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an emission limit is prescribed in §61.65(b)(6)(i) after opening the equipment and using Method 106, a portable hydrocarbon detector, or an alternative method. The method of measurement is to meet the requirements in §61.67(g)(5)(i)(A) or (g)(5)(i)(B).

- (d) A RVD that is ducted to a control device that is continually operating while emissions from the release are present at the device is subject to the following requirements:
- (1) A discharge from a control device other than a flare shall not exceed 10 ppm (average over a 3-hour period) as determined by the continuous emission monitor system required under §61.68. Such a discharge is subject to the requirements of §61.70.
- (2) For a discharge routed to a flare, the flare shall comply with the requirements of \$60.18.
- (i) Flare operations shall be monitored in accordance with the requirements of §§ 60.18(d) and 60.18(f)(2). For the purposes of §60.18(d), the volume and component concentration of each relief valve discharge shall be estimated and calculation shall be made to verify ongoing compliance with the design and operating requirements of §§ 60.18 (c)(3) through (c)(6). If more than one relief valve is discharged simultaneously to a single flare, these calculations shall account for the cumulative effect of all such relief valve discharges. These calculations shall be made and reported quarterly for all discharges within the quarter. Failure to comply with any of the requirements of this paragraph will be a violation of §61.65(d)(2). Monitoring for the presence of a flare pilot flame shall be conducted in accordance with \ \ \ 60.18(f)(2). If the results of this monitoring or any other information shows that the pilot flame is not present 100 percent of the time during which a relief valve discharge is routed to the flare, the relief valve discharge is subject to the provisions of §61.65(a).
- (ii) A report describing the flare design shall be provided to the Administrator not later than 90 days after the adoption of this provision or within 30 days of the installation of a flare system for control of relief valve discharge whichever is later. The flare design report shall include calculations

based upon expected relief valve discharge component concentrations and net heating values (for PVC this calculation shall be based on values expected if a release occurred at the instant the polymerization starts); and estimated maximum exit velocities based upon the design throat capacity of the gas in the relief valve.

[41 FR 46564, Oct. 21, 1976; 41 FR 53017, Dec. 3, 1976, as amended at 42 FR 29006, June 7, 1977; 51 FR 34910, Sept. 30, 1986; 53 FR 36972, Sept. 23, 1988; 55 FR 28348, July 10, 1990; 65 FR 62151, Oct. 17, 2000]

§ 61.66 Equivalent equipment and procedures.

Upon written application from an owner or operator, the Administrator may approve use of equipment or procedures which have been demonstrated to his satisfaction to be equivalent in terms of reducing vinyl chloride emissions to the atmosphere to those prescribed for compliance with a specific paragraph of this subpart.

[51 FR 34912, Sept. 30, 1986]

§ 61.67 Emission tests.

- (a) Unless a waiver of emission testing is obtained under §61.13, the owner or operator of a source to which this subpart 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 Administrator at least 30 days prior notice of an emission test to afford the Administrator 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 Administrator based on representative performance of the source.
- (d) [Reserved]
- (e) When at all possible, each sample is to be analyzed within 24 hours, but

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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 Administrator 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 Administrator, for a minimum of 3 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 B to this part for each test as required by paragraphs (g)(1), (g)(2), (g)(3), (g)(4), and (g)(5) of this section, unless an alternative method has been approved by the Administrator. If the Administrator finds reasonable grounds to dispute the results obtained by an alternative method, he may require the use of a reference method. If the results of the reference and alternative methods do not agree, the results obtained by the reference method prevail, and the Administrator may notify the owner or operator that approval of the method previously considered to be alternative is withdrawn. Whenever Method 107 is specified, and the conditions in Section 1.2, "Applicability" of Method 107A are met, Method 107A may be used.
- (1) Method 106 is to be used to determine the vinyl chloride emissions from any source for which an emission limit is prescribed in $\S61.62(a)$ or (b), $\S61.63(a)$, or $\S61.64(a)(1)$, (b), (c), or (d), or from any control system to which reactor emissions are required to be ducted in $\S61.64(a)(2)$ or to which fugitive emissions are required to be ducted in $\S61.65(b)(1)(ii)$, (b)(2), (b)(5), (b)(6)(ii), or (b)(9)(ii).
- (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:

Equivalent diameter = 2(length)(width)/(length + width)

The 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 contain a minimum volume of 50 liters (1.8 ft³) corrected to standard conditions and is to be taken over a period as close to 1 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 that 10 percent oxygen, the concentration of vinyl chloride as determined by Method 106 is to be corrected to 10 percent oxygen (dry basis) for determination of emissions by using the following equation:

$$C_{b(corrected)} = C_b (10.9)/(20.9 - percent O_2)$$

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

 C_b = The concentration of vinyl chloride as measured by 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 Method 3 of appendix A of part 60 of this chapter.

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

$$C_{BX} = \frac{C_b D_{VC} Q K \left(10^{-6}\right)}{Z}$$

Where:

 C_{BX} = Vinyl chloride emissions, g/kg (lb/lb) product.

 C_b = Concentration of vinyl chloride as measured by Test Method 106, ppmv.

 D_{VC} = Density of vinyl chloride at standard conditions, 2.60 kg/m³ (0.162 lb/ft³).

Q = Volumetric flow rate as determined by Method 2 of appendix A to part 60 of this chapter, m³/hr (ft³/hr).

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K = Unit conversion factor, 1,000 g/kg (1 lb/ lb).

 10^{-6} = Conversion factor for ppm.

Z = Production rate, kg/hr (lb/hr).

- (2) Method 107 or Method 601 (incorporated by reference as specified in §61.18) is to be used to determine the concentration of vinyl chloride in each inprocess wastewater stream for which an emission limit is prescribed in §61.65(b)(9)(i).
- (3) When a stripping operation is used to attain the emission limits in §61.64(e) and (f), emissions are to be determined using 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 Administrator 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 Administrator.
- (iv) At the prior request of the Administrator, 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) 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) Method 107 is to be used to determine the concentration of vinyl chloride in each inprocess wastewater stream subject to the emission limit prescribed in §61.64(e). Vinyl chloride mass emissions are to be determined using the following equation:

$$C_{BX} = \frac{C_{rvc}Q_{water}D_{water}QK(10^{-6})}{Z}$$

Where:

- $C_{\rm BX}=$ Vinyl chloride emissions, g/kg (lb/lb) product in each inprocess wastewater stream.
- $C_{\rm rvc}$ = Concentration of vinyl chloride in wastewater, as measured by Method 107, ppmw.
- $\begin{array}{ll} D_{water} = Density \ of \ wastewater, \ 1.0 \ kg/m^3 \\ (0.0624 \ lb/ft^3). \end{array}$
- Q_{water} = Wastewater flow rate, determined in accordance with a method which has been submitted to and approved by the Administrator, m³/hr (ft³/hr).
- K = Unit conversion factor, 1,000 g/kg (1 lb/ lb).

 10^{-6} = Conversion factor for ppm.

- Z = Production rate, kg/hr (lb/hr), determined in accordance with a method which has been submitted to and approved by the Administrator.
- (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 Administrator 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:

$$C_{BX} = C_b \frac{V_R D_{VC} Q K (10^{-6})}{Z}$$

Where:

 C_{BX} = Vinyl chloride emissions, g/kg (lb/lb) product.

- C_b = Concentration of vinyl chloride, in ppmv, as determined by Method 106 or a portable hydrocarbon detector which measures hydrocarbons with a sensitivity of at least 10 ppmv.
- V_R = Capacity of the reactor, m³ (ft³).
- D_{VC} = Density of vinyl chloride at standard conditions, 2.60 kg/m³ (0.162 lb/ft³).
- K = Unit conversion factor, 1,000 g/kg (1 lb/ lb).
- 10^{-6} = Conversion factor for ppm.
- Z = Production rate, kg/hr (lb/hr).
- (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.

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- (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 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), which is the product of the average batch weight and the number of batches produced since the reactor was last opened to the atmosphere, is to be determined by a method submitted to and approved by the Administrator.
- (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 Administrator as an alternative method for determining reactor opening loss for postpolymerization reactors in the manufacture of bulk resins. Calculation methods based on techniques other than repeated evacuation of the reactor may be approved by the Admin-

- istrator 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 Administrator 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 of vinyl chloride in resin after stripping, measured according to paragraph (g)(3) of this section:
- (B) The reactor vacuum at end of strip from plant instrument; and
- (C) The reactor temperature at the 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 of water in the reactor at the end of strip from the following table:

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Reactor vapor temperature (°C)	H₂O vapor pressure (mm Hg)	Reactor vapor temperature (°C)	H ₂ O vapor pres- sure (mm Hg)	Reactor vapor temperature (°C)	H₂O vapor pressure (mm Hg)
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		

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Reactor vapor temperature (°F)	H ₂ O vapor pressure (psia)	Reactor vapor temperature (°F)	H ₂ O vapor pressure (psia)	Reactor vapor temperature (°F)	H₂O vapor pressure (psia)			
104	1.07	144	3.167	183	8.060			
106	1.13	145	3.314	185	8.384			
108	1.19	147	3.467	187	8.719			
109	1.25	149	3.626	189	9.063			
111	1.32	151	3.792	190	9.419			
113	1.39	153	3.964	192	9.786			
115	1.46	154	4.142	194	10.17			
117	1.54	156	4.326	196	10.56			
118	1.62	158	4.519	198	10.96			
120	1.70	160	4.716	199	11.38			
122	1.79	162	4.923	201	11.81			
124	1.88	163	5.138	203	12.26			
126	1.974	165	5.360	205	12.72			
127	2.073	167	5.590	207	13.19			
129	2.175	169	5.828	208	13.68			
131	2.282	170 172	6.074	210	14.18			
133 135	2.394	172	6.329 6.594	212	14.70			
136	2.510	174						
138	2.632 2.757	178	6.866 7.149					
138	2.757	180	7.149					
140	3.024	181	7.443					
142	3.024	101	7.740					

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

$$PP_{VC} = P_{ATM} - P_{RV} - P_{W}$$

Where:

 PP_{VC} = Partial pressure of vinyl chloride, mm Hg (psia)

 P_{ATM} = Atmospheric pressure at 0 °C (32 °F), 760 mm Hg (14.7 psia)

 P_{RV} = Absolute pressure of reactor vacuum, mm Hg (psia)

 P_W = Vapor pressure of water, mm Hg (psia)

(C) The reactor vapor space volume at the end of the strip from the following equation:

$$V_{RVS} = V_R - V_W - \frac{W_{PVC}}{D_{PVC}}$$

Where

 V_{RVS} = Reactor vapor space volume, $m^3 \ (ft^3)$ V_R = Reactor capacity, $m^3 \ (ft^3)$

 $V_W = Volume$ of water in reactor from recipe, $m^3 (ft^3)$

 W_{PVC} = Dry weight of polyvinyl chloride in reactor from recipe, kg (lb)

 D_{PVC} = Typical density of polyvinyl chloride, 1,400 kg/m³ (87.4 lb/ft³)

(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:

$$C_{\rm BX} = K_1 \left({\rm PPM_{\rm VC}} \right) \ + \ \frac{\left({\rm PP_{\rm VC}} \right) \left(V_{\rm RVS} \right) \left(R_{\rm VC} \right)}{\left(M_{\rm VC} \right) \left(T_{\rm R} + K_{\rm T} \right)}$$

Where:

 $C_{\rm BX}$ = Vinyl chloride emissions, g/kg (lb/lb) product.

 $\mbox{PPM}_{\mbox{\scriptsize VC}}=\mbox{Concentration}$ of vinyl chloride in resin after stripping, ppmw

$$\begin{split} K_1 &= \text{Conversion factor from ppmw to units} \\ &\text{of emission standard, 0.001 (metric units)} \\ &= 0.002 \, (\text{English units}) \end{split}$$

 $\begin{array}{ll} PP_{VC} = Partial \ pressure \ of \ vinyl \ chloride \ determined \quad according \quad to \quad paragraph \\ (g)(6)(ii)(B) \ of \ this \ section, \ mm \ Hg \ (psia) \end{array}$

 V_{RVS} = Reactor vapor space volume determined according to paragraph (g)(6)(ii)(C) of this section, m³ (ft³)

 R_{VC} = Ideal gas constant for vinyl chloride, 1,002 g- $^{\circ}$ K/(mm Hg-m 3) [5.825 lb- $^{\circ}$ R/(psia-ft 3)]

 M_{PVC} = Dry weight of polyvinyl chloride in reactor from recipe, kg (lb)

 $T_R = \text{Reactor temperature}, ^{\circ}C (^{\circ}F)$

 K_T = Temperature conversion factor for °C to °K, 273 (°F to °R, 460)

(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 vinvl 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 D2267-68, 78, or 88 or D4420-94 (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 vinvl chloride content clearly does not exceed 10 percent. When an owner or operator and the Administrator 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.

[41 FR 46564, Oct. 21, 1976, as amended at 42 FR 29007, June 7, 1977; 47 FR 39486, Sept. 8, 1982; 50 FR 46295, Nov. 7, 1985; 51 FR 34912, Sept. 30, 1986; 65 FR 62152, Oct. 17, 2000]

§61.68 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), and for any control system to which reactor emissions are required to be ducted in §61.64(a)(2) 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).
- (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. The vinyl chloride monitoring system used to meet the requirements in $\S61.65(b)(8)(i)$ may be used to meet the requirements of this section.
- (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), 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), 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 §61.67. The calibration is to be done with either:
- (1) A calibration gas mixture prepared from the gases specified in Sections 7.2.1 and 7.2.2 of Method 106 and in accordance with Section 10.1 of Method 106, or