



## Project Summary

# Sampling and Analysis of Butadiene at a Synthetic Rubber Plant

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Butadiene emission samples were collected from the process vent stream of a plant manufacturing synthetic rubber from styrene and butadiene. Samples were collected by modification of the evacuated container sampling procedure, outlined in Section 7.1.1 of EPA Method 18. On-site analysis of samples was performed using a gas chromatograph equipped with a flame ionization detector. The precision of butadiene concentrations determined from simultaneous samples collected at a nominal sampling rate of 0.050 L/min, rather than at the recommended sampling rate of 0.5 L/min, was determined. In addition, simultaneous samples were collected at both 0.20 L/min and 0.050 L/min and analyzed to determine if the mean values or precisions of the measured concentrations were influenced by the sampling rate. Acceptable precision was observed upon analysis of emission samples collected at both sampling rates, and the mean values and precisions of butadiene levels determined were statistically equal for simultaneous samples collected using the two sampling rates.

*This Project Summary was developed by EPA's Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see*

*Project Report ordering information at back).*

### Procedure

The principles of sampling and analysis followed the general procedures described in EPA Method 18, with the exception that emission samples were collected at flow rates of 0.050 L/min and 0.20 L/min, rather than 0.5 L/min.

The precision of the sampling and analysis techniques was determined using quad-trains. During the field test, gases were withdrawn from a duct carrying process emissions in route to an open flare, and all quad-trains drew gases from a common manifold. A schematic of the sampling apparatus is included as Figure 1. Samples were collected in quadruplicate in the 5 L Tedlar bags. In addition, during two of the twelve sampling runs, samples were collected using dual quad-trains. One train utilized 5 L bags and the other train utilized 20 L bags. All bags were analyzed on-site, as was an audit sample. The results from analysis of the four bags were averaged and a standard deviation, variance, and 95% confidence interval for each sampling run were calculated.

One small bag sample from nine of the first ten sampling runs was returned to the base laboratory for reanalysis by Entropy. All bags collected during the final two sampling runs, except one sample from the twelfth run that leaked, were also retained. A full complement of four large and four small bags was available as the eleventh sampling run

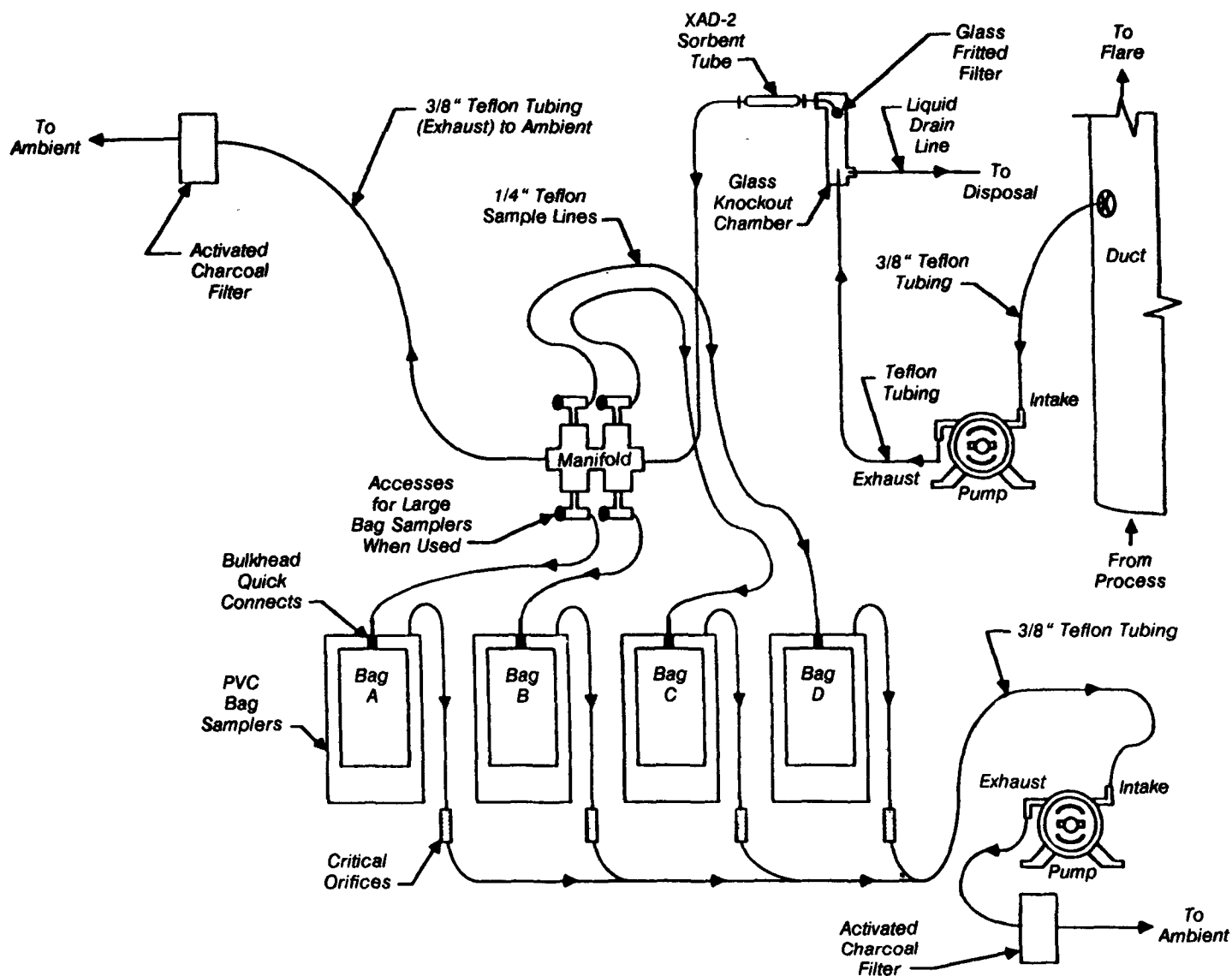


Figure 1. Sample collection apparatus.

involved sample collection using the dual quad-train setup. These samples were analyzed within one week of completion of the field test. Following reanalysis at Entropy's base laboratory, selected bag samples were made available to EMSL-RTP, Quality Assurance Division (QAD) personnel for independent verification of butadiene concentrations measured.

Analyzed cylinders containing approximately 10, 150, and 2000 ppm<sub>v</sub> of gaseous butadiene in nitrogen were purchased from a supplier of high purity gases and used to calibrate the gas chromatograph. The cylinders were analyzed after final blending by the supplier, who certified the butadiene concentrations to  $\pm 2\%$ .

Instrument response was obtained from a least squares fit of the calibration data. An audit of these results was conducted daily by assaying the concentration of a blind audit sample provided under the EPA's performance audit program. The audit sample contained butadiene diluted with nitrogen gas at a concentration in the ppm<sub>v</sub> range.

The accuracy of the butadiene determinations was examined by the on-site analysis of a blind audit sample provided by Research Triangle Institute, Research Triangle Park, North Carolina under the EPA's performance audit program, which utilizes cylinder gases containing volatile organics in the ppm<sub>v</sub> range. The audit cylinders available were known to contain

butadiene in the 5-60 ppm<sub>v</sub> range. Field and laboratory analyses of the cylinders provided a quality assurance check of the three-point calibration curves covering the approximate range 10 to 2000 ppm<sub>v</sub>.

Several other organic components in addition to butadiene were present in samples collected from the plant's process vent. In particular, several butane/butene isomers were observed. Because the chromatographic characteristics of some of these are quite similar to butadiene, a chromatographic system capable of high resolving power was necessary. During the field test, sample analysis involved a chromatographic system utilizing two packed GC columns connected in series as part of a back

flush-to-vent configuration. The first column, a 10' x 1/8" stainless steel column containing 20% SP-2100/0.1% Carbowax 1500 on 100/120 mesh Supelcoport, effected the separation of butadiene and other permanent gases from the higher boiling components within approximately three minutes. In that time these gases had passed into the second column, a 2 m x 1/8" stainless steel column containing 0.19% picric acid on 80/100 mesh Carbowax C. The sampling valve was returned to the load/isolate position at this point to direct a separate carrier flow through the second column allowing for the separation of butadiene from other permanent gases present, while the original carrier flow was simultaneously reversed through the first column to backflush higher boiling sample components to a vent. The separation was performed isothermally at 60°C, and both carrier flows were approximately 20 mL/min in the forward direction.

## Results and Discussion

The range and sensitivity were determined for the Tedlar bag sampling technique prior to conducting the field test. An estimation of the limit of detection and quantifiable limit was carried out. Using a sample size of 1 mL, these values were determined to be 0.43 ppm<sub>v</sub> and 2.0 ppm<sub>v</sub>, respectively.

The upper limit of detection, where the GC column becomes saturated and/or the detector response becomes non-linear, was also estimated. The peak shapes observed for prepared samples that contained butadiene at levels of approximately one percent indicated that the column was saturated. The retention time observed for these prepared samples was also significantly shortened. The shift in retention time was potentially great enough to prevent the complete separation of butadiene from other components observed in samples collected during the field tests.

The results from analysis of the four bags composing each quad-train were averaged and a standard deviation, variance, and 95% confidence interval were calculated. This information is summarized in Table 1.

Two samples could be discarded as statistical outliers at a confidence level of 95%. Two estimates for measures of the precision of the method are given, one in which the outliers are included and one in which they are not.

The average coefficient of variation observed for all the small bag samples

**Table 1.** Summary of Analytical Results and Precision of Data

| Date | Run ID | Mean* | Std. Dev. | Coef. of Var. (%) | Variance |
|------|--------|-------|-----------|-------------------|----------|
| 4/28 | 51     | 322   | 7.4       | 2.3               | 55       |
| 4/28 | 52@    | 24    | 5.7       | 24                | 32       |
| 4/28 | 53     | 30    | 3.7       | 7.8               | 61       |
| 4/28 | L54**  | 444   | 47        | 11                | 2200     |
| 4/28 | 54     | 459   | 39        | 8.5               | 1500     |
| 4/28 | 55     | 171   | 17        | 9.8               | 279      |
| 4/28 | 56@    | 546   | 150       | 27                | 21000    |
| 4/29 | 61     | 426   | 76        | 18                | 5700     |
| 4/29 | 62     | 29    | 3.0       | 10                | 9.0      |
| 4/29 | 63     | 114   | 11        | 10                | 120      |
| 4/30 | 71     | 149   | 6.6       | 4.5               | 44       |
| 4/30 | L72    | 14    | 0.6       | 5                 | 0.3      |
| 4/30 | 72     | 13    | 0.4       | 3                 | 0.2      |
| 4/30 | 73     | 3480  | 40        | 1.2               | 1800     |

\*Butadiene concentrations in ppm<sub>v</sub>.

\*\* One bag sample collected during this run was found to leak; the results from analysis of this bag are not included in any statistical evaluation of the data.

@The results summarized below are obtained for sample runs 52 and 56 when statistical outliers are excluded.

| Date | Run ID | Mean* | Std. Dev. | Coef. of Var. (%) | Variance |
|------|--------|-------|-----------|-------------------|----------|
| 4/28 | 52     | 27    | 1.4       | 5.1               | 2        |
| 4/28 | 56     | 473   | 15        | 3.1               | 217      |

was approximately 11%, but dropped to 6.9% when the two statistical outliers were eliminated from their respective sample sets and the means and standard deviations of those samples recalculated. The average coefficient of variation observed for the two sampling runs utilizing the large Tedlar bags was approximately 8%; the analysis of one large bag sample collected as part of these runs was discarded because the bag did not pass a post-analysis leak check.

During one dual quad-train sampling run, the butadiene level determined using samples collected in the small Tedlar bags at an approximate flow rate of 0.050 L/min was 459 ppm<sub>v</sub> and the standard deviation observed among the four replicates was 39 ppm<sub>v</sub>. The level determined using the large bag samples collected at a flow rate of about 0.20 L/min was 444 ppm<sub>v</sub> and the observed standard deviation was 47 ppm<sub>v</sub>. For the other dual quad-train run, the level measured using the small bags was 13 ppm<sub>v</sub>, with a standard deviation of 0.6 ppm<sub>v</sub>, while the respective data collected using the large bags were 13 ppm<sub>v</sub> and 0.4 ppm<sub>v</sub>. A variance-ratio test, or F-test, showed that standard deviations obtained

using the different bag sizes and flow rates were not significantly different at the 95% confidence level for either of the two sampling runs. This fact, and the similarity of the average coefficients of variation calculated after analysis of samples collected using both sampling rates, suggests that the precisions for the two sampling protocols are invariant. Likewise, when the means of butadiene levels determined using the small and large Tedlar bags were compared for the two sampling runs using a Student's t test and the null hypothesis, they were found to be equivalent at the 95% confidence level.

Selected samples were returned from the field for reanalysis. Because the reanalysis results were in overall agreement with the results obtained during the original on-site analyses, the two sets of measurements were used to estimate within- and between-laboratory precision. The average coefficient of variation for the Entropy's field and laboratory analyses of samples collected in small bags was 9.5%; the average coefficient of variation was 13% when the precisions of both small and large bags are included. The average coefficient of variation for the laboratory analysis of

selected bag samples by Entropy and EMSL, QAD was 4.9%.

Several analyses of the audit cylinder were conducted while analyzing samples collected during the field test. The average value obtained for the concentration of the audit cylinder was approximately 6% below the certified concentration.

Although the retention of butadiene by Tedlar bags was not rigorously evaluated, experiments were conducted to demonstrate that bags containing field samples could be reused after they had been reblanked. Bags were emptied of sample by complete evacuation and flushed twice with compressed air before being filled to half their capacities. After allowing the bags to stand overnight, analysis of the contained gas showed them to be essentially free of butadiene.

## Conclusions and Recommendations

Four principal conclusions were drawn from the data collected and from the observations made during the field test. The sampling and analytical protocol used was fully validated, including the use of the lowered sampling rate utilized for collection of emission samples in small Tedlar bags. The physical and chemical composition of the process effluent encountered in this investigation leads to two important conclusions/ recommendations concerning sampling methodology and to two important conclusions/ recommendations concerning sample analysis.

1. Butadiene levels determined in samples collected in 5 L Tedlar bags at an approximate flow rate of 0.050 L/min and in samples collected in larger, 20 L bags at an approximate flow rate of 0.20 L/min were not significantly different at the 95% confidence level. Because a sampling rate of 0.5 L/min yields a more convenient sample size than that obtained using the sampling rate recommended by EPA Method 18 and the two differing sampling rates utilized for collection of bag samples during this study did not affect the values or precisions of the determinations made, the lowered sampling rate is recommended for collection of bag samples.
2. The presence of aspirated organic droplets in the process vent stream made the precise quantitation of gaseous butadiene levels very difficult. The precision among quadrupole samples was effectively improved by using of filtering media designed to eliminate such liquid while passing butadiene gas. The average coefficient of variation observed for the 0.050 mL/min sampling rate was approximately 7%. The elimination of similar liquids from other process effluents is highly desirable during collection of bag samples. Further investigation of filtering media designed to accomplish this while passing the sample component of interest is recommended.
3. The presence of several butane isomers in the sample stream necessitated the use of chromatography column capable of separating butadiene from these potential interferants. A 2 m x 1/8" stainless steel column containing 0.19% picric acid on 80/100 mesh Carbopack C was utilized during this investigation. This column, or another column similarly able to resolve butadiene from these potential interfering hydrocarbons
4. The presence of high boiling sample components in the collected emission samples made use of a chromatographic system utilizing a two column backflush-to-vent configuration highly desirable. The forward column, a 10' 1/8" stainless steel column containing 20% SP-2100/0.1% Carbowax 150 on 100/120 mesh Supelcopor effected the separation of butadiene and other permanent gases from higher boiling sample components before completion of the separation on the picric acid column. Sample analysis was complete in under 1 minutes, far more rapidly than possible with a conventional single column system. The use of a similar system is recommended to speed the analysis of butadiene samples whenever significant quantities of higher boiling organics are present.

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Jimmy C. Pau is the EPA Project Officer (see below).

The complete report, entitled "Sampling and Analysis of Butadiene at a Synthetic Rubber Plant," (Order No. PB 89-151 534/AS; Cost: \$15.95, subject to change) will be available only from:

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