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Research Triangle Park NC 27711

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Project Summary

Sampling and Analysis of Butadiene at a Neoprene Plant

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Butadiene has been listed as a hazardous air pollutant by the United States Environmental Protection Agency (EPA). This document details a field study commissioned by the EPA's Atmospheric Research and Exposure Assessment Laboratory, Quality Assurance Division, Research Triangle Park, North Carolina, that validates a method for the sampling and analysis of butadiene emissions from a plant manufacturing neoprene from butadiene/chlorine mixtures. Gaseous samples were collected from the process vent of one such plant using a modification of the evacuated container sampling procedure, outlined in Section 7.1.1 of EPA Method 18. The samples were collected at a sampling rate of 0.04 L/min, rather than at 0.5 L/min as specified in the method. Sample collection at the lowered sampling rate yields a total sample volume of approximately 3 L, rather than the 30 L obtained when using the specified sampling rate. On-site analysis of samples was performed using a gas chromatograph equipped with a flame ionization detector.

The method precision was determined by collection and analysis of simultaneous, quadruplicate samples. The relative standard deviation for quad-train samples collected at the lowered sampling rate ranged from 1.7 - 6.4 percent with emission levels ranging from about 2 to 40%.

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 0.04 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 During the field test, gases were withdrawn from a duct carrying process emissions to the atmosphere, and all quad-trains drew gases from a common manifold.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 5 L Tedlar bags using a newly designed sampling system. 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 at 95% confidence level for each sampling run were calculated.

One bag sample from each of the sampling runs was returned to the base laboratory for reanalysis by Entropy. These samples were analyzed 13 to 15 days following completion of the field test. Following reanalysis at Entropy's laboratory, selected bag samples were made available to AREAL, QAD personnel for independent verification of butadiene concentrations measured.

Analyzed cylinders containing approximately 2000 ppm, 1.3%, and 3.8% of gas-

eous 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 ± 5 ppm.

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 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 Figure 1. Quad-train sampling system program, which utilizes cylinder gases containing volatile organics in the ppm range. The audit cylinders available were known to contain butadiene in the 5 - 60 ppm range. Field and laboratory analyses of the cylinder provided a quality assurance check of the three-point calibration curves.

During the field test, sample analysis involved a chromatographic system utilizing a 2 m x 1/8-inch stainless steel column containing 0.19% picric acid on 80/100 mesh Carbopack C. The separation was performed isothermally at 80°C, and the carrier flow was approximately 30 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 made. Using a sample size of 1 mL, these values were determined to be 0.43 ppm and 2.0 ppm, respectively.

The results from analysis of the four bags composing each quad-train were averaged, and a standard deviation at 95% confidence level were calculated. The relative standard deviation was also calculated for each of the 12 sampling runs. One relative standard deviation was discarded as a statistical outlier at a confidence level of 90%. Two estimates for measures of the precision of the method are given, one in which the outlier is included and one in which it is not. The relative standard deviations ranged from 1.7 to 6.4 percent. During the quad-train sampling runs, the average butadiene level determined using samples collected in the bags at a flow rate of 0.04 L/min was approximately 27%. This information is summarized in Table 1.

A stability study of the samples collected indicated that butadiene at these high levels (2-40%) is not necessarily stable over long periods of time. After 13 days, the samples began to show signs of polymerization of the butadiene.

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 only 4% above the certified concentration.

Table 1. Summary of Analytical Results and precision of Data

Date	Run ID	Mean Conc. (%)	Coefficient of Variation (%)
4/2/90	1	25.7	4.44
4/3/90	2	33.9	1.70
4/3/90	3	35.5	2.46
4/3/90	4	37.5	2.53
4/3/90	5	20.2	6.03
4/3/90	6	24.0	5.77
4/4/90	7	41.4	2.28
4/4/90	8	34.2	1.86
4/4/90	9	22.8	6.40
4/4/90	10	2.55	13.5
4/4/90	11*	15.7	4.83
4/4/90	12	26.9	6.01

*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.

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 blanked. Bags were emptied of sample by complete evacuation and flushed four times 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

The sampling and analytical protocol used was fully validated, incorporating the use of the lowered sampling rate for collection of emission samples in small Tedlar bags. The physical and chemical composition of the process effluent encountered in this investigation leads to several important conclusions/recommendations concerning sampling methodology and sample analysis.

1. A sample flow rate (approximately 0.05 L/min) is recommended for the collection of butadiene at neoprene plants. This flow rate which has been proven acceptable at the 95% confidence level greatly reduces the sample size. This reduced sample size allows sample collection in much smaller and more convenient sample containers.
2. The precision ranges from 1.7 to 6.4 percent for this method based on the relative standard deviations obtained in the field evaluation.
3. The possible presence of butane/butene isomers in the sample stream necessitates the use of a chromatography column capable of separating butadiene from these potential interferents. A 2 m x 1/8-inch stainless steel column containing 0.19% picric acid on 80/100 mesh Carbopack C was utilized during this investigation. Use of this column or another one of similar design capable of resolving butadiene from these potentially interfering hydrocarbons is highly recommended.
4. Sample stability is a concern when collecting butadiene at neoprene plants due to the high concentrations (2 - 40%) observed. Samples appear to be stable up to two weeks, but no longer. Rapid analysis of the samples is highly recommended and will eliminate the possibility of polymerization of butadiene before sample analysis.

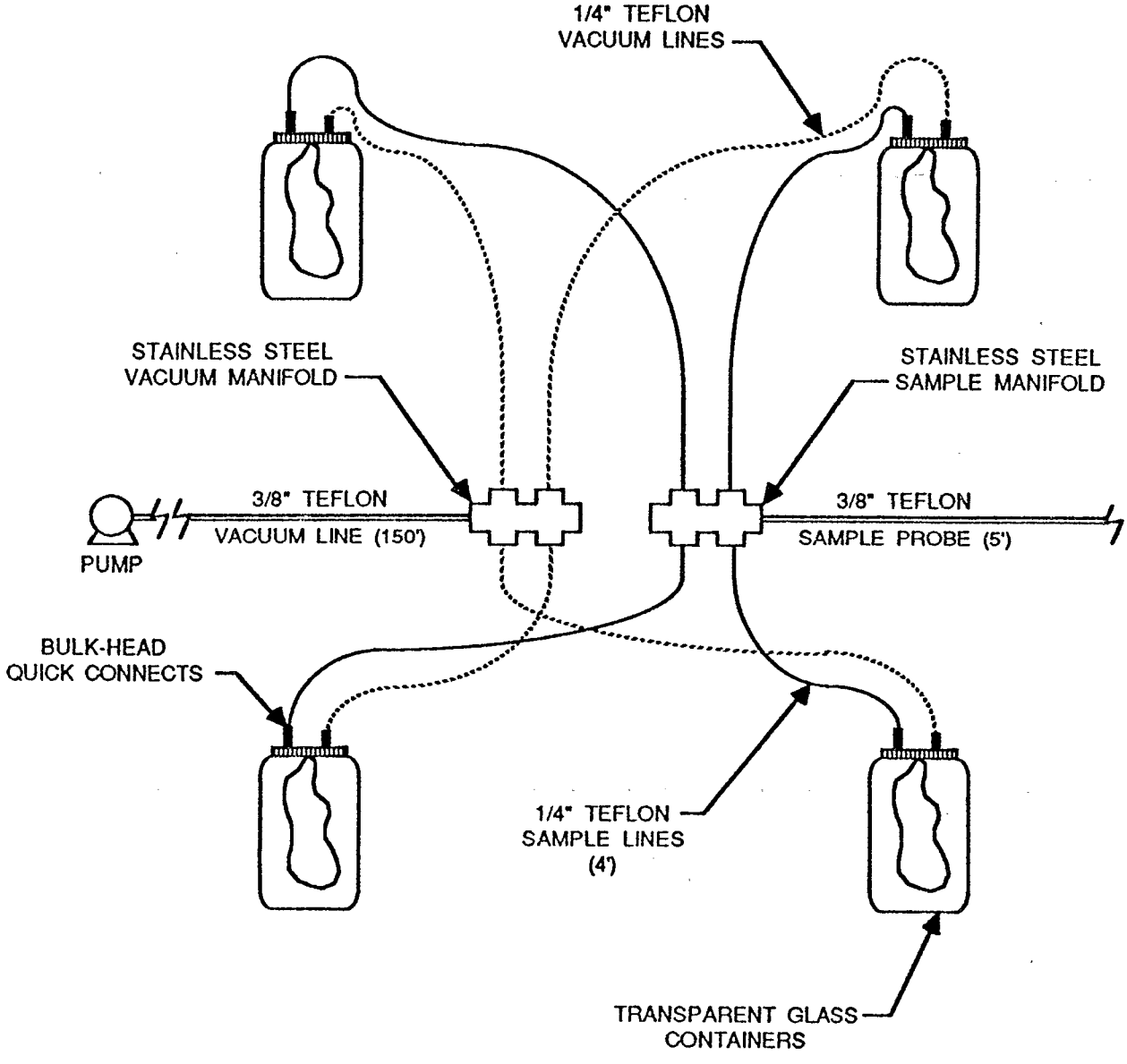

Figure 1. *Quad-train sampling system.*

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The complete report, entitled "Sampling and Analysis of Butadiene at a Neoprene Plant," (Order No. PB90-261 546/AS; Cost: $17.00, cost subject to change) will be available only from:
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