

### 3.5 Vinyl Chloride - Ethylene Dichloride, Vinyl Chloride, and PolyVinyl Chloride Plants

#### 3.5.1 Applicability

- (a) This source category applies to plants which produce:
  - (1) Ethylene dichloride by reaction of oxygen and hydrogen chloride with ethylene,
  - (2) Vinyl chloride by any process, and/or
  - (3) One or more polymers containing any fraction of polymerized vinyl chloride.
- (b) This section does not apply to equipment used in research and development if the reactor used to polymerize the vinyl chloride processed in the equipment has a capacity of no more than 0.19 m<sup>3</sup> (50 gal.).

#### 3.5.2 Emission Tests

- (a) Unless a waiver of emission testing is obtained, the owner or operator of a source to which this source category applies shall test emissions from the source,
  - (1) Within 90 days of the effective date in the case of an existing source or a new source which has an initial startup date preceding the effective date, or
  - (2) Within 90 days of startup in the case of a new source, initial startup of which occurs after the effective date.
- (b) The owner or operator shall provide the Director at least 30 days prior notice of an emission test to afford the Director the opportunity to have an observer present during the test.
- (c) Any emission test is to be conducted while the equipment being tested is operating at the maximum production rate at which the equipment will be operated and under other relevant conditions as may be specified by the Director based on representative performance of the source.
- (d) [Reserved]
- (e) When at all possible, each sample is to be analyzed within 24 hours, but in no case in excess of 72 hours of sample collection. Vinyl chloride emissions are to be determined within 30 days after the emission test. The owner or operator shall report the determinations to the Director by a registered letter dispatched before the close of the next business day following the determination.
- (f) The owner or operator shall retain at the plant and make available, upon request, for inspection by the Director, for a minimum of 2 years, records of emission test results and other data needed to determine emissions.
- (g) Unless otherwise specified, the owner or operator shall use the Test Methods in Appendix A of this text for each test as required by paragraphs (g)(1), (g)(2), (g)(3), (g)(4), and (g)(5) of this section, unless an equivalent method or an alternative method has been approved by the Director. If the Director finds reasonable grounds to dispute the results obtained by an equivalent or alternative method, he may require the use of a reference method. If the results of the reference and equivalent or alternative methods do not agree, the results obtained by the

reference method prevail, and the Director may notify the owner or operator that approval of the method previously considered to be equivalent or alternative is withdrawn.

(1) Test Method 106 is to be used to determine the vinyl chloride emissions from any source for which an emission limit is prescribed, or from any control system to which reactor emissions are required to be ducted or to which fugitive emissions are required to be ducted.

(i) For each run, one sample is to be collected. The sampling site is to be at least two stack or duct diameters downstream and one half diameter upstream from any flow disturbance such as a bend, expansion, contraction, or visible flame. For a rectangular cross section, an equivalent diameter is to be determined from the following equation:

$$C_{\text{equivalent diameter}} = 2 \frac{(\text{length})(\text{width})}{\text{length} + \text{width}}$$

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sampling point in the duct is to be at the centroid of the cross section. The sample is to be extracted at a rate proportional to the gas velocity at the sampling point. The sample is to be taken over a minimum of one hour, and is to contain a minimum volume of 50 liters corrected to standard conditions and is to be taken over a period as close to one hour as practicable.

(ii) Each emission test is to consist of three runs. For the purpose of determining emissions, the average of results of all runs is to apply. The average is to be computed on a time weighted basis.

(iii) For gas streams containing more than 10 percent oxygen, the concentration of vinyl chloride as determined by Test Method 106 is to be corrected to 10 percent oxygen (dry basis) for determination of emissions by using the following equation:

$$C_{b(\text{corrected})} = C_b \frac{10.9}{20.9 - \text{percent } O_2}$$

Where:

$C_{b(\text{corrected})}$  = The concentration of vinyl chloride in the exhaust gases, corrected to 10 percent oxygen.

$C_b$  = The concentration of vinyl chloride as measured by Test Method 106.

20.9 = Percent oxygen in the ambient air at standard conditions.

10.9 = Percent oxygen in the ambient air at standard conditions, minus the 10.0 percent oxygen to which the correction is being made.

Percent  $O_2$  = Percent oxygen in the exhaust gas as measured by Reference Method 3 in Appendix A of this text.

- (iv) For those emission sources where the emission limit is prescribed in terms of mass rather than concentration, mass emissions in kg/100 kg product are to be determined by using the following equation:

$$C_{BX} = \frac{[C_b(2.60)Q(10^{-6})][100]}{Z}$$

Where:

- $C_{BX}$  = kg vinyl chloride/100 kg product.
- $C_b$  = The concentration of vinyl chloride as measured by Test Method 106.
- 2.60 = Density of vinyl chloride at one atmosphere and 20°C in kg/m<sup>3</sup>.
- Q = Volumetric flow rate in m<sup>3</sup>/hr as determined by Reference Method 2 of Appendix A of this text.
- 10<sup>-6</sup> = Conversion factor for ppm.
- Z = Production rate (kg/hr).
- (2) Test Method 107 or Method 601 (incorporated by reference--see Section 1.6) is to be used to determine the concentration of vinyl chloride in each in-process wastewater stream for which an emission limit is prescribed in §61.65(b)(9)(i).
- (3) Where a stripping operation is used to attain the emission limit in §61.64(e) and (f), emissions are to be determined using Test Method 107 as follows:
- (i) The number of strippers (or reactors used as strippers) and samples and the types and grades of resin to be sampled are to be determined by the Director for each individual plant at the time of the test based on the plant's operation.
  - (ii) Each sample is to be taken immediately following the stripping operation.
  - (iii) The corresponding quantity of material processed by each stripper (or reactor used as a stripper) is to be determined on a dry solids basis and by a method submitted to and approved by the Director.
  - (iv) At the prior request of the Director, the owner or operator shall provide duplicates of the samples required in paragraph (g)(3)(i) of this section.
- (4) Where control technology other than or in addition to a stripping operation is used to attain the emission limit in §61.64(e), emissions are to be determined as follows:
- (i) Test Method 106 is to be used to determine atmospheric emissions from all of the process equipment simultaneously. The requirements of paragraph (g)(1) of this section are to be met.
  - (ii) Test Method 107 is to be used to determine the concentration of vinyl chloride in each in-process wastewater stream subject to the emission limit prescribed in §61.64(e). The mass of vinyl chloride in kg/100 kg product in

each in-process wastewater stream is to be determined by using the following equation:

$$C_{BX} = \frac{[C_d R 10^{-6}] [100]}{Z}$$

Where:

- $C_{BX}$  = kg vinyl chloride/100 kg product.
- $C_d$  = The concentration of vinyl chloride as measured by Test Method 107.
- $R$  = Water flow rate in 1/hr., determined in accordance with a method which has been submitted to and approved by the Director.
- $10^{-6}$  = Conversion factor for ppm.
- $Z$  = Production rate (kg/hr), determined in accordance with a method which has been submitted and approved by the Director.

(5) The reactor opening loss for which an emission limit is prescribed in §61.64(a)(2) is to be determined. The number of reactors for which the determination is to be made is to be specified by the Director for each individual plant at the time of the determination based on the plant's operation.

(i) Except as provided in paragraph (g)(5)(ii) of this section, the reactor opening loss is to be determined using the following equation:

$$C = \frac{W (2.60) (10^{-6}) (C_b)}{YZ}$$

Where:

- $C$  = kg vinyl chloride emissions/kg product.
- $W$  = Capacity of the reactor in  $m^3$ .
- $2.60$  = Density of vinyl chloride at one atmosphere and  $20^\circ C$  in  $kg/m^3$ .
- $10^{-6}$  = Conversion factor for ppm.
- $C_b$  = ppm by volume vinyl chloride as determined by Test Method 106 or a portable hydrocarbon detector which measures hydrocarbons with a sensitivity of at least 10 ppm.
- $Y$  = Number of batches since the reactor was last opened to the atmosphere.
- $Z$  = Average kg of polyvinyl chloride produced per batch in the

number of batches since the reactor was last opened to the atmosphere.

- (A) If Method 106 is used to determine the concentration of vinyl chloride ( $C_b$ ), the sample is to be withdrawn at a constant rate with a probe of sufficient length to reach the vessel bottom from the manhole. Samples are to be taken for 5 minutes within 6 inches of the vessel bottom, 5 minutes near the vessel center, and 5 minutes near the vessel top.
  - (B) If a portable hydrocarbon detector is used to determine the concentration of vinyl chloride ( $C_b$ ), a probe of sufficient length to reach the vessel bottom from the manhole is to be used to make the measurements. One measurement will be made within 6 inches of the vessel bottom, one near the vessel center and one near the vessel top. Measurements are to be made at each location until the reading is stabilized. All hydrocarbons measured are to be assumed to be vinyl chloride.
  - (C) The production rate of polyvinyl chloride (Z) is to be determined by a method submitted to and approved by the Director.
- (ii) A calculation based on the number of evacuations, the vacuum involved, and the volume of gas in the reactor is hereby approved by the Director as an alternative method for determining reactor opening loss for postpolymerization reactors in the manufacture of bulk resins.
- (6) For a reactor that is used as a stripper, the emissions of vinyl chloride from reactor opening loss and all sources following the reactor used as a stripper for which an emission limit is prescribed in §61.64(f) are to be determined. The number of reactors for which the determination is to be made is to be specified by the Director for each individual plant at the time of the determination based on the plant's operation.
- (i) For each batch stripped in the reactor, the following measurements are to be made:
    - (A) The concentration (ppm) of vinyl chloride in resin after stripping, measured according to paragraph (g)(3) of this section;
    - (B) The reactor vacuum (mm Hg) at end of strip from plant instrument; and
    - (C) The reactor temperature ( $^{\circ}$ C) at end of strip from plant instrument.
  - (ii) For each batch stripped in the reactor, the following information is to be determined:
    - (A) The vapor pressure (mm Hg) of water in the reactor at end of strip from the following table:

Reactor temperature	H <sub>2</sub> O vapor pressure (mm Hg)	Reactor temperature	H <sub>2</sub> O vapor pressure (mm Hg)	Reactor temperature	H <sub>2</sub> O vapor pressure (mm Hg)
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(°C)		(°C)		(°C)	
40	55.3	62	163.8	84	416.8
41	58.3	63	171.4	85	433.6
42	61.5	64	179.3	86	450.9
43	64.8	65	187.5	87	468.7
44	68.3	66	196.1	88	487.1
45	71.9	67	205.0	89	506.1
46	75.6	68	214.2	90	525.8
47	79.6	69	223.7	91	546.0
48	83.7	70	233.7	92	567.0
49	88.0	71	243.9	93	588.6
50	92.5	72	254.6	94	610.9
51	97.2	73	265.7	95	633.9
52	102.1	74	277.2	96	657.6
53	107.2	75	289.1	97	682.1
54	112.5	76	301.4	98	707.3
55	118.0	77	314.1	99	733.2
56	123.8	78	327.3	100	760.0
57	129.8	79	341.0		
58	136.1	80	355.1		
59	142.6	81	369.7		
60	149.4	82	384.9		
61	156.4	83	400.6		

- (B) The partial pressure (mm Hg) of vinyl chloride in reactor at end of strip from the following equation:

$$PPVC = 760 - RV - VPW$$

Where:

PPVC = partial pressure of vinyl chloride, in mm Hg

760 = atmospheric pressure at 0°C, in mm Hg

RV = absolute value of reactor vacuum, in mm Hg

VPW = vapor pressure of water, in mm Hg

- (C) The reactor vapor space volume (m<sup>3</sup>) at end of strip from the following equation:

$$RVSV = RC - WV - \frac{PVCW}{1,400}$$

Where:

RVSV = reactor vapor space volume, in m<sup>3</sup>

RC = reactor capacity, in m<sup>3</sup>

WV = volume of water in reactor from recipe, in m<sup>3</sup>

PVCW = dry weight of polyvinyl chloride in reactor from

recipe, in kg

1,400 = typical density of polyvinyl chloride, in kg/m<sup>3</sup>

- (iii) For each batch stripped in the reactor, the combined reactor opening loss and emissions from all sources following the reactor used as a stripper is to be determined using the following equation:

Where:

$$C = (PPMVC)(10^{-3}) + \frac{(PPVC)(RVSV)(1,002)}{(PVCW)(273 + RT)}$$

C = g vinyl chloride/kg polyvinyl chloride product

PPMVC = concentration of vinyl chloride in resin after stripping, in ppm

10<sup>-3</sup> = conversion factor for ppm

PPVC = partial pressure of vinyl chloride determined according to paragraph (g)(6)(ii)(B) of this section, in mm Hg

RVSV = reactor vapor space volume determined according to paragraph (g)(6)(ii)(C) of this section, in m<sup>3</sup>

1,002 = ideal gas constant in g-°K/mm Hg-m<sup>3</sup> for vinyl chloride

PVCW = dry weight of polyvinyl chloride in reactor from recipe, in kg

273 = conversion factor for °C to °K

RT = reactor temperature, in °C

- (h) (1) Each piece of equipment within a process unit that can reasonably contain equipment in vinyl chloride service is presumed to be in vinyl chloride service unless an owner or operator demonstrates that the piece of equipment is not in vinyl chloride service. For a piece of equipment to be considered not in vinyl chloride service, it must be determined that the percent vinyl chloride content can be reasonably expected not to exceed 10 percent by weight for liquid streams or contained liquid volumes and 10 percent by volume for gas streams or contained gas volumes which also includes gas volumes above liquid streams or contained liquid volumes. For purposes of determining the percent vinyl chloride content of the process fluid that is contained in or contacts equipment, procedures that conform to the methods described in ASTM Method D-2267 (incorporated by reference as specified in §61.18) shall be used.
- (2) (i) An owner or operator may use engineering judgment rather than the procedures in paragraph (h)(1) of this section to demonstrate that the percent vinyl chloride content does not exceed 10 percent by weight for liquid streams and 10 percent by volume for gas streams, provided that the engineering judgment demonstrates that the vinyl chloride content clearly does not exceed 10 percent. When an owner or operator and the Director do not agree on whether a piece of equipment is not in vinyl chloride service,

however, the procedures in paragraph (h)(1) of this section shall be used to resolve the disagreement.

- (ii) If an owner or operator determines that a piece of equipment is in vinyl chloride service, the determination can be revised only after following the procedures in paragraph (h)(1) of this section.
- (3) Samples used in determining the percent vinyl chloride content shall be representative of the process fluid that is contained in or contacts the equipment.

### 3.5.3 Emission Monitoring

- (a) A vinyl chloride monitoring system is to be used to monitor on a continuous basis the emissions from the sources for which emission limits are prescribed in §§61.62(a) and (b), 61.63(a), and 61.64(a)(1), (b), (c) and (d)<sup>\*</sup>, and for any control system to which reactor emissions are required to be ducted in §61.64(a)(2)<sup>\*</sup>, or to which fugitive emissions are required to be ducted in §61.65(b)(1)(ii) and (b)(2), (b)(5), (b)(6)(ii) and (b)(9)(ii)<sup>\*</sup>.
- (b) The vinyl chloride monitoring system(s) used to meet the requirement in paragraph (a) of this section is to be a device which obtains representative samples from one or more applicable emission points on a continuous sequential basis and analyzes the samples with gas chromatography or, if the owner or operator assumes that all hydrocarbons measured are vinyl chloride, with infrared spectrophotometry, flame ion detection, or an alternative method.
- (c) A daily span check is to be conducted for each vinyl chloride monitoring system used. For all of the emission sources listed in paragraph (a) of this section, except the one for which an emission limit is prescribed in §61.62(b)<sup>\*</sup>, the daily span check is to be conducted with a concentration of vinyl chloride equal to 10 ppm. For the emission source for which an emission limit is prescribed in §61.62(b)<sup>\*</sup>, the daily span check is to be conducted with a concentration of vinyl chloride which is determined to be equivalent to the emission limit for that source based on the emission test required by 3.5.2. The calibration is to be done with either:
  - (1) A calibration gas mixture prepared from the gases specified in Sections 5.2.1 and 5.2.2 of Test Method 106 and in accordance with Section 7.1 of Test Method 106, or
  - (2) A calibration gas cylinder standard containing the appropriate concentration of vinyl chloride. The gas composition of the calibration gas cylinder standard is to have been certified by the manufacturer. The manufacturer must have recommended a maximum shelf life for each cylinder so that the concentration does not change greater than  $\pm 5$  percent from the certified value. The date of gas cylinder preparation, certified vinyl chloride concentration and recommended maximum shelf life must have been affixed to the cylinder before shipment from the manufacturer to the buyer. If a gas chromatograph is used as the vinyl chloride monitoring system, these gas mixtures may be directly used to prepare a chromatograph calibration curve as described in Section 7.3 of Test Method 106. The requirements in Sections 5.2.3.1 and 5.2.3.2 of Test Method 106 for certification of cylinder standards and for establishment and verification of calibration standards are to be followed.
- (d) When exhaust gas(es), having emission limits that are subject to the requirement of paragraph (a) of this section, are emitted to the atmosphere without passing through the control system and required vinyl chloride monitoring system, the vinyl chloride content of the emission shall be calculated (in units of each applicable emission limit) by best practical engineering judgment based on the discharge duration and known VC concentrations in the affected equipment as



determined in accordance with §61.67(h)<sup>1</sup> or other acceptable method.

- (e) For each 3-hour period, the vinyl chloride content of emissions subject to the requirements of paragraphs (a) and (d) of this section shall be averaged (weighted according to the proportion of time that emissions were continuously monitored and that emissions bypassed the continuous monitor) for purposes of reporting excess emissions under §61.70(c)(1)<sup>1</sup>.
- (f) For each vinyl chloride emission to the atmosphere determined in accordance with paragraph (e) of this section to be in excess of the applicable emission limits, the owner or operator shall record the identity of the source(s), the date, time, and duration of the excess emission, the cause of the excess emission, and the approximate total vinyl chloride loss during the excess emission, and the method used for determining the vinyl chloride loss. This information shall be retained and made available for inspection by the Director as required by §61.71(a)<sup>1</sup>.

3.5.4 Reporting [Reserved]

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<sup>1</sup>Code of Federal Regulations, Title 40, Part 61.