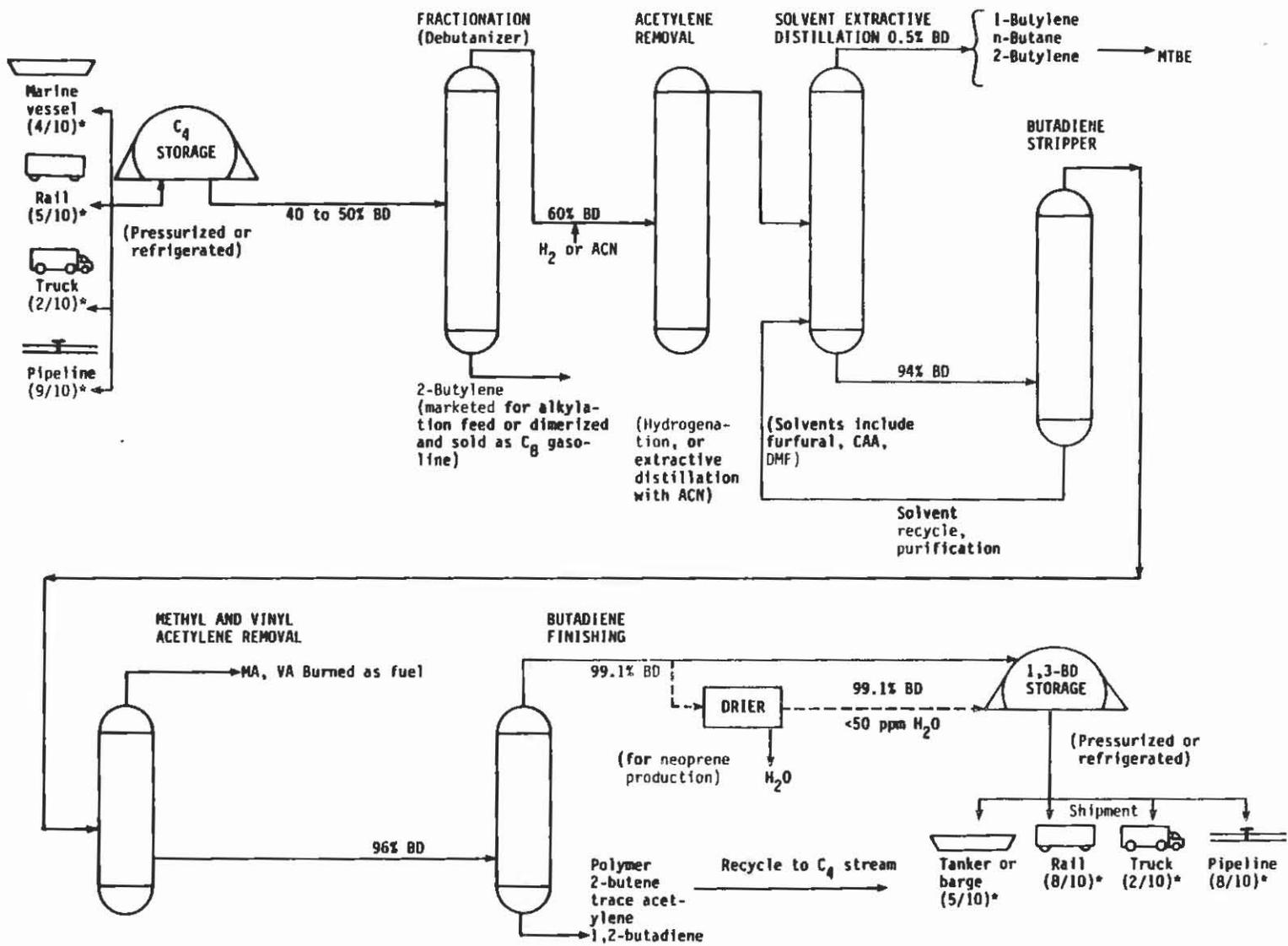
At the 1,3-butadiene plant, the C₄ feed stream is fed to a fractionation column (debutanizer) where 2-butylene is removed. The butylene is either sent to storage to be sold for alkylation feed or dimerized and sold as C₈ gasoline. Both single-stage and two-stage extractive distillation processes are employed.³ In a two-stage system, 1,3-butadiene and acetylenes are first separated from the butenes and butanes, and the 1,3-butadiene is subsequently separated from the acetylenic compounds. In a single-stage extractive distillation system, the acetylenes are separated by conventional distillation. Alternatively, the 1,3-butadiene-containing fractions can be treated before purification by hydrogenation to remove the acetylenes. The 1,3-butadiene stream is hydrogenated to convert any small amounts of acetylene to olefins. Butanes and butylenes are then separated from the C₄ stream by extractive distillation. The butane and butylenes may be removed as a by-product for conversion to products such as methyl tertiary butyl ether (MTBE) or converted to additional 1,3-butadiene by dehydrogenation.

The bottom stream from the solvent extraction column is fed to a stripping column in which 1,3-butadiene along with some residual impurities are removed from the extraction solvent. The 1,3-butadiene stream is then fed to another column where residual acetylenes are vented and burned as fuel. The bottoms stream is given a final purification in a finishing column where 2-butene, trace acetylene, and 1,2-butadiene are removed. The finished product contains greater than 99 percent 1,3-butadiene.

Dehydrogenation Processes

Neither of the two types of dehydrogenation processes are in commercial use today. The principal difference between the catalytic dehydrogenation and oxidative dehydrogenation processes is that oxygen is introduced in the latter to combine with excess hydrogen and form water. Removal of this water allows the reaction forming 1,3-butadiene to proceed further toward completion, thus increasing the yields. Brief descriptions of the dehydrogenation processes are presented below.

The Houdry process is commonly used for dehydrogenation of n-butane. In this process, 95+ percent n-butane is used as feed and conditions can be varied to produce either 1,3-butadiene or n-butenes. The process consists mainly of a battery of fixed-bed catalytic dehydrogenation reactors which operate on a



* Number of plants using this mode/number of plants visited.

Figure 2. Flow diagram for recovery of 1,3-Butadiene from C₄ streams.

cycle, during which the reactor is sequentially heated by burning off the coke deposit, cooled by addition of the butane feed, and purged of hydrocarbon vapors.²⁷ To remain close to optimum conditions during the cycle, the temperature is kept within close limits. The reactor normally operates in the range of 1000° to 1200°F at a pressure of 1/6 atmosphere or higher. The reactor effluent is compressed and sent to a vapor recovery unit to produce a stream containing around 11 percent 1,3-butadiene. This is sent to a butylene splitter where 1,3-butadiene is separated by extractive distillation using furfural or cuprous ammonium acetate as the solvent. Overall yields are about 56 percent.²⁸

The oxidative dehydrogenation process requires lower energy input and results in higher yields of 1,3-butadiene. In this process, the hydrogen generated as a product of the dehydrogenation reaction is removed from the reactor by conducting the reaction in the presence of oxygen. The oxygen reacts with the hydrogen gas and the product is removed as water. The removal of the hydrogen gas serves to drive the reaction further toward completion.²⁷ In the process, n-butene feed, recycled butenes, and steam are preheated and mixed with compressed air. It is then passed through the reactors at 900° to 1100°F in the presence of a catalyst. The catalyst is regenerated in the presence of steam and air in the reactor.²⁶ The oxidative dehydrogenation process results in a 34 percent conversion to 1,3-butadiene per pass. Extraction processes to raise the 1,3-butadiene yield are similar to those used in the ethylene coproduct and Houdry processes.

STUDY DESIGN

SITE SELECTION CRITERIA

Walk-through Survey Site Selection Criteria

At the time of this study, 1,3-butadiene was produced by the ethylene coproduct process by 10 companies at 12 different plant locations. The criterion for selection for the walk-through surveys was essentially a 100 percent sample size of the 10 producers. The ten companies were contacted and walk-through surveys arranged at ten sites. Information collected during the walk-through surveys more clearly defined the process description, plant description, work practices, engineering controls, the number of workers potentially exposed, personnel records, and the industrial hygiene, safety and medical programs.

In-depth Survey Site Selection Criteria

The purpose of the in-depth site selection strategy was to obtain a representative subset of monomer plants from which to characterize exposures by job title and work environment. To achieve this, the 10 monomer production plants were divided into distinct subpopulations (strata) representing observed differences in the workplace environment. The strata were the presence or absence of three specific types of engineering controls, the mode of transportation (pipeline, rail car, tank truck, and/or marine vessel) of the C₄ feed and the 1,3-butadiene product, and the existence of other production

processes or final products at the plant. A single plant within each stratum was selected based on a scoring system that quantified the relative representativeness of each site. Four plants emerged as best representing the diversity of work environments seen in the 1,3-butadiene monomer industry.

The information obtained during each of the four in-depth industrial hygiene monitoring surveys is discussed in subsequent sections titled "Facilities Surveyed" and "NIOSH Sampling Results". During the in-depth surveys, considerable additional information was collected on the nature of the process operations, workforce, work practices, potential routes of exposure, engineering and administrative controls, and personal protective equipment. In addition, industrial hygiene air sampling for 1,3-butadiene was conducted. Both personal and area monitoring samples were taken at controlled and uncontrolled process operations in an effort to determine employee exposure and to assess the efficacy of the engineering controls in use at the time of the survey. These results represent a unique body of exposure information because improved sampling and analytical techniques not previously available to industry or government were used for their collection.

SAMPLING AND ANALYTICAL METHODS

The major limitation at the start of the study was the sensitivity and selectivity of the current analytical method for 1,3-butadiene (NIOSH Method S-91²⁹). This method was developed to meet compliance monitoring needs associated with the current OSHA standard of 1000 ppm (2200 mg/m³); therefore, the S-91 method was validated over a limited range of concentrations: 481 to 2237 ppm (1065 to 4950 mg/m³). Because of new animal test data indicating toxicity at much lower concentrations, it was necessary for NIOSH to develop and validate an analytical method that had a lower detection limit. The existing method (NIOSH S-91) recommends a 6-m x 3.2-mm outer diameter stainless steel column packed with 10 percent Free Fatty Acid Phase (FFAP) on 80/100-mesh Chromosorb W^R acid washed-dimethyldichlorosilane (AW-DMCS) for the gas chromatographic analysis of 1,3-butadiene. The column provides a convenient separation of 1,3-butadiene from the solvent (carbon disulfide), but 1,3-butadiene and other light hydrocarbons, being non-polar, are poorly retained by the highly polar liquid phase, and consequently are poorly separated from each other. Methods using columns which do not adequately separate the four carbon chain (C₄) hydrocarbons and other potential interferences probably overestimate the 1,3-butadiene content of the sample. To improve the resolution of the C₄ hydrocarbons, NIOSH researchers selected a 50-m x 0.32-mm inner diameter fused silica, porous layer open tubular column coated with Al₂O₃/KCl, and used methylene chloride as the extraction solvent. Assuming a 25-liter sample volume the upper limit of the sampler is 100 ppm. The range of the analytical method is 0.02 to 8 ppm. The range may be extended by diluting the desorbed sample. Below 0.4 ppm, the desorption efficiency falls below 75 percent and allowances should be made for the decreased accuracy. A detailed description of the new NIOSH method is provided in Appendix A.

During the in-depth surveys both personal and area sampling were performed. Samples were collected by drawing a known volume of air from a worker's breathing zone or work area through a sampler by means of an SKC Model 224^R

or Gillian Model HFS-113A-UT^R portable low-flow air-sampling pump. Samples were collected on tandem solid sorbent tubes. The forward tube contained 400 mg of coconut charcoal and acted as the primary collection medium. The backup tube contained 200 mg of charcoal and acted to quantify the level of breakthrough. The charcoal tubes were connected to the pumps with plastic Tygon^R tubing. Samples were collected with low-flow pumps at a flow rate of 0.05 to 0.5 liters per minute (Lpm). Sample air volumes were limited to a minimum of 1 liter and a maximum of 25 liters. 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 and Quality Control procedures.³⁰ Field samples were refrigerated during shipment and storage. Samples are known to remain stable for at least 21 days when kept at -4°C.

At the laboratory, each personal monitoring sample was prepared for analysis by desorbing the collected material with 4 ml of methylene chloride for 30 minutes. The resulting solutions were analyzed by gas chromatography with flame ionization detection, a technique which separates the various chemicals and provides responses that are proportional to the amounts present. Each set of samples was analyzed along with 1) calibration standards prepared by desorbing sampling media that has been spiked with known amounts of selected chemicals (analytes) expected to be in the samples, 2) similar solution standards spiked directly, and 3) blank solutions prepared by desorbing blank sampling media. Compounds in the samples were tentatively identified (based on their chromatographic retention times) and quantitated (based on their observed detector responses) by comparison with the retention times and responses observed for the known analytes in the calibration standards.

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 reported LOD and LOQ vary slightly for different analytical runs. For this study, the LOD for 1,3-butadiene ranged from 1 to 5 micrograms per sample ($\mu\text{g}/\text{sample}$) and the LOQ ranged from 4 to 11 $\mu\text{g}/\text{sample}$. These limits were calculated from the statistics of the calibration curve. Treatment of less-than-detectable results for computing both the means and the geometric standard deviation was accomplished by using the numerical value halfway between zero and the reported limit of detection. This approach should provide an accurate measure of the means and standard deviations since only 16 percent of the total data was below the limit of detection.

SAMPLING STRATEGY

Each of the four in-depth surveys was planned and scheduled to obtain full-shift (8-hour) sampling during normal production conditions. All job categories identified during the walk-through surveys as having any potential for exposure to 1,3-butadiene were sampled. Area samples covered the major work environments as well as points along the plant perimeter. Both long- and short-term samples were collected. Long-term samples evaluated full-shift exposures, whereas short-term samples evaluated peak exposures. Short- and long-term samples in this study were defined to be of less than 120 minutes duration and of greater than 120 minutes duration (usually 8 hours), respectively. The number of individuals sampled within a given job category was based on the total number of employees in that category and reflected a 95 percent confidence level ($p = 0.05$), so that the highest and lowest exposed individuals would be included in the sampling.

At least one worker in each job category was monitored for a full shift. During each in-depth survey, the survey team monitored for a total of three shifts over the course of three work days. Auxiliary jobs in the production area, in which exposure to 1,3-butadiene is intermittent, or thought to be nonexistent, were also monitored. Nonproduction jobs involving maintenance and laboratory workers were also evaluated to determine their potential for exposure. The area sources and personal sampling included the following operations: 1) quality control sampling activities, 2) laboratory analysis, 3) pump maintenance and seal changing activities, 4) process area pump alleys, 5) control room operations, 6) tank farm operations, and 7) transportation vehicle loading activities.

FACILITIES SURVEYED

SITE DESCRIPTION

Walk-through surveys were conducted at ten U.S. facilities that produce 1,3-butadiene^a. In-depth industrial hygiene monitoring surveys were conducted at four of these facilities. These four facilities, designated as Plants A, B, C, and D in this report, are described in this section. For each plant, information is presented on plant history, process description, workforce, engineering controls, past worker exposures, medical, safety, and industrial hygiene programs, and personnel recordkeeping.

Plant A

Plant A, located in southeast Texas, covers approximately 2400 acres. Construction began in 1970 and was accomplished in phases. The No. 1 high-density polyethylene (PE) resins unit went on line in 1970 and began production in 1971. The No. 1 and No. 2 olefins units, which recover 1,3-butadiene from the ethylene coproduct stream, began production in 1975 and 1977, respectively. The nameplate capacity of each of these units is 292,000 pounds of 1,3-butadiene per day. The combined production rate of both units at the

^a An additional walk-through survey was conducted by the survey team at a facility that only produced C₄ crude feedstock.

time of the survey was 330,000 pounds per day. In addition to 1,3-butadiene and high-density polyethylene, Plant A produces ethylene, propylene, and polypropylene resins.

Plant B

Plant B, located in southeast Texas, began production of 1,3-butadiene in 1944 by the dehydrogenation of butane and butylene feedstocks. 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.

Plant C

The facility at Plant C is a large refinery/chemical complex. Plant C is also located in southeast Texas. The chemical plant was built in 1941. Shortly after this date, the company built the world's first commercial size 1,3-butadiene plant, which was in production from 1942 to 1945. Two new extractive distillation units were built in 1978 and 1981. An older unit, built in 1969, was closed in 1981. All 1,3-butadiene is produced as a C₄ ethylene coproduct.

The company's total nameplate capacity for 1,3-butadiene at Plant C is 780 million pounds per year. Over the 43-year history of the plant, it has expanded in size and product line. The complex, including the refinery, covers approximately 1500 acres. A variety of chemical, gasoline, and petroleum products are produced at the facility.

Plant D

Plant D is also located in southeast Texas. The Texas division of this company began operations in 1941. Today, the complex covers approximately 3000 acres and consists of 77 processing facilities producing about 700 finished chemicals. The 1,3-butadiene production area covers approximately 4 acres. 1,3-Butadiene production began at the plant in 1951 by the ethylene coproduct process. The facility's total nameplate capacity for 1,3-butadiene monomer production is 85 million pounds per year. Annual 1,3-butadiene monomer production is a function of the ethylene coproduct (C₄) production rates at the two on-site ethylene plants. In addition to 1,3-butadiene, products manufactured at the complex include chlorine, caustic, light hydrocarbons (e.g., ethylene, propylene), and resins (e.g., epoxy, polyethylene).

PROCESS DESCRIPTION

A detailed description of the ethylene coproduct process for manufacturing 1,3-butadiene, which is used by all four plants surveyed, is provided in the Manufacturing Processes section of this report. The major highlights of the

chemical process and handling characteristics are presented in this section for each of the four facilities.

Plant A

Chemical Process--

The crude ethylene coproduct (C₄ feed), which is a blend of four-carbon chain hydrocarbons, is produced on-site at the olefins units and also purchased from outside suppliers. The crude contains approximately 40 to 58 percent 1,3-butadiene. The crude is fed to a primary extraction tower, which uses acetonitrile (ACN) as the extraction solvent. The lighter, mixed butylenes stream from the tower is washed to remove ACN and then pumped via pipeline to another location for storage. The heavier stream, which contains 1,3-butadiene, is separated from ACN in a secondary extraction tower, and the recovered ACN is recycled to the process. The final product, which contains 99 percent 1,3-butadiene, is stored in refrigerated spheres. None of the 1,3-butadiene monomer is consumed at the plant; it is shipped to several customers, either by rail or by barge.

Chemical Handling--

As previously mentioned, the ethylene coproduct is produced on site and transported to the monomer process via pipeline. During the production process, workers collect samples of the ethylene coproduct in various stages of refinement and of the finished 1,3-butadiene. These samples are collected for quality control purposes. The collected samples are then transported to an on-site analytical laboratory for analysis.

Plant B

Chemical Process--

The crude ethylene coproduct (C₄ feed) used at Plant B is a blend from several suppliers. It is received from other producers by pipeline, marine vessel, rail, and truck. The majority is received via ship or barge. The extraction solvent used at Plant B is beta-methoxy propionitrile (BMOP) and furfural. The process includes on-line gas chromatographs for quality control determinations. The finished 1,3-butadiene has a purity greater than 99 percent and is stored in pressurized storage tanks. The on-site storage capacity at Plant B for 1,3-butadiene is 106,000 barrels. The 1,3-butadiene monomer product is shipped primarily by pipeline to other plants in Texas. Small quantities are shipped by barge and rail. None of the 1,3-butadiene monomer is consumed at the 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. Quality control samples are obtained during various stages of the production process and analyzed at an on-site analytical laboratory.

Plant C

Chemical Process--

The crude ethylene coproduct (C₄ feed) used at Plant C is transferred from the Olefins plant to the 1,3-butadiene extraction unit via pipeline. The C₄ fraction contains 40 to 45 percent 1,3-butadiene. The extraction solvent used at Plant C is acetonitrile (ACN). The C₄ feedstock is fed to the extractive distillation unit where butylenes are removed. The extract from the ACN tower (containing 1,3-butadiene) is sent to a finishing tower which produces the final product containing 99.9 percent 1,3-butadiene and a butadiene bottoms byproduct. The finished product is pumped to one of three storage spheres prior to shipment by rail car, tank truck, pipeline, or marine vessel. This facility does not consume any of the 1,3-butadiene monomer on site. The process includes on-line gas chromatographs for quality control determinations.

Chemical Handling--

The C₄ fraction is quality control tested for 1,3-butadiene content before entering the process. Samples are also collected of the intermediates and finished 1,3-butadiene for quality control purposes. All samples are transported to an on-site analytical laboratory for analysis.

Plant D

At Plant D, the crude C₄ feed to the process is a blend of C₄ streams from the two on-site ethylene plants, and contains 50 to 67 percent 1,3-butadiene. Acetonitrile (ACN) has been used as the extraction solvent for further purification of 1,3-butadiene since 1965. (Cuprous ammonium acetate was also used as an extraction solvent by Plant D from 1951 to 1982). The bottoms from the ACN tower are sent to a finishing tower which produces the final product containing 99 percent 1,3-butadiene and a butadiene bottoms byproduct. Other byproducts include butylene and a green oil consisting of heavy organic compounds. The 1,3-butadiene monomer product is stored in pressurized spheres. Most of the 1,3-butadiene monomer is shipped via rail tank cars to outside customers; a fraction is delivered in rail tank cars to the plant's styrene-butadiene latex production facility located approximately seven miles from the 1,3-butadiene monomer production facility.

Chemical Handling--

The C₄ feedstock for the 1,3-butadiene monomer recovery unit is transported via pipeline from the two on-site ethylene plants. The process includes a number of on-line gas chromatographs for quality control. In addition, workers collect samples of the C₄ feed, feed to the ACN extractive distillation unit, butylene byproduct, butadiene bottoms, and finished 1,3-butadiene monomer product for quality control purposes. Samples are then taken to the plant laboratory for analysis.

WORKFORCE CHARACTERIZATION

Five distinct job categories were identified as having potential for occupational exposure to 1,3-butadiene in the monomer plants. Generic titles for these job categories (indicating their associated work locations in the plant) and job descriptions are outlined below. Specific deviations from these descriptions unique to the individual plants are described in the workforce description section for each plant. A summary of the workforce distribution by job category for the ten 1,3-butadiene production facilities visited by NIOSH and PEI is presented in Table 3.

Table 3. Workforce distribution at 1,3-butadiene monomer production facilities.³¹

Job category	Total number of workers per plant *		
	Range		
	Minimum	Maximum	Median
Process Technician/Control Room	2	8	3
Process Technician/Process Area	3	107	8
Process Technician/Loading Area	2	20	3
Laboratory Technician	2	24	4
Maintenance Technician	4	106	6

* Data obtained from the ten NIOSH/PEI walk-through surveys.

The 1,3-butadiene monomer plants operate 24 hours per day, 7 days per week, on either 8-hour or 12-hour rotating shifts. Process technicians in the control room and process area are employed on each shift, whereas the loading area process technicians, laboratory technicians, and most maintenance technicians usually work only during the day shift.

Process Technician/Control Room

This operator holds the most senior position at a monomer production unit and is responsible for its overall operation and production. Duties include implementing written production orders, monitoring process conditions in the control room, and conducting periodic supervision of production and maintenance activities. Typically, 90 percent of this process technician's time is spent in the control room. Because the control room is enclosed and ventilated and somewhat separate from the actual production area, exposures in this job category are generally low. Those activities which increase this process technician's potential for exposure to 1,3-butadiene include troubleshooting, conducting routine inspection, supervising maintenance activities,

and investigating leaks from process equipment. Most plants generally employ one process technician/control room per shift.

Process Technician/Process Area

The process technician/process area is responsible for the day-to-day operation of the inplant process equipment. Duties include controlling and monitoring the process, collecting quality control samples, decontaminating equipment prior to maintenance, monitoring lines and pumps, and performing general housekeeping. This process technician's time is split between the actual process area and the control room, with the majority of the time being spent in the vicinity of the process equipment. Those activities which result in high exposures to 1,3-butadiene include quality control sampling and decontamination of pumps and process equipment. On the average, these process technicians daily collect 8 to 12 quality control samples of the feed, intermediates, and product; pressurized steel cylinders (often referred to as "bombs") are used for collection of the 1,3-butadiene containing samples. Monomer plants generally employ about 3 process area technicians per shift.

Process Technician/Loading Area

The process technician in the loading area is responsible for transferring the crude C₄ ethylene coproduct feed and the 1,3-butadiene monomer product to and from transportation vehicles such as rail tank cars, tank trucks, and marine vessels. Duties include connecting and disconnecting of hoses through which the contents are transferred, monitoring the level in the tanks being loaded or unloaded, purging/venting transfer lines, and taking quality control samples of the materials being loaded or unloaded. They may also be responsible for monitoring the tanks, spheres, and pumps in the tank farm storage area of the plant. The nature of these activities results in a high potential for exposure, frequently resulting from short-term releases of 1,3-butadiene. These exposures are intermittent because the technicians do not continuously load or unload 1,3-butadiene-containing material during their work shift. Plants employing rail tank cars for transporting 1,3-butadiene generally load 1 to 2 cars per day. These loading activities usually take about 2 to 2½ hours per rail car. Other chemicals handled by these technicians may include chemicals such as butylene and pentanes. This job is generally accomplished by 1 to 2 technicians per shift, depending upon the number and type of transportation modes present at the plant.

Laboratory Technician

This job category includes laboratory technicians, chemists, and laboratory supervisors. All monomer plants employ laboratory technicians for the handling and analyses of quality control samples. Duties of the laboratory technician include conducting analyses on the 1,3-butadiene samples for both purity (gas chromatographic analysis) and impurities (wet chemical analysis), and purging sample cylinders upon completion of the analyses. The laboratory technicians daily conduct gas chromatographic and wet chemical analyses on approximately 8 to 12 quality control samples containing 1,3-butadiene. In some plants, the laboratory technicians are also responsible for collecting

quality control samples. The level of exposure associated with this job category is dependent on the laboratory technician's work practices and the effectiveness of laboratory ventilation. There are usually 2 to 3 laboratory technicians per shift associated with the 1,3-butadiene monomer recovery process.

Maintenance Technician

Maintenance technicians at the 1,3-butadiene monomer plant may be either contract personnel or plant employees. The maintenance technician is involved in scheduled and unscheduled maintenance and repair of equipment both inside and outside of the monomer processing area. This job category includes various craftsmen such as machinists, electricians, pipefitters, boiler makers, and welders. The tasks performed by members of this category are dependent on the specific craft of the worker. Exposures during maintenance activities generally fall into two categories: 1) high exposures during the repair of leaking equipment, and 2) lower exposures during the repair of decontaminated equipment. In the latter case, the exposure may be limited to ambient concentrations typical of those in the process area. The potential for exposure to 1,3-butadiene for maintenance technicians is highly variable because they can spend a large portion of their time outside the 1,3-butadiene process area. On an average, there are a total of approximately 6 workers per shift in any plant who may work on 1,3-butadiene process equipment.

Plant A

Plant A employs approximately 815 production and administrative personnel. At each of the two olefins units there are a total of 213 employees (64 salaried and 149 hourly). The following information is unique to Plant A in reference to the job categories with potential for exposure to 1,3-butadiene.

- ° During the survey, only the No. 2 olefins unit was in operation. In the process area of each unit, there is one process technician per shift during normal operations. During upset conditions, two or three process technicians may be in the process area. Responsibility for the process area is regularly rotated among four process technicians. Process technicians work a 12-hour shift, 4 days on and 4 days off.
- ° Rail cars are loaded daily during the day shift by the process technician/loading area. In addition, each shift has a foreman whose responsibilities include the overseeing of process technicians.
- ° Laboratory technicians in Plant A work a 12-hour shift, 4 days on and 4 days off.
- ° The maintenance technicians are employees of Plant A; contract maintenance is limited to major projects, such as shutdowns, which require additional manpower. Maintenance tasks are performed by six employees per olefins unit. The total maintenance staff for the olefins units is 43.

Plant B

Plant B employs a total of 330 employees (100 salaried and 230 hourly). Additions to and clarifications of the different job classifications as outlined previously are as follows:

- ° Process technicians/loading area load rail cars daily during the day shift, while the barges and vessels are loaded as they are received, night or day.
- ° Plant B operates 24 hours a day, 7 days a week, on 8-hour rotating shifts. Maintenance technicians work during the day shift, 5 days a week; laboratory technicians work 7 days a week, two shifts per day.

Plant C

As of May 1984, the Plant C complex employed a total of 3200 employees. In the 1,3-butadiene production area, the department is divided into two areas of responsibilities. The department operates three 8-hour rotating shifts with six production employees on each shift. In the administrative area, there are four employees on the first shift, and one supervisor on each of the second and third shifts for a total of 24 employees (not including maintenance personnel associated with the production of 1,3-butadiene). The maintenance department in the Olefins unit is also responsible for the 1,3-butadiene unit. The maintenance department has 30 employees with approximately 4 to 6 employees assigned on the day shift to the 1,3-butadiene unit. The job duties of the process technician/loading area are separated into three job titles: Tank Truck Operator, Tank Car Operator, and Pump Gauger. The Tank Truck Operator and Tank Car Operator are responsible for duties associated with loading and unloading tank trucks and tank cars, respectively. The Pumper Gauger's duties include starting and stopping pumps, collecting crude cargo samples, cleaning drip pans, hoses, and manifold areas; performing minor pipework and starting pumps for transfers.

Plant D

Plant D employs approximately 7000 personnel. Research and development staff are not included in this total. Additional information on each of the job classifications with potential for exposure to 1,3-butadiene at Plant D are listed below:

- ° The Control A Operator classification at the plant corresponds to the generic process technician/control room job category. There are four Control A Operator positions at the plant; one operator is on duty per 8-hour shift.
- ° The process technician/process area job category corresponds to the Control B Operator classification at Plant D. The three Control B Operators at the plant work an 8-hour, round-the-clock shift with one operator on each shift.

- ° Control C - Loading Operator is the job title at Plant D for the generic job category of process technician/loading area. On an average, two 1,3-butadiene cars are loaded every three days. There are two loading operators who work either on the day or evening shift; one operator per shift is responsible for loading 1,3-butadiene.
- ° Laboratory technicians work an 8-hour day shift plus some evening coverage. There are three employees per shift in the laboratory.
- ° The maintenance department is comprised of both Plant D personnel and contract personnel. This includes six full-time Plant D craftsmen and four outside contractors. These technicians work an 8-hour day shift. Approximately one-third of the maintenance personnel's time is allocated to maintenance activities in the 1,3-butadiene production area.

CONTROLS

Production of 1,3-butadiene monomer occurs in enclosed process systems at open-air plants. Typically, the 1,3-butadiene monomer manufacturing plant is part of a larger chemical production complex. The different processing operations and high production rates of the monomer at these facilities necessitates the use of a wide variety of process equipment. These operations incorporate a number of controls designed 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 worker exposures, which can arise from inhalation or skin contact, whereas others are intended to abate environmental releases. Frequently, the environmental controls can function indirectly to reduce the level of toxic contaminants in the workplace air.

The survey team examined each of the four monomer production facilities during the in-depth monitoring surveys to identify those controls that directly or indirectly reduce workplace exposures. This section presents a description of the existing controls in 1,3-butadiene monomer plants by process operation or work task they are designed to control. Both engineering controls and administrative controls are discussed. The controls identified at each plant during the in-depth surveys are presented following the general discussion on controls.

Engineering Controls

Engineering controls are implemented in three operational categories:

A. Process Flow--Leak prevention from pumps at 1,3-butadiene monomer facilities is accomplished through the use of various types of seals which isolate the interior of the pump from the atmosphere.

Mechanical seals offer better protection against leaks than packed seals. These seals are further categorized as either single or dual mechanical

seals. Figure 3 shows a typical single mechanical seal. In a single mechanical seal application, the rotating seal ring and stationary element faces of the motor shaft are lapped to a very high degree of flatness to maintain contact throughout their entire mutual surface area. The faces are held together by a combination of pressure supplied by a spring and pump pressure transmitted through the fluid which is being pumped. The close contact between the two surfaces is designed to prevent leakage. If these faces wear out or become misaligned, however, a single mechanical seal will release the material being transferred directly into the work environment.³² Figures 4 and 5 present two different configurations for a dual mechanical seal: back-to-back and tandem. In both configurations, a liquid, usually oil, is circulated through the cavity between the two mechanical seals. The circulating liquid is normally maintained at a higher pressure than the process fluid. Any leakage across the seal face causes the seal liquid to be released first, indicating seal failure, before releasing the material being transferred, thus providing additional protection over a single mechanical seal.³²

B. Quality Control (QC) Samples--A QC program typically requires workers to perform three major tasks: 1) collection of 1,3-butadiene samples using sampling cylinders or "bombs", 2) laboratory analysis of the samples, and 3) purging/cleaning of the sampling cylinders. Each task has individual controls associated with it.

- 1) Sample collection--In general, there are two types of sampling methods--the use of on-line gas chromatographs and manual sampling employing either an "open-loop" or "closed-loop" system. The use of on-line gas chromatographs may decrease the need for some manual sampling.

Manual collection of samples consists of attaching the bomb to fittings on the process equipment, opening the process stream in order to allow the sample to flow through the bomb, closing off the sampling stream, and disconnecting the bomb. Open-loop or closed-loop manual sampling may be done.

Open-loop atmospheric sampling systems represent the older technology and present greater potential for exposure. In these systems, the bomb is attached to a process release valve, opened at both ends, and a sample is taken following release of 1,3-butadiene through the bomb directly into the workplace. This stream of 1,3-butadiene detracts from the air quality in the work environment, and may result in exposure to workers through both inhalation and direct dermal contact.

The potential for worker exposure during sampling is greatly minimized by the use of closed-loop sampling techniques. Figure 6 depicts a closed-loop sampling system. These systems represent a recent solution towards minimizing the release of process fluid to the work environment during bomb sampling. The closed-loop system allows the sampled fluid to circulate from the process through the bomb, and back to the process. Sampling occurs by "grabbing" a

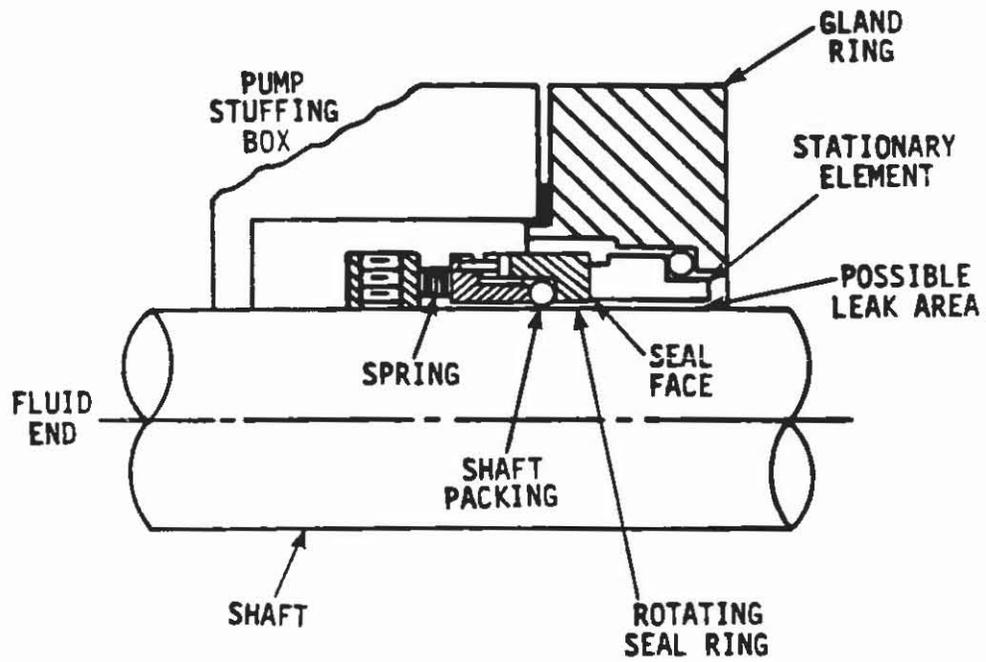


Figure 3. Diagram of a single mechanical seal.

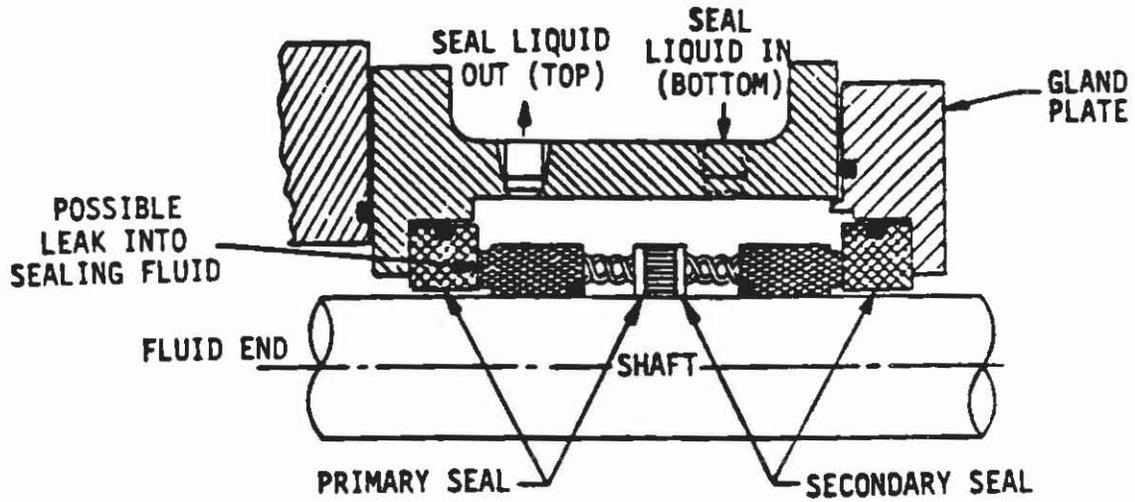


Figure 4. Diagram of a dual mechanical seal (back-to-back arrangement).

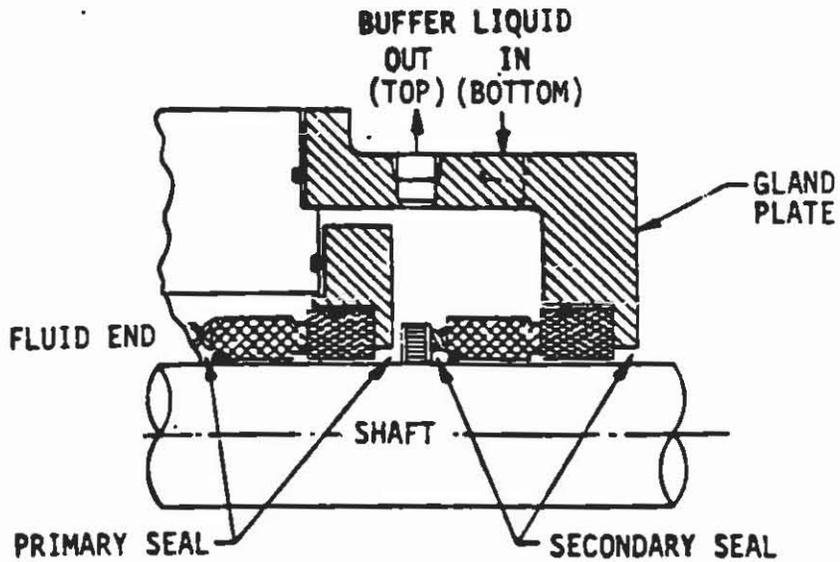
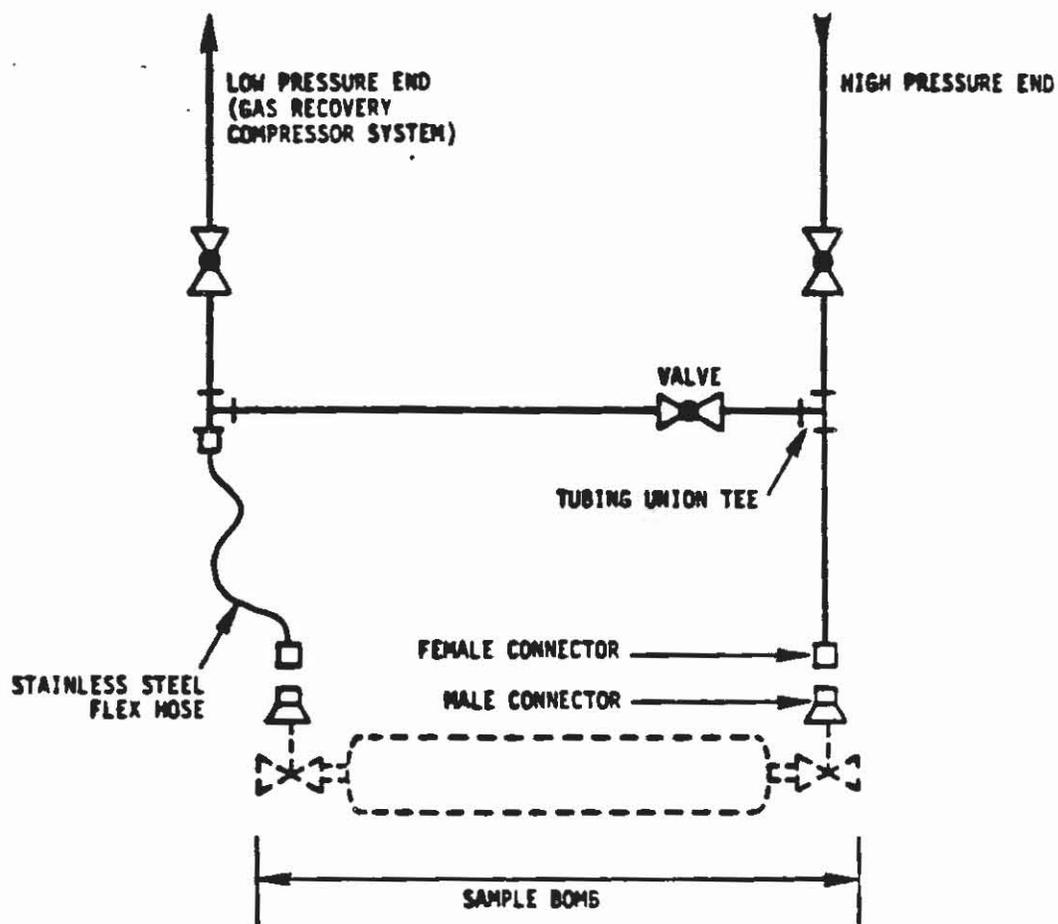


Figure 5. Diagram of a dual mechanical seal (tandem arrangement).



- Figure 6. A closed-loop sampling system.

sample of the process stream as it passes through the bomb. Sampling lines connecting the process to the bomb are a permanent part of the process equipment. Properly designed closed-loop systems also have provisions to purge or evacuate the sample lines of 1,3-butadiene before removing the bomb. Improperly purged sampling lines are a source of 1,3-butadiene during the disconnecting of the bomb because the sampling line is under pressure with respect to the work environment.

- 2) Laboratory analysis--Laboratory analyses of the quality control samples may present a potential for additional exposures through dermal contact or inhalation. The sample bombs are taken to the plant laboratory for analysis by instrumental methods (gas chromatography) and wet chemical procedures. The release of the 1,3-butadiene sample for analysis can consist of either direct connection of the sample bomb to analytical equipment (e.g., gas chromatograph) or release of a small volume of the sample from the bomb into an open container. The connection of the bomb to analytical equipment can result in small releases of 1,3-butadiene into the laboratory workplace. Engineering controls in the laboratory may include dilution ventilation of the laboratory air, the use of laboratory hoods with adequate face velocities, and the employment of sample connections that minimize leakage and dead volume.
- 3) Sample cylinder purging--The complete voiding or purging of sample cylinders (bombs) is performed following analysis in order to evacuate the bomb and make it available for reuse. Bomb voiding may be accomplished by several methods: 1) manual or uncontrolled voiding of the bombs directly to the atmosphere, 2) controlled voiding under laboratory hoods or enclosed vacuum, vents, and 3) controlled voiding of bombs by recycling to the process.

C. Transportation--The transportation of crude C_4 feedstock and 1,3-butadiene product to and from the monomer production facilities is accomplished using four transfer methods: pipelines, rail tank cars, tank trucks, and marine vessels. Of these methods, only pipeline transfer (which is a totally enclosed system) represents a situation where no exposure to or release of 1,3-butadiene occurs.

Monitoring of the loading/unloading of the rail tank cars, tank trucks, and marine vessels may present a potential for 1,3-butadiene exposure. For rail tank cars, two types of "fill" gauges are used to monitor the loading/unloading process: slip-tube and magnetic.

- 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 process technician that the 1,3-butadiene in the tank car has reached a predetermined level.
- 2) The magnetic gauge, which is a completely sealed metering system operating 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 steel rod projects out over the top of the car. The extent of this projection is monitored by the loading area process technician and provides an accurate measure of the level of 1,3-butadiene in the tank car.

The monitoring of the loading/unloading operation for tank trucks differs from that of rail tank cars in that the gauging system on the trucks is an open-ended rotameter which releases 1,3-butadiene into the atmosphere, thereby creating an increased potential for 1,3-butadiene exposure.

Marine vessels typically utilize slip-tube gauges similar to those used by rail tank cars for monitoring the loading/unloading process.

Administrative Controls

Administrative controls are changes in work practices or procedures which act to decrease the potential for employee exposure to a harmful agent.

As an administrative control, some plants require 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. The decontamination procedures produce two effects, the latter of which can be classified as an administrative control:

- 1) The most qualified personnel (process area technicians) shut down and clean the equipment.
- 2) Exposures to maintenance technicians are limited to the time it takes to repair the equipment, not to the full decontamination/repair task.

The specific engineering and administrative controls employed at each of the four plants surveyed are described below.

Plant A

Engineering Controls--

A. Process Flow--All process pumps located in the 1,3-butadiene recovery area (pump alley) at Plant A are equipped with single mechanical seals.

B. Quality Control Samples--

- 1) Sample collection--The use of on-line gas chromatographs decreases the need for some manual sampling at Plant A. At the time of the survey, most of the QC sampling locations for manual sampling in the 1,3-butadiene production area at Plant A had been converted

from open-loop to closed-loop systems. A problem with leaking fittings prevented their proper use at some sample points; however, those fittings had been repaired by the third day of the survey. Plant A workers use 500 cc stainless steel cylinders for collecting QC samples.

- 2) Laboratory analysis--At Plant A, laboratory analyses are performed in a facility with 100 percent makeup air. Transfer of 1,3-butadiene samples from sample cylinder to laboratory glassware, and weathering steps are completed in laboratory hoods. The mean face velocity of laboratory hoods at the Plant A facility was 83 linear feet per minute (lfpm) with a range of 63 to 118 lfpm. Gas chromatograph (GC) injections are completed using a liquid sample valve in a closed system. Residual 1,3-butadiene is vacuumed from the system and vented outside the laboratory.
- 3) Sample cylinder purging--At Plant A, after a sufficient quantity of 1,3-butadiene has been removed for analysis, the cylinders are moved from the laboratory to an outside steam manifold for purging of the remaining sample, steam-cleaning, and nitrogen purging. Excess 1,3-butadiene is exhausted to the atmosphere through an enclosed system that vents the sample to an exhaust stack above the laboratory building.

C. Transportation--The method of transportation of 1,3-butadiene product used by Plant A is rail tank cars. Both slip-tube and magnetic gauges were in use at Plant A for monitoring the loading process.

Administrative Controls--

Plant A requires that decontamination procedures be followed as an administrative control measure for 1,3-butadiene exposure. Process area technicians isolate, decommission, and nitrogen-purge process equipment before maintenance workers enter the area. Maintenance technicians install "blinds" prior to repairing process equipment.

Plant B

Engineering Controls--

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.

B. Quality Control Samples--

- 1) Sample collection--Two control options are in use at Plant B: on-line gas chromatographs and the replacement of manual open-loop cylinder samples with closed-loop systems. At the time of the survey, only a few QC sampling locations had been converted to closed-loop systems. The company is planning to convert all their existing sample locations to a closed-loop system.

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

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 GC analyses is equipped with a single hood having a mean face velocity of 138 lfpm.

- 3) Sample cylinder purging--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--Plant B utilizes rail tank cars for transportation of 1,3-butadiene. Both slip-tube and magnetic gauges were in use for monitoring the loading of 1,3-butadiene into the rail tank cars.

Administrative Controls--

Plant B also requires that certain decontamination procedures be followed during the repair, maintenance, or cleaning of process equipment. Process technicians "blind", decommission, steam, and nitrogen-purge process equipment before maintenance technicians enter the area.

Plant C

Engineering Controls--

A. Process Flow--All of the process pumps located in the 1,3-butadiene recovery area of Plant C are equipped with single mechanical seals.

B. Quality Control Samples--

- 1) Sample collection--Plant C uses on-line gas chromatographs and a combination of open- and closed-loop manual sampling systems.
- 2) Laboratory analysis--Analyses are performed in a laboratory facility with 50 percent makeup air. Transfer of 1,3-butadiene samples for wet analysis from sample bomb to laboratory glassware is performed under laboratory hoods. GC analyses are conducted with the sample cylinders mounted in exhausted enclosures with the cylinders directly connected to the GC units.

The mean face velocity of the laboratory hoods used to conduct the wet (impurity) analysis was 110 lfpm. During dry (purity) GC

analysis of the samples, two hoods were frequently used to house bombs prior to transfer to the exhausted enclosures; the mean face velocity of these hoods were 70 lfpm.

- 3) Sample cylinder purging--After a sufficient quantity of 1,3-butadiene has been removed for analysis, the bombs are taken from the laboratory to an outside exhausted enclosure for purging of the remaining sample. Excess 1,3-butadiene is vacuum-vented to the atmosphere through an enclosed system that releases the unused 1,3-butadiene to an exhaust stack located outside and on top of the laboratory. Following vacuum venting, the bombs are transferred to a nearby steam manifold for purging. Figure 7 is a diagram of the vacuum-vented enclosure.

C. Transportation--Both slip-tube and magnetic gauges were in use at Plant C for monitoring the filling of rail tank cars used in transportation of 1,3-butadiene.

Administrative Controls--

Decontamination procedures are required to be followed at Plant C to decrease potential exposure to maintenance technicians. Process area technicians decommission and nitrogen-purge process equipment before maintenance workers enter the area to open equipment. Often, water flushing is performed before opening equipment so that the equipment is relatively free of residual 1,3-butadiene prior to maintenance operations.

Plant D

Engineering Controls--

A. Process Flow--Dual mechanical (tandem) seals have been retrofitted on all pumps in the storage and 1,3-butadiene recovery areas of Plant D. The seal system is integrated into Plant D's existing auxiliary systems (e.g., flare system, panel alarms).

B. Quality Control Samples--

- 1) Sample collection--Both on-line gas chromatographs and closed-loop manual sampling systems are in use at Plant D. Since 1981, a closed-loop sampling system has been implemented at all manual sampling locations, whereby the 1,3-butadiene stream sampled circulates from the process through the bomb to a flare. Thus, the potential for worker exposure during sampling is greatly reduced. A flexible hose, about 12 inches long, is attached to one side of the bomb when making connections.
- 2) Laboratory analysis--Chemical analyses are performed in a laboratory ventilated at a rate of 12 air changes per hour. Laboratory technicians perform dry tests by connecting the bombs directly to a gas chromatograph. Wet chemistry tests for tertiary butyl catechol (inhibitor), peroxides (impurity), and ACN (extraction solvent) are

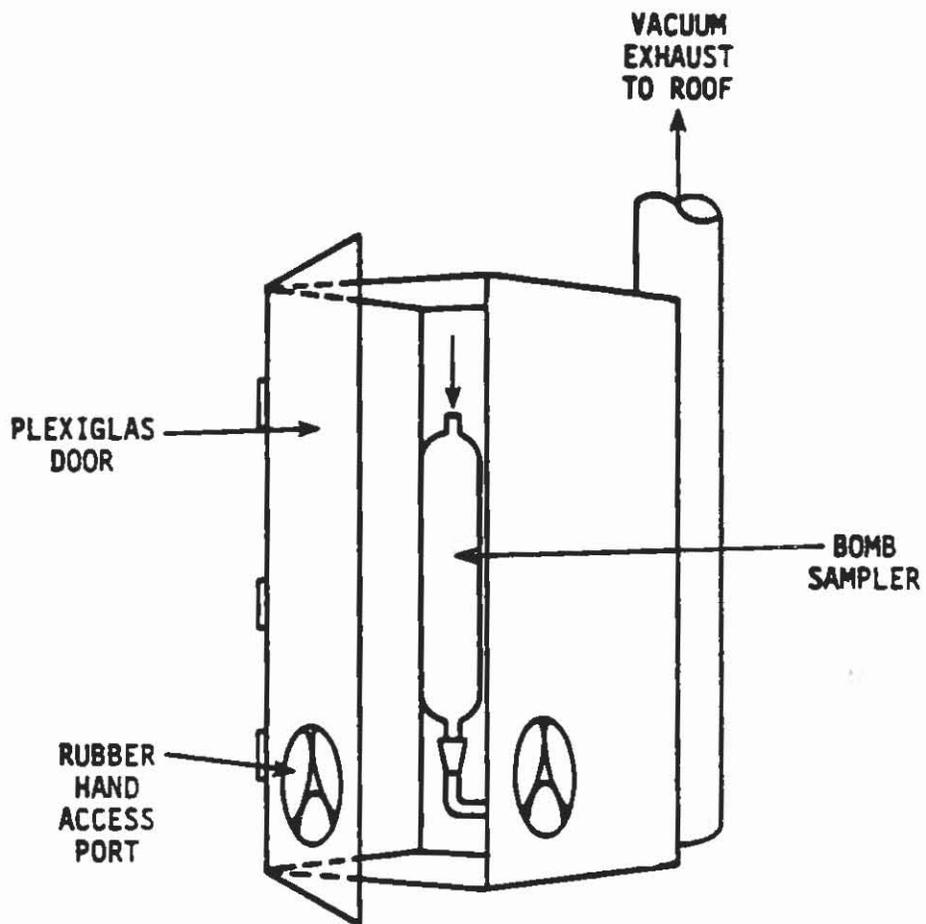


Figure 7. Diagram of vacuum vented enclosure at Plant C for voiding of sample bombs.

performed by releasing a small volume of sample from the bombs into a beaker under one of the three laboratory hoods. The mean face velocities measured during the survey in two of the hoods were 178 lfpm and 163 lfpm, with a range of 130 to 240 lfpm.

- 3) Sample cylinder purging--After a sufficient quantity of the sample has been removed for analysis, the bombs are removed from the laboratory for voiding. This operation consists of purging with nitrogen to a flare.

C. Transportation--Magnetic gauges are fitted to all rail tank cars owned by the company. Occasionally, however tank cars from other companies fitted with slip-tube gauges must be loaded. Only tank cars fitted with magnetic gauges were loaded during the survey at Plant D. After completing the loading operation (approximately 2½ hours per car), the transfer lines are purged of 1,3-butadiene with nitrogen and vented to a flare.

Administrative Controls--

Plant D performs decontamination procedures similar to those performed by the other 3 plants in an effort to reduce exposures to maintenance technicians during repair, maintenance, or cleaning of process equipment.

PAST WORKER EXPOSURES

This section presents the results of the historical monitoring data for 1,3-butadiene collected by the respective companies at Plants A, B, C, and D.

Plant A

This company has been conducting personal sampling for 1,3-butadiene since 1982. A total of 56 full-shift time-weighted average (TWA) and short-term samples have been collected. Table 4 presents a summary of Plant A's historical personal monitoring results. Full-shift TWAs ranged from 0.1 to 7.1 ppm; short-term exposures ranged from 1 to 220 ppm. The weighted mean full-shift TWA for the process-related jobs (process and maintenance technicians) was 2.0 ppm. The weighted mean full-shift TWA for laboratory personnel was approximately 0.3 ppm.

All personal samples were reported to have been collected on charcoal tubes with low-flow pumps²⁹ and analyzed by gas chromatographic techniques similar to NIOSH Method S-91.

Plant B

Industrial hygiene data on 1,3-butadiene is available for the period 1981 through 1984 for Plant B. Table 5 presents a summary of Plant B's historical personal monitoring results. Geometric mean 8-hour TWAs for all job descriptions were below 2 ppm. Arithmetic mean 8-hour TWAs above 5 ppm for maintenance technicians (pipefitters, machinists) were primarily due to a few very high measurements.

Table 4. Summary of Plant A's personal monitoring results for 1,3-butadiene in process, loading, and laboratory areas, 1982-1984^a

Job title/location	TWA ^{b,c} , ppm				Short-term peak exposures ^c , ppm			
	No. of samples	Duration, minutes	Range	Arithmetic mean	No. of samples	Duration, hours	Range	Arithmetic mean
Process technician/ process area	5	12	0.1 - 7.1	2.6	34	30	<1 - 81	5.8
Process technician/ loading area	2	12	0.5	0.5	5	30	<1 - 28	7.0
Maintenance technician	1	12	2.3	2.3	1	5	220	220
Laboratory analyst								
Wet	4	8	0.2 - 0.8	0.5				
GC	4	8	<0.1 - 0.5	<0.2				

^a NIOSH Method S-91 was used for sampling and analysis.

^b Time-weighted average.

^c Data presented as reported by the company.

Table 5. Summary of Plant B's personal monitoring results for 1,3-butadiene, 1981-1984^a

Job title	No. of samples	8-hour TWA ^b , ppm		
		Range	Geometric mean	Arithmetic mean
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
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
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 (include yard)	40	0.16 - 22.49	1.80	4.24

^a NIOSH Method S-91 was used for sampling and analysis.

^b Time-weighted average; data presented as reported by the company.

Again, 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-91.²⁹

Plant C

Personal monitoring data has been collected by the company between 1979-1983 for job categories with the highest potential for exposure to 1,3-butadiene. Table 6 presents a summary of Plant C's historical personal monitoring results. Process area technicians who comprise the majority of the exposed employees have 8-hour TWAs below 6 ppm. For employees involved in tank car and tank truck loading operations, the highest exposures range from 55 to 142 ppm, but with a substantially lower geometric mean of 4.3 to 8.3 ppm.

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

Plant D

Plant D's industrial hygiene data on 1,3-butadiene is available from two sampling surveys. The first major sampling survey was conducted by the company in 1981, and the second survey was conducted in 1984. Tables 7 and 8 present Plant D's 1,3-butadiene personal monitoring data for 1981 and 1984. The reported mean 8-hour TWAs for all categories were below 10 ppm (present TLV) for both the 1981 and 1984 data. Mean 8-hour TWA exposures above 5 ppm were reported for the process area technician in the 1981 survey and for the loading area process technician in the 1984 survey.

The sampling method for Plant D's historical monitoring surveys consisted of collection using 1 gram (Qazi-Ketchum) charcoal tubes at a flow rate of 90 cc/min; the analytical procedure consisted of desorption with carbon disulfide and analysis by flame ionization gas chromatography.

It should be noted that prior to 1981, the method used by Plant D for obtaining QC samples was the old method of attaching a sample bomb to the process release valve using a screw-type fitting, and releasing the 1,3-butadiene through the bomb to the atmosphere. Since 1981, a closed-loop sampling system has been implemented which circulates the 1,3-butadiene from the process through the bomb and back to the process or to a flare. Thus, the potential for exposure to the process area technicians during sampling is greatly reduced.

MEDICAL, SAFETY, AND INDUSTRIAL HYGIENE PROGRAMS

Plant A

Medical Program--

Plant A conducts preemployment and annual physicals for all production and maintenance workers. The secretarial staff and other clerical employees who

Table 6. Summary of Plant C's personal monitoring results for 1,3-butadiene, 1979 - 1983^a

Job title	8-hour TWA ^b , ppm	
	Range	Geometric mean
Process technician/process area	1 ^c - 6	1.2
Tank truck operator	1 - 55	4.3
Tank car operator	1 - 142	8.2

^a NIOSH Method S-91 was used for sampling and analysis.

^b Time-weighted average; data presented as reported by the company.

^c Limit of detection.

Table 7. Summary of Plant D's personal monitoring results for 1,3-butadiene, 1981^a

Job title	8-hour TWA ^{b,c} , ppm				
	No of samples	Range	Geo-metric mean	Arithmetic mean	Range of short-term peak exposures ^{c,d} , ppm
Control A operator	5	2.18 - 14.63	4.16	5.48	0.40 - 749
Control B operator	5	1.50 - 11.77	5.62	6.86	0.17 - 1176
Control C operator	5	0.97 - 8.23	3.80	4.74	4.60 - 75.2
Control C loading operator	5	0.45 - 4.62	1.12	1.87	0.56 - 9240
Laboratory technician	2	0.19 - 0.58	0.33	0.39	0.17 - 15.8

^a NIOSH Method S-91 was used for sampling and analysis.

^b Time-weighted average.

^c Data presented as reported by the company.

^d Based on samples of less than one minute duration.

Table 8. Summary of Plant D's personal monitoring results for 1,3-butadiene, 1984^a

Job title	8-hour TWA ^{b,c} , ppm				
	No of samples	Range	Geo-metric mean	Arithmetic mean	Range of short-term peak exposures ^{c,d} , ppm
Control A operator	3	0.2 - 2.1	0.8	1.1	-
Control C operator	3	1.0 - 6.2	2.5	3.2	0.9 - 963
Control C loading operator	1	6.2	6.2	6.2	2.8 - 335

^a NIOSH Method S-91 was used for sampling and analysis.

^b Time-weighted average.

^c Data presented as reported by the company.

^d Based on samples of less than one minute duration.

Plant A

Personal Sampling--

A total of 16 personal air samples were collected during the in-depth survey at Plant A. These samples represented four job descriptions:

1. Process technicians/process area
2. Process technicians/loading area
3. Process technicians/control room
4. Laboratory technicians

Table 9 presents a summary of the personal samples collected at Plant A. It shows the number of samples taken, the arithmetic mean, the minimum and maximum, the geometric mean, and the geometric standard deviation for each job description. The geometric standard deviation is used as an indicator of the variability of the data. The raw data on personal samples (including date, sample I.D., air volume, duration, and concentration) are presented by job description in Appendix B, Table B-1.

Table 9. Summary of NIOSH's personal samples collected at Plant A, 1985 (ppm)

Job description	Number of samples	Arithmetic mean	Range		Geometric mean	Geometric standard deviation
			Min.	Max.		
Process technician/ process area	6	0.66	0.18 ^a	1.71	0.51	0.76
Process technician/ loading area	1	-	-	0.30	-	-
Process technician/ control room	3	<0.02	<0.02	<0.02	-	-
Laboratory technician						
Wet	3	0.09	0.05 ^a	0.15	0.08	1.75
GC	3	0.51	0.03 ^a	0.87	0.25	6.39

^a Laboratory analysis of analyte was below limit of quantitation (4 µg/sample).

The sample results indicate that worker exposures to 1,3-butadiene are below the OSHA PEL of 1000 ppm and the current ACGIH TLV of 10 ppm. The arithmetic mean, full-shift, time-weighted exposures across all job categories are less than 1 ppm. Process technicians working in the process area have the highest mean exposure (0.66 ppm) of all job categories measured. A process technician

working in the pump alley received the highest individual TWA exposure (1.71 ppm) of any Plant A employee monitored. Laboratory technicians as a group have the second highest arithmetic mean exposure (0.51 ppm). A laboratory technician conducting a GC analysis of 1,3-butadiene QC samples received the second highest individual TWA exposure (0.87 ppm) of all employees monitored.

Area Sampling--

A total of 26 area air samples were collected during the in-depth survey. These samples represented four work environments and the background ambient air:

1. Process area/pump alley
2. Process area/rail car loading dock
3. Storage area/during normal and leak conditions
4. Laboratory/wet and GC analysis and cylinder voiding
5. Background/ambient air

Table 10 summarizes the area samples collected at Plant A. It presents the number of samples taken, the arithmetic mean, the minimum and maximum, the geometric mean, and the geometric standard deviation by work environment. The raw data on the area samples is presented in Appendix B, Table B-2.

The area sample results indicate that under normal operating conditions, the arithmetic mean airborne concentration of 1,3-butadiene in all work environments is less than 2 ppm. The highest arithmetic mean concentrations were found in the tank farm area (0.81 ppm) and the pump alley of the process area (0.36 ppm). The highest individual 8-hour TWA airborne concentrations were also detected in the tank farm and pump alley (1.76 and 1.23 ppm, respectively). Under an "upset" condition experienced in the storage tank area (leaking circulation pump handling 1,3-butadiene), airborne concentrations reached a value of 23.80 ppm for an 8-hour period. Although no employees were present in the area when the leak occurred, this sampling result indicates a potential for personal exposures higher than the levels measured during the survey.

Perimeter concentrations measured during the survey were all less than the analytical limit of detection. Ambient airborne concentrations were less than 0.03 ppm. The area monitors were located both upwind and downwind of the 1,3-butadiene process.

Plant B

Personal Sampling--

A total of 39 personal air samples were collected during the in-depth survey at Plant B. These samples represented five job categories.

1. Process technicians/process area
2. Process technicians/loading area
3. Process technicians/control room
4. Process technicians/storage area
5. Laboratory technicians

Table 10. Summary of NIOSH's area samples collected at Plant A, 1985
(ppm)

Work environment	Number of samples	Arithmetic mean	Range		Geometric mean	Geometric standard deviation
			Min.	Max.		
Process/pump alley	5	0.36	0.07 ^a	1.23	0.20	3.09
Process/rail car loading	2	0.16	0.10 ^a	0.22	-	-
Storage area/ tank farm						
General	3	0.81	0.15	1.76	0.52	3.43
Leak	2	18.29	12.77	23.80	-	-
Laboratory						
Wet	3	0.07	0.03 ^a	0.12	0.06	2.00
GC	3	0.06 _b	0.04 ^a _b	0.07 ^a _b	0.06	1.34
Cylinder voiding	2	<0.05 ^b	<0.05 ^b	<0.05 ^b	-	-
Background/ ambient air						
North	2	<0.03 ^a	0.02 ^a	0.03 ^a _b	-	-
East	1	-	-	<0.02 ^b _b	-	-
South	1	-	-	<0.02 ^b _b	-	-
West	2	<0.02 ^b	<0.02 ^b	<0.02 ^b	-	-

^a Laboratory analysis of analyte was below limit of quantitation (4 µg/sample).

^b Laboratory analysis of analyte was below limit of detection (1 µg/sample).

Table 11 presents a summary of the personal samples collected at Plant B. It shows the number of samples taken, the range of measurements, the arithmetic mean, the geometric mean, and the geometric standard deviation for each job description. The raw data on personal samples are presented by job category in Appendix B, Table B-3.

The sampling results indicate that exposures to 1,3-butadiene are below the OSHA PEL and the current ACGIH TLV. 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 11. Summary of NIOSH's personal samples collected at Plant B, 1985 (ppm)

Job description	Number of samples	Arithmetic mean	Range		Geometric mean	Geometric standard deviation
			Min.	Max.		
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 ^b	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
Chromatograph	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 (3 µg/sample).

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

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 category, process technicians in the loading area have the second highest arithmetic mean exposure (63.77 ppm).

Area Sampling--

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

1. Process area/pump alley
2. Process area/control room
3. Laboratory/wet and dry analysis and cylinder voiding

Table 12 summarizes the results from the area samples collected at Plant B by work environment. The raw data on area samples are presented in Appendix B, Table B-4.

Area samples collected in the production area during the in-depth survey indicated that under normal operating conditions arithmetic mean airborne concentrations of 1,3-butadiene in all work environments measured was less than 2 ppm. However, the highest arithmetic mean concentration (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.

Plant C

Personal Sampling--

A total of 26 personal air samples were collected during the in-depth survey at Plant C. These samples represented five job categories:

1. Process technicians/process area
2. Process technicians/loading area
3. Process technicians/control room
4. Maintenance technicians
5. Laboratory technicians

Table 13 presents a summary of the personal samples collected at Plant C. It shows the number of samples taken, the range of measurements, the arithmetic mean, the geometric mean, and the geometric standard deviation by job description. The raw data on personal samples are presented by job description in Appendix B, Table B-5.

The industrial hygiene survey of Plant C's 1,3-butadiene production facility has demonstrated that all workers' exposures to 1,3-butadiene are well below the OSHA PEL and that a majority of the employees are below the 10 ppm ACGIH TLV.

Table 12. Summary of NIOSH's area samples collected at Plant B, 1985 (ppm)

Work environment	Number of samples	Arithmetic mean	Range		Geometric mean	Geometric standard deviation
			Min.	Max.		
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	-	-	-	-

Table 13. Summary of NIOSH's personal samples collected at Plant C, 1985 (ppm)

Job description	Number of samples	Arithmetic mean	Range		Geometric mean	Geometric standard deviation
			Min.	Max.		
Process technician/ process area	4	1.45	0.09	4.19	0.56	5.83
	2 ^a	3.65	<0.33	6.96	-	-
Process technician/ loading area						
Rail car	3	0.24	0.12	0.46	0.19	2.12
Tank truck	3	2.65	0.08	5.46	1.02	9.38
Process technician/ control room	2	<0.08	<0.04 ^b	<0.11 ^b	-	-
Maintenance technician	2	14.46	12.09 ^c	16.83 ^c	-	-
Laboratory technician						
Wet	4	0.39	0.12	0.89	0.30	2.28
Dry	3	0.30	0.04 ^{b,c}	0.63 ^c	0.18	4.03
Bomb voiding	3	<1.58	<0.10 ^{b,c}	4.50 ^c	<0.39	8.38

^a Short-term sample not time weighted to 8-hours (no respirator worn).

^b Laboratory analysis of analyte was below limit of detection (2 µg/sample).

^c Short-term samples not time weighted to 8-hours (respirator was worn).

The mean, full-shift, time-weighted exposures vary greatly across different job categories. As a job category, process technicians in the loading area had the highest mean 8-hour TWA exposure (2.65 ppm). Process technicians performing equipment maintenance had the highest mean exposure (14.46 ppm) of any job category, although this represents a short-term mean exposure. One process technician working on a faulty process pump received the highest individual exposure (16.83 ppm) of any Plant C employee monitored although this was a short-term exposure. It should be noted that technicians performing maintenance of process equipment are required to wear respirators. Therefore, the exposure value cited represents a potential and not an actual exposure.

Area Sampling--

A total of 30 area air samples were collected during the in-depth survey at Plant C. These samples characterize six work environments:

1. Process area/pump alley
2. Process area/control room
3. Process area/loading tank trucks
4. Process area/loading rail cars
5. Laboratory/wet and dry analysis and cylinder voiding
6. Background/ambient air

Table 14 summarizes the area samples collected at Plant C. The raw data on the area samples are presented by work environment in Appendix B, Table B-6. Area samples collected during the in-depth survey demonstrate that, under normal operating conditions, the arithmetic mean 8-hour TWA airborne concentrations of 1,3-butadiene in all work environments vary considerably. The highest mean area concentration (n=5) for a specific work environment was 15.78 ppm and was found in the loading area during a 2½-hour loading operation of rail cars. The highest individual area airborne concentration (64.29 ppm) was also detected near a rail car during a 2½-hour loading operation.

Plant D

Personal Sampling--

A total of 30 personal air samples were collected during the in-depth survey at Plant D. These samples represented five job categories:

1. Process technicians/process area
2. Process technicians/loading area
3. Process technicians/control room
4. Laboratory technicians
5. Maintenance technicians

Table 15 presents a summary of the personal samples collected at Plant D. The raw data on personal samples are presented by job category in Appendix B, Table B-7.

Table 14. Summary of NIOSH's area samples collected at Plant C, 1985 (ppm)

Work environment	Number of samples	Arithmetic mean	Range		Geometric mean	Geometric standard deviation
			Min.	Max.		
Process/pump alley	6	0.98	0.09	1.73	0.71	2.97
Process/loading area						
Rail cars	5	15.78	1.40	64.29	5.36	4.65
Tank truck	6	<0.58	<0.04 ^a	1.92	0.23	4.53
Laboratory						
Wet	3	<0.16	0.07	0.19	0.14	1.86
Dry	3	<0.27	<0.04 ^a	0.67	0.13	4.27
Background/ambient air						
North	1	-	-	0.13	-	-
East	2	<0.09	<0.06 ^a	<0.11	-	-
South	2	<0.08	<0.04 ^a	<0.11	-	-
West	1	<0.05	-	-	-	-

^a Laboratory analysis of analyte was below limit of detection (5 µg/sample or 2 µg/sample depending on the day the sample was analyzed).

Table 15. Summary of NIOSH's personal samples collected at Plant D, 1985 (ppm)

Job description	Number of samples	Range		Arithmetic mean	Geometric mean	Geometric standard deviation
		Min.	Max.			
Process technician/ process area (Control B Operator)	7	0.08 ^a	2.98	1.16	0.67	3.56
Process technician/ process area (Control C Operator)	4	0.76 ^b	10.44 ^b	3.52 ^c	1.91 ^c	3.41
° Bomb sampling						
Process technician loading area (Control C Operator)	3	0.50	1.44	1.08	0.98	1.79
Process technician/ control room (Control A Operator)	2	0.25	0.52	0.38	0.36	-
Laboratory technician						
° Wet	3	0.25	1.96	0.95	0.68	2.80
° Dry	3	0.34	1.04	0.58	0.50	1.88
° Supervisor	3	0.08 ^a	0.10	0.09	0.09	1.12
Maintenance technician	5	0.05 ^{a,b}	6.08 ^b	1.45 ^c	0.34 ^c	7.44

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

^b Short-term samples; values were not time weighted to 8-hour concentrations.

^c Averages of short-term samples.

The industrial hygiene survey of Plant D has demonstrated that the workers' exposures to 1,3-butadiene are well below the current ACGIH TLV of 10 ppm and the OSHA PEL of 1000 ppm.

The arithmetic mean, full-shift, TWA exposures across all job categories were less than 1.2 ppm. Process technicians working in the process area had the highest mean 8-hour TWA exposure (1.16 ppm) among the different job categories. Process technicians in the loading area had the second highest mean 8-hour TWA exposure of 1.08 ppm. A process technician performing bomb sampling in the process area received the highest short-term (20-minute) exposure of 10.44 ppm. The second highest short-term exposure of 6.08 ppm was observed for a maintenance technician.

Area Sampling

A total of 33 area air samples were collected during the in-depth survey at Plant D. These samples characterize five work environments:

1. Process area/pump alley
2. Process area/rail car loading
3. Process area/rail car unloading
4. Laboratory/dry analysis
5. Background/ambient air

Table 16 summarizes the area samples collected at Plant D. The raw data on the area samples are presented by work environment in Appendix B, Table B-8.

Area samples collected during the in-depth survey demonstrate that, under normal operating conditions, the arithmetic mean airborne concentrations of 1,3-butadiene in all work environments were less than 13 ppm. The two highest mean concentrations of 12.81 ppm and 10.47 ppm were found in the rail car unloading and loading areas, respectively. The highest individual full-shift airborne concentration of 50.43 ppm was observed in the rail tank car loading area.

Arithmetic mean area background concentrations measured during the survey were less than 0.20 ppm. The area monitors were located both upwind and downwind of the 1,3-butadiene production area.

DISCUSSION

The monitoring effort conducted during the in-depth surveys at the 1,3-butadiene monomer plants was designed to characterize both occupational exposures to the five job categories discussed earlier (i.e., personal monitoring), and airborne concentrations for several process areas in the plant that were associated with unique worker activities (i.e., area monitoring). The personal and area monitoring results for each plant were discussed separately in the previous section. This section summarizes and discusses the personal and area monitoring results for all four plants collectively to assess the 1,3-butadiene exposure potential in the monomer industry.

Table 16. Summary of NIOSH's area samples collected at Plant D, 1985 (ppm)

Work environment	Number of samples	Range		Arithmetic mean	Geometric mean	Geometric standard deviation
		Min.	Max.			
Process area/pump alley	9	<0.04 ^a	0.77	0.40	0.32	2.40
Process area/rail car loading	5	0.09 ^b	50.43	10.47	0.88	11.58
Process area/rail car unloading	6	1.14	30.33	12.81	6.54	4.08
Laboratory						
° Dry	1	-	0.11 ^b	-	-	-
Background/ambient air						
North	3	0.08 ^b	0.37	0.20	0.16	2.16
East	3	<0.04 ^a	<0.05 ^a	<0.04	-	-
South	3	<0.05 ^a	0.07 ^b	<0.06	0.06	1.18
West	3	<0.02 ^a	0.50 ^b	0.19	0.07	5.44

^a Laboratory analysis of analyte was below limit of detection (2 µg/sample).

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

PERSONAL MONITORING DATA

A total of 111 personal samples (comprised of 88 full-shift and 23 short-term samples) were collected during the four 1,3-butadiene monomer facility in-depth surveys. Figure 8 presents a cumulative percentage distribution of the full-shift personal monitoring results. Excluding the three high full-shift exposures greater than 10 ppm, it appears that the personal monitoring data collected on workers at 1,3-butadiene monomer plants is lognormally distributed. This is consistent with earlier research which suggests that concentrations in random occupational environmental samples are lognormally and independently distributed both within any particular workshift and over many daily exposure averages.³⁹ Assuming that the worker population sampled during the surveys is representative of the entire workforce in the 1,3-butadiene monomer industry, Figure 8 shows that 70 percent of the exposed population have full-shift exposures below 1 ppm and approximately 95 percent of the exposures are below 5 ppm.

Tables 17 and 18 provide a breakdown by job category/worker activity of the full-shift and short-term personal monitoring results, respectively, and present averages, ranges, and standard deviations for the measured 1,3-butadiene concentrations. The geometric standard deviation is a measure of the variability of the data about the geometric mean. The process technician/storage area was a job category employed at only one of the four 1,3-butadiene monomer plants. Full-shift exposures for the different job categories range from a low of 0.01 to a high of 373.54 ppm (Table 17), whereas short-term exposures range from 0.05 to 146.60 ppm (Table 18). The short-term personal monitoring was conducted with the intention of identifying peak exposures during high-risk activities. However, because continuous, real-time monitors were not available for measuring 1,3-butadiene concentrations, it was not possible to ensure that the short-term sampling would succeed in detecting peak concentrations over the entire workshift. The short-term monitoring data in Table 18 shows exposures to 1,3-butadiene greater than 10 ppm for all three types of periodic inplant activities, but does not appear to have consistently detected peak levels (i.e., some full-shift results showed higher concentrations than the short-term results for the same operation). Among the different job categories, the maximum average full-shift and short-term exposures were both observed for laboratory technicians in charge of cylinder voiding, with arithmetic means of 125.52 and 22.90 ppm, respectively; corresponding geometric means were 7.46 and 1.95 ppm, respectively. It should be noted, however, that the mean for the full-shift cylinder voiding samples was based on only 3 measurements. Table 17 clearly shows that the only job categories that experience full-shift 1,3-butadiene exposures greater than 10 ppm are the process area technicians, rail car loading area process technicians, and laboratory technicians who perform cylinder voiding. These job categories had geometric mean exposures of 0.64, 1.00, and 7.46 ppm, respectively. Geometric mean exposures for all other job categories were at or below approximately 1 ppm. Maximum exposures for some job categories exceeded 100 ppm with one exposure for a laboratory technician reaching a full-shift TWA of approximately 375 ppm. These high exposures were associated with poor work practices or uncontrolled emissions, and should not be considered typical of cylinder voiding activities observed in the industry.

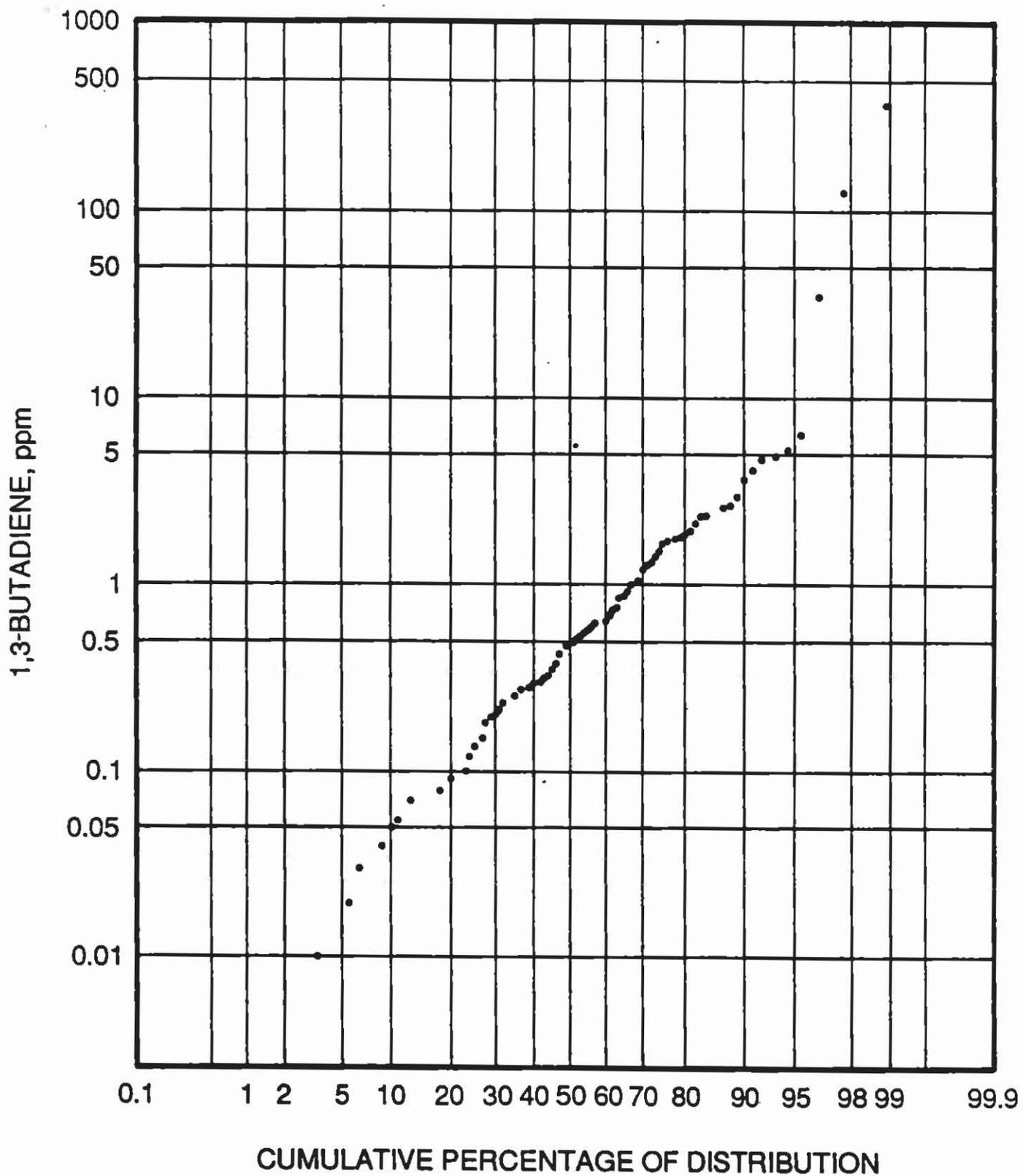


Figure 8. Probability plot of full-shift 1,3-butadiene personal exposures.

Table 17. Summary of full-shift personal samples collected at 1,3-butadiene monomer production facilities

Job category	1,3-butadiene concentration, ppm						
	Number of samples	Arithmetic mean	Median	Range		Geometric mean	Geometric standard deviation
				Minimum	Maximum		
Process technician/ control room	10	0.45	0.07	<0.02 ^a	1.87	0.09	8.01
Process technician/ process area	28	2.23	0.64	<0.08 ^a	34.90	0.64	4.30
Process technician/ loading area							
- rail car	9	14.64	0.50	0.12	123.57	1.00	8.46
- tank truck	3	2.65	2.40	0.08	5.46	1.02	9.38
Laboratory technician	29	1.06	0.36	0.03	6.31	0.40	4.36
Laboratory technician - cylinder voiding	3	125.52	2.61	0.42	373.54 ^b	7.46	33.58
Maintenance technician	1	-	-	-	0.21	-	-
Process technician/ tank farm	5	0.44	0.20	<0.04 ^a	1.53	0.20	4.75

^a Minimum measurement represents the lower limit of detection achieved with the new NIOSH sampling and analytical method.

^b This abnormally high exposure was due to poor work practices at one plant and is not typical of cylinder voiding activities observed in the industry.

Table 18. Summary of short-term personal samples collected at 1,3-butadiene monomer production facilities

Job category	1,3-butadiene concentration, ppm						
	Number of samples	Arithmetic mean	Median	Range		Geometric mean	Geometric standard deviation
				Minimum	Maximum		
Process technician/ process area							
- cylinder sampling	10	17.25	1.45	<0.34 ^a	146.60	2.01	7.70
Laboratory technician							
- cylinder voiding	6	22.90	3.02	<0.10 ^a	108.44	1.95	22.13
Maintenance technician	7	5.17	0.57	0.05	16.83	0.99	11.63

^a Minimum measurement represents the lower limit of detection achieved with the new NIOSH sampling and analytical method.

AREA MONITORING DATA

Analysis of the area monitoring data for the four 1,3-butadiene monomer plants yielded a total of 100 valid area measurements comprised of 97 full-shift and 3 short-term samples. Figure 9 presents a cumulative percentage distribution of the full-shift area monitoring results. The area monitoring data also appear to be lognormally distributed. Figure 9 shows that approximately 75 percent of the airborne concentrations are below 1 ppm and approximately 90 percent of the concentrations are below 5 ppm.

Table 19 provides a breakdown by work environment of the full-shift area monitoring results, and presents averages, ranges, and standard deviations for the measured 1,3-butadiene concentrations. Full-shift 1,3-butadiene concentrations in the work areas ranged from a low of 0.02 to a high of 64.29 ppm (Table 19). Three area samples collected to assess short-term 1,3-butadiene concentrations around cylinder voiding operations ranged from 0.05 to 1.91 ppm, with an arithmetic mean of 0.67 ppm and a geometric mean of 0.17 ppm. The maximum average full-shift area concentrations were observed for the rail car loading area, with an arithmetic mean of 10.58 ppm. A review of the area monitoring results indicates that only two work areas are associated with 1,3-butadiene concentrations greater than 10 ppm: the rail car loading area and the tank storage farm area. These areas had geometric mean concentrations of 1.77 and 2.12 ppm, respectively. Other work areas had geometric mean concentrations of less than 1 ppm. No full-shift area samples exceeded 100 ppm of 1,3-butadiene. Ambient air concentrations of 1,3-butadiene detected at the plant perimeter locations were extremely low, with a geometric mean of 0.04 ppm.

CONCLUSIONS

In summary, the monitoring results from the present NIOSH study for the 1,3-butadiene monomer industry show that full-shift exposures for all job categories are well below the current OSHA PEL of 1000 ppm. Geometric mean full-shift exposures for all job categories are also below the ACGIH TLV of 10 ppm. A few individual exposures exceed 10 ppm for three job categories comprised of process technicians in the process area, process technicians in the rail car loading area, and laboratory technicians responsible for cylinder voiding. These high exposures are associated with either inadequate engineering controls or poor work practices.

A noteworthy finding of the in-depth monitoring surveys is the relatively low overall concentrations of 1,3-butadiene in the monomer production industry. Historical monitoring data from the monomer plants show somewhat higher full-shift exposures with a greater frequency of exposures above 10 ppm. The discrepancy between the study results and those from the historical monitoring data may be attributed to improved engineering controls implemented at the monomer production sites over the past few years. Also the improved selectivity of the new NIOSH method minimized interferences to the 1,3-butadiene analysis from other C₄ compounds.

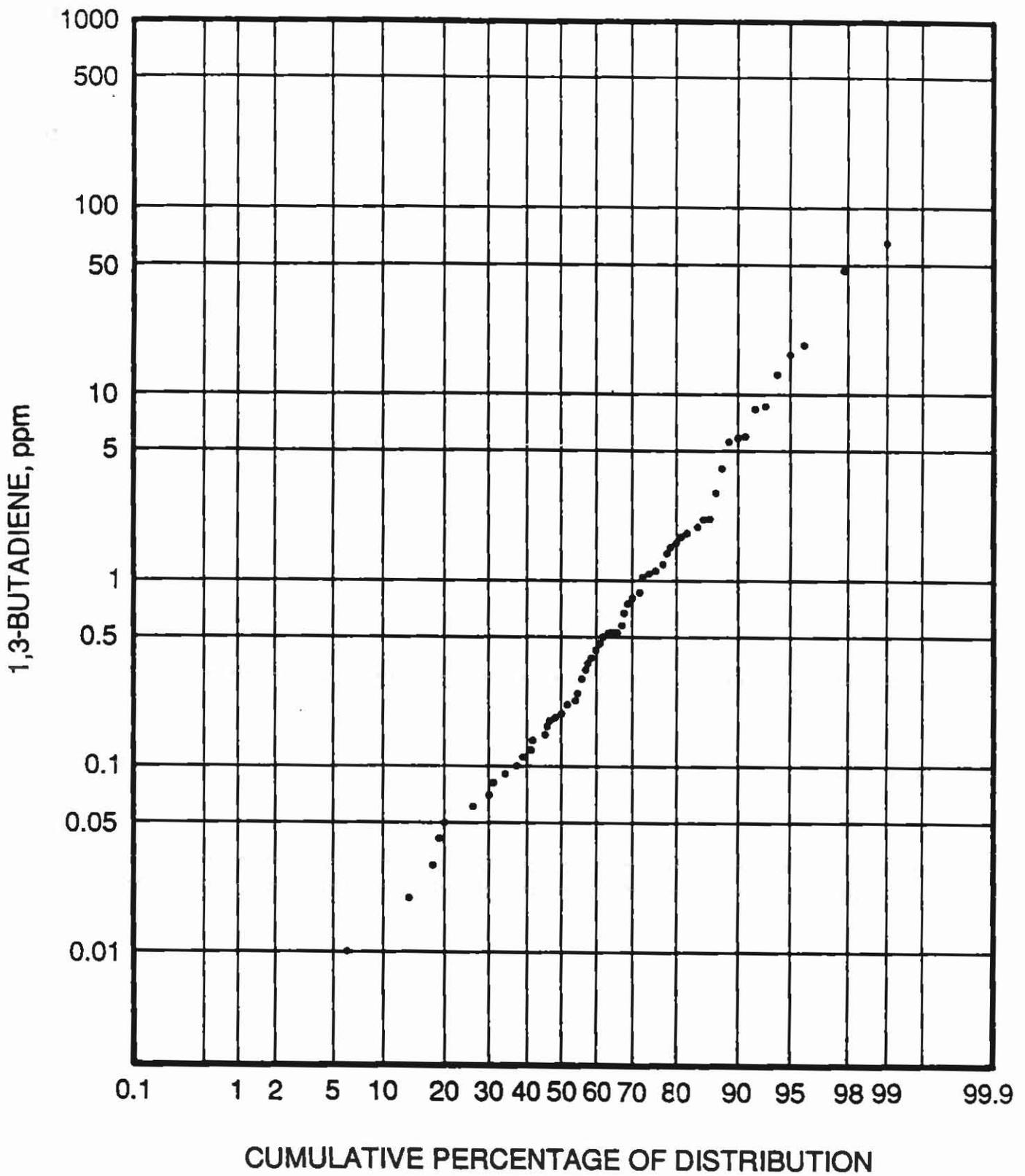


Figure 9. Probability plot of full-shift 1,3-butadiene area concentrations.

Table 19. Summary of full-shift area samples collected at 1,3-butadiene monomer production facilities

Work environment	1,3-butadiene concentration, ppm						
	Number of samples	Arithmetic mean	Median	Range		Geometric mean	Geometric standard deviation
				Minimum	Maximum		
Process/pump alley	24	0.50	0.35	<0.04 ^a	1.73	0.31	2.98
Control room	1	-	-	-	2.13	-	-
Loading area							
- rail car terminal	20	10.58	1.46	<0.04 ^a	64.29	1.77	9.36
- tank truck terminal	4	0.57	0.14	0.10	1.92	0.24	4.01
Laboratory	18	1.03	0.12	<0.04 ^a	5.88	0.21	6.14
Storage/tank farm	5	7.80	1.76	0.15	23.80	2.12	8.36
Ambient air	25	0.07	0.03	<0.02 ^a	0.50	0.04	3.14

^a Minimum measurement represents the lowest limit of detection achieved with the New NIOSH sampling and analytical method.

RECOMMENDATIONS

In the context of the current OSHA PEL for 1,3-butadiene (1000 ppm) and the ACGIH TLV of 10 ppm, the NIOSH study results indicate that the control programs in the monomer industry appear to maintain personal exposures below the applicable limits. However, because of certain job-related exposures and the concern that 1,3-butadiene may present both a carcinogenic and teratogenic risk, the following additional control measures are recommended for monomer production plants that may not already be implementing such controls:

- 1) For obtaining quality control cylinder samples, plants should consider conversion to a closed-loop sampling system to lower the mean exposure of process technicians working in the process area.
- 2) Leaking pumps present an exposure potential to process technicians in the process area. The release of 1,3-butadiene from such equipment can be controlled through the use of dual mechanical seals. Plants should consider retrofitting of pumps having single mechanical seals with the more effective dual mechanical seals.
- 3) Because magnetic gauges are known to limit the release of 1,3-butadiene (and hence exposures to process technicians in the loading area) during the loading of rail cars, plants should consider a program to convert to 100 percent magnetic gauges for monitoring rail car filling operations.
- 4) As evident from the monitoring results for laboratory technicians conducting cylinder voiding, workers assigned to this task may be exposed to relatively high levels of 1,3-butadiene. Consideration should be given to the use of a laboratory hood or a vacuum exhaust with an enclosure for cylinder voiding. Furthermore, workers should be trained in the proper conduct of tasks such as cylinder voiding and cylinder sampling.
- 5) Maintenance technicians should use respirators with organic vapor cartridges when performing maintenance-related activities on process equipment.

As evident from the results of the NIOSH monitoring study, the use of analytical methods specific to 1,3-butadiene is preferred for assessing 1,3-butadiene exposures. The new NIOSH sampling and analytical method for 1,3-butadiene is recommended in areas of potentially low exposures and where there is a potential for interference with other C₄ compounds.

REFERENCES

1. Matanoski GM, Schwartz L, Sperrazza J., Tonascia J.: Mortality of workers in the styrene-butadiene rubber polymer manufacturing industry. Final report. Unpublished report submitted to The International Institute of Synthetic Rubber Producers, Inc. by Johns Hopkins University School of Hygiene and Public Health, Baltimore, Maryland (June 1982).
2. Downs TD, Crane MM, Kim KK: Mortality among workers at a butadiene production facility. Report concerning Neches Butane, Port Neches, Texas. Submitted by Research Statistics, Inc., to Texaco, Inc. (October 18, 1985).
3. Meinhardt TJ, Lemen RA, Crandall MS, Young, RJ.: Environmental epidemiologic investigation of the styrene-butadiene rubber industry: Mortality patterns with discussion of the hematopoietic and lymphatic malignancies. Scan J Work Environ. Health 8:250-259 (1982).
4. Kirk-Othmer Encyclopedia of Chemical Technology. Third Edition. Butadiene, John Wiley & Sons, New York, New York, Vol. 4 , pp. 313-337 (1979).
5. Tatken R, Lewis RJ (ed): Registry of Toxic Effects of Chemical Substances. 1981-2 edition. DHHS (NIOSH) Publication No. 83-107. U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, Cincinnati, Ohio, Volume 1 (June, 1983)
6. Cox JP: Odor Control and Olfaction. Edited by Ralph B. Duclos, Pollution Sciences Publishing Company, Lynden, Washington, p. 161 (1975).
7. Owen PE: The toxicity and carcinogenicity of butadiene gas administered to rats by inhalation for approximately 24 months. Final Report. Volumes 1-4, Addendum. Unpublished report submitted to the International Institute of Synthetic Rubber Producers, Inc. by Hazleton Laboratories Ltd, Harrogate, England (November 1981).
8. Powers M: Board Draft of NTP technical report on the toxicology and carcinogenesis studies of 1,3-butadiene (CAS No. 106-99-0) in B6C3F₁ mice (inhalation studies). NTP-83-071/NIH Publication No. 84-2544. ¹ U.S. Department of Health and Human Services, Public Health Service, National Institutes of Health, National Toxicology Program (October 28, 1983).

9. Owen PE, Irvine LFH: 1,3-Butadiene: Inhalation teratogenicity study in the rat. Final Report. Unpublished report submitted to The International Institute of Synthetic Rubber Producers, Inc. by Hazleton Laboratories Ltd, Harrogate, England (November 1981).
10. Carpenter CP, Shaffer CB, Weil CS, et al.: Studies on the inhalation of 1,3-butadiene; with a comparison of its narcotic effect with benzol, toluol, and styrene, and a note on the elimination of styrene by the human. J Ind Hlth Tox 26(3):69-78 (1944).
11. Occupational Diseases: A Guide to Their Recognition. Revised Edition. DHEW (NIOSH) Publication No. 77-181. U.S. Department of Health, Education, and Welfare, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, Cincinnati, Ohio pp. 138-139 (June 1977).
12. Weaver NK: International Labor Organization Encyclopedia of Occupational Health and Safety. Third (Revised) Edition, 1,3-butadiene. International Labor Office, Geneva, Volume 1 A-K, pp. 347-348 (1982).
13. American Conference of Governmental Industrial Hygienists; Threshold Limit Values of Air-borne Contaminants for 1968, Recommended and Intended Changed. ACGIH, Cincinnati, Ohio (1968).
14. Code of Federal Regulations, U.S. Department of Labor, Occupational Safety and Health Administration, 29 CFR 1910.1000, Table Z-1 (1982).
15. American Conference of Governmental Industrial Hygienists; TLVs^R Threshold Limit Values for Chemical Substances and Physical Agents in the Work Environment and Biological Exposure Indices with Intended Changes for 1986-87. ACGIH, Cincinnati, Ohio (1986).
16. National Institute for Occupational Safety and Health, Cincinnati, Ohio. Current Intelligence Bulletin No. 41 - 1,3-Butadiene. DHHS (NIOSH) Publication No. 84-105 (February 9, 1984).
17. Chemical Week. Butadiene Producers Travel a Rough Road (November 6, 1985).
18. U.S. Environmental Protection Agency, Washington, D.C. EPA Advance Notice Initiating Regulatory Action to Determine Ways to Control Exposure to 1,3-Butadiene. Published in the Federal Register of May 14, 1984 (49 FR 20524).
19. PEI Associates, Inc., Cincinnati, Ohio. Control of Occupational Exposure to 1,3-Butadiene at Monomer Production Facilities. Prepared for U.S. Environmental Protection Agency, Office of Pesticides and Toxic Substances, Washington, D.C. (February 22, 1985).
20. U.S. International Trade Commission. Synthetic Organic Chemicals, United States Production and Sales: 1979 (1980).

21. U.S. International Trade Commission. Synthetic Organic Chemicals, United States Production and Sales: 1984 (1985).
22. SRI International, Menlo Park, California. 1984 Directory of Chemical Producers, 1983: United States of America (1984).
23. Kirk-Othmer Encyclopedia of Chemical Technologies, 3rd Edition, Vol. 9, Ethylene. John Wiley and Sons, New York, New York (1980).
24. The Petroleum Publishing Company. U.S. Petrochemicals, Technologies, Markets, and Economics. Arthur M. Brownstein, Ed (1972).
25. SRI International, Menlo Park, California. Chemical Economics Handbook (1985).
26. Standifer, R. L. Butadiene. Organic Chemicals Manufacturing. Volume 10: Selected Processes. Report 7. Prepared for U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina (1980).
27. Hahn, Albert V. G. The Petrochemical Industry, Market and Economics, McGraw-Hill, Inc. (1980).
28. Hutson, T., Jr., R. D. Skinner, and R. S. Logan. Phillips' New Butadiene Process. Hydrocarbon Processing (June 1974).
29. National Institute for Occupational Safety and Health, Cincinnati, Ohio. NIOSH Manual of Analytical Methods. 3rd Edition. Vol. 1 DHHS (NIOSH) Publication No. 84-100 (1984).
30. Lunsford RA, Gagnon Y: NIOSH Manual of Analytical Methods. 3rd Edition. Method 1024. U.S. Department of Health and Human Services, DHHS (NIOSH) Publication No. 84-100 (1984), 1986 Supplement, in press.
31. PEI Associates, Inc., Cincinnati, Ohio. Analysis of Occupational Exposure to 1,3-Butadiene in the Monomer Production Industry. Prepared for U.S. Environmental Protection Agency, Office of Pesticides and Toxic Substances, Washington, D.C. (January 20, 1987).
32. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. VOC Fugitive Emissions in Synthetic Organic Chemicals Manufacturing Industry - Background Information for Proposed Standards. EPA-450/3-80-033a (November 1980).
33. Leidel NA, Busch KA, Lynch JR: Occupational Exposure Sampling Strategy Manual. U.S. Department of Health, Education, and Welfare. National Institute for Occupational Safety and Health, Cincinnati, Ohio (January 1977).

APPENDIX A

NEW NIOSH SAMPLING AND ANALYTICAL
METHOD FOR 1,3-BUTADIENE

FORMULA: C₄H₆, CH₂=CHCH=CH₂

1,3-BUTADIENE

M.W.: 54.09

METHOD: 1024
ISSUED: 5/15/86

OSHA: 1000 ppm
NIOSH: potential carcinogen [1]
ACGIH: 10 ppm; suspect carcinogen
(1 ppm = 2.21 mg/m³ @ NTP)

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

SYNONYMS: CAS #106-99-0

SAMPLING	MEASUREMENT
SAMPLER: SOLID SORBENT TUBE (coconut charcoal, 400- and 200-mg in separate tubes)	! TECHNIQUE: GAS CHROMATOGRAPHY, FID ! ! ANALYTE: 1,3-butadiene !
FLOW RATE: 0.01 to 0.5 L/min	! DESORPTION: 4 mL methylene chloride; 30 min !
VOL-MIN: 3 L -MAX: 25 L @ 100 ppm	! INJECTION: 1 µL !
SHIPMENT: separate front and back tubes, chill below -4 °C	! TEMPERATURE-INJECTION: 200 °C ! -DETECTOR: 250 °C ! -COLUMN: see APPENDIX A !
SAMPLE STABILITY: at least two months for quality assurance blind spikes stored in a freezer	! CARRIER GAS: Helium ! ! MAKEUP GAS: Nitrogen, 30 mL/min !
BLANKS: 10% of samples	! COLUMNS: fused silica, 10-m x 0.50-mm ID ! 1.8-µm CP WAX 57 CB (backflushable ! pre-column), and 50-m x 0.32-mm ID ! Al ₂ O ₃ /KCl PLOT (see APPENDIX A) !
! . . .	
! CALIBRATION: vapor-spiked sampling media !	
! RANGE: 1.1 to 480 µg per sample !	
! ESTIMATED LOD: 0.2 µg per sample !	
! PRECISION (s _p): 0.025 !	
! . . .	
APPLICABILITY: Assuming 25-L sampling volumes: the upper limit of the sampler is 220 mg/m ³ (100 ppm); the analytical range covers 0.04 to 18 mg/m ³ (0.02 to 8 ppm); at higher levels, desorbed samples may require dilution; below 0.9 mg/m ³ (0.4 ppm), the desorption efficiency falls below 75% and allowance should be made for decreased accuracy.	
INTERFERENCES: Pentane, methyl acetylene, or vinylidene chloride may chromatographically interfere at high levels. High humidity (>80% RH) or other hydrocarbons present at permissible levels may significantly decrease the sampler's capacity for 1,3-butadiene.	
OTHER METHODS: This method revises S91 [2].	

REAGENTS:

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

*See Special Precautions.

EQUIPMENT:

1. Sampler: Tandem charcoal tubes. Each tube is flame-sealed glass (8.5 cm long, 8-mm OD, 6-mm ID), has plastic caps for resealing, and contains activated coconut shell charcoal (such as SKC Lot 120) preceded by silylated glass wool and followed by a 3-mm urethane foam plug. The front tube holds 400 mg charcoal. The back tube holds 200 mg.
2. Personal sampling pump, 0.01 to 0.5 L/min, with flexible connecting tubing.
3. Refrigerant, bagged (e.g., Blue Ice or dry ice), and insulated shipping container.
4. Gas chromatograph, flame ionization detector, integrator, and column (see APPENDIX A).
5. Ice, wet.
6. Vials, 5-mL, 2-mL, 1-mL, and other convenient sizes, with PTFE-lined septum caps.
7. Pipettes, TD, 4-, 2-, and 1-mL.
8. Syringes, gas-tight, 250-, 100-, 25-, and 10- μ L.
9. Beaker, 150-mL.
10. 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 carcinogen, teratogen, and reproductive hazard [1]. Methylene chloride is toxic, very volatile, and a suspect carcinogen [3]. Work should be performed in a well-ventilated fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Immediately before sampling, break ends of sampler tubes. 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 0.5 L/min for a sample size of 3 to 25 L.
4. Separate the tubes, cap, and pack securely for shipment. Chill below -4°C during shipment and storage.

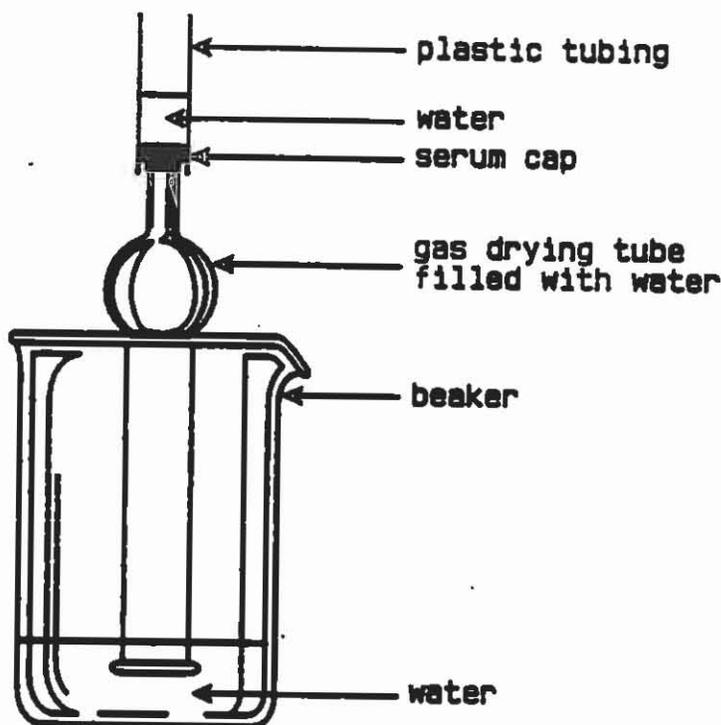
SAMPLE PREPARATION:

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 cap 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. Even a slight obstruction (e.g., flakes of PTFE from the plunger tip which obstruct the needle) 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 μL of 1,3-butadiene gas in 1 mL solution, and both 200 and 50 μL of gas in 4 mL solution:
- 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.



- Pipet 1 or 4 mL of methylene chloride into a 1- or 5-mL vial, cap, and thoroughly chill.
 - Take a known amount (50 or 200 μL) of 1,3-butadiene from the drying tube with a 100- or 250- μL gas-tight syringe. Bracket the gas in the syringe with small amounts of water (5 to 10% of syringe volume) 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.
 - Slowly inject the 1,3-butadiene and water below the surface of the methylene chloride.
 - 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 μL 1,3-butadiene gas per sample:
- Break ends of larger sampler and attach to personal sampling pump with flexible tubing.
 - Take pure gas (50 or 200 μL , as in step 9.c) for the higher levels, or 40 μL of stock solution for lower levels.
 - 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.
 - Seal tube with plastic caps.
 - Store at temperature below $-4\text{ }^{\circ}\text{C}$ overnight, then desorb (steps 5 through 8).
 - Analyze media standards and blanks together with samples (steps 13 and 14).
 - Convert gas volumes to masses, correcting for compressibility and water vapor (see APPENDIX 8), and prepare a calibration graph (peak areas or heights vs. concentration of 1,3-butadiene taken in $\mu\text{g}/\text{mL}$).

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) with methylene chloride to extend the range of standards down to 0.1 µg/mL. 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. $DE = (\text{mass found} - \text{blank mass})/(\text{mass taken})$.
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 1024-1. 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.

NOTE: Vinylidene chloride, an impurity in methylene chloride, elutes just after 1,3-butadiene and may be used as an internal standard.

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 responses determined for triplicate standard solutions at each of five levels were linear over the range 0.3 to 440 µg per sample. The pooled s_p was 0.038. The estimated limit of detection was 0.02 µg/mL.

The capacity of a 400-mg charcoal sorbent section was 31 L for a sample at 80% RH and approximately 56 ppm 1,3-butadiene. When exposed to 0.7 and 2.5 mL of pure 1,3-butadiene gas followed by 80% RH air, breakthrough occurred after 35 L and 28.5 L, respectively. The corresponding respective time-weighted average concentrations were 20 and 88 ppm.

For the analysis of media standards at levels of 1.1, 4.4, 18, 125, and 480 µg per sample, the pooled s_p was 0.025, and the desorption efficiencies were 67%, 68%, 75%, 102%, and 97%.

respectively. Adding water to media standards just after spiking or during desorption had no significant effect on desorption efficiencies.

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 frozen 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 1,3-butadiene via calibrated sampling valve. The recovery was 102.2% versus media standards (corrected for desorption efficiency) and 96.8% versus standard solutions (uncorrected for desorption efficiency); the s_r of the response was 0.016. Subsequently, simulated samples were exposed to known amounts 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 with thermal conductivity detection. Media standards were prepared via calibrated sampling valves. The recovery from six simulated samples at 463 µg per sample was 101.6% versus media standards and 91.3% versus standard solutions; the s_r of the response was 0.047. At 45.3 µg per sample, the recovery was 112.3% versus media standards and 102.9% versus standard solutions; the s_r of the response was 0.048. At 4.64 µg per sample, the recovery was 80.3% versus media standards and 103.8% versus standard solutions; the s_r of the response was 0.011. In the latter experiment, the two lowest levels of media standards appeared to be high, possibly due to absorption and release of 1,3-butadiene by internal parts of the sampling valve. The study was repeated at 4.71 µg, with the three lowest levels of media standards prepared as in step 10. The recovery was 129.5% versus media standards and 91.2% versus standard solutions; the s_r of the response was 0.023. The s_r of the response 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), apparent biases may 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, based on the linear response and near-zero intercept observed for the standard solution calibrations and the higher than expected desorption efficiencies for the samples, there appeared to be a positive bias in the preparation of the simulated samples.

The method has been used in six industrial hygiene surveys, for a total of 621 samples, most of which were collected under conditions of high ambient temperature and humidity. Only two samples showed severe breakthrough ($W_b > W_f/10$). Results for field samples at levels as high as 7.3 mg per sample were not significantly changed by dilution and reanalysis. In all, over 2000 analyses were made over a period of six months without any deterioration of the chromatographic columns. During the course of the analyses, twenty sets of standard solutions and media standards were prepared and analyzed, each set consisting of triplicates at each of five levels corresponding to 1.08 to 1.10, 4.32 to 4.40, 17.3 to 17.6, 108 to 110, and 432 to 441 µg per sample. For the five levels of standard solutions, the respective pooled relative standard deviations of the observed responses were 0.093, 0.074, 0.059, 0.055, and 0.071. For each set of standard solutions, the deviations of the responses were determined relative to the line resulting from a weighted linear regression of response on concentration. The 95% confidence intervals for the mean relative deviations from linearity for the five levels were -0.002 ± 0.003 , 0.000 ± 0.003 , -0.020 ± 0.002 , 0.002 ± 0.002 , and -0.019 ± 0.002 , respectively. For the media standards, the respective pooled relative standard deviations for the observed responses at the five levels were 0.109, 0.080, 0.050, 0.064, and 0.037; the respective 95% confidence intervals for the mean percent recoveries relative to the standard solution calibrations were 60.4 ± 0.4 , 66.4 ± 0.3 , 70.5 ± 0.2 , 86.2 ± 0.3 , and 91.2 ± 0.2 .

The analysis of quality assurance blind spikes provided additional data indicating that samples were stable when stored below -4°C , and that average recoveries, calibrated against media standards, ranged from 96 to 107%. Seventy-seven blind spikes were prepared at six levels, 19.9 to 21.9, 48.6 to 52.6, 104 to 110, 199 to 219, 398 to 438, and 663 μg per sample, stored in a freezer, and analyzed along with the field samples. The storage times ranged from 3 to 134 days; the average was 59 days. For the six levels of blind spikes, the respective relative standard deviations for recoveries were 0.210, 0.092, 0.054, 0.091, 0.126, and 0.056; the respective 95% confidence intervals for the mean recoveries were 0.986 ± 0.032 , 0.961 ± 0.014 , 0.994 ± 0.008 , 1.029 ± 0.015 , 1.064 ± 0.021 , and 1.074 ± 0.021 . Prior to linear regression of the recoveries versus the amounts spiked and/or days stored, three results, two high and one low, were determined to be outliers by application of one-sided Grubbs tests [4] at the 2.5% significance level and were dropped from the data set. Linear regression of percent recovery on days stored for the data segregated by level resulted in respective slopes and 95% confidence intervals of 0.060 ± 0.080 , 0.005 ± 0.128 , -0.003 ± 0.092 , 0.060 ± 0.179 , 0.249 ± 0.188 , and 0.018 ± 0.247 percent per day. Thus, the only statistically significant correlation between recovery and days stored was at the next to highest level, for a gain rather than loss over time. Over all levels, the slopes and 95% confidence intervals for recovery versus amounts spiked and days stored were 0.017 ± 0.009 percent per μg and 0.045 ± 0.051 percent per day, respectively. Thus, according to the latter model: the recovery for the blind spikes increased at a rate corresponding to approximately 11% over the range prepared; as stored, the blind spikes appeared to be stable — the 95% confidence interval of the slope over time indicated a maximum gain of 5.7% or loss of 0.4% during the average 59-day storage period.

REFERENCES:

- [1] NIOSH Current Intelligence Bulletin 41, "1,3-Butadiene," U.S. Department of Health and Human Services, Publ. (NIOSH) 84-105 (1984).
- [2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 2, S91, U.S. Department of Health Education, and Welfare, Publ. (NIOSH) 77-157-8 (1977).
- [3] NIOSH Current Intelligence Bulletin 46, "Methylene Chloride," U.S. Department of Health and Human Services, Publ. (NIOSH) 86-114 (1986).
- [4] Grubbs, F. E. "Procedures for Detecting Outlying Observations in Samples," *Technometrics*, V. 11, No. 1, 1-21 (February 1969).
- [5] MacCallum, R. N., and J. J. McKetta. "Low Pressure Z_5 of C_4 Hydrocarbons," *Hydrocarbon Process. Petrol. Refiner*, V. 42, No. 5, 191-4 (May 1963).

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

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

Any column which separates 1,3-butadiene from the other substances present, and which otherwise provides satisfactory chromatographic performance, is acceptable. The column specified in NIOSH Method S91 [2] is 6-m x 3-mm OD stainless steel, packed with 10% FFAP on 80/100 mesh Chromosorb W AW-DMCS. It provides a convenient separation of 1,3-butadiene from the desorbing solvent. However, if other C₄ to C₆ hydrocarbons are present, interferences are likely. For the development of this method, a 50-m x 0.32-mm ID fused-silica porous-layer open-tubular (PLOT) column coated with Al₂O₃/KCl (Cat. # 7515, Chrompack, Bridgewater, NJ) was chosen as the analytical column because it provides a very efficient separation at temperatures above ambient. However, water from the samples deactivates the aluminum oxide, reducing retention times, and high-boiling or polar substances may accumulate on the column and irreversibly degrade the separation. The degradation was eliminated by using a backflushable pre-column, i.e., 10-m x 0.5-mm ID fused-silica CP Wax 57 CB (Cat. # 7648, Chrompack, Bridgewater, NJ). 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 Hewlett-Packard 5880A gas chromatograph with split-splitless capillary inlet systems installed in the "B" and "C" injector positions. The only change to the "B" system involves the normally closed (NC) port of the "B" solenoid valve. Originally, it was connected to the capped port of the tee in the "B" septum purge line. (If desired, switching between normal operation of the "B" system and backflushable pre-column operation could be easily achieved by adding a manually operated three-way valve.) Replumb the components of the "C" system as shown, and extend lines from the normally open (NO) port of the "C" solenoid and the "C" backpressure regulator into the oven. Connect the lines and columns with a zero-dead-volume cross (e.g., Part # ZX1, Valco, Houston, TX) and graphite ferrules.

Set the initial oven temperature to 50 °C and the "C" backpressure regulator to 185 kPa. With the solenoid valves activated (inject mode), set the "C" flow control to 20 mL/min and the "B" controls so that the effluent from the analytical column and the "C" split vent total 10 mL/min. Then, with the solenoid valves deactivated (backflush or normal mode), adjust the "B" backpressure regulator until the flow from the "C" split vent returns to the value previously measured. This establishes a reverse flow of 10 mL/min through the pre-column. Program the oven to hold the initial temperature (50 °C) for 2 min, then rise to 120 °C at 20 °C/min, and hold for 8 min. Adjust the time from injection to backflush by injecting standards and progressively decreasing the time from 2 min until the methylene chloride peak is removed without attenuating the butadiene response. It may be necessary to clear higher hydrocarbons from the analytical column by programming the oven to 200 °C at 30 °C/min and holding 4 min. Program the solenoid valves to be activated at the end of each run to prepare for the next injection.

Using the backflushable pre-column, there remains a slight problem with retention drift. While in inject mode, the pre-column strips residual water from the carrier gas. This activates the aluminum oxide surface of the analytical column and causes retention to increase. The effect is most noticeable when starting up after the system has been idle. When beginning a sequence of samples, it is advisable to analyze solvent blanks until the retention drift (e.g., of vinylidene chloride) becomes tolerable.

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

MacCallum and McKetta [5] 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 , 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:

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

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 ($\text{g} \cdot \text{mol}^{-1}$)
 62.36 = gas constant ($\text{mm Hg} \cdot \text{L} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)
 273.2 = absolute temperature of 0 °C (K)

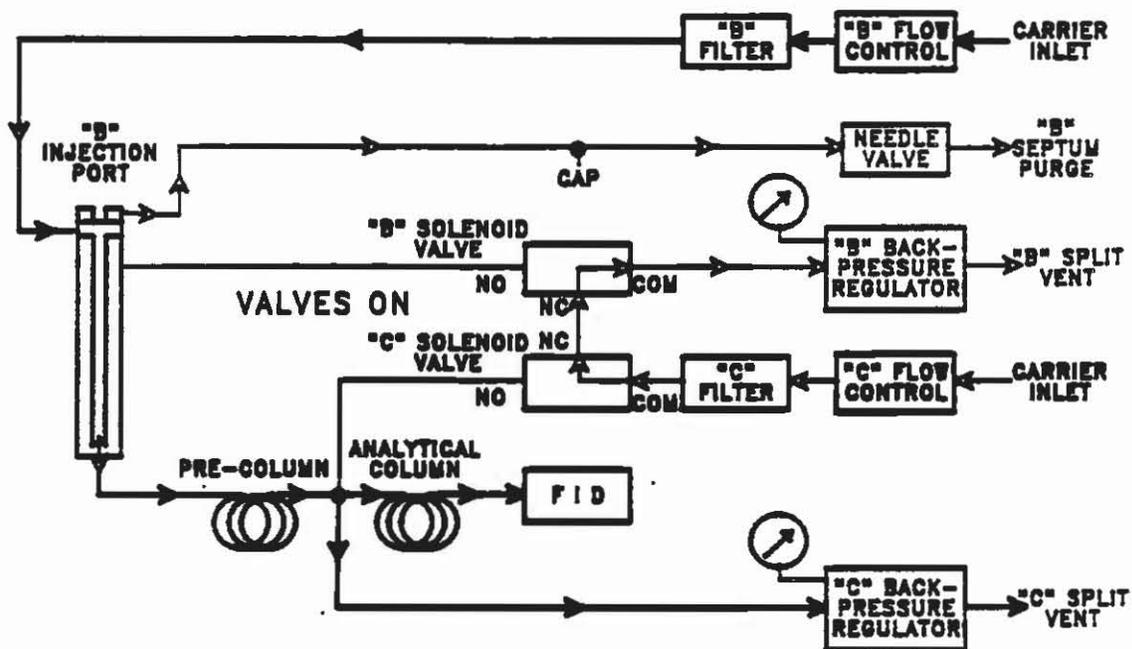


Figure 1. Flow diagram for pre-column system in inject mode.

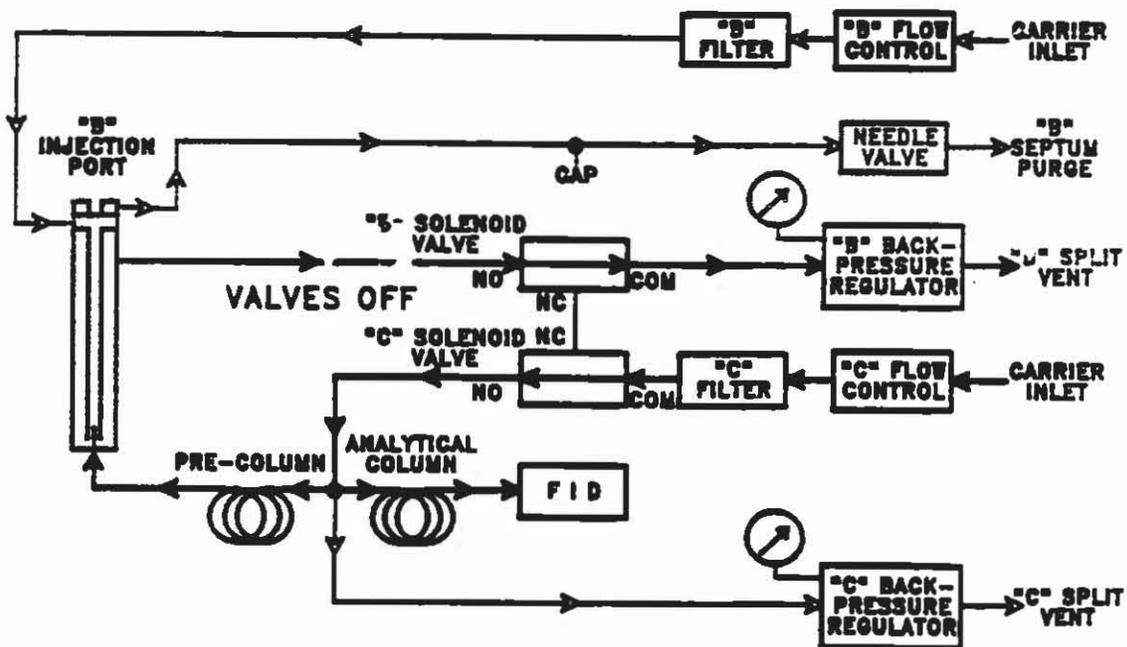


Figure 2. Flow diagram for pre-column system in backflush (normal) mode.

APPENDIX B

NIOSH PERSONAL AND AREA MONITORING
DATA COLLECTED AT PLANTS, A, B, C, AND D

Table B-1. Personal sampling data collected by NIOSH at Plant A.

Job description	Date	Sample ID	Air volume, liters	Duration, min.	Concentration, ppm
Process technician/ process area	3/26	A-5	19.5	90 ^c	0.36
	3/26	A-7	21.3	506	1.71
	3/27	A-56	20.9	460	0.57
	3/27	A-68	22.8	470	0.18 ^a
	3/28	A-26	22.5	457	0.74
	3/28	A-32	23.7	489	0.37
Process technician/ loading area	3/27	A-60	10.9	213	0.30
Process technician/ control room	3/26	A-4	24.1	485	<0.02 ^b
	3/27	A-78	20.7	466	<0.02 ^b
	3/28	A-18	21.8	447	<0.02 ^b
Lab analyst					
Wet	3/26	A-3	23.3	492	0.15
	3/27	A-61	23.9	486	0.07
	3/28	A-31	23.3	484	0.05 ^a
GC	3/26	A-1	21.8	478	0.87
	3/27	A-62	22.8	487	0.03 ^a
	3/28	A-25	23.5	483	0.62

^a Laboratory analysis of analyte was below limit of quantitation (4 µg/sample).

^b Laboratory analysis of analyte was below limit of detection (1 µg/sample).

^c Short term samples not time weighted.

Table B-2. Area sampling data collected by NIOSH at Plant A.

Work environment	Date	Sample ID	Air volume, liters	Duration, min.	Concentration, ppm	
Process/pump alley	3/26	A-14	21.2	486	1.23	
	3/27	A-65	24.0	477	0.17	
	3/27	A-70	24.4	479	0.24	
	3/28	A-20	19.2	424	0.07 ^a	
	3/28	A-21	21.7	452	0.09	
Process/railcar loading	3/27	A-52	9.5	196	0.10 ^a	
	3/27	A-53	9.8	195	0.22	
Process/control room	-	-	-	-	-	
Storage area/tank farm	3/26	A-8	24.2	503	0.15	
	3/26	A-9	23.3	477	1.76	
	3/26	A-10	24.4	483	23.80 ^c	
	3/28	A-28	20.3	456	12.77 ^c	
	3/28	A-30	24.1	470	0.53	
Laboratory Wet	3/26	A-2	21.2	498	0.12	
	3/27	A-48	23.3	485	0.06 ^a	
	3/28	A-27	21.4	481	0.03 ^a	
Laboratory Dry	3/26	A-6	24.9	439	0.06 ^a	
	3/27	A-24	22.6	450	0.04 ^a	
	3/28	A-67	21.7	486 ^d	0.07 ^a	
Cylinder voiding	3/27	A-76	7.6	15 ^d	<0.05 ^b	
	3/27	A-77	7.7	15 ^d	<0.05 ^b	
Background ambient air	North	3/26	A-16	19.4	474	<0.02 ^b
		3/27	A-55	15.4	346	<0.02 ^b
	East	3/26	A-13	23.0	473	<0.02 ^b
	South	3/26	A-11	17.5	393	<0.02 ^b
	West	3/26	A-12	25.4	565	<0.02 ^b
		3/27	A-69	18.9	370	<0.02 ^b

^a Laboratory analysis of analyte was below limit of quantitation (4 µg/sample).

^b Laboratory analysis of analyte was below limit of detection (1 µg/sample).

^c Pump leaked 1,3-butadiene.

^d Short term samples not time weighted.

Table B-3. Personal sampling data collected by NIOSH at Plant B

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	22.60	448	34.90
	4/9	T24	22.15	456	0.29
° Instrumentation	4/11	T54	21.81	430	2.55 ^b
	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 ^b
	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-3 (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-4. Area sampling data collected by NIOSH at Plant B

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 ^a
	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
° Chromato- graph	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).

Table B-5. Personal sampling data collected by NIOSH at Plant C.

Job description	Date	Sample ID	Air volume, liters	Duration, min.	Concentration, ppm*
Process technician/ process area	4/25	S54	21.2	436	0.09
	4/25	S53	22.9	437	1.34 ^b
	4/25	S28	21.5	435	0.19 ^b
	4/24	S32	6.4	13	6.96
	4/24	S38	2.7	5	<0.33 ^a
	4/23	S9	21.5	432	4.19
Process technician/ loading area					
Rail car	4/25	S44	9.9	442	0.46 ^b
	4/24	S35	11.6	260	0.12 ^b
	4/24	S36	23.9	474	0.13 ^b
Tank truck	4/25	S47	22.3	446	0.08
	4/24	S26	23.9	474	5.46
	4/23	S2	24.4	484	2.40
Process technician/ control room	4/24	S27	22.2	442	<0.04 ^a
	4/23	S8	21.1	425	<0.11 ^c
Process technician/ maintenance	4/23	S10	12.3	25	16.83
	4/23	S1	13.4	25	12.09
Laboratory technician					
Dry	4/25	S70	22.2	441	0.63 ^b
	4/24	S25	23.5	464	0.04 ^b
	4/23	S20	23.4	370	0.23
Wet	4/25	S62	22.4	451	0.12
	4/24	S37	8.1	159	0.89 ^b
	4/23	S23	22.4	449	0.28 ^b
	4/23	S17	22.4	449	0.28
Bomb voiding	4/25	S69	9.5	18	<0.10 ^c
	4/24	S46	7.0	13	<0.13 ^a
	4/23	S19	8.0	15	4.50

^a Laboratory analysis of analyte was below limit of detection (2 µg/sample) for first analytical run.

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

^c Laboratory analysis of analyte was below limit of detection (5 µg/sample) for second analytical run.

* Short-term samples were not time weighted to 8 hours.

Table B-6. Area sampling data collected by NIOSH at Plant C.

Work environment	Date	Sample ID	Air volume, liters	Duration, min.	Concentration, ppm
Process/pump alley	4/25	S61	10.0	188	0.86
	4/25	S51	19.6	440	1.58
	4/24	S31	20.8	410	1.04
	4/24	S23	20.1	412	0.09 ^a
	4/23	S14	22.4	416	1.73
	4/23	S6	18.7	420	0.58
Laboratory					
Dry	4/25	S55	22.3	441	0.67 ^b
	4/24	S40	24.7	462	<0.04 ^b
	4/23	S18	25.1	470	<0.09 ^b
Wet	4/25	S66	20.5	442	0.07
	4/24	S39	18.7	458	0.22 ^a
	4/23	S12	21.9	474	0.19 ^a
Process/loading area					
Tank truck	4/23	S3	22.7	450	0.12
	4/25	S52	21.5	433	0.15
	4/25	S57	22.0	435	0.10
	4/24	S24	25.8	472	1.92
Rail car	4/25	S59	9.3	195	8.23
	4/25	S58	10.1	203	2.94
	4/25	S41	10.7	221	1.14
	4/24	S21	8.8	177	2.04
	4/24	S49	9.0	181	1.40
	4/24	S50	7.7	153	64.29 ^b
	4/24	S22	22.6	450	<0.04 ^b
Background ambient air	4/25	S60	14.9	488	<0.06 ^b
	4/25	S56	17.8	498	<0.05 ^b
	4/24	S29	20.5	420	<0.04 ^b
	4/23	S16	20.9	415	<0.11 ^b
	4/23	S5	20.4	410	<0.11 ^b
	4/23	S4	20.2	416	0.13 ^a
	4/23	S7	19.4	395	<0.12 ^b

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

^b Laboratory analysis of analyte was below limit of detection (5 µg/sample).

Table B-7. Personal sampling data collected by NIOSH at Plant D

Job category	Date	Sample ID	Air volume, liters	Duration, min ^b	Concentration, ppm
Process technician/ process area (Control B Operator)	5/14	D1	23.4	451	0.46
	5/14	D6	13.1	260	0.27 ^a
	5/15	D32	24.4	452	1.23
	5/15	D42	22.4	454	2.98
	5/16	D51	23.0	452	2.37
	5/16	D57	21.4	437	0.70
Process technician/ process area (Control B Operator)	5/14	D15	12.5	25	0.79
	5/15	D43	10.2	20	10.44
	5/15	D49	20.5	41	2.11
° Bomb sampling	5/16	D69	16.0	31	0.76
Process technician/ loading area (Control C - Loading Operator)	5/14	D13	21.6	427	1.29
	5/15	D18	21.1	428	1.44
	5/16	D53	20.6	415	0.50
Process technician/ control room (Control A Operator)	5/14	D5	23.1	455	0.25
	5/15	D24	22.2	451	0.08 ^a
	5/16	D64	21.8	452	0.52
Laboratory technician					
° Wet	5/14	D4	23.4	463	0.25
	5/15	D40	24.2	490	0.63
	5/16	D60	19.8	410	1.96
° Dry	5/14	D3	23.7	467	0.36
	5/15	D41	24.2	498	1.04
	5/16	D52	22.4	418	0.34
° Supervisor	5/14	D2	21.5	392	0.10 ^a
	5/15	D31	23.6	463	0.08 ^a
	5/16	D59	19.8	395	0.09 ^a
Maintenance technician	5/14	D22	24.6	49	0.05 ^a
	5/14	D23	26.4	51	0.05 ^a
	5/15	D61	35.2	68	0.57
	5/15	D72	32.2	68	0.52
	5/16	D74	4.1	8	6.08

^a Laboratory analysis of analyte was below limit of quantification (11 µg/sample).

^b Short term samples not time weighted to 8-hours.

Table B-8. Area sampling data collected by NIOSH at Plant D

Work environment	Date	Sample ID	Air volume, liters	Duration, min	Concentration, ppm
Process area/pump alley	5/14	D9	18.7	396	0.36
	5/14	D19	20.4	377	0.42
	5/15	D21	24.9	493	0.77 ^b
	5/15	D35	23.9	494	<0.04 ^b
	5/16	D48	20.6	456	0.46
	5/16	D50	20.6	453	0.52
	5/16	D54	18.0	361	0.18 ^a
	5/16	D55	18.6	375	0.51
	5/16	D66	16.4	453	0.30
Process area/rail car loading	5/14	D7	14.1	282	1.10
	5/14	D14	15.0	289	0.51
	5/15	D20	23.2	463	0.21
	5/15	D34	21.2	464	50.43
	5/16	D63	19.8	422	0.09 ^a
Process area/rail car unloading	5/14	D10	14.4	280	29.29
	5/14	D11	14.3	278	1.51
	5/15	D26	9.8	194	1.14
	5/15	D33	9.4	190	30.33
	5/16	D58	20.3	422	5.80
	5/16	D62	16.5	324	8.79
Laboratory					
° Dry	5/15	D39	16.6	365	0.11 ^a
Background ambient air					
North	5/14	D16	21.1	413	0.08 ^a
	5/15	D27	17.6	487	0.15 ^a
	5/16	D65	19.6	432	0.37
East	5/14	D12	18.1	406	<0.05 ^b
	5/15	D37	22.9	489	<0.04 ^b
	5/16	D67	20.3	430	<0.04 ^b
South	5/14	D8	15.9	423	<0.06 ^b
	5/15	D38	20.3	481	0.07 ^a
	5/16	D56	17.9	444	<0.05 ^b
West	5/14	D17	20.1	427	<0.02 ^b
	5/15	D25	22.0	487	0.50 ^b
	5/16	D68	20.7	418	<0.04 ^b

^a Laboratory analysis of analyte was below limit of quantification (11 µg/sample).

^b Laboratory analysis of analyte was below limit of detection (2 µg/sample).