



INDUSTRYWIDE STUDIES REPORT
OF AN IN-DEPTH SURVEY AT
E.I. duPONT deNEMOURS AND COMPANY
SABINE RIVER WORKS
ORANGE, TEXAS

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August 25-28, 1986

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PURPOSE OF SURVEY:	To conduct an in-depth survey of a plant using 1,3-butadiene as a raw material, and to assess the extent of worker exposure, the status and nature of existing engineering controls, and current industrial hygiene programs.
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EMPLOYEE REPRESENTATIVES CONTACTED:	Employees are not unionized
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ABSTRACT

An in-depth industrial hygiene survey was conducted at the Sabine River Works of E.I. duPont de Nemours and Company in Orange, Texas on August 25-28, 1986. The purpose of the survey was to assess the extent of worker exposure at a 1,3-butadiene processing facility and to determine the status and nature of existing engineering controls and industrial hygiene programs. The impetus for this investigation came from recent toxicological studies that have identified 1,3-butadiene as an animal and potential human carcinogen.

The Sabine River Works, which was constructed in 1946, began producing adiponitrile (ADN) with its present technology in 1971. The plant has a capacity to produce 490 million pounds/year of ADN by synthesis of 1,3-butadiene and hydrogen cyanide. The 1,3-butadiene monomer is delivered to the site by barge and pipeline. DuPont uses ADN primarily for captive use in the production of hexamethylenediamine (HMDA), which is a principal ingredient in the production of nylon-66.

During the in-depth survey, descriptive information was collected on the company's control technology, workforce, past employee exposures, means of recordkeeping, and medical, safety, and industrial hygiene programs. A detailed industrial hygiene monitoring effort was conducted by NIOSH to characterize employee exposures to 1,3-butadiene for the ADN process.

Personal and area monitoring was performed using a new sampling and analytical method developed by NIOSH. Personal exposures were characterized for all job categories with potential for exposure to 1,3-butadiene, and area concentrations were determined for nine work environments and at points along the plant perimeter. Arithmetic and geometric mean full-shift exposures across all job categories, with the exception of the shipping technicians, were found to be below 0.20 ppm. The arithmetic and geometric mean full-shift exposures for two shipping technicians were 14.6 and 4.69 ppm, respectively. A shipping technician received the highest full-shift-exposure of 28.5 ppm. The same shipping technician also received the highest short-term exposure of 210 ppm during the sampling of a barge for 1,3-butadiene. Arithmetic and geometric mean area concentrations in the work environments were found to be at or below approximately 0.60 ppm. 1,3-Butadiene concentrations at the plant perimeter were very low (≤ 0.02 ppm).

Recommendations are made regarding the use of additional controls to reduce worker exposures to the shipping technicians.

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INTRODUCTION

The total U.S. demand for 1,3-butadiene in 1985 was 3.25 billion pounds,¹ of which about 2.45 billion pounds was domestically produced. The predominant uses of 1,3-butadiene are in the manufacture of synthetic rubbers, plastics, and resins. Of the synthetic rubbers, styrene-butadiene rubber (SBR) and polybutadiene rubber (PBR) make up more than half of the demand for 1,3-butadiene, representing 45 and 20 percent, respectively, of the total 1,3-butadiene consumption.

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

The offspring of pregnant rats exposed to 1,3-butadiene at 8,000 ppm had major skeletal defects. In addition, fetal toxicity was observed when pregnant dams were exposed to 200 ppm, 1,000 ppm, and 8,000 ppm.⁴

Epidemiological studies of workers employed in facilities producing SBR have indicated an increased, but not statistically significant, risk of mortality from leukemia and from neoplasms of the lymphatic and hematopoietic tissues.^{5,6}

Based on these data, the National Institute for Occupational Safety and Health (NIOSH) recommends that 1,3-butadiene be regarded as a potential occupational carcinogen and teratogen and as a possible reproductive hazard.⁷ Because of the number of workers potentially exposed to 1,3-butadiene and the resulting potential health risk, NIOSH researchers are conducting an extent-of-exposure study of the 1,3-butadiene polymer production industry.

The NIOSH study of the polymer industry is divided into three phases. The first phase consisted of a literature review, a definition of the industry, and the development of a study design. The second phase involved conducting a series of walk-through surveys at 17 plants producing various types of 1,3-butadiene polymers (or other chemicals), and then selecting facilities for in-depth industrial hygiene surveys. The nature of the process, the process controls, available information on exposure levels, number of workers potentially exposed, and the company's industrial hygiene, safety, and medical programs are discussed in a walk-through report written for each of the facilities visited. The final phase involved conducting in-depth industrial hygiene surveys at five selected facilities. The site selection criteria for the in-depth surveys included type of polymer (or chemical) produced, type of process, number of polymers (or chemicals) produced at the plant, age of the plant, and the number of potentially exposed employees at the plant. As part of the final phase, an in-depth survey report has been written for each of the companies visited.

APPLICABLE STANDARDS AND RECOMMENDED LIMITS

The current Permissible Exposure Limit (PEL) enforced by the Occupational Safety and Health Administration (OSHA) for 1,3-butadiene is 1000 ppm for an 8-hour time-weighted averaged (TWA).⁸ OSHA has 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.⁹ A Threshold Limit Value (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.⁷

HISTORY AND DESCRIPTION OF THE PLANT

The Sabine River Works, located in Orange, Texas, is owned and operated by E.I. duPont de Nemours and Company. The plant was constructed on 750 acres in 1946; the adiponitrile (ADN) process, which consumes 1,3-butadiene, was built in 1971. The plant has a capacity to produce 490 million pounds/year of ADN. ADN is captively used by DuPont in the production of hexamethylene diamine (HMDA), which is a principal ingredient in the production of nylon-66.

Other products manufactured at the facility include HMDA, adipic acid, ethylene, high and low density polyethylenes, and ethylene copolymers.

PROCESS DESCRIPTION

Figure 1 is the process flow diagram for production of ADN. The 1,3-butadiene monomer is received by barge and pipeline from Texaco Chemical Company, Port Neches, Texas. It is dried using molecular sieves and continuously fed to the pentenenitrile synthesis unit where it is reacted with hydrogen cyanide (HCN) and reportedly totally consumed. The resulting pentenenitriles contain part-per-million concentrations of residual 1,3-butadiene at this point. The pentenenitriles may be sold commercially or refined further on-site. On-site processing begins with distillation for use in the next reaction, dinitrile synthesis. In the dinitrile synthesis unit, the mononitriles are further hydrocyanated for conversion to dinitriles. The resulting mixture of 6-carbon dinitriles is refined by distillation. The final product, ADN, a colorless liquid with the viscosity of water, is stored in tanks and then pumped via pipeline to the HMDA unit for hydrogenation. Some ADN (approximately 5 percent of the total production) is transported by barge to DuPont's plant in Victoria, Texas.

Most of the byproducts produced are burned in a boiler due to their fuel value. One of the mononitrile byproducts is sold as a commercial product. 1,3-butadiene content of this material is reported to be non-detectable by DuPont's standard laboratory analysis which has a limit of detection of 200 to 400 ppm by weight.

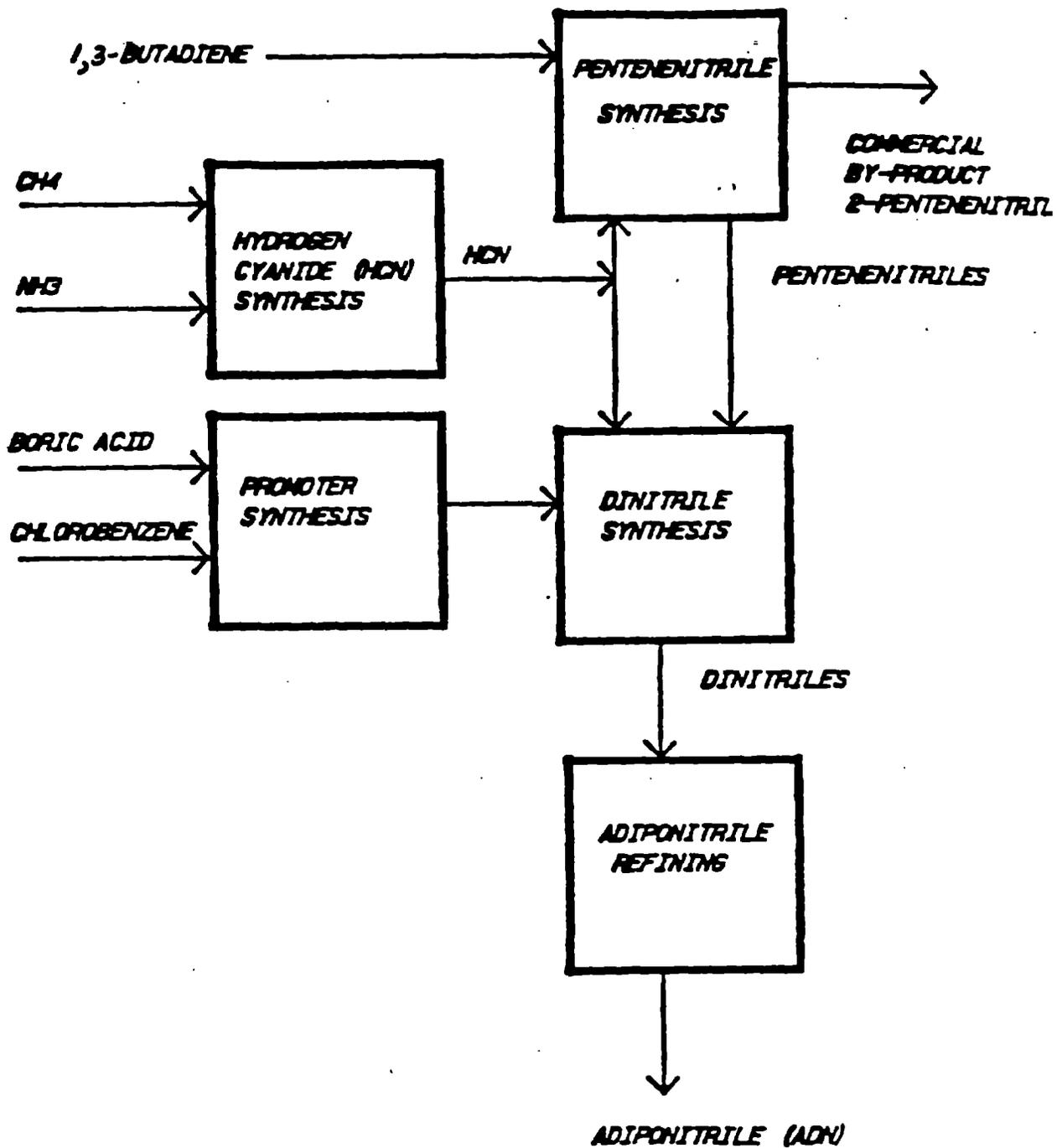


Figure 1. Process flow diagram for production of adiponitrile at DuPont's Sabine River Works in Orange, Texas.

All ADN produced at the plant is stored in nitrogen-padded storage tanks equipped with both conservation and emergency vents. Normal operating pressure is 4 inches of water. All process equipment is totally enclosed; process vapors are exhausted to a flare stack for burning.

Quality Control

Quality control (QC) is assured by distinct procedures during each step of ADN production. The QC method for each step in the process is as follows:

HCN Synthesis - Product quality is ensured by a combination of on-line analyzers, key temperature measurements, and spot sampling.

Promoter Synthesis - Product quality is ensured by tight control of the ingredients added to the batch reactions. In the continuous part of the process, quality is inferred by distillation column temperatures. Spot sampling is used for verification.

Pentenenitrile Synthesis - Quality of the pentenenitriles is inferred by temperatures in the reactors and the distillation columns. Spot sampling verifies these measurements. Sampling bulk 1,3-butadiene or 1,3-butadiene-containing streams is not routinely done. When sampling is required, however, gas bags at atmospheric pressure are used.

Dinitrile Synthesis - Quality of the dinitriles is inferred by on-line analysis of the dinitrile reactors and key temperatures in the subsequent distillation columns.

Adiponitrile Refining - Quality of refined dinitriles is inferred by column temperatures and verified by spot sampling.

The company has not conducted analysis of the ADN product for residual 1,3-butadiene. (NIOSH analyzed a bulk sample of ADN and found 1,3-butadiene to be non-detectable. The limit of detection was 0.04 ng/mg by weight.)

CONTROL DESCRIPTION

The DuPont Sabine River Works incorporates 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, while others have been added for a specific purpose. Some controls are designed to reduce worker exposures, whereas others are intended to abate environmental releases. Frequently, the environmental controls also function indirectly to reduce the level of toxic contaminants in the workplace air.

The survey team examined the process associated with ADN production at Sabine River Works to identify those controls that directly or indirectly reduce workplace exposures. Controls identified during the survey are presented by the process operation or work task that they are designed to control.

Engineering Controls

Several engineering controls are in place at the Sabine River Works facility that directly or indirectly control the release of 1,3-butadiene to the work environment.

A. Process Flow

Pumps in service at the barge dock and 1,3-BD storage sphere have single mechanical seals. Figure 2 is a schematic of a 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 mutual surface area. The faces are held together by a combination of pressures: pressure exerted by a mechanical spring and pump pressure transmitted through the liquid being pumped. Single mechanical seals represent an improvement over packed seals for protection against leakage. Ten pumps handling 1,3-butadiene in the ADN production building are equipped with dual mechanical seals flushed with high boiling dinitriles. Figure 3 is a schematic of a dual mechanical seal. In a dual mechanical seal, a liquid is circulated through the cavity between the two mechanical seals. The circulating liquid (dinitriles at the ADN plant) is maintained at a higher pressure than the process fluid. In this case, any leakage across the primary seal face causes the seal liquid to be released into the 1,3-butadiene being transferred. Any leakage across the secondary seal face causes the high boiling seal liquid to be released before the 1,3-butadiene, thus providing additional protection over a single mechanical seal. Centrifugal pumps on the process line and transfer pumps in the tank farm are overhauled every six months.

At the DuPont ADN plant, there are numerous valves that are in use at the ends of open pipes. These valves are normally used during the cleanup of the pipelines and equipment in the plant. DuPont's normal procedure is to use blind flanges on these lines as caps. In addition to the normal steps taken to prevent leaks from valves, DuPont has recently replaced 14 plug valves at the 1,3-butadiene molecular sieves with disk valves incorporating special seats, packing and gaskets in order to reduce both the potential for personnel exposure and flammable vapor cloud formation.

All major pieces of equipment and pipelines have relief valves, many of which were installed to meet ASME pressure codes. In addition, the 1,3-butadiene storage sphere is also equipped with a rupture disk. Potential releases of 1,3-butadiene from relief valves on process equipment are collected and routed to a flare.

B. Quality Control (QC) Samples

The QC program at DuPont's Sabine River Works requires workers to perform three major tasks: 1) collection of the 1,3-butadiene samples, 2)

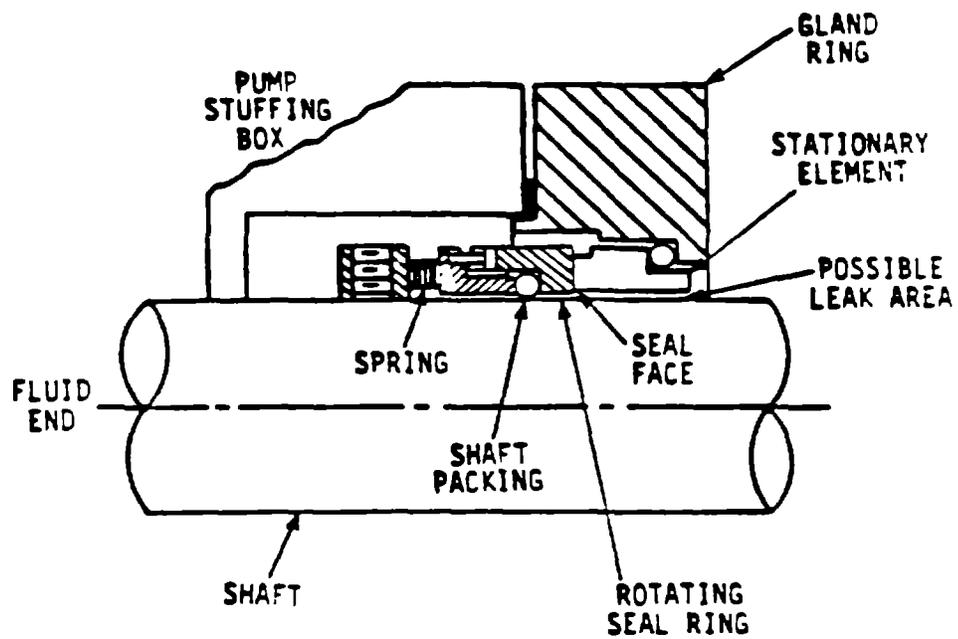


Figure 2. Diagram of a single mechanical seal.

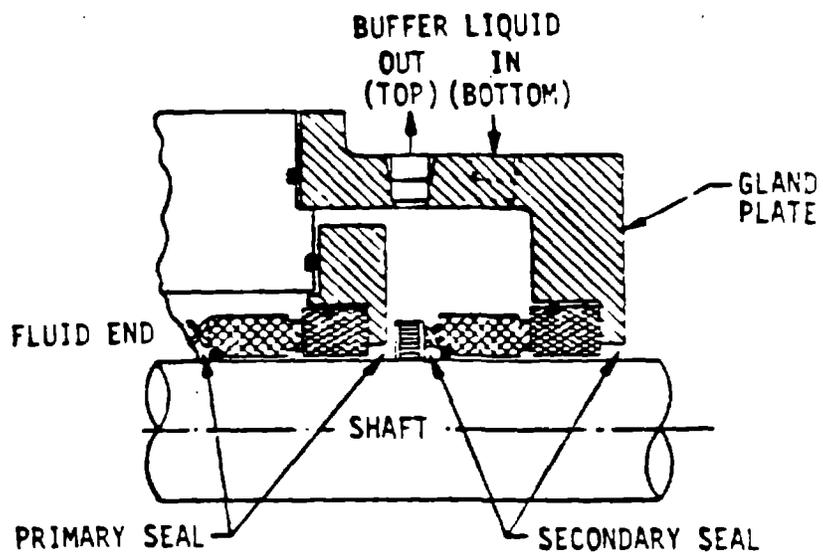


Figure 3. Diagram of a dual mechanical seal.
(tandem arrangement)

laboratory analysis of the samples, and 3) purging/cleaning of the sample cylinders.

No routine QC sampling of the 1,3-butadiene streams is performed in the ADN process; gas bags, however, are used whenever any sampling is required. There is thus minimal potential for exposure from QC sampling of the process. QC sampling, however, is performed on all incoming 1,3-butadiene prior to unloading of the barges. Shipping technicians collect QC samples with 500 cubic centimeter (cc) stainless steel sample cylinders. The sample cylinder is attached to an open-loop system by fittings and hoses to the high-pressure side of the sampling connection; valves are then opened to fill the cylinder. Cylinder sampling has the greatest potential for exposure to 1,3-butadiene. The use of closed-loop sampling systems as an engineering control measure was not observed at DuPont's Sabine River Works. Open-loop sampling permits the escape of 1,3-butadiene to the atmosphere, thereby potentially exposing the worker via inhalation and dermal routes.

Samples are analyzed in the laboratory by gas chromatography and wet chemistry tests both performed under a Class A laboratory hood. The mean face velocity measured during the survey in the laboratory hood (dimensions: 2 ft 6 in. x 1 ft 10 in.) was 158 linear feet per minute (lin ft/min), with a range of 110 to 180 lin ft/min. Sample cylinders are emptied inside the laboratory hood, following completion of the analyses. The general ventilation in the laboratory is designed for "once-through" air.

C. Transportation

The level of 1,3-butadiene in barges is monitored by two types of gauges: slip-tube and magnetic. The slip-tube gauges are the original equipment on each barge. Six magnetic gauges, however, were installed in 1983 to minimize personnel exposures during level checks of the barges. The magnetic gauges monitor the level of liquid from the full level down to a 12-inch depth. The slip-tube gauges measure the level below the 12-inch depth. The slip-tube gauge indicates the level of 1,3-butadiene by releasing a plume of 1,3-butadiene vapor to the ambient air. The vapor acts as a visual signal to the shipping technician that the 1,3-butadiene in the vessel has reached a predetermined level. This type of gauge can be considered an engineering control, to the extent that it negates the need for the process technician to be in close proximity to the tank port. The magnetic gauge, on the other hand, is a completely sealed metering system in which a magnetic ring or "doughnut" located inside the barge floats on the surface of the 1,3-butadiene. As the level of 1,3-butadiene in the barge changes, the ring rises over an enclosed shaft. Inside the shaft is a metered rod which projects out over the top of the barge. The extent of this projection provides an accurate measure of the level of 1,3-butadiene in the barge.

There is a vapor recovery system at the barge unloading area. In this area, DuPont has also installed a vent stack that is used during the

connection and disconnection of barges, to disperse 1,3-butadiene vapors and to prevent areas of high concentrations of 1,3-butadiene from forming at the ground level.

Administrative Controls

DuPont requires that certain decontamination procedures be followed during the repair, maintenance, or cleaning of process equipment. These procedures are designed to assure that maintenance workers are not overexposed to 1,3-butadiene during the performance of their tasks. Decontamination procedures include the draining of all process fluids into an enclosed and sealed sump system. The equipment is then steamed at 175 psig to remove residual organics, and purged with nitrogen. The resulting vapors are burned in a flare. After the equipment is opened, an explosimeter is used to ensure total decontamination of flammables. Explosibility must be at zero percent before maintenance can begin.

DuPont's decontamination procedures produce two effects, the latter of which can be classified as an administrative control:

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

PERSONAL PROTECTIVE EQUIPMENT

Required safety equipment at DuPont's Sabine River Works includes safety glasses, hard hats, and steel-toed safety shoes in the production areas. All operators in the ADN area must also wear nitrile butadiene rubber (NBR) gloves which are impermeable to the process organics (as determined by DuPont's Haskell Laboratory). Laboratory technicians wear rubber gloves during QC analyses and emptying of sample cylinders.

Operators and mechanics involved in sampling, stripping, and connection/disconnection procedures for barges use the following personal protective equipment to minimize the potential for exposure to 1,3-butadiene:

- ° MSA Ultra-Twin Full Face Organic Vapor Respirator or MSA Comfo II Half Face Organic Vapor Respirator, and coverall goggles.
- ° Heavy leather gloves.

Respirators are not routinely used in the nitrile section of the ADN process area where 1,3-butadiene is handled. The Sabine River Works facility uses approximately 600 respirator cartridges per year. The plant has a formal respirator program.

Showers and separate clothing change rooms are available. Lunchrooms are separate from the production area. Smoking areas are designated for use; these areas are reportedly free of process vapors.

DESCRIPTION OF THE WORKFORCE

DuPont employs 2,100 people at Sabine River Works, of which 305 (15 percent) are dedicated to ADN production. The majority of the employees, 210 of 305, work 8-hour day shifts which include some day shift mechanics. The production employees (95) work 12-hour rotating shifts. The nitrile area of the ADN process employs a total of 124 employees: 36 production (12-hour shift) workers and 88 (8-hour shift) day workers. (This is an area which DuPont identified as having potential for 1,3-butadiene exposure.) Only four employees per day (two process operators and two mechanics, one of each per shift) work in the Step I pentenenitrile synthesis area, where 1,3-butadiene is brought in as a raw material and is consumed in the synthesis reaction. ADN production-related job descriptions for potentially exposed employees are as follows:

Tank Farm Operator:	Responsible for monitoring the storage tanks. Obtains QC samples from the storage tanks.
Outside Operator:	Responsible for monitoring the equipment at the tank farm and at the multi-purpose storage tanks. Transfers QC samples to the laboratory. Drives truck and runs errands in the ADN production area.
Synthesis Operator A:	Responsible for monitoring the 1,3-butadiene equipment and the synthesis equipment for pentenenitrile synthesis. Obtains QC samples from the reactors. Decontaminates equipment prior to maintenance operations
Synthesis Operator B:	Responsible for monitoring the equipment for dinitrile synthesis. Checks for leaks on pumps. Obtains QC samples. Decontaminates equipment prior to maintenance operations.
ADN Recovery Operator:	Responsible for recovery equipment. Obtains QC samples from this equipment.
ADN Refining Operator:	Works in ADN product refining area. Obtains QC samples from the refining system and from the product storage tanks. There are a total of two operators per shift in the east and west sections of the refining area.

HCN Boiler Operator:
(Power Operator) Responsible for monitoring the flame arrestor, refrigeration unit, and condensate receivers in the HCN area. Regenerates 1,3-butadiene molecular sieves. Obtains QC samples of the feed water and the blowdown from the boiler.

Control Room Operator: Responsible for monitoring the control room equipment.

Shipping Technician: Responsible for operations involving unloading of 1,3-butadiene barges. Conducts barge sampling and stripping. Seventeen of the twenty-three qualified operators are licensed "tankermen," having passed the necessary examinations which define procedures for handling 1,3-butadiene barges.

Laboratory Technician: Performs gas chromatographic and wet chemical analyses of the 1,3-butadiene QC samples.

Maintenance Technician: Responsible for maintenance and repair of process equipment. Connects and disconnects barges for 1,3-butadiene unloading.

The workforce is 88 percent male. The turnover rate is estimated to be less than 3 percent, indicating a stable workforce. The mean age of the employees is 38.7 years.

DESCRIPTION OF PAST WORKER EXPOSURES

The process used to produce ADN has been basically unchanged since start-up in 1971.

DuPont has conducted personal monitoring for 1,3-butadiene since 1978. However, in 1976, Draeger detector tubes were used for area monitoring for 1,3-butadiene. Table 1 summarizes the data for employees exposed to 1,3-butadiene in the barge loading and unloading area, the ADN process area, and the analytical laboratory. The weighted mean of the 8-hour time-weighted average (TWA) mean exposures for all job categories is 4.1 ppm (n = 157). The TWA exposures for 1983-1985 are significantly lower than those for previous years; mean TWAs for all job categories during these years are at or below 1 ppm. DuPont has used three different sampling methods since 1976.

1976 = Draeger Detector Tubes
 1978 = DuPont P-200 Pump and Charcoal Tube
 1980-1985 = Pro-Tek Organic Vapor Air Monitoring Badge

All samples were analyzed by a gas chromatographic method similar to NIOSH Method S-91.¹⁰ N-pentane was used as a calibration standard.

TABLE 1. SUMMARY OF DuPONT'S PERSONAL MONITORING FOR 1,3-BUTADIENE AT SABINE RIVER WORKS, ORANGE, TEXAS, 1978-1985

Job category/ year	No. of samples (n)	Range, TWA ^a	Arithmetic mean, (n)
<u>BARGE LOADING AND UNLOADING AREA</u>			
<u>Shipping Technician, Sample Barge</u>			
1978	7	<0.01 - 31	5.1 (7)
1980	1	62.7	62.7 (1)
1981	13	<0.01 - 31.6	7.7 (13)
1982	22	<0.01 - 34.2 (162) ^b	5.0 (21)
1983	11	<0.01 - 1.2	0.3 (11)
1984	14	<0.01 - 8.6	1.0 (14)
<u>Shipping Technician, Unloading Barge</u>			
1978	12	<0.01 - >25 ^c	3.9 (12)
1981	5	<0.01 - <0.01	<0.01 (5)
1982	1	12.2	12.2 (1)
1984	2	<0.1 - <0.1	<0.1 (5)
<u>Shipping Technician - Clearing for Barge Connect</u>			
1981	5	<0.1 - <0.1	<0.1 (5)
<u>Shipping Technician - Stripping Barge</u>			
1981	7	<0.1 - 16 (147;865) ^b	10.7 (5)
1982	3	<0.1 - 3.4 (145) ^b	1.7 (2)
1983	2	<0.1 - <0.1	<0.1 (2)
1984	6	0.23	0.15 (6)
<u>Shipping Technician - Clearing for Disconnect</u>			
1981	3	2.8 - 35	24.2 (3)
1982	1	<0.1	<0.1 (1)
1984	1	<0.1	<0.1 (1)
<u>Mechanic - Connecting and Disconnecting Barge</u>			
1978	10	<0.1 - 2.3	0.6 (10)
1980	4	2.7 - 71 (543) ^b	39.9 (3)
1984	8	<0.1 - 0.7	0.1 (8)
1985	4	0.1 - 2.7	0.9 (4)

Job category/ year	No. of samples (n)	Range, TWA ^a	Arithmetic mean, (n)
<u>ADIPONITRILE PROCESS AREA</u>			
<u>Synthesis Operator A</u>			
1984	6	<0.01 - 0.04	0.02 (6)
<u>Refining Operator</u>			
1984	2	<0.01 - <0.01	<0.01 (2)
<u>ANALYTICAL LABORATORY</u>			
<u>Lab Technician</u>			
1983	1	<0.1	<0.1 (1)
1984	11	<0.1 - 1.4	<u>0.5 (11)</u>
			4.1 (157)

^a Time-weighted average (8-hr).

^b Suspect values (outlier).

^c Breakthrough observed into rear section of charcoal tube.

Under normal conditions, one 1,3-butadiene barge arrives every 7 to 10 days. The barge unloading process usually takes two shifts (24 hours) to complete. Under normal conditions, two shipping technicians are responsible for the unloading, sampling, and purging operations while two mechanics connect and disconnect the liquid/vapor lines from the unloading station to the pump.

Operators are potentially exposed to 1,3-butadiene while sampling 1,3-butadiene during the barge unloading operation. Barge stripping operations involve using an atmosphere slip-tube to measure the last 12 to 13 inches remaining in the barge. Operators are instructed to stand upwind of the vent when either operating the stripping slip-tube or purging the sample cylinder.

DESCRIPTION OF PERSONNEL RECORD SYSTEM

Personnel records are maintained on terminated as well as current employees. Upon retirement or termination, however, some items in the personnel folders of the employees are destroyed. Approximately 4000 records are on file, dating back to 1946. The records contain a work history as well as the following types of information:

1. Name
2. Social Security Number
3. Date of Birth
4. Work History
5. Termination Information
6. Benefits Package Information

DESCRIPTION OF MEDICAL, SAFETY, AND INDUSTRIAL HYGIENE PROGRAMS

Medical Program

The medical program serves all plant employees. There are two full-time physicians and one full-time physician's assistant. The medical team also has six registered nurses. Personnel trained in first aid (on each shift) include one nurse and eight laboratory analysts who also serve as ambulance drivers. All employees receive periodic physicals as well as pre-employment exams. Medical tests include the following: chest x-rays, hearing tests, vision tests, lung function tests, blood tests, and urine tests. Electrocardiograms (EKGs) are begun at age 30. The plant is located approximately three miles from the nearest hospital.

Safety Program

The Safety Superintendent is responsible for the safety and health programs at the plant. The Safety and Occupational Health Division, comprised of 10 employees, is responsible for an organized safety program at the Sabine River Works facility. Management has established a Central Safety and Health Committee with standing sub-committees. Each production area has an Area Safety Committee and an Area Occupational Health Coordinator. Monthly meetings are held with all personnel.

Personal protective equipment is required as part of the safety program, as discussed in the Personal Protective Equipment section of this report.

Industrial Hygiene Program

The industrial hygiene program is carried out by five full-time employees: Occupational Health Coordinator, Certified Industrial Hygienist, Area Specialist, Laboratory Technician, and Stenographer. Several part-time personnel are responsible for carrying out special sampling surveys such as those for noise, ventilation, and radiation. Each area of the plant has an Area Occupational Health Coordinator.

Since 1978, DuPont has conducted personal monitoring for 1,3-butadiene. In addition to 1,3-butadiene monitoring, air sampling is conducted at varying frequencies for the following substances: cyclohexane, dinitriles, pent-enitriles, diatomaceous earth, nickel, ammonia, asbestos, hydrogen chloride, hydrogen cyanide, benzene, and cresol.

Air monitoring techniques involve the use of several sample media: charcoal tubes, silica gel tubes, DuPont Pro-Tek organic vapor air monitors, or long-duration and spot-check detector tubes (area and personal monitoring).

SAMPLING STRATEGY

The in-depth survey was planned and scheduled to obtain full-shift (8-hour) sampling during normal production conditions. All job categories identified 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. 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 the in-depth survey, the survey team monitored for a total of four 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) maintenance activities, 4) tank farm operations, 5) ADN synthesis area operations, 6) ADN refining area operations, and 7) barge unloading area operations.

SAMPLING AND ANALYTICAL METHODS

A new sampling and analytical method for 1,3-butadiene was used by NIOSH during the DuPont in-depth survey. The new method is similar to the old NIOSH Method S-91 for 1,3-butadiene,¹⁰ but includes changes in both sampling apparatus and analytical procedure.¹¹ A brief summary of the method is presented here; more detailed information is provided in Appendix A.

Sampling, Transport, and Storage

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

Sampling pumps used during the survey were checked for significant air-flow deviation (greater than 5 percent) after each sampling period. To assure the quality of results, sample blanks and quality assurance spikes were generated, analyzed, and reported in accordance with NIOSH Quality Assurance/Quality Control procedures.¹⁰

Samples were collected with separable 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.

For this method, samples are collected with low-flow pumps at a flow rate of 0.05 to 0.5 liter per minute. Sample air volumes are generally limited to a minimum of 1 liter and a maximum of 25 liters.

Field samples were refrigerated during shipment and storage. Samples were considered to remain stable for at least 21 days when kept at -4°C .

Desorption and Analysis

All front sections and 17 percent of the back sections of the samples submitted were analyzed. Media standards and spiked charcoal tube standards were prepared. The field samples and the spiked standards were each desorbed with methylene chloride along with four blind spikes and three charcoal tube blanks. The analytical method followed was NIOSH Method 1024 (see Appendix A).

All analyses were performed using a Hewlett-Packard 5880 computer-controlled gas chromatograph (GC) equipped with an integrator and an auto-sampler with refrigerated sample trays (10°C). Helium was used as a carrier gas, and the detection was accomplished using a flame ionization detector (FID).

The resulting chromatograms were reconstructed by the main computer and were further examined in detail to confirm the identification of 1,3-butadiene by retention time. Vinylidene chloride, an impurity in the methylene chloride solvent, was used as an internal standard to monitor the quality of the

injections. Peak areas for 1,3-butadiene were corrected when the vinylidene chloride peak areas varied more than $\bar{x} \pm 2\sigma$. Seventeen samples that indicated concentrations of 1,3-butadiene above 8 $\mu\text{g}/\text{tube}$ were selected for analysis of their back sections.

To verify the presence of 1,3-butadiene, six samples exhibiting high 1,3-butadiene concentrations were submitted for analysis by GC-mass spectrometry. In addition, the sample which had the heaviest loading was further analyzed to identify other organics besides 1,3-butadiene. This sample indicated the following compounds to be present: cyclohexane, isooctane, and tetrahydrofuran.

The point at which an 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).¹⁰ For the 1,3-butadiene analyses performed, the LOD was 0.3 μg per sample, and the LOQ was 1.1 μg per sample. Twenty-eight percent of the samples indicated nondetectable 1,3-butadiene concentrations.

RESULTS

Personal Sampling

A total of 43 personal samples were collected over four shifts during the in-depth survey. These samples represented all of the job categories for the ADN production process described earlier (see section on Description of the Workforce) with potential for exposure to 1,3-butadiene. The control room operator was not monitored; area samples, however, were taken in the control room. Table 2 presents a summary of the personal samples collected at DuPont. It includes the number of samples taken, range of measurements, arithmetic mean, median, geometric mean, and geometric standard deviation for each of the job categories monitored. 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 a fairly accurate measure of the means for the DuPont personal monitoring data; the standard deviation, however, may not be as accurate because a significant portion of the total data (28 percent) was below the limit of detection. The raw data on personal samples (including date, sample ID, air volume, duration, and concentration) are presented by job category in Appendix B, Table B-1. The data include both long- and short-term sampling results. Short-term samples collected during this survey are defined to be of less than 150 minutes duration, whereas long-term samples are of greater than 150 minutes duration, and are usually full-shift, 8-hour samples. The long-term concentrations, however, were not time-weighted to 8-hour values.

TABLE 2. SUMMARY OF PERSONAL SAMPLES, DuPONT'S SABINE RIVER WORKS,
ORANGE, TEXAS, AUGUST 26-28, 1986
(ppm)

Job category	Number of samples	Arithmetic mean	Median	Range		Geo-metric Mean	Geo-metric standard deviation
				Minimum	Maximum		
Tank farm operator	4	0.027	0.025	0.011 ^a	0.048	0.022	2.10
Outside operator	4	0.197	0.048	0.009 ^a	0.682	0.060	6.14
Synthesis operator A	4	0.143	0.140	0.043	0.250	0.114	2.27
Synthesis operator B	4	0.064	0.062	0.028	0.105	0.054	1.98
ADN recovery operator	4	0.051	0.019 ^a	<0.006 ^b	0.164	0.021	5.09
ADN refining operator	6	0.024	0.026	0.009 ^a	0.036	0.022	1.73
HCN boiler operator	4	0.011	0.007 ^a	<0.006 ^b	0.026 ^a	0.007	2.99
Shipping technician	2	14.6	14.6	0.770	28.5	4.69	12.9
Shipping technician-barge sampling	2	116.0	116.0 ^c	21.7 ^c	210.0 ^c	67.4	4.98
Laboratory technician	3	0.150	0.016 ^a	<0.009 ^b	0.429	0.031	10.6
Laboratory technician	1	-	-	-	0.682 ^c	-	-
Maintenance technician	4	0.019	0.020 ^a	0.011 ^a	0.026 ^a	0.018	1.41
Maintenance technician	1	-	-	-	0.306 ^c	-	-

^a Laboratory analysis of analyte was below limit of quantitation (1.1 µg/sample).

^b Laboratory analysis of analyte was below limit of detection (0.3 µg/sample).

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

Area Sampling

A total of 51 area samples were collected over three shifts during the in-depth survey. These samples characterize nine work environments and points along the plant perimeter:

1. Control room
2. 1,3-Butadiene incoming pipe, 1st floor - synthesis area
3. 1,3-Butadiene Sundyne pumps, 1st floor - synthesis area
4. 1,3-Butadiene molecular sieves, 2nd floor - synthesis area
5. 1,3-Butadiene vent header, 2nd floor - synthesis area
6. Synthesis column, 1st floor - synthesis area
7. ADN refining area
8. HCN boiler area
9. Barge unloading area
10. Perimeter (north, east, south, west)

Table 3 summarizes the area samples collected at DuPont. It presents the number of samples taken, the range of measurements, arithmetic mean, median, geometric mean, and geometric standard deviation for each work environment monitored. Treatment of less-than-detectable results for computing means and the standard deviation was again accomplished by using the numerical value halfway between zero and the reported limit of detection. This approach is again subject to the caveat mentioned for the personal monitoring data. The raw data for the area samples (including date, sample ID, air volume, duration, and concentration) are presented by work environment in Appendix B, Table B-1.

DISCUSSION

The industrial hygiene survey of the DuPont Sabine River Works ADN production facility has demonstrated that the workers' full-shift exposures to 1,3-butadiene (with the exception of a shipping technician's exposure of 28.5 ppm) are below both the ACGIH TLV of 10 ppm⁹ and the present OSHA PEL of 1000 ppm.⁸

Arithmetic and geometric mean full-shift exposures across all job categories (with the exception of the shipping technician) were less than 0.20 ppm. The arithmetic and geometric mean full-shift exposures for shipping technicians were 14.6 and 4.69 ppm, respectively. A shipping technician received the highest individual TWA 1,3-butadiene exposure (28.5 ppm) of any worker monitored. The same shipping technician also received the highest short-term exposure of 210 ppm during the sampling of a barge for 1,3-butadiene. Short-term 1,3-butadiene exposures on a laboratory technician conducting chemical analysis on QC samples and a maintenance technician replacing spool pieces on 1,3-butadiene Sundyne pumps in the synthesis area were 0.68 and 0.31 ppm, respectively.

Area samples collected during the in-depth survey demonstrate that, under normal operating conditions, the arithmetic and geometric mean airborne concentrations of 1,3-butadiene in all work environments were at or below

TABLE 3. SUMMARY OF AREA SAMPLES, DuPONT'S SABINE RIVER WORKS,
ORANGE, TEXAS, AUGUST 26-28, 1986
(ppm)

Work environment	Number of samples	Arithmetic mean	Median	Range		Geo-metric Mean	Geo-metric standard deviation
				Minimum	Maximum		
Control room	5	0.007	<0.006 ^a	<0.006 ^a	0.014 ^b	0.005	2.318
1,3-Butadiene incoming pipe, 1st floor - synthesis area	4	0.093	0.086	0.015 ^b	0.185	0.067	2.922
1,3-Butadiene Sundryne pumps, 1st floor - synthesis area	9	0.167	0.074	0.010 ^b	0.426	0.103	3.281
1,3-Butadiene molecular sieves, 2nd floor - synthesis area	7	0.614	0.238	0.033	2.697	0.253	4.393
1,3-Butadiene vent header, 2nd floor - synthesis area	4	0.604	0.539	0.380	0.956	0.564	1.524
Synthesis column, 1st floor - synthesis area	1	-	-	-	0.530	-	-
ADN refining area	7	0.010	0.005 ^b	0.007 ^b	0.022	0.009	1.928
HCN boiler area	1	-	-	-	0.007 ^b	-	-
Barge unloading area	1	-	-	-	0.460	-	-
Perimeter							
North	3	0.005	<0.006 ^a	<0.006 ^a	<0.016 ^a	0.004	1.760
East	3	0.005	<0.007 ^a	<0.006 ^a	<0.015 ^a	0.004	1.655
South	3	0.007	0.010 ^b	<0.006 ^a	<0.015 ^a	0.006	1.889
West	3	0.004	<0.006 ^a	<0.006 ^a	<0.015 ^a	0.004	1.738

^a Laboratory analysis of analyte was below limit of detection (0.3 µg/sample).

^b Laboratory analysis of analyte was below limit of quantitation (1.1 µg/sample).

approximately 0.60 ppm. Concentrations of 1,3-butadiene measured during the survey at the plant perimeter were less than approximately 0.02 ppm. The area monitors were located both upwind and downwind of the ADN production process.

CONCLUSIONS

Based on an evaluation of both DuPont's historical monitoring data and the results of the NIOSH in-depth survey, several observations can be made:

- 1) The historical TWA exposure data supplied by DuPont (Table 1) are in general agreement with the NIOSH personal monitoring results (Table 2) for the Step I and ADN refining area process operator job categories as well as the laboratory technicians. The higher exposures observed for the tankermen during the NIOSH in-depth survey are also in keeping with the sporadic high exposures measured for this job category in previous DuPont monitoring efforts.
- 2) Individual short-term exposures greater than 10 ppm, specifically 21.7 and 210 ppm, were measured during the NIOSH survey for tankermen collecting 1,3-butadiene QC samples from barges; no short-term measurements, however, had previously been recorded by DuPont to allow a direct comparison of these data. TWA exposures ranging up to 62.7 ppm, however, had been previously measured by DuPont for this operation.
- 3) The current exposure control programs in the ADN production process at DuPont's Sabine River Works (see section on Control Description) serve to maintain mean 8-hour worker exposures in the process area well below 10 ppm (the present ACGIH TLV) of 1,3-butadiene.

RECOMMENDATIONS

In the context of the present OSHA PEL for 1,3-butadiene (1000 ppm) and the ACGIH TLV (10 ppm), the control programs for the ADN production process at DuPont's Sabine River Works appear to result in exposure levels within the present standards. However, because of certain job-related exposure excursions for the tankermen in the barge unloading area and the concern that 1,3-butadiene may present both a carcinogenic and teratogenic risk, the following additional precautions should be considered:

- 1) DuPont should consider conversion to a closed-loop sampling system for obtaining 1,3-butadiene QC samples from barges. This conversion should serve to lower the mean and peak exposures of shipping technicians when sampling barges before unloading.
- 2) DuPont presently uses both slip-tube and magnetic gauges to monitor the level of 1,3-butadiene on barges. Because magnetic gauges are known to limit the release of 1,3-butadiene during unloading, a program to convert to 100 percent magnetic gauges should be considered, if technically feasible.

REFERENCES

1. Key Chemicals: Butadiene. Chemical & Engineering News. p. 15 (June 9, 1986).
2. 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, Incorporated, by Hazelton Laboratories Ltd, Harrogate, England (November 1981).
3. Powers M: Board Draft of NTP technical report on the toxicology and carcinogenesis studies of 1,3-butadiene (CAS No. 106-99-0) in B6C3F mice (inhalation studies). NTP-83-071/NIH Publication No. 84-2544. U.S. Department of Health and Human Services, Public Health Service, National Institute of Health, National Toxicology Program (October 28, 1983).
4. 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 Hazelton Laboratories Ltd, Harrogate, England (November 1981).
5. Meinhardt TJ, Lemen RA, Crandall MS, et al.: Environmental epidemiologic investigation of the styrene-butadiene rubber industry: Mortality patterns with discussions of the hematopoietic and lymphatic malignancies. Scan J. Work Environ. Health 8:250-359 (1982).
6. Matanoski GM, Schwarts L, Sperrazza J, et al.: 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 John Hopkins University School of Hygiene and Public Health, Baltimore, Maryland (June 1982).
7. Current Intelligence Bulletin No. 41 - 1,3-butadiene. U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health (NIOSH), Cincinnati, Ohio, Publication No. 84-105 (February 9, 1984).
8. U.S. Department of Labor. OSHA Permissible Exposure Limit for 1,3-Butadiene. Code of Federal Regulations. 29 CFR 1910.1000, Subpart Z, Toxic and Hazardous Substances. Occupational Safety and Health Administration (March 11, 1983).
9. 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).
10. National Institute for Occupational Safety and Health. NIOSH Manual of Analytical Methods. 3rd Edition. Vol. 1, DHHS (NIOSH) Publication No. 84-100, 1984.

11. 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.

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: insignificant loss after 21 days below -4 °C	!CARRIER GAS: Helium !
BLANKS: 10% of samples	!MAKEUP GAS: Nitrogen, 30 mL/min !
	!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 440 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 require dilution. Below 1.1 mg/m ³ (0.5 ppm), the desorption efficiency falls below 80% and allowance should be made for decreased accuracy.	
INTERFERENCES: Pentane or methyl acetylene may interfere chromatographically 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.

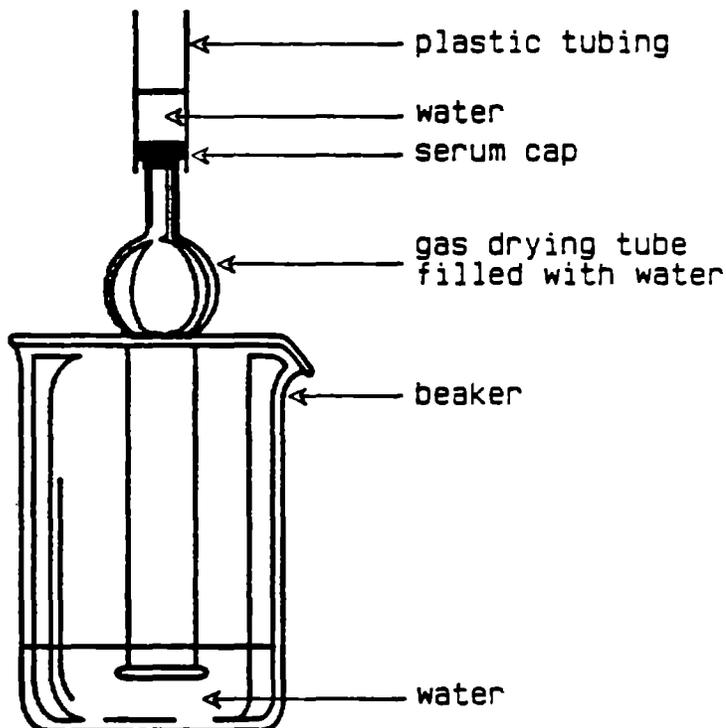
SAMPLE PREPARATION:

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 B), 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 response to standard solutions was linear over the range 0.07 to 110 µg/mL. The pooled s_p was 0.038. (Higher concentrations overload the analytical column, but field samples as high as 1820 µg/mL have not caused a problem.) The estimated limit of detection for the measurement method was 0.02 µg/mL or 6 picograms on the analytical column.

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

per sample, the pooled s_p was 0.025, and the desorption efficiencies were 67%, 68%, 75%, 102%, and 97%, respectively.

In a study of temperature effects on storage stability, 400-mg charcoal tubes were spiked with 26 μg 1,3-butadiene and stored either at ambient temperature or in a freezer below -4°C . Recoveries were measured relative to media standards stored overnight in the freezer. The recoveries (and days stored) were 94% (7), 93% (14), and 98% (21) for the 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 via calibrated sampling valve. The recovery was 102.2% versus media standards and 96.8% versus standard solutions; the s_p was 0.016. Subsequently, charcoal tubes 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 and thermal conductivity detection. Media standards were prepared via calibrated sampling valves at all levels. At 463 μg , the recovery was 101.6% versus media standards and 91.3% versus standard solutions; the s_p was 0.047. At 45.3 μg , the recovery was 112.3% versus media standards and 102.9% versus standard solutions; the s_p was 0.048. At 4.64 μg , the recovery was 80.3% versus media standards and 103.8% versus standard solutions; the s_p was 0.011. The two lowest levels of media standards appeared to be high, possibly due to absorption of 1,3-butadiene by internal parts of the sampling valve. The study was repeated at 4.71 μg , with media standards prepared as in step 10. The recovery was 129.5% versus media standards and 91.2% versus standard solutions; the s_p was 0.023. The s_p pooled for all levels was 0.033. Assuming a sampling pump error of 0.05, the precision of the total sampling and analytical method was 0.060. For levels at and above 45 μg (0.8 ppm in 25 L), the apparent bias could be attributed to experimental errors in the preparation and analysis of standards and samples rather than a true bias in the method. At lower levels, a primary source of error appeared to be the preparation and analysis of media standards.

The method was field tested under conditions of high ambient temperature and humidity with over 650 samples from five surveys. Only one percent showed significant breakthrough. Quality assurance blind spikes (16 per survey), stored with the samples and ranging from approximately 20 to 650 μg per sample, were stable for at least 10 weeks. Including selected back sections and standards, over 1250 analyses were made without any deterioration of the chromatographic columns.

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

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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 [4] 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)

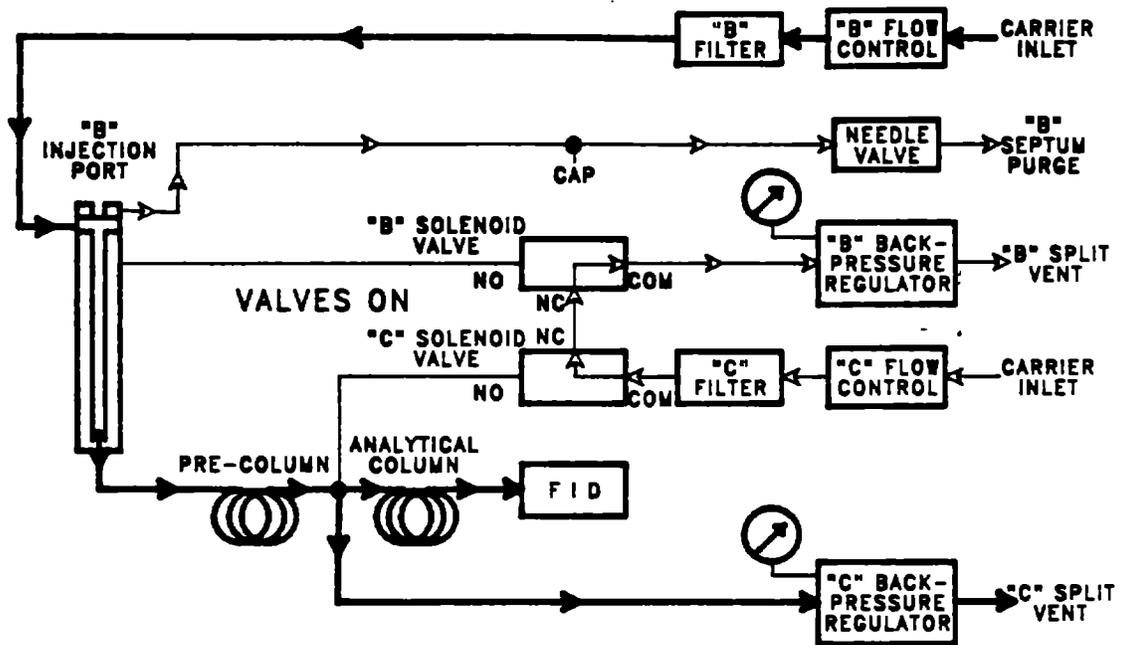


Figure 1. Flow diagram for pre-column system in inject mode.

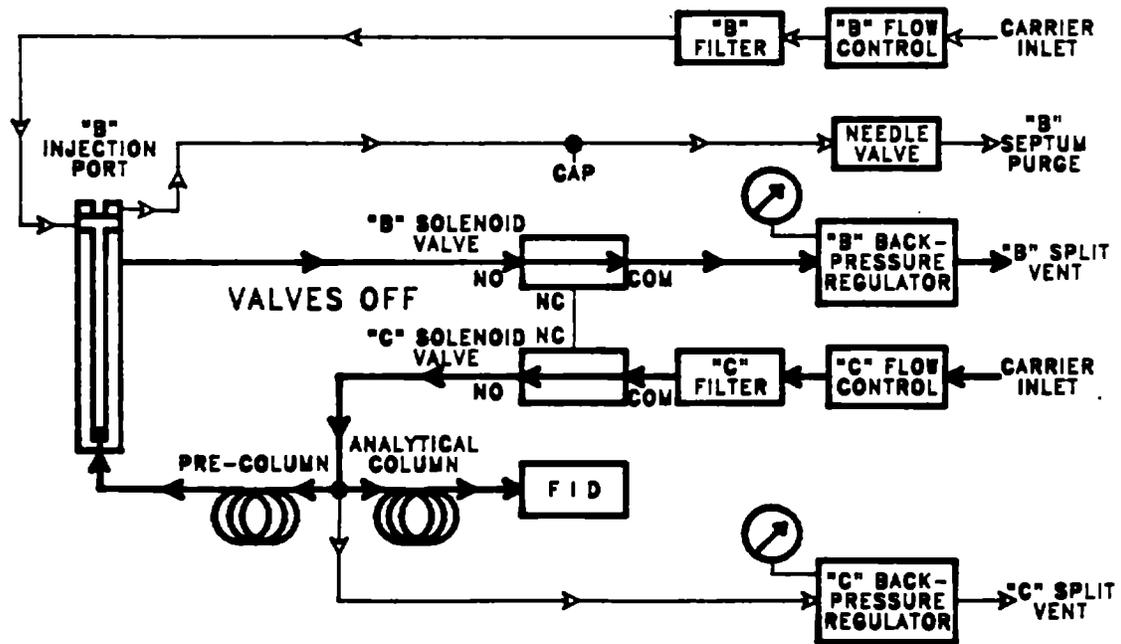


Figure 2. Flow diagram for pre-column system in backflush (normal) mode.

APPENDIX B

NIOSH SAMPLING DATA FOR IN-DEPTH
SURVEY AT DuPONT'S SABINE RIVER WORKS
ORANGE, TEXAS
AUGUST 26-28, 1986

DuPONT'S SABINE RIVER WORKS
ORANGE, TEXAS, AUGUST 26-28, 1986

Job category	Date (1986)	Sample ID	Air volume, liters	Duration, min	Concentration, ppm
Tank farm operator	8/26	DP8	21.48	467	0.011 ^a
	8/27	DP50	23.77	466	0.013 ^a
	8/27	DP60	22.82	496	0.036
	8/28	DP91	17.86	406	0.048
Outside operator	8/26	DP18	21.84	455	0.033
	8/27	DP47	21.57	469	0.682
	8/27	DP71	23.86	487	0.063
	8/28	DP86	20.20	396	0.009 ^a
Step I operator	8/26	DP16	24.16	493	0.043
	8/27	DP51	23.60	472	0.079
	8/27	DP55	21.91	498	0.250
	8/28	DP85	19.65	401	0.200
Step II operator	8/26	DP20	23.47	489	0.033
	8/27	DP52	22.80	475	0.028
	8/27	DP65	24.26	495	0.105
	8/28	DP81	20.40	408	0.091
ADN recovery operator	8/26	DP9	22.04	469	<0.006 ^b
	8/27	DP38	23.10	462	0.018 ^a
	8/27	DP59	23.18	483	0.164
	8/28	DP84	19.55	399	0.021 ^a
ADN refining operator	8/26	DP15	24.00	480	0.009 ^a
	8/27	DP40	23.10	462	0.014 ^a
	8/27	DP42	23.25	465	0.021 ^a
	8/27	DP61	24.38	508	0.032
	8/28	DP99	20.35	424	0.033
	8/28	DP87	21.30	426	0.036
HCN boiler operator	8/26	DP10	23.18	473	<0.006 ^b
	8/27	DP39	23.08	471	0.012 ^a
	8/27	DP69	24.35	497	<0.006 ^b
	8/28	DP98	19.15	399	0.026 ^a
Tankerman	8/28	DP79	15.78	30	210.0 ^c
	8/28	DP88	10.99	229	28.5 ^d
	8/28	DP92	15.72	31	21.7 ^c
	8/28	DP94	11.52	245	0.770 ^d
Laboratory technician	8/28	DP75	15.50	310	<0.009 ^b
	8/28	DP83	16.99	354	0.429
	8/28	DP93	17.04	355	0.016 ^a
	8/28	DP101	71.06	141	0.682 ^c
Maintenance technician	8/26	DP3	19.34	403	0.026 ^a
	8/26	DP4	19.70	402	0.011 ^a
	8/26	DP6	19.65	401	0.021 ^a
	8/26	DP7	19.25	401	0.019 ^a
	8/27	DP58	11.09	22	0.306 ^c

^a Laboratory analysis of analyte was below limit of quantitation (1.0 µg/sample).

^b Laboratory analysis of analyte was below limit of detection (0.3 µg/sample).

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

^d Values were not time-weighted to 8-hour concentrations.

TABLE B-2. AREA SAMPLING DATA FOR 1,3-BUTADIENE
 DuPONT'S SABINE RIVER WORKS
 ORANGE, TEXAS, AUGUST 26-28, 1986

Job category	Date (1986)	Sample ID	Air volume, liters	Duration, min	Concen- tration, ppm
Control room	8/26	DP17	24.10	482	<0.006 ^a
	8/26	DP19	23.62	482	<0.006 ^a
	8/27	DP46	22.13	461	<0.006 ^a
	8/27	DP67	24.91	519	0.013 ^b
	8/28	DP96	18.96	395	0.014 ^b
1,3-butadiene incoming pipe, 1st floor - synthesis area	8/26	DP5	21.60	450	0.069
	8/27	DP48	19.54	444	0.185 ^b
	8/27	DP62	24.11	492	0.015 ^b
	8/28	DP90	11.09	231	0.102
1,3-butadiene Sundyne pumps, 1st floor - synthesis area (east)	8/26	DP21	17.43	379	0.273
1,3-butadiene Sundyne pumps, 1st floor - synthesis area (west)	8/26	DP24	17.11	372	0.064
1,3-butadiene Sundyne pumps, 1st floor - synthesis area	8/26	DP25	17.66	368	0.074
1,3-butadiene Sundyne pumps, 1st floor - synthesis area (east)	8/27	DP43	20.74	461	0.059
1,3-butadiene Sundyne pumps, 1st floor - synthesis area (west)	8/27	DP49	20.88	464	0.063
1,3-butadiene Sundyne pumps, 1st floor - synthesis area (east)	8/27	DP68	23.52	490	0.010 ^b
1,3-butadiene Sundyne pumps, 1st floor - synthesis area (west)	8/27	DP70	24.65	493	0.184
1,3-butadiene Sundyne pumps, 1st floor - synthesis area (west)	8/28	DP100	17.86	397	0.426
1,3-butadiene Sundyne pumps, 1st floor - synthesis area (east)	8/28	DP95	20.70	398	0.348

(continued)

TABLE B-2 (continued)

Job category	Date (1986)	Sample ID	Air volume, liters	Duration, min	Concentration, ppm
1,3-butadiene molecular sieve, 2nd floor - synthesis area (east)	8/26	DP22	17.01	362	0.439
1,3-butadiene molecular sieve, 2nd floor - synthesis area (west)	8/26	DP23	16.42	357	2.69
1,3-butadiene molecular sieve, 2nd floor - synthesis area	8/26	DP26	17.62	367	0.033
	8/26	DP29	18.41	354	0.057
	8/27	DP45	19.96	434	0.238
	8/27	DP64	24.30	486	0.632
	8/28	DP89	19.50	390	0.200
1,3-butadiene vent header, 2nd floor - synthesis area	8/26	DP27	16.10	350	0.427
	8/27	DP44	18.14	432	0.651
	8/27	DP66	22.03	479	0.956
	8/28	DP73	18.48	385	0.380
Step II column, 1st floor - synthesis area	8/27	DP41	20.68	440	0.530
ADN refining area	8/26	DP2	15.44	315	<0.009 ^a
	8/26	DP28	14.81	322	<0.009 ^a
	8/26	DP30	13.90	316	<0.010 ^a
	8/27	DP34	21.02	438	0.015 ^b
	8/27	DP57	23.81	486	0.013 ^b
	8/27	DP63	24.55	501	0.022 ^b
	8/28	DP82	18.24	380	0.007 ^b
HCN boiler area	8/26	DP11	24.90	498	0.007 ^b
Barge unloading area	8/28	DP77	10.72	233	0.460
Perimeter					
North	8/26	DP12	22.42	467	<0.006 ^a
	8/27	DP36	23.85	477	<0.006 ^a
	8/28	DP74	8.70	174	<0.016 ^a
East	8/26	DP1	20.88	454	<0.007 ^a
	8/27	DP35	21.55	449	<0.006 ^a
	8/28	DP76	8.87	181	<0.015 ^a
South	8/26	DP13	23.45	469	0.010 ^b
	8/27	DP33	23.40	468	<0.006 ^b
	8/28	DP78	8.95	179	<0.015 ^a
West	8/26	DP14	22.51	469	<0.006 ^a
	8/27	DP37	24.20	484	<0.006 ^a
	8/28	DP80	8.98	176	<0.015 ^a

^a Laboratory analysis of analyte was below limit of detection (0.3 µg/sample).

^b Laboratory analysis of analyte was below limit of quantitation (1.0 µg/sample).