

METHOD 27

REF: Reg 11-6

DETERMINATION OF VINYL CHLORIDE IN EFFLUENT

1) PRINCIPLE

This method is applicable to the measurement of vinyl chloride (chloroethene) in stack gases from ethylene dichloride, vinyl chloride, and polyvinyl chloride manufacturing processes. An intergrated bag sample of stack gas containing vinyl chloride is determined by gas chromatography, using a flame ionization detector (**FID**).

1.1 Interferences. Acetaldehyde, which can occur in some vinyl chloride source will interfere with the vinyl chloride peak from the chromasorb 102. See Sections **2.2** and **4.9**.

2) APPARATUS

2.1 Gas Chromatograph. The unit is equipped with a compatible recorder, a FID and 1.0 to 5.0 ml heated sample loop valve. It must be capable of detecting at least 1 ppm vinyl chloride.

2.2 Chromatographic Column. Stainless steel, 2 m x 3.2 mm, containing 80/100 mesh Chromasorb 102. A secondary column of GE SF-96, 20 percent on 60/80 mesh AW Chromasorb P, stainless steel, 2m x 3.2 mm or Porapak T, 80/100 mesh, stainless steel, 1 m x 3.2 mm is required if acetaldehyde is present. If used, a secondary column is placed after the Chromasorb 102 column. The combined columns should then be operated at 120°C.

2.3 Flow Meters. Rotameter type, 0 to 100 ml/min capacity, with flow control valves and a rotameter type, 0 to 1000 ml/min range accurate to $\pm 1\%$, to meter nitrogen in preparation of standard gas mixtures.

2.4 A 1.0 to 5.0 ml heated sample valve loop.

2.5 Diaphragm Air Pump. Leak free with a minimum range of 100 ml/min.

2.6 Teflon Tubing.

2.7 Gas Tight Syringes. 0 - 50 μ l and 0 - 250 μ l capacity.

2.8 Stop-Watch.

2.9 16 in. square Tedlar bag for the preparation of standards.

3) REAGENTS

3.1 Helium or Nitrogen Zero Carrier Gas.

3.2 Hydrogen Zero Gas.

3.3 Oxygen Gas or Air Zero Gas.

3.4 Vinyl Chloride, 99.9% + Purity.

3.5 Nitrogen Zero Gas for the Preparation of Standard Gas Mixtures.

3.6 Charcoal Tube.

4) ANALYTICAL PROCEDURE.

4.1 **Sample storage.** Sample bags must be kept out of direct sunlight. When at all possible analysis is to be performed within 24 hours, but in no case in excess of 72 hours of sample collection.

4.2 **General Column and Instrument Parameters:**

	100°C	Column	Temperature
Temperature	120°C	Combined	Column
	150°C	Detector	Temperature
		Sample Valve Loop	70°C

4.2.1 Establish the flow rates consistent with the manufacturer's requirement for satisfactory operation, using helium or nitrogen zero gas as the carrier gas, and hydrogen and air to the FID.

4.3 To the outlet side of the sampling valve, connect the 0 to 500 ml/min range rotameter, a charcoal trap and a small diaphragm air pump.

4.4 Purge the heated sample loop for at least 30 seconds at a rate of about 100 ml/min.

- 4.5 Stop the pump and immediately activate the sampling valve. Inspect the chromatogram to insure that the heated sample loop is free of residual vinyl chloride.
- 4.6 Connect the Tedlar sample bag to the inlet of the gas sampling valve with teflon tubing. Start the diaphragm air pump and purge the sample loop for at least 30 seconds at a rate of about 100 ml/min.
- 4.7 Stop the pump and immediately activate the sampling valve to transfer the sample to the analytical column.
- 4.8 Measure the peak height and peak area of the vinyl chloride peak. Repeat the sample injection at least twice or until consecutive vinyl chloride peak heights and areas do not vary more than 5%. The average value of the peak heights or areas will be used to compute the vinyl chloride concentration.
- 4.9 Compare the ratio of peak height to peak area for the vinyl chloride sample with the same ratio for the standard peak which is closest in height. If the ratios differ by greater than 10%, the vinyl chloride peak may be contaminated with acetaldehyde, and the combined columns must be used.

5) PREPARATION OF STANDARD CALIBRATION CURVE

5.1 Preparation of Standard Curve.

- 5.1.1 Evacuate a sixteen inch square Tedlar bag that has passed a leak check and meter in accurately 5.0 liters of nitrogen by means of a 0 to 1000 ml/min rotameter for a specific time, utilizing a stopwatch.
- 5.1.2 While the bag is filling, use the 250 μ l syringe to inject 250 μ l of vinyl chloride thru the wall of the bag. Upon withdrawing the syringe needle, immediately cover the resulting hole with adhesive tape.
- 5.1.3 The Tedlar bag now contains a vinyl chloride concentration of 50 ppm. In a similar manner, prepare gas mixtures of 10 and 5 ppm vinyl chloride.
- 5.1.4 Place each bag on a smooth surface and alternately depress opposite sides of the bag at least 20 times to aid the mixing process.
- 5.1.5 Let the bags set for at least 30 minutes, prior to taking a sample.

- 5.2 Analyze the Tedlar bag standards as described in 4.1 thru 4.9.
- 5.3 Using the three different concentrations of standard gas mixtures, plot the respective vinyl chloride concentrations vs. the peak heights and peak areas on a rectilinear graph paper.
- 5.4 Perform the calibration daily or before and after each set of bag samples, which ever is more frequent.
- 5.5 These gas standards mixtures may be used for 10 days from the date of preparation.

6) CALCULATIONS

- 6.1 From the calibration curve described in 5.3, determine the value of the vinyl chloride concentration (**PPM**) that corresponds to the sample peak height or area.

7) REFERENCE

- 7.1 Method 106, Reference Method for the "**Determination of Vinyl Chloride from Stationary Sources**", 40 CFR Part 61 N, Appendix B.