1,3-BUTADIENE 1024

$H_2C=CHHC=CH_2$ MW: 54.09   CAS: 106-99-0   RTECS: EI9275000

METHOD: 1024, Issue 2	EVALUATION: FULL	Issue 1: 15 August 1987 Issue 2: 15 August 1994

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

PROPERTIES: gas; vapor density 1.9 (air = 1); BP –4.4 °C; explosive range 2.0 to 11.5% v/v in air

SYNONYMS: butadiene; biethylene; divinyl

SAMPLING	MEASUREMENT
SAMPLER: SOLID SORBENT TUBE (coconut charcoal, 400- and 200-mg in separate tubes)	**TECHNIQUE:** GAS CHROMATOGRAPHY, FID
FLOW RATE: 0.01 to 0.5 L/min	**ANALYTE:** 1,3-butadiene
VOL-MIN: 5 L @ 100 ppm **-MAX:** 25 L	**DESORPTION:** 4 mL methylene chloride; 30 min
SHIPMENT: separate front and back tubes, chill below –4 °C	**INJECTION:** 1 µL

SAMPLE STABILITY: at least two months for quality assurance blind spikes stored in a freezer	**TEMPERATURE-INJECTION:** 200 °C
	  -DETECTOR: 250 °C
	  -COLUMN: see APPENDIX A

	CARRIER GAS: helium
BLANKS: 2 to 10 field blanks per set	**MAKEUP GAS:** nitrogen, 30 mL/min

ACCURACY	
RANGE STUDIED:	0.19 to 19 mg/m³ (25-L samples)
BIAS:	0.1%
OVERALL PRECISION ($\hat{S}_{rT}$):	0.060
ACCURACY:	±11.32%

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

CALIBRATION: vapor-spiked sampling media

RANGE: 1 to 480 µg per sample

ESTIMATED LOD: 0.2 µg per sample

PRECISION ($\bar{S}_r$): 0.025

APPLICABILITY: The working range is 0.02 to 100 ppm (0.04 to 220 mg/m³) for a 25-L air sample. At the higher levels, desorbed samples may require dilution. Below 0.9 mg/m³ (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 revises Method S91 [1].

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 [2]. 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 5 to 25 L.
4. Separate the tubes, cap, and pack securely for shipment. Chill below –4 °C during shipment and storage.
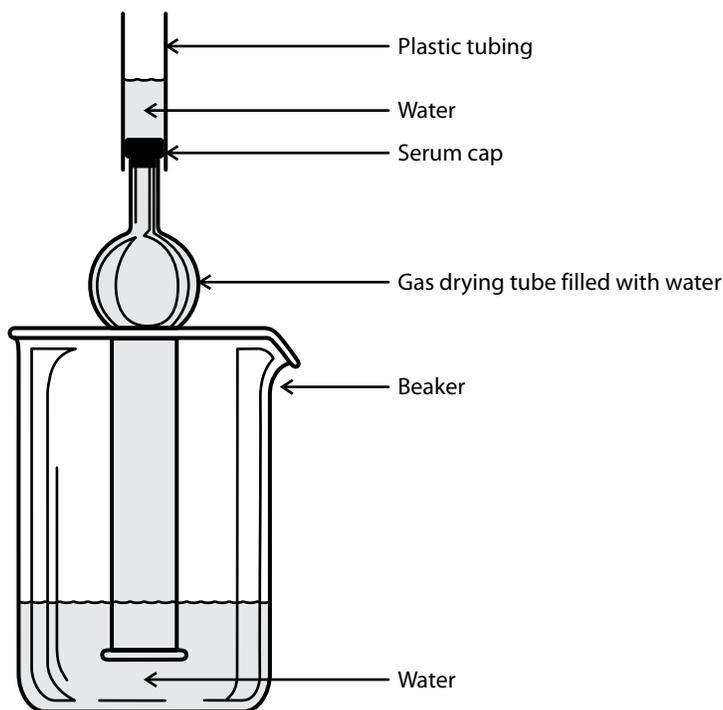
SAMPLE PREPARATION:

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. 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.

Plastic tubing

Water

Serum cap

Gas drying tube filled with water

Beaker

Water

   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 six 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, D, mL, 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.

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

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 $\overline{S}_r$ was 0.038. The estimated LOD 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 $\overline{S}_r$ 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 $\bar{S}_r$ 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 $\bar{S}_r$ 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 $\bar{S}_r$ 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 $\bar{S}_r$ 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 $\bar{S}_r$ of the response was 0.023. The $\bar{S}_r$ of the response pooled for all levels was 0.033. Assuming a sampling pump error of 0.05, the precision ($\hat{S}_{rT}$) 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 significant 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 $\bar{S}_r$ for the observed responses at the five levels were 0.109, 0.080, 0.050, 0.064, and 0.037; the respective 95% confidence intervals for the mean percent recoveries relative to the standard solution calibrations were 60.4 ± 0.4, 66.4 ± 0.3, 70.5 ± 0.2, 86.2 ± 0.3, and 91.2 ± 0.2.

The analysis of quality assurance blind spikes provided additional data indicating that samples were stable when stored below –4 °C, and that average recoveries, calibrated against media standards, ranged from 96 to 107%. Seventy-seven blind spikes were prepared at six levels, 19.9 to 21.9, 48.6 to 52.6, 104 to 110, 199 to 219, 398 to 438, and 663 µg per sample, stored in a freezer, and analyzed along with the field samples. The storage times ranged from 3 to 134 days; the average was 59 days. For the six levels of blind spikes, the respective relative standard deviations for recoveries were 0.210, 0.092,

0.054, 0.091, 0.126, and 0.056; the respective 95% confidence intervals for the mean recoveries were 0.986 ± 0.032, 0.961 ± 0.014, 0.994 ± 0.008, 1.029 ± 0.015, 1.064 ± 0.021, and 1.074 ± 0.021. Prior to linear regression of the recoveries versus the amounts spiked and/or days stored, three results, two high and one low, were determined to be outliers by application of one-sided Grubbs tests [4] at the 2.5% significance level and were dropped from the data set. Linear regression of percent recovery on days stored for the data segregated by level resulted in respective slopes and 95% confidence intervals of 0.060 ± 0.080, 0.005 ± 0.128, –0.003 ± 0.092, 0.060 ± 0.179, 0.249 ± 0.188, and 0.018 ± 0.247 percent per day. Thus, the only statistically significant correlation between recovery and days stored was at the next to highest level, for a gain rather than loss over time. Over all levels, the slopes and 95% confidence intervals for recovery versus amounts spiked and days stored were 0.017 ± 0.009 percent per μg and 0.045 ± 0.051 percent per day, respectively. Thus, according to the latter model: the recovery for the blind spikes increased at a rate corresponding to approximately 11% over the range prepared; as stored, the blind spikes appeared to be stable—the 95% confidence interval of the slope over time indicated a maximum gain of 5.7% or loss of 0.4% during the average 59-day storage period.

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd. ed., V. 2, S91, U.S. Department of Health Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

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

[3] NIOSH Current Intelligence Bulletin 46, "Methylene Chloride," U.S. Department of Health and Human Services, Publ. (NIOSH) 86-114 (1986).

[4] Grubbs, F. E. "Procedures for Detecting Outlying Observations in Samples," *Technometrics*, *11*(1), 1–21, (February, 1969).

[5] MacCallum, R. N., and J. J. McKetta. "Low-Pressure Zs of C_4 Hydrocarbons," *Hydrocarbon Process. Petrol. Refiner*, *42*(5), 191–194 (1963).

METHOD WRITTEN BY:

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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 [1] is 6 m × 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 × 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 × 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 peak. 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 after each run to prepare for the next injection.

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

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

MacCallum and McKetta [5] determined the compressibility factor, Z, which corrects for non-ideal behavior, for 1,3-butadiene at temperatures, T, ranging from 10 to 75 °C, and pressures, P, from approximately 420 to 1050 mm Hg. Multiple regression of the observed values against P, PT, and PT^2, yields the following equation (standard error of the estimated Z is 0.000635 for 13 degrees of freedom):

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

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

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

$$M = \frac{(P - P_v) \times V \times 54.09}{Z \times 62.36 \times (T - 273.2)}, \text{ µg,}$$

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·mol^{-1}),
      62.36 = gas constant (mm Hg·L·mol^{-1}·K^{-1}),
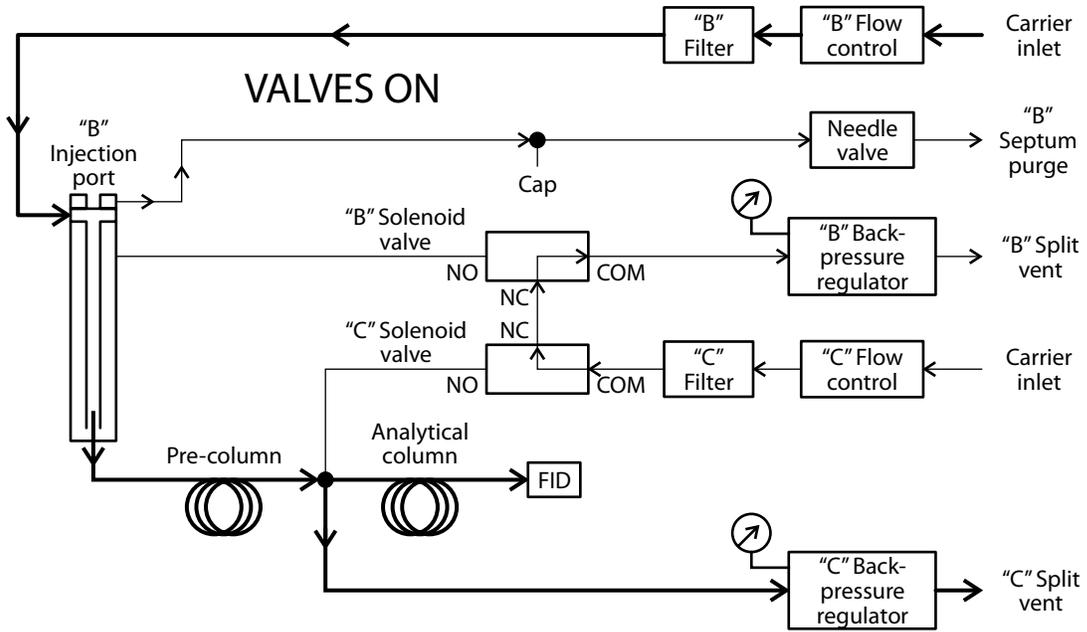   273.2 = absolute temperature of 0 °C (K).

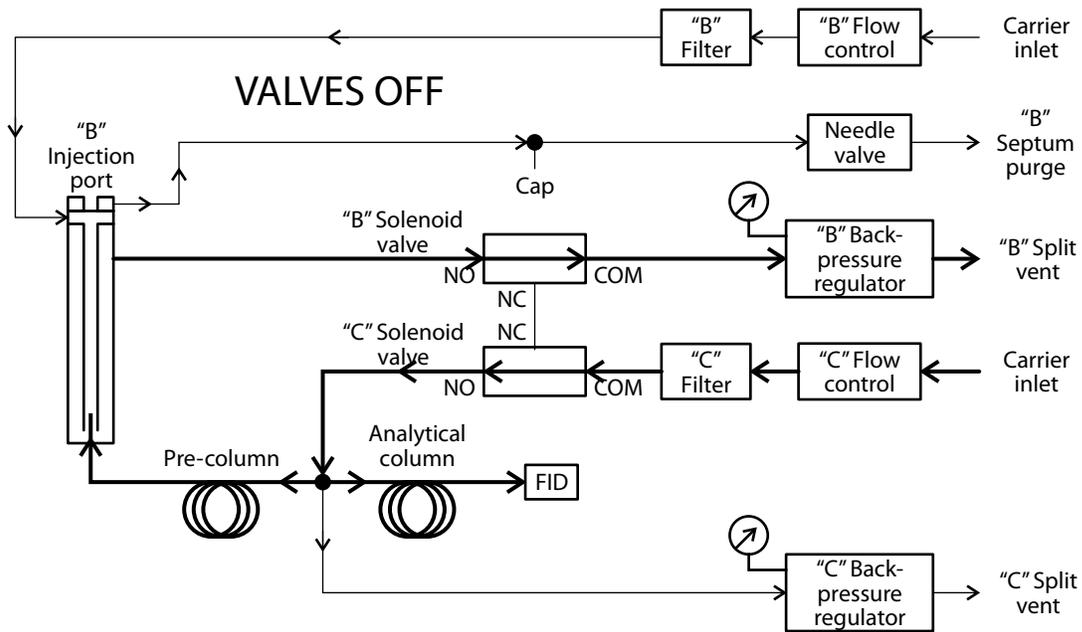**Figure 1.** Flow diagram for pre-column system in inject mode.

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