

Determination of Butadiene Emissions

1. APPLICABILITY, PRINCIPLE, INTERFERENCES, PRECISION, BIAS, AND STABILITY.

1.1 Applicability. This method is applicable to the determination of 1, 3-butadiene (hereafter butadiene) present in waste gases emitted from synthetic rubber plants.

1.2 Principle.

1.2.1 Emission samples are collected in 5-liter Tedlar bags housed in rigid, air-tight polyvinyl chloride (PVC) containers at a flow rate of 50 ml/min over a 1-hr period by evacuating the space surrounding the bag.

1.2.2 Cylinders of dilute gaseous butadiene in nitrogen are used as standards to calibrate the gas chromatograph with a flame ionization detector (GC/FID), which are then used to determine the concentration of butadiene in the field samples.

1.3 Potential Interferences. Several C_4 and unsaturated C_4 hydrocarbons are potential interferents but may be eliminated with the use of a GC column capable of separating butadiene from these potential interferents.

1.4 Precision. The within-laboratory relative standard deviation observed for the collection and analysis of quadruplicate samples during field validation of this method was approximately 7 percent.

1.5 Stability. Samples should be analyzed within two weeks of collection.

2. SAFETY

Butadiene has been listed as a hazardous air pollutant in the Federal Register since serious health effects result from exposure to the gas; therefore, inhalation of butadiene, and of other potentially harmful vapors present in source samples, must be rigorously avoided. The use of electrical equipment for sampling in potentially explosive areas requires additional precautionary measures.

3. APPARATUS AND MATERIALS

NOTE: Mention of trade names or products does not constitute endorsement by the Environmental Protection Agency.

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3.1 Sampling Apparatus. The sampling train is shown in Figure 1, and component parts are discussed below.

3.1.1 Probe. Teflon tubing, 3/8-in. OD, with appropriate connecting fittings.

3.1.2 Glass Wool. Borosilicate or quartz. Use a small wad of glass wool at the inlet of the probe to remove particulate matter, if present in the sample stream.

3.1.3 Primary Sampling Pump. Leak-free Teflon-coated diaphragm-type pump, or equivalent. Connect directly to the anterior end of the Teflon probe line.

3.1.4 Liquid Knockout Chamber. Elongated glass vessel with 1/4-in. openings at both ends, with a fritted glass filter at the outlet end and a perpendicular sidearm near the inlet end. The use of the knockout chamber is optional, but is highly recommended to eliminate entrained liquids when they are present in the process stream. Mount the chamber vertically with the outlet end and glass filter facing upward. Connect to the outlet of the sampling pump with Teflon tubing so that sample gas and entrained liquid enter the tube at the bottom. The perpendicular sidearm located at the lower end allows any liquid collecting in the tube to be forced out by a portion of the sample flow allowed to vent at this point. The fritted glass filter located at the top of the chamber transports gases to be subsequently sampled.

3.1.5 Liquid Drain Line. Rubber surgical tubing or other convenient material used in conjunction with the optional liquid knockout chamber. Attach to the sidearm of the knockout chamber. Provide for the collection and disposal of liquid exiting at the end of line and for appropriate venting of sample gas (refer to Section 3.1.9).

3.1.6 Flow Control Valves. Connect in-line after the sampling manifold, and adjust to maintain slight positive pressures in the sampling apparatus. If the optional liquid knockout chamber is used, include a flow control valve to regulate the flow rate of sample vented via the liquid drain line.

3.1.7 XAD-2 Adsorption Tube. The use of the adsorption tube is optional, but is highly recommended to eliminate entrained liquid when visible quantities are carried past the optional liquid knockout chamber. Place the XAD-2 tube, which will largely pass butadiene, in-line between the knockout chamber and sampling manifold to trap fine liquid droplets.

3.1.8 Sampling Manifold. Stainless steel, with the appropriate fittings

necessary to obtain simultaneous samples and to connect a manometer. In general, two or more samples are collected. Flow through all parts of the manifold should be unrestricted and uniform. Connect downstream of the sampling pump using Teflon tubing.

3.1.9 Activated Charcoal Filters. Place behind auxiliary sampling pump to adsorb gas vented in the event of sampling bag rupture. Also place behind sampling manifold to filter gas, if excess is vented to the atmosphere rather then to emission conduit.

3.1.10 Manometer. U-tube water manometer, 76-cm, to measure pressure in the sampling manifold.

3.1.11 Sample Lines. Teflon tubing, 1/4-in OD, to conduct gas from the manifold to the Tedlar gas sampling bags.

3.1.12 Quick-Connects. Stainless steel, self-sealing, male quick-connects. Attach to the bag end of each sample line. Mating female, stainless steel, bulkhead quick-connects are affixed in the lid of rigid containers and directly adjoined on the underside to an enclosed Tedlar gas sampling bag.

3.1.13 Rigid, Evacuation Containers. PVC, or other suitable rigid material, to house leak-free Tedlar sampling bags. The design of one such container is shown in Figure 2.

3.1.14 Tedlar Gas Sampling Bags. Unused, double-seamed, with nominal capacities of 5 liters.

3.1.15 Auxiliary Sampling Pump. For evacuation of bag containers. Sample flow into each gas sampling bag is produced by controlled, partial evacuation of container space surrounding the sample bags.

3.1.16 Critical Orifices. Glass or other suitable material, to fix the flow exiting the containers, and, in turn, to regulate the sample flow entering the sample bags. Sonic flow through each orifice should be approximately 0.050 liter/min. Calibrate and place in-line between auxiliary sampling pump and bag.

3.1.17 Vacuum Tubing. To connect the rigid containers to the auxiliary sampling pump.

3.1.18 Rate Meter. To be used in leak-check procedures.

3.2 Gas Standards. Dilute gaseous butadiene in nitrogen at concentrations certified to ±2 percent, commercially available from suppliers of high purity gases. Purchase cylinders containing nominal butadiene concentrations of 10, 100, and 1000 ppm, or at three other concentrations, to bracket the emission concentrations expected. Order the desired concentrations four or more weeks in advance of need to allow time for custom blending of gases by suppliers, when necessary.

3.3 Gas Chromatographic System. General criteria for the GC and

peripheral hardware necessary for analysis of samples are outlined below.

3.3.1 Gas Chromatograph. Transportable, incorporating an FID, appropriate separation columns, a temperature-controlled gas sampling valve, and a column oven capable of maintaining stable temperatures of 30-100°C.

3.3.2 Carrier Gas. Oxygen/hydrocarbon-free nitrogen gas for optimum performance of separation columns and noiseless operation of detector. Minimum acceptable purity specifications recommended for carrier gas are dependent on specific column and specific brand of detector used. Two carrier flows are required to create the backflush-to-vent configuration that is required for rapid sample analysis (refer to Figure 3 and Sections 3.3.4 and 3.3.5).

3.3.3 Recorder/Integrator. To record the output of the detector. If a strip chart recorder is used, provisions must be made for estimating the recorded peak areas.

3.3.4 GC Columns. Two packed GC columns, serially combined in a backflush-to-vent configuration (refer to Figure 3 and Section 3.3.5). Resolution of closely related hydrocarbons from butadiene occurs on the rear column of the series, while high boiling sample components are backflushed and vented from the forward column. The first column separates butadiene and other permanent gases from the higher boiling sample components. One column adequate for this purpose is a 10-ft x 1/8-in. stainless steel column containing 20 percent SP-2100/0.1 percent Carbowax 1500 on 100/120 mesh supelcoport. A 2-m x 1/8-in. stainless steel column similarly able to resolve C_4 and unsaturated C_4 hydrocarbons, is used for the final chromatographic separation.

3.3.5 Gas Sampling Valve. Stainless steel with ten ports and an inert gas sample loop. A schematic of the required backflush-to-vent sample valve configuration is included as Figure 3. Maintain the entire valve/column assembly at a constant temperature in the GC column oven.

3.3.6 Gas Sample Loop. Stainless steel or Teflon. The sample loop's precise volume need not be known, but sample loop volumes of 0.1 to 1.0 ml are convenient for most analyses.

3.3.7 Gas Sample Loop Pump. To draw collected emissions samples from a gas sample bag through the sample loop at a nominal flow rate of 100 ml/min.

3.3.8 Rate Meter. To measure sample flow during loading of sample loop.

4. SAMPLING PROCEDURE

4.1 Pretest Leak-Checks. Leak-check the Tedlar gas sampling bags and the rigid containers before traveling to the test site.

4.1.1 Leak-Check of Tedlar Gas Sampling Bags. Leak-check each Tedlar bag before sealing it in a rigid container. A compression fitting incorporated during construction of each bag allows direct connection of the bag to the

bulkhead female quick-connect fixed in the lid of individual rigid containers. Screw the bags tightly to this quick-connect on the underside of the container lids and inflate bags to rigidity. Discard bags that show any loss of rigidity after standing overnight. After leak-checking, completely deflate the bags.

4.1.2 Leak-Check of Rigid Containers. After ensuring that leak-free bags are attached to the lid of each rigid container, liberally coat the rubber gaskets positioned atop the open container tops with silicone vacuum grease before screwing the lids tightly in place. To leak-check individual rigid containers, attach a water manometer to the male bulkhead compression fitting that is imbedded in each container lid. This fitting provides access to the space between the container and the enclosed sample bag, and allows the pressure changes within the container to be monitored. Seal other "open" fittings. Create a positive pressure of 25 cm H_2O in the container by slowly filling the sample bag with a small volume of zero air quick-connect connected via the female EMTIC CM-001 CM TEST METHOD Page 5

to the enclosed bag. Any visible change in the level of water in the manometer during a 30-second period indicates a leak. Isolate any leaks detected in the rigid containers with a leak detection fluid.

4.2 Set-up of Sampling Apparatus.

4.2.1 Attach the rear of the 3/8-in. OD Teflon probe line to the intake of primary sampling pump. Connect the outlet of the primary sampling pump to the sampling manifold. If a glass knockout chamber is used, mount it vertically and use Teflon tubing to connect the pump output to the inlet of the knockout chamber. Attach the liquid drain line and associated flow control valve to the horizontal sidearm of the knockout, and connect the inlet of the stainless steel manifold, using Teflon tubing, to the outlet of the knockout chamber. Place the XAD-2 adsorption tube, if used, between the knockout and sampling manifold.

4.2.2 Use Teflon tubing to return excess sample gas to the emission conduit, or when the concentrations of process gases present create no explosion risk, pass excess sample gas through an activated charcoal filter before venting to the atmosphere a safe distance from sampling personnel. Attach sample lines to the steel manifold.

4.2.3 Place the rigid containers used to house the Tedlar bags in position for connection to the manifold sample lines using the quick-connects affixed in their lids. Do not connect the rigid containers to the sampling manifold or to the auxiliary sampling pump until leak-check procedures are completed.

4.3 On-Site Leak-Checks of Sampling Apparatus. The sampling apparatus is leak-checked on-site in three sections.

4.3.1 Leak-Check of Evacuation Systems. Plug the open ends of the vacuum tubing used to evacuate the bag containers. Connect the flow meter to the outlet of the auxiliary sampling pump, and start the pump. If the flow meter indicates any residual flow after a time sufficient to evacuate the vacuum lines, then a leak is present. Shut off the pump and unplug the vacuum lines when the leak-check is complete.

4.3.2 Leak-Check of Probe and Primary Sampling Pump. Remove the line leading from the outlet of the primary sampling pump to the sampling manifold, or to the glass knockout chamber when used, and attach the flow meter to the outlet of the pump. Plug the open end of the probe, and start the pump. If the flow meter indicates any residual flow after a time sufficient to evacuate the vacuum lines, then a leak is present. Shut off the pump, and unplug the probe when the leak-check is complete.

4.4 Final Assembly of Sampling Apparatus and Purge Procedure. Immediately before sampling, check the Tedlar bags for residual gas, and evacuate as necessary. A large volume of in-drawn ambient air indicates that the bag may have leaked during transport. Attach the vacuum lines to the rigid containers. Insert the probe into the stack. Once the connection between the stack and sampling apparatus is deemed leakfree, start the sample pump. Purge the delivery system for at least 5 minutes. During the purge, adjust the sample flow so that a positive pressure of approximately 10 cm H_2O , as measured by the water manometer attached to the sampling manifold, exists in the system.

4.5 Sample Collection. Following the purge of the delivery system, mate the quick-connects at the end of the manifold sample lines with the quick-connects joined to the gas sampling bags. Immediately start the auxiliary sampling pump to begin sampling. Adjust the sample flow at this point if the system pressure drops below approximately 4 cm H_2O , as measured by the water manometer. A leak in the surrounding container is indicated by rapid filling of an individual Tedlar bag. Monitor the manifold pressure every 10 minutes; a drop in system pressure indicates a leak has formed in the delivery system. At the end of the 60-minute sampling period, switch off the auxiliary pump, and detach the manifold sample lines from the rigid containers. Then, switch off the primary sampling pump.

5. GC ANALYSIS

5.1 Column Configuration Used to Resolve Butadiene. Samples are rapidly and conveniently analyzed using an analytical system that includes two packed

GC columns connected in series and incorporated in a backflush-to-vent sample valve configuration (see Figure 3). Such a system provides adequate separation of closely related hydrocarbons from butadiene on the second column in the series, while high boiling sample components are separated, backflushed, and vented from the forward column. One column adequate for the first column is a 10-ft x 1/8-in. stainless steel column containing 20 percent SP-2100/0.1 percent Carbowax 1500 on 100/120 mesh Supelcoport. A 2-m x 1/8-in. stainless steel column containing 0.19 percent picric acid

on 80/100 mesh Carbopack C, or other column similarly able to resolve $\rm C_4$ and unsaturated $\rm C_4$ hydrocarbons, is used for the final chromatographic separation.

5.2 Instrument Operating Parameters.

5.2.1 Operating Parameters for Detector. For all analyses, fix the hydrogen and air flows to the FID at rates that give a stable flame. If the GC used includes internal metering orifices, supplying these gases at constant regulator pressures will accomplish this. The detector response should be optimized according to the instructions provided by the manufacturer.

5.2.2 Temperatures of Heated Components. When using the columns listed in Section 5.1, set the oven to operate isothermally at 60° C. Maintain the detector temperature at 300° C.

5.2.3 Carrier Gas Flows. When using the columns listed in Section 5.1, set the forward flow through both columns at approximately 20 ml/min.

5.3 GC Equilibration. Prior to sample analysis, establish a stable baseline. Inject a nitrogen blank to distinguish any peaks arising from sample injection.

5.4 Introduction of Samples.

5.4.1 Introduce cylinder standards directly into the sample loop at regulator pressures of approximately 140 kPa. Draw emission samples from the Tedlar bags and through the sample loop at nominal flow rates of 100 ml/min using a small pump. During sample loop loading of either standard cylinder gases or bag samples, purge the sample loop for a minimum of one minute. After cessation of standard or sample gas purge, allow the sample loop pressured to equilibrate to ambient pressure over a 10 second period before injecting loaded samples.

5.4.2 When using the recommended valve/column assembly, return the gas sample valve to its initial position approximately three minutes after injection of a gas sample. the resulting redirection of carrier flows isolates butadiene and other permanent gases, which have passed into the second column, from higher boiling sample components, which are backflushed from the first column to a vent. Butadiene and related C_4 and C unsaturated hydrocarbons elute from the second column within about 12 minutes of the initial sample injection. The retention time of butadiene in Figure 4, the example gas chromatogram, is 10.09 minutes.

5.5 Calibration Curve for Gas Chromatograph. Analyze the cylinder gas calibration standards as outlined in EPA Method 18. Use the peak areas resulting from analysis of these standards to establish a linear calibration curve relating detector response to the concentration of butadiene present in a sample.

5.6 Audit Analysis. Perform the analysis of audit samples, during calibration of the detector response, as set forth in EPA Method 18.

5.7 Calculation of Measured Butadiene Concentrations. Calculate the concentration of butadiene in the field samples using the detector responses as set forth in EPA Method 18.

7. BIBLIOGRAPHY

- 1. <u>Federal Register</u>, <u>51</u>, No. 62, pp 11021-11022, April 1, 1986.
- Method 18: Measurement of Gaseous Organic Compound Emissions by Gas Chromatography, 40 CFR Part 60, July 1, 1987.