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Industrywide Studies Report
of an Indepth Survey at
Firestone Tire and Rubber Company
Des Moines, Iowa

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16. Abstract (Limit: 200 words)

For the purpose of determining worker exposure to 1,3-butadiene (106990), an indepth industrial hygiene survey was conducted at the Firestone Tire and Rubber Company (SIC-3011), Des Moines, Iowa. Large farm and truck tires were manufactured on site as well as temporary spare tires for passenger cars. A total of 900 employees work in the production area of the facility with 200 more employed as office and supervisory personnel. There were three shifts, with the facility functioning around the clock. Employees with the greatest potential exposures included banbury operators, cooling conveyor operators, calendering operators, mill tenders, extruder operators, wire winders, tire builders (tractor and heavy duty tires), curing operators (passenger and heavy duty), and tire buffer and repair men. Personal air samples were collected over the three shifts. Gas chromatographic analysis revealed that none of the 90 charcoal tube front sections contained 1,3-butadiene. The back sections of ten selected samples which indicated a high organic concentration in their front sections were analyzed and no breakthrough was demonstrated. Mass spectrometry of four selected samples indicated that all contained toluene (108883) and saturated aliphatic hydrocarbons. No measurable exposure to 1,3-butadiene was demonstrated at this facility

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PURPOSE OF SURVEY:	To conduct an indepth survey of a 1,3-butadiene polymer consuming plant and to assess the extent of worker exposure to 1,3-butadiene.
EMPLOYER REPRESENTATIVES CONTACTED:	Bernie Young, Plant Manager Jim Allpress, Safety Engineer Ted Georgiados, Corporate Industrial Hygienist
EMPLOYEE REPRESENTATIVES CONTACTED:	Steve Larson, Safety Representative United Rubber Workers Local 310 125 N.W. Broadway
STANDARD INDUSTRIAL CLASSIFICATION (SIC) CODE:	3011 - Tires and Inner Tubes

ABSTRACT

An indepth industrial hygiene survey was conducted at the Firestone Tire and Rubber Company in Des Moines, Iowa on October 5-8, 1987. The purpose of the survey was to assess the extent of worker exposures at a 1,3-butadiene polymer consuming plant. The impetus for this investigation came from recent toxicological studies that have identified 1,3-butadiene as an animal and potential human carcinogen.

The Firestone Tire and Rubber Company, which opened in 1945, manufactures an assortment of large farm and truck tires as well as a temporary spare tire for passenger cars.

During the indepth survey, descriptive information was collected on the company's workforce, process, and medical, safety and industrial hygiene programs. A detailed industrial hygiene monitoring effort was conducted by NIOSH to characterize employee exposure to 1,3-butadiene.

Personal 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. All the analytical results were below the limit of detection of 0.3 ug/tube. The results of this survey did not demonstrate measurable exposure to 1,3-butadiene at this tire manufacturing facility.

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 consumption. Because SBR is the leading consumer of 1,3-butadiene a tire plant was selected for an indepth industrial hygiene survey.

Inhalation exposure of rats and mice to 1,3-butadiene induced a carcinogenic response at multiple sites. Mammary fibroadenomas/carcinomas, uterine sarcomas, Leydig cell adenomas of the testes, thyroid follicular cell adenomas, exocrine tumors of the pancreas, and Zymbal gland carcinomas were identified in rats exposed at concentrations of 1000 to 8000 ppm of 1,3-butadiene. Mice exposed to 625 or 1250 ppm of 1,3-butadiene developed a high incidence of malignant lymphomas; and 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 8000 ppm had major skeletal defects. In addition, fetal toxicity was observed when pregnant dams were exposed at 200 ppm, 1000 ppm, and 8000 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 end-user industry (tire and rubber products).

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 average (TWA).[8] OSHA has initiated new rulemaking action intended to reduce 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 numerical TLV of 10 ppm has been assigned to 1,3-butadiene.

NIOSH in their Current Intelligence Bulletin recommends that 1,3-butadiene be regarded as a potential occupational carcinogen and teratogen and as a possible reproductive hazard.[7]

HISTORY AND DESCRIPTION OF THE PLANT

The Firestone Tire and Rubber Company manufactures an assortment of large farm and truck tires as well as a temporary spare tire for passenger cars at its plant in Des Moines, Iowa. The production facility, which was originally constructed in 1945, covers approximately 105 acres of which approximately 57 acres are under roof.

Annual production in 1985 used approximately 131,500,000 pounds of raw materials including steel bead wire, natural rubber, synthetic rubber, fabric, chemicals and pigments. Normal production capacity is over 2,000,000 tires a year, however, at the present time the plant is at 75% capacity. The plant is in the process of producing new product lines which will increase production and employment at the plant

PROCESS DESCRIPTION

Figure 1 is a graphic flow diagram of the tire manufacturing process.

DESCRIPTION OF THE WORKFORCE

The company employs 1,100 persons which include 900 in production and 200 in office and supervisory capacities. Production workers are represented by the United Rubber Workers Local No. 310 Maintenance electricians are represented by Local No. 347 of the International Brotherhood of Electrical Workers.

The plant operates 24 hours per day. There are three shifts per day with maintenance and administrative personnel working the day shift only.

The job descriptions for employees which were identified by NIOSH to have the greatest potential for exposure to 1,3-butadiene are as follows:

Banbury Operator:
Sets up controls and scales according to mixing specifications in order to manually or automatically operate and/or attend one or more banbury mixers on a continuous operations. Check on separate scale, total weight per specified tolerance of every pigment prior to loading it to banbury.

Check controls and weights periodically and make necessary adjustments to assure adherence to mixing chamber either manually or automatically as required. Accurately record production tally and delay time on production forms provided. Keep a record of stocks in storage bins. Communicate with Tower Operator, Pelletizer Attendant, Pellet Storage Bin Attendant and Cooling Conveyor Operator as specified on stock changes, also equipment and quality problems. Notify supervision immediately when equipment or quality problems occur. Manually load into banbury as required, loose pellets, slab rubber, slit TMA, chunk rubber, mill batch off, etc. Assist in correcting delays. Maintain a continuous flow of production on banbury mixing operation throughout the shift and at shift change. Service banbury weigh

FIRESTONE PRECISION TIRE MANUFACTURING

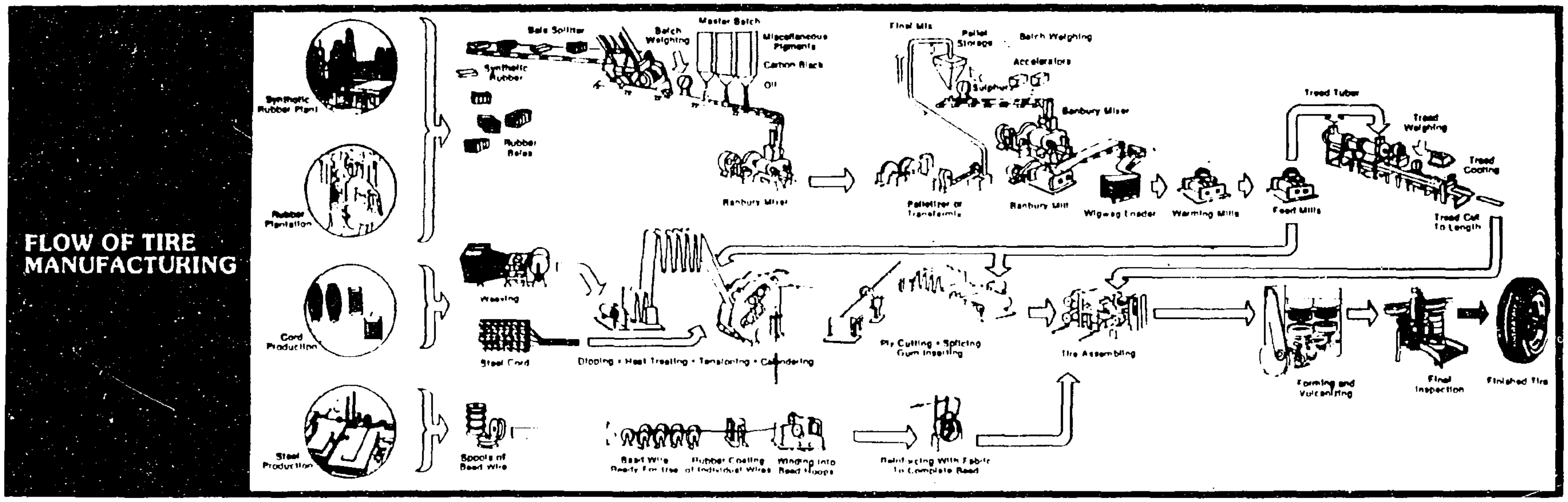

Figure 1. Tire Manufacturing Process at the Firestone Tire & Rubber Company, Des Moines, Iowa (Figure provided by Firestone)

hopper rejects, asiding part batches into proper containers and identify properly. Scrape banbury feed door and plunger as needed. Maintain area in neat and orderly manner, picking up loose pellets, and aside into proper containers.

Perform other typical duties consistent with the job actors as required or that may be requested by supervision.

Cooling Conveyor Operator:
Operate all controls for automatic discharge mills, batch off conveyors, slab mills, cooling conveyors, wig way, slab dip unit and marking device to process stock from discharge mills to stock skids. Properly identify each load with correct stock number, date, shift, machine, and load number. Cut samples as specified and deliver to mill room control as directed. Operate and service slab marking device. Provide full and/or partial skid loads of stock to designated area and place empty skid in position under wig wag. Communicate with Banbury Operator on stock change and mechanical or quality problems. Contact supervision immediately when mechanical or quality problems occur. Assist in correcting delays as necessary or directed by supervision. Keep production in tally on forms provided. Maintain discharge mills, batch off conveyors, slab off mills, cooling conveyors, and wig wag area in neat and orderly manner. Maintain a continuous flow of production on banbury mixing operation throughout the shift and at shift change.

Calendering Operator:
Control the automatic application of a variety of rubber skim stocks to both sides of treated and untreated fabric (both cord and square woven) in a single pass thru a four roll calender. Observe charts and indicators during calendering operation to insure correct conditions such as: speed, cushion and contour pressure, fabric width, roll temperature, and gauge. Make necessary corrections to insure proper quality of product and to maintain normal production. Maintain calender feed strips and stock banks. Adjust calender trim knives. Trim edges of calender fabric. Alert crew members of any changes in stock (fabric or rubber) or any other irregularities. Observe fabric for dirt, tears, improper dip or style. Order stock according to production schedule or production tags. Maintain crew production record and record appropriate delays.

Mill Tender:
Operates warmup mills, surge mills, and feed mills. Breakdown, heat, soften, and blend stock to required plasticity for tubing by normally cutting through rubber on mill roll thus feeding bank through mill bite. Send stock to surge and/or feed mill. Set rollers to feed stock across mills, operates blending belts, sets feed strips to specified width, starts feed strip, maintains proper temperatures on mills by regulating water, adjust mill rolls for specified gauge, "pigs", rubber, takes samples of each mill load and sends with identification ticket to Mill Room Control.

Extruder Operator:
Operate a dual tuber producing treads, sidewall, retreads, and other extruding rubber materials in amounts specified on printed schedule. Using Card-X, conveyor tread scale and tension gauge, etc., adjust tuber speeds to produce materials of the correct dimensions and weight as shown on the Card-X file. Use feed strips of specified width and gauge. Keep extrusion and booking temperatures within specifications by adjusting tuber head cooling water and conveyor belt speeds. Communicates with mill tender to obtain feed strips when needed and so that only the required amount of the correct stock is warmed up. Check extruded rubber frequently to make sure all dimensions are correct. Responsible for complete tubing operation, correct tread marking, cushion and cement application, booking length and weight, and scrapping defective treads.

Wire Winder:
Insulate and wind wire to be used in making beads by running strands of wire through a wire winding insulating machine. Rubber insulation is automatically fed into hopper of insulating machine from insulation containers. Turn on steam valve to heat die head, insert end of wire into winding wheel and turn on machine. The machine automatically covers strands of wire with rubber insulation and then runs it through a wax and cooling unit.

Tire Builder - Tractor and Heavy Duty Tires:
Build pneumatic tires on mechanically rotated drum type or automatic sequence control tire building machines. Apply drum cement to surface of metal drum to make it adhesive. Wind each ply of rubberized fabric around drum and press overlapping ends together to splice by adhesion. Build up carcass with desired number of innerliner and plies, hand form over drum edges and distribute buckles at ply edges. Operate "ply down" tools on automatic equipment. Rotate drum and press or "stitch" plies together by working over surface with special hand tools and machine operated ply stitching rollers. Place head in edge of fabric plies and fasten by forming edges of plies around them. Wind on, splice, and roll down tread or cap plies and reinforcing strips or "chafers" at point of rim contact by aligning with overhead guidelights. Apply unit tread, tread edges and sidewall also by aligning with overhead guidelights. Use solvent and rubber cement to improve adhesive qualities of fabric and rubber during construction. Apply gumstrips over splices and defective spots where necessary. Press whole surface of tire with mechanical and hand stitching tools to stitch all parts together. Trim excess fabric at edges and operate trimmer to trim sidewalls. Apply wire tread ply or steel fortified stock as directed by specifications. Recycle limit switch or automatic sequence units to assure proper machine sequence. Visually inspect tires, removing any surface wrinkles with wrinkle hook and place builder's identification tag on tire. Collapse drum, remove tire from drum manually or with pneumatic hoist. Make necessary repairs and place tire on conveyors, pallet, or pin rack.

Curing Operator (Passenger and Heavy Duty):
Attend lines of semi-automatic (Bag-O-Matic) single and dual mold curing presses operating in rotation or random according to cure time and when loaded: load molds with green tires manually or with hoist. Unload press after old opens manually or with hoist. Post inflate cured tires as required. Molds open automatically. Spray molds as necessary with tire releasing dope. Remove stuck tires from mold either manually and/or with mechanical apparatus.

Tire Buffer and Repair:
Performs finishing, repair, and final inspection operations to Truck, Bus, Heavy Duty, Rear Tractor, and A-2 tires after the classifying operation. Operator will pull tire from temporary storage and will roll tire to and from various repair stations. Operators will inspect tires; cutout, fill in, cure, buff, trim, cement, and other miscellaneous duties to repair defects and to meet specifications: reinspect tire to assure a quality operation; and will move tire by lifting, rolling, and pushing tire (or some A-2 tires by hoist) to temporary storage. Operators will determine extent and type of repair, will get repair materials from central storage locations; change wheels, cutting and buffing heads and make minor repairs to equipment, and cure tires for specified periods.

DESCRIPTION OF MEDICAL, SAFETY, AND INDUSTRIAL HYGIENE PROGRAMS

Medical Program:
Firestone has one contract, part-time physician and 3 full-time registered nurses (one per shift) on-site. Each new employee is given a pre-employment examination before being assigned to permanent job responsibilities. This physical includes a chest roentgenogram, urinalysis, blood chemistry, hearing tests, vision tests, and lung function tests. Annual physical examinations are offered through the union benefits package.

Safety Program:
Firestone has an on-site safety program at the Des Moines plant. The program is administered through a central safety committee. The plant safety engineer chairs the committee. Labor is represented by a Health and Safety Representative for each shift as well as a full time Health and Safety Representative.

The committee meets monthly for two days and inspects the plant for health and safety problems. The entire plant is evaluated every four months. Identified mechanical problems are assigned a work order number and are corrected by the maintenance department.

There is no standard personal protective equipment required to be worn throughout the plant. The requirements vary by department and job. Appropriate personal protective equipment is available for those job that require protection.

Industrial Hygiene Program:
Firestone does not have an industrial hygienist at the Des Moines plant. The corporate industrial hygienist conducts annual industrial hygiene audits as well as a comprehensive industrial hygiene survey every two years. Emphasis is placed on dust sampling in the Banbury and compounding departments, solvents, noise, and radiation.

Corporate headquarters provide consultation to the plant on technical matters and provides support staff to resolve specific problems.

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. 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 identified job category was monitored for a full shift. During the in-depth survey, the survey team monitored for a total of three shifts over the course of three work days.

SAMPLING AND ANALYTICAL METHODS

A new sampling and analytical method for 1,3-butadiene was used by NIOSH during the Firestone 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 Firestone plant, personal sampling was performed. The samples were collected with 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 liters 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 9 percent of the back sections of the samples submitted were analyzed. Media standards and 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 the 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 x ±2 .

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 quanitation" (LOQ).[10] For the 1,3-butadiene analyses performed, the LOD was 0.3 ug/per sample.

RESULTS

A total of 90 personal samples were collected over three shifts during the indepth survey. These samples represented all of the job categories previously discussed (see section on Description of the Workforce) with potential for exposure to 1,3-butadiene. Table 1 presents a summary of the personal samples collected at Firestone.

Gas chromatographic analysis indicated that none of the 90 charcoal tube front sections analyzed contained 1,3-butadiene; the LOD was 0.3 ug per tube. The back sections of 10 selected samples which indicated a high concentrations of organics in their front sections were analyzed and indicated that no breakthrough occurred.

Mass spectrometric analysis of four selected samples indicated that all contained toluene and saturated aliphatic hydrocarbons (empirical formulas C_6H_{14}, C_7H_{16}) such as hexane, heptane, and methylpentanes.

Table 1
Summary of Personal Samples for 1,3-Butadiene
Firestone Tire and Rubber Company
Des Moines, Iowa
October 5-8, 1987

Job Description	Number of Samples	Results
Banbury Operator	6	N.D.*
Cooling Conveyor Operator	6	N.D.
Calendering Operator	13	N.D.
Extruder Operator	11	N.D.
Wire Winder	3	N.D.
Tube Machine Operator	9	N.D.
Tire Builder	15	N.D.
Curing Operator	21	N.D.
Tire Repair and Buffer	6	N.D.
Total	90	

*N.D. = Non Detectable (Limit of Detection is 0.3 ug/sample)

CONCLUSIONS

The analytical results indicate that 1,3-butadiene is nondetectable in all the departments surveyed. These results support the current thinking that workers in the end user industry do not currently have measurable exposures to 1,3-butadiene.

RECOMMENDATIONS

Based on the negative results of this survey it is not necessary to make any recommendations to Firestone for control of 1,3-butadiene.

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APPENDIX A

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

FORMULA: C_4H_6, $CH_2{=}CHCH{=}CH_2$

1,3-BUTADIENE

METHOD: 1024
ISSUED: 5/15/86

M.W.: 54.09

OSHA: 1000 ppm
NIOSH: potential carcinogen [1]
ACGIH: 10 ppm; suspect carcinogen
(1 ppm = 2.21 mg/m^3 @ 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

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SYNONYMS: CAS #106-99-0

SAMPLING

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

FLOW RATE: 0.01 to 0.5 L/min

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

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

SAMPLE STABILITY: at least two months for quality assurance blind spikes stored in a freezer

BLANKS: 10% of samples

ACCURACY

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

BIAS: see EVALUATION OF METHOD

OVERALL PRECISION (s_r): 0.060

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: 1,3-butadiene

DESORPTION: 4 mL methylene chloride; 30 min

INJECTION: 1 µL

TEMPERATURE-INJECTION: 200 °C
-DETECTOR: 250 °C
-COLUMN: see APPENDIX A

CARRIER GAS: Helium

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_2O_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_r): 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-µL.
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.

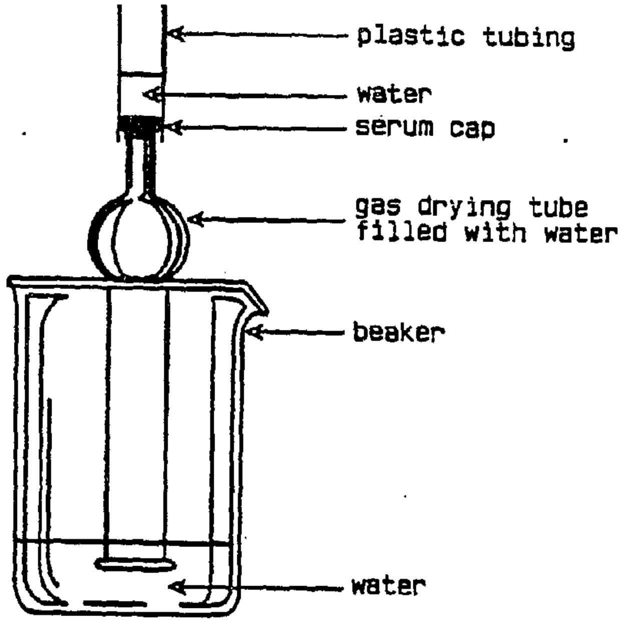
SAMPLE PREPARATION:

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:
   a. Prepare a beaker and drying tube assembly as shown below. Bubble 1,3-butadiene under the lower edge of the drying tube so that water is displaced and the gas is trapped in the tube.



   b. Pipet 1 or 4 mL of methylene chloride into a 1- or 5-mL vial, cap, and thoroughly chill.
   c. 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.
   d. Slowly inject the 1,3-butadiene and water below the surface of the methylene chloride.
   e. Agitate and continue to chill the vial to complete dissolution.

10. Calibrate daily with media blanks and triplicate independent media standards of at least five levels ranging from, e.g., 0.5 to 200 µL 1,3-butadiene gas per sample:
    a. Break ends of larger sampler and attach to personal sampling pump with flexible tubing.
    b. Take pure gas (50 or 200 µL, as in step 9.c) for the higher levels, or 40 µL of stock solution for lower levels.
    c. Inject the gas and surrounding water plugs or the stock solution at a point inside the sampler near the glass wool plug while drawing clean air through tube at 0.05 L/min. Continue to draw air through the tube for 5 min or just until the stock solution evaporates.
    d. Seal tube with plastic caps.
    e. Store at temperature below -4 °C overnight, then desorb (steps 5 through 8).
    f. Analyze media standards and blanks together with samples (steps 13 and 14).
    g. Convert gas volumes to masses, correcting for compressibility and water vapor (see APPENDIX B), and prepare a calibration graph (peak areas or heights vs. concentration of 1,3-butadiene taken in µg/mL).

11. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in calibration range (step 10).
    a. Dilute the stock solutions (step 9) 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 = (mass found - blank mass)/(mass taken).
12. Analyze three quality control blind spikes to insure that calibration graph (step 10) is in control.

MEASUREMENT:

13. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 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_r 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_r 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.

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[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_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 C_4 to C_6 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 Al_2O_3/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 noticable 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:

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

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 ($g \cdot mol^{-1}$)

62.36 = gas constant ($mm\ Hg \cdot L \cdot mol^{-1} \cdot K^{-1}$)

273.2 = absolute temperature of 0 °C (K)

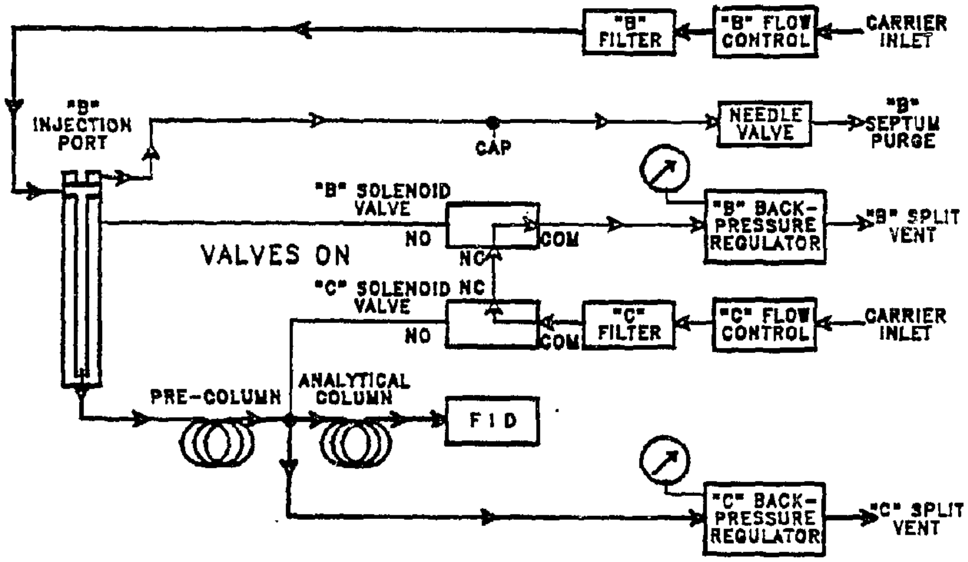

Figure 1. Flow diagram for pre-column system in inject mode.

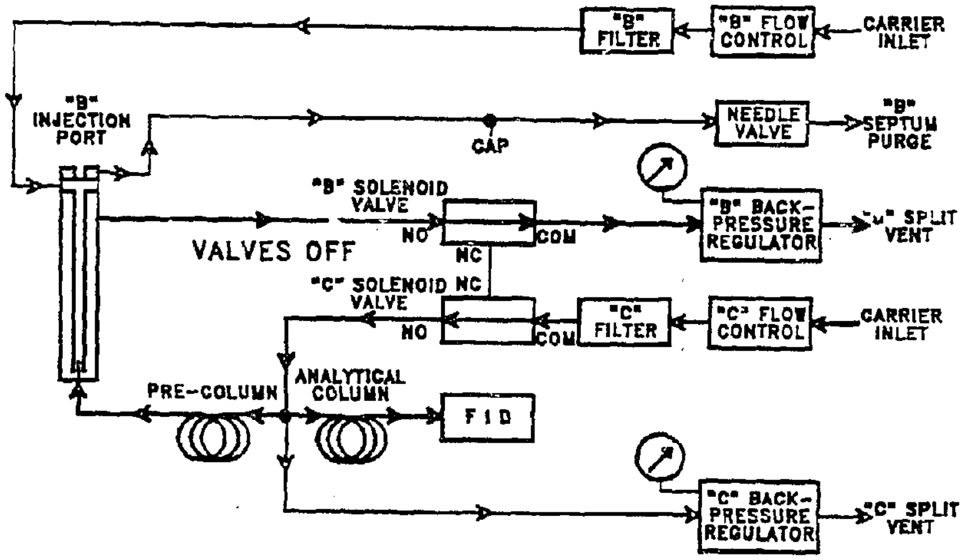

Figure 2. Flow diagram for pre-column system in backflush (normal) mode.