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**THURSDAY, OCTOBER 21, 1976**



**PART II:**

# **ENVIRONMENTAL PROTECTION AGENCY**

## **NATIONAL EMISSION STANDARDS FOR HAZARDOUS AIR POLLUTANTS**

**Standard For Vinyl Chloride**

**federal register**

## RULES AND REGULATIONS

## Title 40—Protection of Environment

## CHAPTER I—ENVIRONMENTAL PROTECTION AGENCY

## SUBCHAPTER C—AIR PROGRAMS

[FR 618-1]

## PART 61—NATIONAL EMISSION STANDARDS FOR HAZARDOUS AIR POLLUTANTS

## Standard for Vinyl Chloride

On December 24, 1975, under section 112 of the Clean Air Act, as amended (42 U.S.C. 1857), the Environmental Protection Agency (EPA) added vinyl chloride to the list of hazardous air pollutants (40 FR 59477) and proposed a national emission standard for it (40 FR 59532). The standard covers plants which manufacture ethylene dichloride, vinyl chloride, and/or polyvinyl chloride.

EPA decided to regulate vinyl chloride because it has been implicated as the causal agent of angiosarcoma and other serious disorders, both carcinogenic and noncarcinogenic, in people with occupational exposure and in animals with experimental exposure to vinyl chloride. Reasonable extrapolations from these findings cause concern that vinyl chloride may cause or contribute to the same or similar disorders at present ambient air levels. The purpose of the standard is to minimize vinyl chloride emissions from all known process and fugitive emission sources in ethylene dichloride-vinyl chloride and polyvinyl chloride plants to the level attainable with best available control technology. This will have the effect of furthering the protection of public health by minimizing the health risks to the people living in the vicinity of these plants and to any additional people who are exposed as a result of new construction.

Interested parties participated in the rulemaking by sending comments to EPA. The comments have been carefully considered, and where determined by the Administrator to be appropriate, changes have been made to the regulation as promulgated.

## SUMMARY OF THE STANDARD

In ethylene dichloride-vinyl chloride plants, the standard limits vinyl chloride emissions from the ethylene dichloride and vinyl chloride formation and purification processes to 10 ppm. For the oxychlorination process, vinyl chloride emissions are limited to 0.2 g/kg of ethylene dichloride product.

In polyvinyl chloride plants, the standard limits vinyl chloride emissions from equipment preceding and including the stripper in the plant process flow to 10 ppm. Emissions from equipment following the stripper are to be controlled by stripping dispersion resins to 2000 ppm and other resins to 400 ppm, or by using equivalent controls. Vinyl chloride emissions from reactor opening are to be reduced to 0.02 g/kg polyvinyl chloride product.

In both ethylene dichloride-vinyl chloride and polyvinyl chloride plants, relief valve discharges and manual venting of gases are prohibited except under emergency conditions. Fugitive emissions

are required to be captured and controlled.

## HEALTH AND ENVIRONMENTAL IMPACTS

EPA prepared a document entitled the *Quantitative Risk Assessment for Community Exposure to Vinyl Chloride* which estimates the risk from vinyl chloride exposure to populations living in the vicinity of vinyl chloride-emitting plants before and after implementation of controls to meet the standard. There are no dose-response data for the concentrations of vinyl chloride found in the ambient air. Therefore, assessments of risk at ambient levels of exposure were extrapolated from dose-response data from higher levels of exposure using both a linear model and a log-probit model. Extrapolations made with each of these models entailed using different sets of assumptions. Because different assumptions can be made in extrapolating to low doses, the health risks are reported in ranges.

It was estimated that 4.6 million people live within 5 miles of ethylene dichloride-vinyl chloride and polyvinyl chloride plants and that the average exposure around these plants before installation of controls to meet the standard is 17 parts per billion. The exposure levels for uncontrolled plants were calculated based on estimated 1974 emission levels. Using the linear dose-response model, EPA found that the rate of initiation of liver angiosarcoma among people living around uncontrolled plants is expected to range from less than one to ten cases of liver angiosarcoma per year of exposure to vinyl chloride. The log-probit model gave predictions that are 0.1 to 0.01 times this rate. This wide range is an indication of the uncertainties in extrapolation to low doses. Due to the long latency time observed in cancer cases resulting from vinyl chloride exposure, increases initiated by exposure this year will not be diagnosed until the 1990's or later. Vinyl chloride is also estimated to produce an equal number of primary cancers at other sites, for a total of somewhere between less than one and twenty cases of cancer per year of exposure among residents around plants. The number of these effects is expected to be reduced at least in proportion to the reduction in the ambient annual average vinyl chloride concentration, which is expected to be 5 percent of the uncontrolled levels after the standard is implemented.

Changes in the standard since proposal do not affect the level of control required. Thus, the environmental impact of the promulgated standard is, with one exception, the same as that described in Chapter 6 of Volume I of the *Standard Support and Environmental Impact Statement*. According to data submitted by the Society of Plastics Industry, Inc. (SPI), the impact on water consumption in the draft environmental impact statement was overstated. In estimating the impact on water consumption, EPA based its estimates on worst case conditions. That is, EPA assumed that those control systems with the

greatest water usage would be employed and that there would be no recycling of water. There is no regulation which would require water recycling. According to SPI, the control system utilizing the most water will not be used generally by the industry and economic factors will cause plants to recycle much of the water. Therefore, according to SPI the impact of the standard on water consumption will be negligible.

The environmental impacts of the promulgated standard may be summarized as follows: The primary environmental impacts of the standard are beneficial and will consist of vinyl chloride emission reductions of approximately 94 percent at ethylene dichloride-vinyl chloride plants and 95 percent at polyvinyl chloride plants. Percentage numbers for both source categories are based on an estimated 90 percent reduction in fugitive emissions and 1974 emission levels.

The potential secondary environmental impacts of the standard are either insignificant or will be minimized without additional action, except for one adverse impact. Hydrogen chloride is already emitted by process equipment at ethylene dichloride-vinyl chloride plants and by other petrochemical plants in the complexes where ethylene dichloride-vinyl chloride plants are typically located. An incinerator used to attain the standard at an ethylene dichloride-vinyl chloride plant could increase hydrogen chloride emissions by several fold. Typically, however, due to the corrosion problems which would otherwise occur both on plant property and in the community, plants use scrubbers to control already existing hydrogen chloride emissions. Hydrogen chloride emissions resulting from control of vinyl chloride emissions are expected to be controlled for the same reason. If even a moderately efficient scrubber (98 percent control) were used to control the hydrogen chloride emissions resulting from incineration of vinyl chloride emissions, the increase in hydrogen chloride emissions from a typical ethylene dichloride-vinyl chloride plant due to the standard would be reduced to 35 percent. However, EPA plans to further evaluate the need to control hydrogen chloride emissions, since diffusion model results indicate that under "worst-case" meteorological conditions, the hydrogen chloride emissions from the process equipment and the incinerator combined would cause maximum ambient concentrations of hydrogen chloride in the vicinity of ethylene dichloride-vinyl chloride plants to be in the same range or somewhat higher than existing foreign standards and National Academy of Sciences (NAS) guidelines for public exposure.

## ECONOMIC IMPACT

In accordance with Executive Order 11821 and OMB circular A-107, EPA carefully evaluated the economic and inflationary impact of the proposed standard and alternative control levels and certified this in the preamble to the proposed standard. These impacts are

discussed in Chapter 7 of Volume I of the *Standard Support and Environmental Impact Statement*. Comments on the proposed standard have resulted in only one major change in the economic impact analysis. EPA estimated that there would be four plant closures as a result of the promulgated standard. Of the four plants identified as possible closure candidates, one has given notice that it no longer produces polyvinyl chloride and the other three have indicated that they do not intend to close as a result of the standard.

The economic impacts of the promulgated standard may be summarized as follows: The total capital cost for existing plants to meet the standard is estimated to be \$198 million, of which \$15 million is for ethylene dichloride-vinyl chloride plants and \$183 million is for polyvinyl chloride plants. EPA estimates that these plants will have to spend \$70 million per year to maintain the required emission levels. In addition, the total capital cost for existing plants to meet the EPA's 1983 water effluent guideline limitations is expected to be \$63 million and the total annualized operation cost is \$17 million. The costs to the industry of meeting the OSHA standard cannot be quantified at this time, but they are expected to overlap to some degree with the costs to meet EPA's fugitive emission regulations. The costs of meeting the fugitive emission regulations are included in the total costs cited above for meeting the promulgated regulation. Broken out separately, the capital cost of meeting the fugitive emission regulations is \$37 million and the annualized cost is \$25 million.

The standard is not expected to deter construction of new ethylene dichloride-vinyl chloride plants or most types of new polyvinyl chloride plants. For one type of polyvinyl chloride plant (dispersion process) that represents 13 percent of the industry production, the standard would significantly deter the construction of smaller plants.

It is estimated that the price of polyvinyl chloride resins will rise by approximately 7.3 percent in order to maintain precontrol profitability and also to recover the total annualized control costs necessitated by the standard at ethylene dichloride-vinyl chloride plants and polyvinyl chloride plants. This increase is estimated to translate into a maximum consumer price increase in goods fabricated from polyvinyl chloride resins of approximately 3.5 percent. Recovery of effluent annualized costs plus maintenance of precontrol profitability is estimated to add approximately 2 percent to polyvinyl chloride resin prices and result in an additional maximum consumer price increase of 1 percent.

#### PUBLIC PARTICIPATION

During the public comment period, 50 comment letters on the proposed standard were received. There were 24 from industry; 3 from environmental groups; 15 from Federal, State, and local agencies; and 8 from individual citizens. As required by section 112(b)(1)(B) of the

Act, a public hearing was held on the proposed standard on February 3, 1976, in Washington, D.C. Presentations were made by the Environmental Defense Fund, the Society of the Plastics Industry, Inc., Dow Chemical Company, Diamond Shamrock Corporation, and Air Products and Chemicals, Inc. Copies of the comment letters received, the public hearing record, and a summary of the comments with EPA's responses are available for public inspection and copying at the EPA Public Information Reference Unit, Room 2922 (EPA Library), 401 M Street, SW., Washington, D.C. In addition, copies of the comment summary and Agency responses may be obtained upon written request from the Public Information Center (PM-215), Environmental Protection Agency, 401 M Street, SW., Washington, D.C. 20460 (specify *Standard Support and Environmental Impact Statement, Emission Standard for Vinyl Chloride, Volume II*).

#### SIGNIFICANT COMMENTS AND CHANGES TO THE PROPOSED REGULATION

(1) *Decision to list vinyl chloride as a hazardous air pollutant.* In general, the commenters did not contest EPA's decision to list vinyl chloride as a hazardous air pollutant. However, three commenters (two companies and one Federal agency) argued that EPA placed undue emphasis on factors suggesting that vinyl chloride presented a health risk and ignored factors suggesting that no significant risk was involved. Under section 112, however, EPA could remove vinyl chloride from the list of hazardous air pollutants only if information were presented to EPA that shows that vinyl chloride is clearly not a hazardous air pollutant. As discussed more fully in the comment summary, the commenters did not provide conclusive evidence that vinyl chloride is not a hazardous air pollutant which causes or contributes to death or serious illness, nor did they conclusively prove that the health risk factors emphasized by EPA were insignificant.

Several other commenters agreed with EPA's decision to list vinyl chloride as a hazardous air pollutant, but argued that EPA had overstated the health problem, the emission levels, and the projected ambient air concentrations around uncontrolled plants. With regard to the alleged overstated health problem, the commenters stated, for example, that the U.S. worker EPA discussed as having been exposed to vinyl chloride levels lower than those usually encountered in polyvinyl chloride production has been dropped from the National Institute of Occupational Safety and Health's listing of workers with angiosarcoma. EPA agrees that there are questions concerning the level of exposure and in some cases the pathology of these cases not involved directly in polyvinyl chloride and vinyl chloride production. These uncertainties are stated in the appropriate footnotes of the *Scientific and Technical Assessment Report on Vinyl Chloride and Polyvinyl Chloride (STAR)* where the angiosarcoma cases are listed. However, in spite of these uncertainties, in view of

the possible exposure patterns, these cases cannot be ignored in the evaluation of the potential public health problems.

With regard to the alleged overstated emission levels, the uncontrolled emission levels reported by EPA were based on 1974 data. This qualification was stated wherever emission data were presented. EPA recognizes that emissions have been reduced since that time, and stated this in the preamble to the proposed standard. EPA decided not to gather more recent data on emission levels, because these emission levels are expected to change, and gathering the data would take considerable time both on the part of EPA and on the part of industry. Since the purpose of the standard is to minimize emissions, these more current data would not affect the standard itself. The 1974 emission levels were also used in diffusion modeling to project maximum ambient air concentrations around uncontrolled plants. These maximum air concentrations would probably be lower if 1976 emission levels were used. This would reduce the relative impact of the standard below that described in the *Standard Support and Environmental Impact Statement*, but would not affect the basis of the standard itself.

(2) *Approach for Regulating Vinyl Chloride Under Section 112.* Two approaches other than using best available control technology were suggested by the commenters for regulating vinyl chloride under section 112. The first was to ban polyvinyl chloride products for which substitutes are currently available and to gradually phase out other polyvinyl chloride products as substitutes are developed.

In the preamble to the proposed standard EPA specified its reasons for not setting a zero emission limit for vinyl chloride, as follows: (1) There are beneficial uses of vinyl chloride products for which desirable substitutes are not readily available; (2) there are potentially adverse health and environmental impacts from substitutes which have not been thoroughly studied; (3) there are a number of employees, particularly in the fabrication industries, who would become at least temporarily unemployed; and (4) control technology is available which is capable of substantially reducing emissions of vinyl chloride into the atmosphere.

EPA agrees that substitutes do exist or could be manufactured for most polyvinyl chloride uses. However, in general, these substitutes do not have some of the more desirable characteristics of polyvinyl chloride, such as nonflammability. If vinyl chloride and polyvinyl chloride were banned, other substitutes with these more desirable characteristics would likely be developed. There is a risk that these substitutes would also have adverse health or environmental effects. Since control measures are available which can reduce vinyl chloride emissions by 90 percent or more, it does not seem prudent to reduce emissions by the remaining percentage and take the risk of introducing new untested chemicals into the environment.

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Another approach suggested by the commenters was to base the standard for each individual emission point on cost versus benefit. Several of the fugitive emission sources were named specifically as ones for which the costs of control were substantially higher than the benefits. Although EPA did determine a cost-benefit ratio for the controls required for a number of emission points, EPA does not believe such a ratio is an appropriate basis on which to set a standard. Section 111 of the Clean Air Act provides for the development of standards based on best control technology (considering costs). Even under section 111, however, standards are not based on a fine balancing of costs versus benefits. Instead, costs are considered in terms of the affordability of the control technology required to achieve a given emission level and the economic impact of possible standards on the industry in question. Unlike section 111, section 112 does not explicitly provide for consideration of costs, so it would clearly be inappropriate to consider costs to a greater extent under section 112 than would be done under section 111. As discussed in the preamble to the proposed standard for vinyl chloride, EPA believes costs may be considered under section 112, but only to a very limited extent; i.e., to assure that the costs of control technology are not grossly disproportionate to the amount of emission reduction achieved. In comparison with other emission points, the costs of controlling the fugitive emission sources mentioned by the commenters are relatively small compared with the amount of emission reduction achieved.

Several commenters recommended adding to the regulation a provision for excess emissions during startup, shutdown, and malfunction. EPA considered this comment, and decided that this addition is not necessary for the vinyl chloride standard. Startup and shutdown of the process has essentially no effect on emissions to the atmosphere for polyvinyl chloride production, and technology exists to avoid excess emissions during startup and shutdown at ethylene dichloride/vinyl chloride plants. We do not believe plants should be allowed to emit excess emissions during malfunctions, and therefore are requiring them to shut down immediately.

(3) *Selection of source categories.* In the preamble to the proposed standard EPA recognized that some small research and development facilities may exist where the emissions of vinyl chloride are insignificant and covering these facilities under the standard would be unnecessary and inappropriate. However, EPA did not have sufficient information available to clearly define which facilities should be excluded from the standard, and encouraged interested parties to submit such information during the comment period. Based on the information submitted, EPA decided to exempt polyvinyl chloride reactors and associated equipment from applicability of all parts of the standard if the reactors are used in research and development and have a

capacity of no more than  $0.19 \text{ m}^3$  (50 gal). Reactors in this size range can generally be found in a laboratory, whereas the larger reactors are typically pilot scale facilities. Emissions from laboratory scale equipment are relatively small, and application of the controls required by the standard would be expensive and impractical. EPA also decided to exempt research and development facilities containing reactors greater than  $0.19 \text{ m}^3$  (50 gal) and no more than  $4.07 \text{ m}^3$  (1100 gal) in capacity from all parts of the standard except the 10 ppm limit for reactors, strippers, monomer recovery systems, and mixing, weighing and holding containers. EPA decided not to require these facilities to meet other parts of the standard because of the technical problems involved in doing so. For example, the standard for reactor opening is based in part on reducing the frequency of opening the reactor. Research and development reactors have to be opened after every batch for thorough cleaning. Also, stripping technology is developed individually for each resin in research and development equipment. Therefore, attainment of the stripping limitations in the research and development equipment would not always be possible. The  $4.07 \text{ m}^3$  (1100 gal) figure was selected as an upper cut-off point because there are no commercial reactors smaller than this.

(4) *Emission limits.* The only major change in the emission limits between proposal and promulgation is the addition of a provision for emergency manual venting of vinyl chloride from reactors to the atmosphere. The proposed standard prohibited all manual venting to the atmosphere. In the preamble to the proposed standard, EPA invited interested persons to comment on whether permitting manual venting to the atmosphere could result in overall lower emissions. There are several methods available for preventing relief discharges from reactors, one of which is manual venting of part of the reactor contents for purposes of cooling and reduction in pressure within the reactor. The higher the temperature and pressure within the reactor, the greater the amount of vinyl chloride which has to be removed to bring the reactor under control. Manual venting can be done at a lower pressure than the pressure required to open the relief valve. For this reason manual venting can result in lower emissions than would occur by allowing the reactor to discharge through the relief valve. Furthermore, a manual vent valve is under the control of an operator and can be closed. A relief valve may become clogged with resin and not close. The result would be loss of all the reactor contents.

The contents of a reactor can be manually vented to a gasholder or other holding vessel. However, in some cases, such as during severe weather conditions, several reactors may be out of control at one time. There would be insufficient holding capacity under these conditions to manually vent the contents of all the reactors to a gasholder. Therefore, when all other measures to prevent relief valve discharges have been exhausted, manual

venting will be permitted as a last resort before the relief valve opens. The same notification procedures are required for manual venting to the atmosphere as are required for relief discharges.

There are several changes in the numerical emission limits in the promulgated standard. Except for the standard for reactor opening loss, these changes simply involve conversion to the International System of Units (SI). There was an error involved in the original calculation used to derive the standard for reactor opening. Correcting this error doubles the allowable emissions. It is emphasized that the change in this standard is a correction, and not a change in the intent for the degree of control required.

The proposed standard required the installation of a rupture disc beneath each relief valve to prevent leakage from the relief valve. A provision has been added to the promulgated standard so that a rupture disc is not required if the relief valve is tied into a process line or recovery system. In this case, any leakage from the relief valve would be contained.

The regulation for obtaining vinyl chloride samples has been changed to an operating procedure. The proposed standard stated that there were to be no emissions from taking the samples. Several commenters pointed out that the use of the word "no" would make this regulation impractical to enforce. Therefore, the promulgated standard specifies the operating procedure which EPA originally intended to be used to control this source. This revision is only a change in wording and does not represent a change in the level of the standard.

The regulation for taking samples has also been revised to apply only to samples containing at least 10 percent by weight vinyl chloride. This is consistent with the other parts of the standard which apply to equipment "in vinyl chloride service." "In vinyl chloride service" distinguishes between situations where vinyl chloride is clearly involved and situations where vinyl chloride is a minor component or contaminant, and as defined in promulgated § 61.61(1) means that a piece of equipment contains or contacts either a liquid that is at least 10 percent by weight vinyl chloride or a gas that is at least 10 percent by volume vinyl chloride.

The proposed standard required a vinyl chloride monitoring system for continuously measuring vinyl chloride levels both within the plant (for leak detection) and within stacks. The proposed standard did not outline required specifications for the monitoring system, except that it was to analyze the samples with gas chromatography, or if all hydrocarbons were assumed to be vinyl chloride, with infrared spectrophotometry, flame ion detection, or equivalent. It required that each plant submit a description of its monitoring system to EPA, so that EPA could determine whether it was acceptable or not. Comments were received indicating a need for EPA to specify some criteria for judging the acceptability of monitoring systems. The accuracy of the monitor-

ing system would be related to the frequency of calibration. Therefore, EPA has included in the promulgated standard requirements for the frequency of calibration and procedures to be carried out in the calibration of the monitoring instruments.

The portable hydrocarbon detector required by the proposed standard was required to have a sensitivity of 5 ppm. Comments were received indicating that instruments in this sensitivity range are delicate and require continuing maintenance. The portable hydrocarbon detector is required for leak detection and for measuring vinyl chloride concentrations inside the equipment before opening it. A 5 ppm sensitivity is not needed in either case, and the required sensitivity has been changed to 10 ppm in the promulgated standard.

The proposed standard contained a single regulation for compressors. The promulgated standard has separate regulations for rotating and reciprocating compressors. This is consistent with having separate regulations for rotating and reciprocating pumps in both the proposed and promulgated standards.

Section 61.66 of the proposed standard provided for the use of equivalent methods of control which have been approved by EPA. The promulgated standard requires that the plant owner or operator submit a request for determination of equivalency within 30 days of the promulgation date if the alternative control method is intended as the initial means of control. The purpose of this is to provide time for EPA to evaluate the method before the plant has to be in compliance (for existing sources, 90 days after the promulgation date). EPA also suggests that this request for determination of equivalency be accompanied by a request for waiver of compliance pursuant to section 112(c)(1)(B)(ii) of the Act. The request for a waiver for compliance should provide for the case where EPA determines that a method is not equivalent and the plant needs to purchase other equipment. In no case will the waiver of compliance be extended beyond two years from the date of promulgation.

There are several wording clarifications which have been made in the promulgated standard. The definition for "in vinyl chloride service" (§ 60.61(1)) has been clarified by stating that it means equipment that contacts vinyl chloride as well as equipment that contains vinyl chloride. This would include such equipment as agitators.

Words have been added in §§ 61.62, 61.63, and 61.64 to clarify that the 10 ppm emission limits do not have to be met when equipment has already been opened in compliance with the regulation for opening of equipment. Equipment that has met the opening of equipment regulation can contain more than 10 ppm vinyl chloride and would be in violation of the standard if this statement were not included.

The requirements for stripping polyvinyl chloride resins to specified levels have been revised in §§ 61.64(e), 61.67

(g)(3)(ii), and 61.70(c)(2)(i) so that measurement of the vinyl chloride levels in the resins is to be made immediately after stripping is completed rather than as the resin is being transferred out of the stripper. This allows a plant to carry out operations in a stripper after stripping has been completed but before it is transferred out of the stripper. This is consistent with the original intent of the standard.

The regulation for loading and unloading lines in § 61.65(b)(1) has been revised to clarify that it applies only to lines that are disconnected after each loading or unloading operation. Permanently installed pipelines that are opened infrequently for inspection or maintenance, for example, are covered by the opening of equipment regulation rather than the loading and unloading line regulation.

The regulation for inprocess wastewater in the proposed standard could have been misinterpreted to require individual treatment of wastewater streams. Section 61.65(b)(9)(i) of the promulgated standard clarifies that wastewater streams that are required to be treated (i.e., those containing greater than 10 ppm vinyl chloride) can be combined to be treated. However, wastewater streams that contain greater than 10 ppm vinyl chloride cannot be combined with wastewater streams that contain less than 10 ppm vinyl chloride before treatment; i.e., dilution cannot be used to meet the standard.

The commenters recommended several changes in the emission limits which have not been incorporated into the promulgated standard. These are discussed in the following paragraphs.

It was recommended that the requirement for double mechanical seals on pumps, compressors, and agitators be removed because the single seals currently used on this equipment have small emissions and are more reliable than double mechanical seals. EPA is aware that each fugitive emission source, such as one pump, taken by itself causes relatively small emissions. Fugitive emissions considered as a whole are a significant source of emissions, however, and the intent of the standard is to reduce these. Double mechanical seal pumps are commonly used in the industry for emission reduction. Sealless pumps or equivalent systems are available as options to double mechanical seals.

The commenters recommended increasing the averaging time for the 10 ppm limits and the emission limits for reactor opening and stripping to 30 days. Some of the commenters apparently thought that the 10 ppm limits had to be met on an instantaneous basis. However, since the performance test for determining compliance consists of three runs for a minimum of an hour each, the averaging time for the 10 ppm limit is at least three hours. Increasing the averaging time to 30 days for any of the emission limits would permit higher peak emission levels. EPA has determined that this is neither desirable nor necessary.

Some commenters requested that the stripping levels for dispersion resins be

made the same as for other resins and others requested that they be made less stringent. EPA decided not to make the standard for stripping dispersion resins the same as for other resins because there is sufficient evidence to indicate that these resins are more difficult to strip than other resins. With regard to making the stripping levels for dispersion resins less stringent, only one of the eight manufacturers of dispersion resins specifically commented that the dispersion resin standard should be made less stringent. Only two of several grades of dispersion resins made by this company cannot meet the 2,000 ppm limit. The proposed standard takes into consideration that some resins are more difficult to strip than others by providing for averaging among different resins.

(5) Testing, reporting, and recordkeeping. There are several relatively minor changes in the testing, reporting, and recordkeeping requirements. A provision has been added to § 61.67 which requires that stack gas samples taken with Test Method 106 are to be analyzed within 24 hours. This is consistent with the requirements in the proposed Test Method 106. The promulgated standard also specifies that in averaging the results of the three runs required by Test Method 106, a time-weighted average is to be used.

One commenter requested that the oxygen content and moisture content be specified for the 10 ppm concentration standards. The proposed standard specified that the vinyl chloride concentration is to be corrected to 10 percent oxygen (wet basis) if combustion is used as the control measure. In the promulgated standard, this requirement has been expanded to all control measures.

A provision has been added to the promulgated standard which states that if a reactor is also used as a stripper, the reactor opening emissions may be determined immediately following the stripping operation. If a reactor is also used as a stripper, the resin is in the reactor when it is opened. This means that vinyl chloride in the resin which has already been stripped to acceptable levels can escape from the resin and become part of the reactor opening loss. It is EPA's intent that once a resin has been stripped to the required levels, that additional controls are not required. Under the new provision, vinyl chloride escaping from the resin after it has been stripped to acceptable levels is not counted as part of the reactor opening loss.

A section requiring continuous monitoring of stack emissions has been added to the promulgated standard. The continuous monitoring of stack emissions was required in the proposed standard. The addition of a specific paragraph for emission monitoring serves only to clarify the requirement.

The standard has been revised so that the initial report requires a "description" rather than a "detailed description" of the equipment used to control fugitive emissions. Several commenters pointed out that a detailed description would contain proprietary information. EPA agrees that a detailed description in the

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initial report is unnecessary. If additional information is needed, EPA can obtain it under section 114 of the Act and the plant can request confidential treatment in accordance with 40 CFR Part 2 for information it believes to be proprietary.

The proposed standard required that a semiannual report be submitted every 180 days. The promulgated standard specifies dates for the submittal of the reports. It also specifies that the first semiannual report does not have to be submitted until at least six months after the initial report is submitted.

The standard has been revised to eliminate the requirement to record the cause of any leak detected by the vinyl chloride detector, the action taken to repair the leak, and the amount of time required to repair the leak. EPA is concerned only that leaks are detected and repaired. That this has been done can be established by looking at the strip chart record of measurements made by the vinyl chloride detector. These records are still required for the portable hydrocarbon detector however.

Several commentators recommended that the companies be allowed an extra two weeks to submit to EPA data from the initial performance test. They also recommended that they submit the data by regular mail rather than registered mail. EPA has not adopted either of these recommendations. A source is supposed to be in compliance with the standard within 90 days of the promulgation of the standard. The standard requires that the emission tests be done within the 90 day period, and permits an extra 30 days for determination of results. The purpose of using registered mail is to document the fact that emission data have been sent and received. This way if the results are lost in the mail, there will be no question that they were sent.

(6) *Test method.* Test Method 106 has been changed to recognize that on a gas chromatograph equipped with a Chromosorb 102 column, acetaldehyde may interfere with the vinyl chloride peak. When a sample is expected to contain acetaldehyde, a secondary column as described in section 4.3.2 must be employed. Mass spectroscopy or another absolute analytical technique is required to confirm the vinyl chloride peak obtained with the gas chromatograph, only if peak resolution with the secondary column is not successful.

In section 4.1.4, aluminized Mylar bags can be substituted for Tedlar bags. EPA now has data to allow this substitution, provided that the samples are analyzed within 24 hours of collection.

In section 5.1.3 of Test Method 106 the requirement to use "oxygen gas" has been replaced with "oxygen gas or air, as required by the detector." Several commentors stated that most gas chromatographs are designed to use hydrogen and air for their flame detectors. When used in this way, they are capable of detecting 0.5 ppm vinyl chloride in air. This is sensitive enough for monitoring the 10 ppm emission limits stipulated in the standard.

In section 6.4 of Test Method 106 the requirement for an automatic integrator has been replaced with a requirement for a disc integrator or planimeter for measuring peak area. This change is in response to a comment which states that automatic integrators are unnecessarily elaborate and expensive.

A new section 6.5 has been added to Test Method 106 which requires determination of the water vapor content of the sampling bag by measuring the ambient temperature and pressure near the bag. The vinyl chloride concentration of the bag can then be reported on a dry basis. A provision for checking the rigid container for leaks has been added to section 7.4 of Test Method 106.

The only change in Test Method 107 is the provision in Section 5.3.2 for use of Carbopak C as well as Carbopak A.

**AUTHORITY:** Section 112 of the Clean Air Act as added by sec. 4(a) of Pub. L. 91-604, 84 Stat. 1685 (42 U.S.C. 1857c-7; Section 114 of the Clean Air Act, as added by sec. 4(a) of Pub. L. 91-604, 84 Stat. 1687, and amended by Pub. L. 93-319, sec. 6(a)(4), 88 Stat. 259 (42 U.S.C. 1857c-9); Section 301(a) of the Clean Air Act, as amended by sec. 15(e)(2) of Pub. L. 91-604, 84 Stat. 1713 (42 U.S.C. 1857g(a)).

Dated: October 12, 1976.

JOHN QUARLES,  
Acting Administrator.

Part 61 of Chapter I, Title 40 of the Code of Federal Regulations is amended as follows: The table of sections for Part 61 is amended by adding a list of sections for new Subpart F and Part 61 is amended by adding a new Subpart F reading as follows:

**Subpart F—National Emission Standard for Vinyl Chloride**

Sec.	
61.60	Applicability.
61.61	Definitions.
61.62	Emission standard for ethylene dichloride plants.
61.63	Emission standard for vinyl chloride plants.
61.64	Emission standard for polyvinyl chloride plants.
61.65	Emission standard for ethylene dichloride, vinyl chloride and polyvinyl chloride plants.
61.66	Equivalent equipment and procedures.
61.67	Emission tests.
61.68	Emission monitoring.
61.69	Initial report.
61.70	Semiannual report.
61.71	Recordkeeping.

**AUTHORITY:** Section 112 of the Clean Air Act as added by sec. 4(a) of Pub. L. 91-604, 84 Stat. 1685 (42 U.S.C. 1857c-7); section 114 of the Clean Air Act, as added by sec. 4(a) of Pub. L. 91-604, 84 Stat. 1687, and amended by Pub. L. 93-319, sec. 6(a)(4), 88 Stat. 259 (42 U.S.C. 1857c-9); section 301(a) of the Clean Air Act, as amended by sec. 15(e)(2) of Pub. L. 91-604, 84 Stat. 1713 (42 U.S.C. 1857g(a)).

**Subpart F—National Emission Standard for Vinyl Chloride**

#### § 61.60 Applicability.

(a) This subpart 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 subpart 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).

(c) Sections of this subpart other than § 61.64(a)(1), (b), (c), and (d) do 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 greater than 0.19 m<sup>3</sup> (50 gal) and no more than 4.07 m<sup>3</sup> (1100 gal).

#### § 61.61 Definitions.

Terms used in this subpart are defined in the Act, in subpart A of this part, or in this section as follows:

(a) "Ethylene dichloride plant" includes any plant which produces ethylene dichloride by reaction of oxygen and hydrogen chloride with ethylene.

(b) "Vinyl chloride plant" includes any plant which produces vinyl chloride by any process.

(c) "Polyvinyl chloride plant" includes any plant where vinyl chloride alone or in combination with other materials is polymerized.

(d) "Slip gauge" means a gauge which has a probe that moves through the gas/liquid interface in a storage or transfer vessel and indicates the level of vinyl chloride in the vessel by the physical state of the material the gauge discharges.

(e) "Type of resin" means the broad classification of resin referring to the basic manufacturing process for producing that resin, including, but not limited to, the suspension, dispersion, latex, bulk, and solution processes.

(f) "Grade of resin" means the subdivision of resin classification which describes it as a unique resin, i.e., the most exact description of a resin with no further subdivision.

(g) "Dispersion resin" means a resin manufactured in such away as to form fluid dispersions when dispersed in a plasticizer or plasticizer/diluent mixtures.

(h) "Latex resin" means a resin which is produced by a polymerization process which initiates from free radical catalyst sites and is sold undried.

(i) "Bulk resin" means a resin which is produced by a polymerization process in which no water is used.

(j) "Inprocess wastewater" means any water which, during manufacturing or processing, comes into direct contact with vinyl chloride or polyvinyl chloride or results from the production or use of any raw material, intermediate product, finished product, by-product, or waste product containing vinyl chloride or polyvinyl chloride but which has not been discharged to a wastewater treatment process or discharged untreated as wastewater.

(k) "Wastewater treatment process" includes any process which modifies

characteristics such as BOD, COD, TSS, and pH, usually for the purpose of meeting effluent guidelines and standards; it does not include any process the purpose of which is to remove vinyl chloride from water to meet requirements of this subpart.

(l) "In vinyl chloride service" means that a piece of equipment contains or contacts either a liquid that is at least 10 percent by weight vinyl chloride or a gas that is at least 10 percent by volume vinyl chloride.

(m) "Standard operating procedure" means a formal written procedure officially adopted by the plant owner or operator and available on a routine basis to those persons responsible for carrying out the procedure.

(n) "Run" means the net period of time during which an emission sample is collected.

(o) "Ethylene dichloride purification" includes any part of the process of ethylene dichloride production which follows ethylene dichloride formation and in which finished ethylene dichloride is produced.

(p) "Vinyl chloride purification" includes any part of the process of vinyl chloride production which follows vinyl chloride formation and in which finished vinyl chloride is produced.

(q) "Reactor" includes any vessel in which vinyl chloride is partially or totally polymerized into polyvinyl chloride.

(r) "Reactor opening loss" means the emissions of vinyl chloride occurring when a reactor is vented to the atmosphere for any purpose other than an emergency relief discharge as defined in § 61.65(a).

(s) "Stripper" includes any vessel in which residual vinyl chloride is removed from polyvinyl chloride resin, except bulk resin, in the slurry form by the use of heat and/or vacuum. In the case of bulk resin, stripper includes any vessel which is used to remove residual vinyl chloride from polyvinyl chloride resin immediately following the polymerization step in the plant process flow.

#### § 61.62 Emission standard for ethylene dichloride plants.

An owner or operator of an ethylene dichloride plant shall comply with the requirements of this section and § 61.65.

(a) Ethylene dichloride purification: The concentration of vinyl chloride in all exhaust gases discharged to the atmosphere from any equipment used in ethylene dichloride purification is not to exceed 10 ppm, except as provided in § 61.65(a). This requirement does not apply to equipment that has been opened, is out of operation, and met the requirement in § 61.65(b) before being opened.

(b) Oxychlorination reactor: Except as provided in § 61.65(a), emissions of vinyl chloride to the atmosphere from each oxychlorination reactor are not to exceed 0.2 g/kg the 100 percent ethylene dichloride product from the oxychlorination process.

#### § 61.63 Emission standard for vinyl chloride plants.

An owner or operator of a vinyl chloride plant shall comply with the requirements of this section and § 61.65.

(a) Vinyl chloride formation and purification: The concentration of vinyl chloride in all exhaust gases discharged to the atmosphere from any equipment used in vinyl chloride formation and/or purification is not to exceed 10 ppm, except as provided in § 61.65(a). This requirement does not apply to equipment that has been opened, is out of operation, and met the requirement in § 61.65(b) (6) (i) before being opened.

#### § 61.64 Emission standard for polyvinyl chloride plants.

An owner or operator of a polyvinyl chloride plant shall comply with the requirements of this section and § 61.65.

(a) Reactor: The following requirements apply to reactors:

(1) The concentration of vinyl chloride in all exhaust gases discharged to the atmosphere from each reactor is not to exceed 10 ppm, except as provided in paragraph (a)(2) of this section and § 61.65(a).

(2) The reactor opening loss from each reactor is not to exceed 0.02 g vinyl chloride/Kg (0.00002 lb vinyl chloride/lb) of polyvinyl chloride product, with the product determined on a dry solids basis. This requirement applies to any vessel which is used as a reactor or as both a reactor and a stripper. In the bulk process, the product means the gross product of prepolymerization and postpolymerization.

(3) Manual vent valve discharge: Except for an emergency manual vent valve discharge, there is to be no discharge to the atmosphere from any manual vent valve on a polyvinyl chloride reactor in vinyl chloride service. An emergency manual vent valve discharge means a discharge to the atmosphere which could not have been avoided by taking measures to prevent the discharge. Within 10 days of any discharge to the atmosphere from any manual vent valve, the owner or operator of the source from which the discharge occurs shall submit to the Administrator a report in writing containing information on the source, nature and cause of the discharge, the date and time of the discharge, the approximate total vinyl chloride loss during the discharge, the method used for determining the vinyl chloride loss, the action that was taken to prevent the discharge, and measures adopted to prevent future discharges.

(b) Stripper: The concentration of vinyl chloride in all exhaust gases discharged to the atmosphere from each stripper is not to exceed 10 ppm, except as provided in § 61.65(a). This requirement does not apply to equipment that has been opened, is out of operation, and met the requirement in § 61.65(b) (6) (i) before being opened.

(c) Mixing, weighing, and holding containers: The concentration of vinyl chloride in all exhaust gases discharged to the atmosphere from each mixing, weighing, or holding container in vinyl chloride service which precedes the

stripper (or the reactor if the plant has no stripper) in the plant process flow is not to exceed 10 ppm, except as provided in § 61.65(a). This requirement does not apply to equipment that has been opened, is out of operation, and met the requirement in § 61.65(b) (6) (i) before being opened.

(d) Monomer recovery system: The concentration of vinyl chloride in all exhaust gases discharged to the atmosphere from each monomer recovery system is not to exceed 10 ppm, except as provided in § 61.65(a). This requirement does not apply to equipment that has been opened, is out of operation, and met the requirement in § 61.65(b) (6) (i) before being opened.

(e) Sources following the stripper(s): The following requirements apply to emissions of vinyl chloride to the atmosphere from the combination of all sources following the stripper(s) [or the reactor(s)] in the plant process flow including but not limited to, centrifuges, concentrators, blend tanks, filters, dryers, conveyor air discharges, baggers, storage containers, and inprocess wastewater:

(1) In polyvinyl chloride plants using stripping technology to control vinyl chloride emissions, the weighted average residual vinyl chloride concentration in all grades of polyvinyl chloride resin processed through the stripping operation on each calendar day, measured immediately after the stripping operation is completed, may not exceed:

(i) 2000 ppm for polyvinyl chloride dispersion resins, excluding latex resins;

(ii) 400 ppm for all other polyvinyl chloride resins, including latex resins, averaged separately for each type of resin; or

(2) In polyvinyl chloride plants controlling vinyl chloride emissions with technology other than stripping or in addition to stripping, emissions of vinyl chloride to the atmosphere may not exceed:

(i) 2 g/kg (0.002 lb/lb) product from the stripper(s) [or reactor(s)] if the plant has no stripper(s) [or for dispersion polyvinyl chloride resins, excluding latex resins, with the product determined on a dry solids basis];

(ii) 0.4 g/kg (0.0004 lb/lb) product from the strippers [or reactor(s)] if the plant has no stripper(s) [or for all other polyvinyl chloride resins, including latex resins, with the product determined on a dry solids basis].

#### § 61.65 Emission standard for ethylene dichloride, vinyl chloride and polyvinyl chloride plants.

An owner or operator of an ethylene dichloride, vinyl chloride, and/or polyvinyl chloride plant shall comply with the requirements of this section.

(a) Relief valve discharge: Except for an emergency relief discharge, there is to be no discharge to the atmosphere from any relief valve on any equipment in vinyl chloride service. An emergency relief discharge means a discharge which could not have been avoided by taking measures to prevent the discharge. Within 10 days of any relief valve discharge,

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the owner or operator of the source from which the relief valve discharge occurs shall submit to the Administrator a report in writing containing information on the source, nature and cause of the discharge, the date and time of the discharge, the approximate total vinyl chloride loss during the discharge, the method used for determining the vinyl chloride loss, the action that was taken to prevent the discharge, and measures adopted to prevent future discharges.

## (b) Fugitive emission sources:

(1) Loading and unloading lines: Vinyl chloride emissions from loading and unloading lines which are opened to the atmosphere after each loading or unloading operation are to be minimized as follows:

(i) After each loading or unloading operation and before opening a loading or unloading line to the atmosphere, the quantity of vinyl chloride in all parts of each loading or unloading line that are to be opened to the atmosphere is to be reduced so that the parts combined contain no greater than  $0.0038 \text{ m}^3$  (0.13 ft<sup>3</sup>) of vinyl chloride, at standard temperature and pressure; and

(ii) Any vinyl chloride removed from a loading or unloading line in accordance with paragraph (b)(1)(i) of this section is to be ducted through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm, or equivalent as provided in § 61.66.

(2) Slip gauges: During loading or unloading operations, the vinyl chloride emissions from each slip gauge in vinyl chloride service are to be minimized by ducting any vinyl chloride discharged from the slip gauge through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm, or equivalent as provided in § 61.66.

(3) Leakage from pump, compressor, and agitator seals:

(i) Rotating pumps: Vinyl chloride emissions from seals on all rotating pumps in vinyl chloride service are to be minimized by installing sealless pumps, pumps with double mechanical seals, or equivalent as provided in § 61.66. If double mechanical seals are used, vinyl chloride emission from the seals are to be minimized by maintaining the pressure between the two seals so that any leak that occurs is into the pump; by ducting any vinyl chloride between the two seals through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm; or equivalent as provided in § 61.66.

(ii) Reciprocating pumps: Vinyl chloride emissions from seals on all reciprocating pumps in vinyl chloride service are to be minimized by installing double outboard seals, or equivalent as provided in § 61.66. If double outboard seals are used, vinyl chloride emissions from the seals are to be minimized by maintaining the pressure between the two seals so that any leak that occurs is into the pump; by ducting any vinyl chloride between the two seals through a control

system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm; or equivalent as provided in § 61.66.

(iii) Rotating compressor: Vinyl chloride emissions from seals on all rotating compressors in vinyl chloride service are to be minimized by installing compressors with double mechanical seals, or equivalent as provided in § 61.66. If double mechanical seals are used, vinyl chloride emissions from the seals are to be minimized by maintaining the pressure between the two seals so that any leak that occurs is into the compressor; by ducting any vinyl chloride between the two seals through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm; or equivalent as provided in § 61.66.

(iv) Reciprocating compressors: Vinyl chloride emissions from seals on all reciprocating compressors in vinyl chloride service are to be minimized by installing double outboard seals, or equivalent as provided in § 61.66. If double outboard seals are used, vinyl chloride emissions from the seals are to be minimized by maintaining the pressure between the two seals so that any leak that occurs is into the compressor; by ducting any vinyl chloride between the two seals through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm; or equivalent as provided in § 61.66.

(v) Agitator: Vinyl chloride emissions from seals on all agitators in vinyl chloride service are to be minimized by installing agitators with double mechanical seals, or equivalent as provided in § 61.66. If double mechanical seals are used, vinyl chloride emissions from the seals are to be minimized by maintaining the pressure between the two seals so that any leak that occurs is into the agitated vessel; by ducting any vinyl chloride between the two seals through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm; or equivalent as provided in § 61.66.

(4) Leakage from relief valves: Vinyl chloride emissions due to leakage from each relief valve on equipment in vinyl chloride service are to be minimized by installing a rupture disk between the equipment and the relief valve, by connecting the relief valve discharge to a process line or recovery system, or equivalent as provided in § 61.66.

(5) Manual venting of gases: Except as provided in § 61.64(a)(3), all gases which are manually vented from equipment in vinyl chloride service are to be ducted through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm; or equivalent as provided in § 61.66.

(6) Opening of equipment: Vinyl chloride emissions from opening of equipment (including loading or unloading lines that are not opened to the atmosphere after each loading or unloading operation) are to be minimized as follows:

(i) Before opening any equipment for any reason, the quantity of vinyl chlo-

ride is to be reduced so that the equipment contains no more than 2.0 percent by volume vinyl chloride or  $0.0950 \text{ m}^3$  (25 gal) of vinyl chloride, whichever is larger, at standard temperature and pressure; and

(ii) Any vinyl chloride removed from the equipment in accordance with paragraph (b)(6)(i) of this section is to be ducted through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm, or equivalent as provided in § 61.66.

(7) Samples: Unused portions of samples containing at least 10 percent by weight vinyl chloride are to be returned to the process, and sampling techniques are to be such that sample containers in vinyl chloride service are purged into a closed process system.

(8) Leak detection and elimination: Vinyl chloride emissions due to leaks from equipment in vinyl chloride service are to be minimized by instituting and implementing a formal leak detection and elimination program. The owner or operator shall submit a description of the program to the Administrator for approval. The program is to be submitted within 45 days of the effective date of these regulations, unless a waiver of compliance is granted under § 61.11. If a waiver of compliance is granted, the program is to be submitted on a date scheduled by the Administrator. Approval of a program will be granted by the Administrator provided he finds:

(i) It includes a reliable and accurate vinyl chloride monitoring system for detection of major leaks and identification of the general area of the plant where a leak is located. A vinyl chloride monitoring system means a device which obtains air samples from one or more 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 equivalent or alternative method.

(ii) It includes a reliable and accurate portable hydrocarbon detector to be used routinely to find small leaks and to pinpoint the major leaks indicated by the vinyl chloride monitoring system. A portable hydrocarbon detector means a device which measures hydrocarbons with a sensitivity of at least 10 ppm and is of such design and size that it can be used to measure emissions from localized points.

(iii) It provides for an acceptable calibration and maintenance schedule for the vinyl chloride monitoring system and portable hydrocarbon detector. For the vinyl chloride monitoring system, a daily span check is to be conducted with a concentration of vinyl chloride equal to the concentration defined as a leak according to paragraph (b)(8)(vi) of this section. The calibration is to be done with either:

(A) A calibration gas mixture prepared from the gases specified in sections 5.2.1 and 5.2.3 of Test Method 106, or

(B) A calibration gas cylinder containing the appropriate concentration of vinyl chloride. If a calibration gas cylinder is used, the analysis must be traceable to the National Bureau of Standards or to a gravimetrically calibrated vinyl chloride permeation tube.

(iv) The location and number of points to be monitored and the frequency of monitoring provided for in the program are acceptable when they are compared with the number of pieces of equipment in vinyl chloride service and the size and physical layout of the plant.

(v) It contains an acceptable plan of action to be taken when a leak is detected.

(vi) It contains a definition of leak which is acceptable when compared with the background concentrations of vinyl chloride in the areas of the plant to be monitored by the vinyl chloride monitoring system. Measurements of background concentrations of vinyl chloride in the areas of the plant to be monitored by the vinyl chloride monitoring system are to be included with the description of the program. The definition of leak for a given plant may vary among the different areas within the plant and is also to change over time as background concentrations in the plant are reduced.

(9) Inprocess wastewater: Vinyl chloride emissions to the atmosphere from inprocess wastewater are to be reduced as follows:

(i) The concentration of vinyl chloride in each inprocess wastewater stream containing greater than 10 ppm vinyl chloride measured immediately as it leaves a piece of equipment and before being mixed with any other inprocess wastewater stream is to be reduced to no more than 10 ppm by weight before being mixed with any other inprocess wastewater stream which contains less than 10 ppm vinyl chloride; before being exposed to the atmosphere, before being discharged to a wastewater treatment process; or before being discharged untreated as a wastewater. The paragraph does apply to water which is used to displace vinyl chloride from equipment before it is opened to the atmosphere in accordance with § 61.64(a)(2) or paragraph (b)(6) of this section, but does not apply to water which is used to wash out equipment after the equipment has already been opened to the atmosphere in accordance with § 61.64(a)(2) or paragraph (b)(6) of this section.

(ii) Any vinyl chloride removed from the inprocess wastewater in accordance with paragraph (b)(9)(i) of this section is to be ducted through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm, or equivalent as provided in § 61.66.

(c) The requirements in paragraphs (b)(1), (b)(2), (b)(5), (b)(6), (b)(7) and (b)(8) of this section are to be incorporated into a standard operating procedure, and made available upon request for inspection by the Administrator. The standard operating procedure is to include provisions for measuring the

vinyl chloride in equipment  $\geq 4.75 \text{ m}^3$  01250 gal in volume for which an emission limit is prescribed in § 61.65(b)(6)

(i) prior to opening the equipment and using Test Method 106, a portable hydrocarbon detector, or an equivalent or alternative method. The method of measurement is to meet the requirements in § 61.67(g)(5)(i)(A) or (g)(5)(i)(B).

#### § 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. For an existing source, any request for using an equivalent method as the initial measure of control is to be submitted to the Administrator within 30 days of the effective date. For a new source, any request for using an equivalent method is to be submitted to the Administrator with the application for approval of construction or modification required by § 61.07.

#### § 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) 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.

(e) All samples are to be analyzed within 24 hours, and 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 2 years records

of emission test results and other data needed to determine emissions.

(g) Unless otherwise specified, the owner or operator shall use 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 equivalent method or an alternative method has been approved by the Administrator. If the Administrator 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 Administrator 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 in §§ 61.62(a) or (b) § 61.63(a), or §§ 61.64(a)(1), (b), (c), or (d), or from 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), (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:

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

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 be taken over a minimum of one hour, and is to contain a minimum volume of 50 liters corrected to standard conditions.

(ii) 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 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 percent oxygen to which the correction is being made.

Percent O<sub>2</sub> = Percent oxygen in the exhaust gas as measured by Reference Method 3 in Appendix A of Part 60 of this chapter.

(iii) For those emission sources where the emission limit is prescribed in terms of mass rather than concentration, mass

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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 to Part 60 of this chapter.

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

$Z$ =Production rate (kg/hr).

(2) Test Method 107 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) Where a stripping operation is used to attain the emission limit in § 61.64(e), emissions are to be determined using Test Method 107 as follows:

(i) The number of 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 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) 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 inprocess 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 l/hr, determined in accordance with a method which has been submitted to and approved by the Administrator.

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

$Z$ =Production rate (kg/hr), determined in accordance with a method which has been submitted and approved by the 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. For a reactor

that is also used as a stripper, the determination may be made immediately following the stripping 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<sup>3</sup>.

2.60=Density of vinyl chloride at one atmosphere and 20°C in kg/m<sup>3</sup>.

$10^{-6}$ =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 Administrator.

(D) 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.

#### S 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 emission 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 air samples from one or more 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 equivalent or alternative method. The vinyl chloride monitoring system used to meet the requirements in § 61.65(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 determined to be equivalent to the emission limit for that source based on the emission test required by § 67.67. The calibration is to be done with either:

(1) A calibration gas mixture prepared from the gases specified in sections 5.2.1 and 5.2.3 of Test Method 106, or

(2) A calibration gas cylinder containing the appropriate concentration of vinyl chloride. If a calibration gas cylinder is used, the analysis must be traceable to the National Bureau of Standards or to a gravimetrically calibrated vinyl chloride permeation tube.

#### S 61.69 Initial report.

(a) An owner or operator of any source to which this subpart applies shall submit a statement in writing notifying the Administrator that the equipment and procedural specifications in §§ 61.65(b)(1), (b)(2), (b)(3), (b)(4), (b)(5), (b)(6), (b)(7), and (b)(8) are being implemented.

(b) (1) In the case of an existing source or a new source which has an initial startup date preceding the effective date, the statement is to be submitted within 90 days of the effective date, unless a waiver of compliance is granted under § 61.11, along with the information required under § 61.10. If a waiver of compliance is granted, the statement is to be submitted on a date scheduled by the Administrator.

(2) In the case of a new source which did not have an initial startup date preceding the effective date, the statement is to be submitted within 90 days of the initial startup date.

(c) The statement is to contain the following information:

(1) A list of the equipment installed for compliance,

(2) A description of the physical and functional characteristics of each piece of equipment.

(3) A description of the methods which have been incorporated into the standard operating procedures for measuring or calculating the emissions for which emission limits are prescribed in §§ 61.65(b)(1)(i) and (b)(6)(i),

(4) A statement that each piece of equipment is installed and that each piece of equipment and each procedure is being used.

#### S 61.70 Semianual report.

(a) (2) is to be determined. The number source to which this subpart applies shall submit to the Administrator on Septem-

ber 15 and March 15 of each year a report in writing containing the information required by this section. The first semi-annual report is to be submitted following the first full 6 month reporting period after the initial report is submitted.

(b) (1) In the case of an existing source or a new source which has an initial startup date preceding the effective date, the first report is to be submitted within 180 days of the effective date, unless a waiver of compliance is granted under § 61.11. If a waiver of compliance is granted, the first report is to be submitted on a date scheduled by the Administrator.

(2) In the case of a new source which did not have an initial startup date preceding the effective date, the first report is to be submitted within 180 days of the initial startup date.

(c) Unless otherwise specified, the owner or operator shall use the Test Methods in Appendix B to this part to conduct emission tests as required by paragraphs (c) (2) and (c) (3) of this section, unless an equivalent or an alternative method has been approved by the Administrator. If the Administrator 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 Administrator may notify the owner or operator that approval of the method previously considered to be equivalent or alternative is withdrawn.

(1) The owner or operator shall include in the report a record of any emissions which averaged over any hour period (commencing on the hour) are in excess of the emission limits prescribed in §§ 61.62(a) or (b), § 61.63(a), or §§ 61.64(a) (1), (b), (c), or (d), or 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), (b) (2), (b) (5), (b) (6) (ii), or (b) (9) (ii). The emissions are to be measured in accordance with § 61.68.

(2) In polyvinyl chloride plants for which a stripping operation is used to attain the emission level prescribed in § 61.64(e), the owner or operator shall include in the report a record of the vinyl chloride content in the polyvinyl chloride resin. Test Method 107 is to be used to determine vinyl chloride content as follows:

(i) If batch stripping is used, one representative sample of polyvinyl chloride resin is to be taken from each batch of each grade of resin immediately following the completion of the stripping, and grade and the date and time the batch is completed. The corresponding quantity of material processed in each stripper batch is to be recorded and identified by resin type and grade and the date and time the batch is completed.

(ii) If continuous stripping is used, one representative sample of polyvinyl chloride resin is to be taken for each grade of resin processed or at intervals

of 8 hours for each grade of resin which is being processed, whichever is more frequent. The sample is to be taken as the resin flows out of the stripper and identified by resin type and grade and the date and time the sample was taken. The corresponding quantity of material processed by each stripper over the time period represented by the sample during the eight hour period, is to be recorded and identified by resin type and grade and the date and time it represents.

(iii) The quantity of material processed by the 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 paragraphs (c) (2) (i) and (c) (2) (ii) of this section.

(v) The report to the Administrator by the owner or operator is to include the vinyl chloride content found in all the samples required in paragraphs (c) (2) (i) and (c) (2) (ii) of this section, averaged separately for each type of resin, over each calendar day and weighted according to the quantity of each grade of resin processed by the stripper(s) that calendar day, according to the following equation:

$$A_{T_i} = \frac{\sum_{j=1}^n P_{G_j} M_{G_j}}{Q_{T_i}}$$

$$= \frac{P_{G_1} M_{G_1} + P_{G_2} M_{G_2} + \dots + P_{G_n} M_{G_n}}{Q_{T_i}}$$

$A$ =24-hour average concentration of type T<sub>i</sub> resin in ppm.  
 $Q$ =Total production of type T<sub>i</sub> resin over the 24-hour period, in kg.  
 $T_i$ =Type of resin;  $j=1, 2, \dots, n$  where  $n$  is total number of resin types produced during the 24-hour period.  
 $M$ =Concentration of vinyl chloride in one sample of grade G<sub>j</sub> resin, in ppm.  
 $P$ =Production of grade G<sub>j</sub> resin represented by the sample, in kg.  
 $G_1$ =Grade of resin, e.g., G<sub>1</sub>, G<sub>2</sub>, and G<sub>3</sub>.  
 $n$ =Total number of grades of resin produced during the 24-hour period.

(vi) The owner or operator shall retain at the source and make available for inspection by the Administrator for a minimum of 2 years records of all data needed to furnish the information required by paragraph (c) (2) (v) of this section: The records are to contain the following information:

(A) The vinyl chloride content found in all the samples required in paragraphs (c) (2) (i) and (c) (2) (ii) of this section, identified by the resin type and grade and the time and date of the sample, and

(B) The corresponding quantity of polyvinyl chloride resin processed by the stripper(s), identified by the resin type and grade and the time and date it represents.

(3) The owner or operator shall include in the report a record of the emissions from each reactor opening for which an emission limit is prescribed in § 61.64(a) (2). Emissions are to be determined in accordance with § 61.67(g) (5), except that emissions for each reactor are to be determined. For a reactor that is also used as a stripper, the determination

may be made immediately following the stripping operation.

#### § 61.71 Recordkeeping.

(a) The owner or operator of any source to which this subpart applies shall retain the following information at the source and make it available for inspection by the Administrator for a minimum of two years:

(1) A record of the leaks detected by the vinyl chloride monitoring system, as required by § 61.65(b) (8), including the concentrations of vinyl chloride as measured, analyzed, and recorded by the vinyl chloride detector, the location of each measurement and the date and approximate time of each measurement.

(2) A record of the leaks detected during routine monitoring with the portable hydrocarbon detector and the action taken to repair the leaks, as required by § 61.65(b) (8), including a brief statement explaining the location and cause of each leak detected with the portable hydrocarbon detector, the date and time of the leak and any action taken to eliminate that leak measured in accordance with § 61.68.

(3) For the relief discharges from reactors subject to the provisions of § 61.65(a), a daily operating record for each reactor, including pressures and temperatures.

2. Appendix B is amended by adding Test Methods 106 and 107 as follows:

#### METHOD 106—DETERMINATION OF VINYL CHLORIDE FROM STATIONARY SOURCES

##### INTRODUCTION

Performance of this method should not be attempted by persons unfamiliar with the operation of a gas chromatograph, nor by those who are unfamiliar with source sampling, as there are many details that are beyond the scope of this presentation. Care must be exercised to prevent exposure of sampling personnel to vinyl chloride, a carcinogen.

##### 1. Principle and Applicability.

1.1 An integrated bag sample of stack gas containing vinyl chloride (chloroethylene) is subjected to chromatographic analysis, using a flame ionization detector.

1.2 The method is applicable to the measurement of vinyl chloride in stack gases from ethylene dichloride, vinyl chloride and polyvinyl chloride manufacturing processes, except where the vinyl chloride is contained in particulate matter.

##### 2. Range and Sensitivity.

The lower limit of detection will vary according to the chromatograph used. Values reported include  $1 \times 10^{-2}$  mg and  $4 \times 10^{-3}$  mg.

##### 3. Interferences.

Acetaldehyde, which can occur in some vinyl chloride sources, will interfere with the vinyl chloride peak from the Chromosorb 102 column. See sections 4.3.2 and 6.4. If resolution of the vinyl chloride peak is still not satisfactory for a particular sample, then chromatograph parameters can be further altered with prior approval of the Administrator. If alteration of the chromatograph parameters fails to resolve the vinyl chloride peak, then supplemental confirmation of the vinyl chloride peak through an absolute analytical technique, such as mass spectroscopy, must be performed.

##### 4. Apparatus.

###### 4.1 Sampling (Figure 1).

4.1.1 Probe—Stainless steel, Pyrex glass, or Teflon tubing according to stack temper-

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ature, each equipped with a glass wool plug to remove particulate matter.

4.1.2 Sample line—Teflon, 6.4 mm outside diameter, of sufficient length to connect probe to bag. A new unused piece is employed for each series of bag samples that constitutes an emission test.

4.1.3 Male (2) and female (2) stainless steel quick-connects, with ball checks (one pair without) located as shown in Figure 1.

4.1.4 Tedlar bags, 100 liter capacity—to contain sample. Teflon bags are not acceptable. Aluminized Mylar bags may be used, provided that the samples are analyzed within 24 hours of collection.

4.1.5 Rigid leakproof containers for 4.1.4, with covering to protect contents from sunlight.

4.1.6 Needle valve—to adjust sample flow rate.

4.1.7 Pump—Leak-free. Minimum capacity 2 liters per minute.

4.1.8 Charcoal tube—to prevent admission of vinyl chloride to atmosphere in vicinity of samplers.

4.1.9 Flow meter—for observing sample flow rate; capable of measuring a flow range from 0.10 to 1.00 liter per minute.

4.1.10 Connecting tubing—Teflon, 6.4 mm outside diameter, to assemble sample train (Figure 1).

4.1.11 Pitot tube—Type S (or equivalent), attached to the probe so that the sampling flow rate can be regulated proportional to the stack gas velocity.

#### 4.2 Sample recovery.

4.2.1 Tubing—Teflon, 6.4 mm outside diameter, to connect bag to gas chromatograph sample loop. A new unused piece is employed for each series of bag samples that constitutes an emission test, and is to be discarded upon conclusion of analysis of those bags.

#### 4.3 Analysis.

4.3.1 Gas chromatograph—with flame ionization detector, potentiometric strip chart recorder and 1.0 to 5.0 ml heated sampling loop in automatic sample valve.

4.3.2 Chromatographic column—Stainless steel, 2.0 × 3.2 mm, containing 80/100 mesh Chromosorb 102. A secondary column of GE SF-96, 20% on 80/80 mesh AW Chromosorb P, stainless steel, 2.0 m × 3.2 mm, will be required if acetaldehyde is present. If used, the SF-96 column is placed after the Chromosorb 102 column. The combined columns should then be operated at 110°C.

4.3.3 Flow meters (2)—Rotameter type, 0 to 100 ml/min capacity, with flow control valves.

4.3.4 Gas regulators—for required gas cylinders.

4.3.5 Thermometer—Accurate to one degree centigrade, to measure temperature of heated sample loop at time of sample injection.

4.3.6 Barometer—Accurate to 5 mm Hg, to measure atmospheric pressure around gas chromatograph during sample analysis.

4.3.7 Pump—Leak-free. Minimum capacity 100 ml/min.

#### 4.4 Calibration.

4.4.1 Tubing—Teflon, 6.4 mm outside diameter, separate pieces marked for each calibration concentration.

4.4.2 Tedlar bags—Sixteen-inch square size, separate bag marked for each calibration concentration.

4.4.3 Syringe—0.5 ml, gas tight.

4.4.4 Syringe—50 µl, gas tight.

4.4.5 Flow meter—Rotameter type, 0 to 1000 ml/min range accurate to  $\pm 1\%$ , to meter nitrogen in preparation of standard gas mixtures.

4.4.6 Stop watch—Of known accuracy, to time gas flow in preparation of standard gas mixtures.

5. Reagents. It is necessary that all reagents be of chromatographic grade.

#### 5.1 Analysis.

5.1.1 Helium gas or nitrogen gas—Zero grade, for chromatographic carrier gas.

5.1.2 Hydrogen gas—Zero grade.

5.1.3 Oxygen gas, or Air, as required by the detector—Zero grade.

#### 5.2 Calibration.

5.2.1 Vinyl chloride, 99.9+ %—For preparation of standard gas mixtures.

5.2.2 Calibration cylinders (3), optional—One each of 50, 10 and 5 ppm vinyl chloride in nitrogen with certified analysis. Analysis must be traceable to NBS (National Bureau of Standards) or to a gravimetrically calibrated vinyl chloride permeation tube.

5.2.3 Nitrogen gas—Zero grade, for preparation of standard gas mixtures.

#### 6. Procedure.

6.1 Sampling. Assemble the sample train as in Figure 106-1. Perform a bag leak check according to Section 7.4. Observe that all connections between the bag and the probe are tight. Place the end of the probe at the centroid of the stack and start the pump with the needle valve adjusted to yield a flow of 0.5 lpm. After a period of time sufficient to purge the line several times has elapsed, connect the vacuum line to the bag and evacuate the bag until the rotameter indicates no flow. Then reposition the sample and vacuum lines and begin the actual sampling, keeping the rate proportional to the stack velocity. Direct the gas exiting the rotameter away from sampling personnel. At the end of the sample period, shut off the pump, disconnect the sample line from the bag, and disconnect the vacuum line from the bag container. Protect the bag container from sunlight.

6.2 Sample storage. Sample bags must be kept out of direct sunlight. When at all possible, analysis is to be performed within 24 hours of sample collection.

6.3 Sample recovery. With a piece of Teflon tubing identified for that bag, connect a bag inlet valve to the gas chromatograph sample valve. Switch the valve to withdraw gas from the bag through the sample loop. Plumb the equipment so the sample gas passes from the sample valve to the leak-free pump, and then to a charcoal tube, followed by a 0-100 ml/min rotameter with flow control valve.

6.4 Analysis. Set the column temperature to 100°C the detector temperature to 150°C, and the sample loop temperature to 70°C. When optimum hydrogen and oxygen flow rates have been determined verify and maintain these flow rates during all chromatograph operations. Using zero helium or nitrogen as the carrier gas, establish a flow rate in the range consistent with the manufacturer's requirements for satisfactory detector operation. A flow rate of approximately 40 ml/min should produce adequate separations. Observe the base line periodically and determine that the noise level has stabilized and that base line drift has ceased. Purge the sample loop for thirty seconds at the rate of 100 ml/min, then activate the sample valve. Record the injection time (the position of the pen on the chart at the time of sample injection), the sample number, the sample loop temperature, the column temperature, carrier gas flow rate, chart speed

and the attenuator setting. Record the laboratory pressure. From the chart, select the peak having the retention time corresponding to vinyl chloride, as determined in Section 7.2. Measure the peak area,  $A_m$ , by use of  $H_m$ , and a disc integrator or a planimeter. Measure the peak height,  $H_m$ . Record  $A_m$  and the retention time. Repeat the injection at least two times or until two consecutive vinyl chloride peaks do not vary in area more than 5%. The average value for these two areas will be used to compute the bag concentration.

Compare the ratio of  $H_m$  to  $A_m$  for the vinyl chloride sample with the same ratio for the standard peak which is closest in height. As a guideline, if these ratios differ by more than 10%, the vinyl chloride peak may not be pure (possibly acetaldehyde is present) and the secondary column should be employed (see Section 4.3.2).

6.5 Measure the ambient temperature and barometric pressure near the bag. (Assume the relative humidity to be 100 percent.) From a water saturation vapor pressure table, determine the record and water vapor content of the bag.

#### 7. Calibration and Standards.

7.1 Preparation of vinyl chloride standard gas mixtures. Evacuate a sixteen-inch square Tedlar bag that has passed a leak check (described in Section 7.4) and meter in 5.0 liters of nitrogen. While the bag is filling, use the 0.5 ml syringe to inject 250 µl of 99.9+ % vinyl chloride through the wall of the bag. Upon withdrawing the syringe needle, immediately cover the resulting hole with a piece of adhesive tape. This gives a concentration of 50 ppm of vinyl chloride. In a like manner use the other syringes to prepare dilutions having 10 and 5 ppm vinyl chloride concentrations. Place each bag on a smooth surface and alternately depress opposite sides of the bag 50 times to further mix the gases.

7.2 Determination of vinyl chloride retention time. This section can be performed simultaneously with Section 7.3. Establish chromatograph conditions identical with those in Section 6.3, above. Set attenuator to X 1 position. Flush the sampling loop with zero helium or nitrogen and activate the sample valve. Record the injection time, the sample loop temperature, the column temperature, the carrier gas flow rate, the chart speed and the attenuator setting. Record peaks and detector responses that occur in the absence of vinyl chloride. Maintain conditions. With the equipment plumbing arranged identically to Section 6.3, flush the sample loop for 30 seconds at the rate of 100 ml/min with one of the vinyl chloride calibration mixtures and activate the sample valve. Record the injection time. Select the peak that corresponds to vinyl chloride. Measure the distance on the chart from the injection time to the time at which the peak maximum occurs. This quantity, divided by the chart speed, is defined as the retention time. Record.

7.3 Preparation of chromatograph calibration curve. Make a gas chromatographic measurement of each standard gas mixture (described in Section 7.1) using conditions identical with those listed in Section 6.3 above. Flush the sampling loop for 30 seconds at the rate of 100 ml/min with each standard gas mixture and activate the sample valve. Record  $C_i$ , the concentrations of vinyl chloride injected, the attenuator setting, chart speed, peak area, sample loop temperature, column temperature, carrier gas flow rate, and retention time. Record the laboratory pressure. Calculate  $A_c$ , the peak area multi-

<sup>1</sup>Mention of trade names on specific products does not constitute endorsement by the Environmental Protection Agency.

plied by the attenuator setting. Repeat until two injection areas are within 5%, then plot those points vs  $C_e$ . When the other concentrations have been plotted, draw a smooth curve through the points. Perform calibration daily, or before and after each set of bag samples, whichever is more frequent.

7.4 Bag leak checks. While performance of this section is required subsequent to bag use, it is also advised that it be performed prior to bag use. After each use, make sure a bag did not develop leaks as follows. To leak check, connect a water manometer and pressurize the bag to 5-10 cm H<sub>2</sub>O (2-4 in H<sub>2</sub>O). Allow to stand for 10 minutes. Any displacement in the water manometer indicates a leak. Also check the rigid container for leaks in this manner.

(NOTE: An alternative leak check method is to pressurize the bag to 5-10 cm H<sub>2</sub>O or 2-4 in H<sub>2</sub>O and allow to stand overnight. A deflated bag indicates a leak.) For each sample bag in its rigid container, place a rotameter in-line between the bag and the pump inlet. Evacuate the bag. Failure of the rotameter to register zero flow when the bag appears to be empty indicates a leak.

#### 8. Calculations.

8.1 Determine the sample peak area as follows:

$$A_e = A_m A_f \quad \text{Equation 106-1}$$

where:

$A_e$ =The sample peak area.

$A_m$ =The measured peak area.

$A_f$ =The attenuation factor.

8.2 Vinyl chloride concentrations. From the calibration curve described in Section 7.3, above, select the value of  $C_e$  that corresponds to  $A_e$ , the sample peak area. Calculate  $C_b$  as follows:

$$C_b = \frac{C_e P_r T_i}{P_i T_r (1 - B_{ws})} \quad \text{Equation 106-2}$$

Where:

$B_{ws}$ =The water vapor content of the bag sample, as analyzed.

$C_e$ =The concentration of vinyl chloride in the bag sample in ppm.

$C_b$ =The concentration of vinyl chloride indicated by the gas chromatograph, in ppm.

$P_r$ =The reference pressure, the laboratory pressure recorded during calibration, mm Hg.

$T_i$ =The sample loop temperature on the absolute scale at the time of analysis, °K.

$P_i$ =The laboratory pressure at time of analysis, mm Hg.

$T_r$ =The reference temperature, the sample loop temperature recorded during calibration, °K.

#### 9. References.

1. Brown, D. W., Loy, E. W. and Stephenson, M. H. "Vinyl Chloride Monitoring Near the B. F. Goodrich Chemical Company in Louisville, Kentucky." Region IV, U.S. Environmental Protection Agency, Surveillance and Analysis Division, Athens, Georgia, June 24, 1974.

2. "Evaluation of A Collection and Analytical Procedure for Vinyl Chloride in Air," by G. D. Clayton and Associates, December 13, 1974. EPA Contract No. 68-02-1408, Task Order No. 2, EPA Report oN. 75-VCL-1.

3. "Standardization of Stationary Source Emission Method for Vinyl Chloride," by Midwest Research Institute, 1976. EPA Contract No. 68-02-1098, Task Order No. 7.

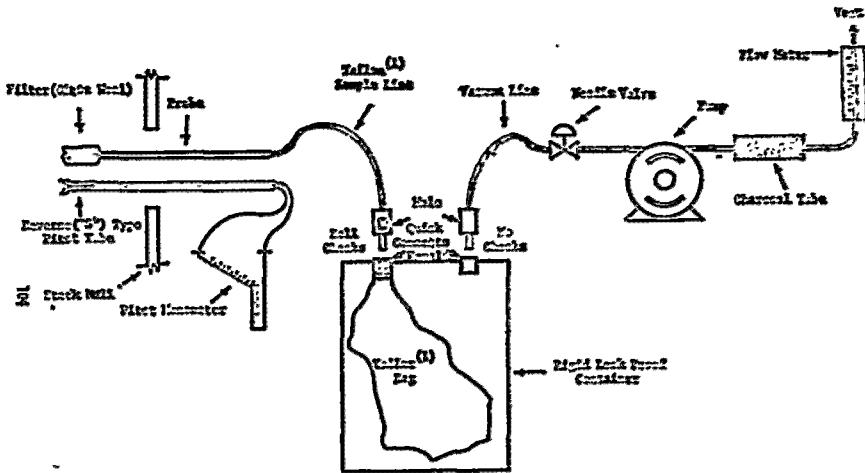


Figure 106-1. Analytical bag sampling train.

(1) Mention of trade names on specific products does not constitute endorsement by the Environmental Protection Agency.

#### METHOD 107—DETERMINATION OF VINYL CHLORIDE CONTENT OF IMPRECISE WASTEWATER SAMPLES, AND VINYL CHLORIDE CONTENT OF POLYVINYL CHLORIDE RESIN, SLURRY, WET CAKE, AND LATEX SAMPLES

##### INTRODUCTION

Performance of this method should not be attempted by persons unfamiliar with the operation of a gas chromatograph, nor by those who are unfamiliar with sampling, as there are many details that are beyond the scope of this presentation. Care must be exercised to prevent exposure of sampling personnel to vinyl chloride, a carcinogen.

##### 1. Principle and Applicability.

1.1 The basis for this method relates to the vapor equilibrium which is established between RVCM, PVC, resin, water, and air in a closed system. It has been demonstrated that the RVCM in a PVC resin will equilibrate in a closed vessel quite rapidly, provided that the temperature of the PVC resin is maintained above the glass transition temperature of that specific resin.

1.2 This procedure is suitable for determining the vinyl chloride monomer (VCM) content of imprecise wastewater samples, and the residual vinyl chloride monomer (RVCM) content of polyvinyl chloride (PVC) resins, wet cake, slurry, and latex samples. It cannot be used for polymer in fused form, such as sheet or cubes. If a resolution of the vinyl chloride peak is not satisfactory for a particular sample, then chromatograph parameters may be altered with prior approval of the Administrator. If there is reason to believe that some other hydrocarbon with an identical retention time is present in the sample, then supplemental confirmation of the vinyl chloride peak through an absolute analytical technique, such as mass spectroscopy, should be performed.

##### 2. Range and Sensitivity.

The lower limit of detection of vinyl chloride will vary according to the chromatograph used. Values reported include  $1 \times 10^{-7}$

mg and  $4 \times 10^{-7}$  mg. With proper calibration, the upper limit may be extended as needed.

##### 3. Precision and Reproducibility.

An interlaboratory comparison between seven laboratories of three resin samples, each split into three parts, yielded a standard deviation of 2.63% for a sample with a mean of 2.63 ppm, 4.16% for a sample with a mean of 1.66 ppm, and 5.23% for a sample with a mean of 62.63 ppm.

##### 4. Safety.

Do not release vinyl chloride to the laboratory atmosphere during preparation of standards. Venting or purging with VCM/air mixtures must be held to a minimum. When they are required, the vapor must be routed to outside air. Vinyl chloride, even at low ppm levels, must never be vented inside the laboratory. After vials have been analyzed, the pressure within the vial must be vented prior to removal from the instrument turn-table. Vials must be vented into an activated charcoal tube using a hypodermic needle to prevent release of vinyl chloride into the laboratory atmosphere. The charcoal must be replaced prior to vinyl chloride breakthrough.

##### 5. Apparatus.

5.1 Sampling.

5.1.1 Bottles—60 ml (2 oz), with waxed lined screw on top, for PVC samples.

5.1.2 Vials—50 ml Hypo-vials,<sup>2</sup> sealed with Teflon faced Tuf-Bond discs for water samples.

5.1.3 Electrical tape—or equivalent, to prevent loosening of bottle tops.

##### 5.2 Sample recovery.

5.2.1 Vials—with seals and caps, Perkin-Elmer Corporation No. 105-0118, or equivalent.

5.2.2 Analytical balance—Capable of weighing to  $\pm 0.001$  gram.

5.2.3 Syringe, 100  $\mu$ l—Precision Series "A" No. 010325, or equivalent.

(2) Mention of trade names on specific products does not constitute endorsement by the Environmental Protection Agency.

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5.2.4 Vial Sealer—Perkin-Elmer No. 105-0106 or equivalent.

5.3 Analysis.

5.3.1 Gas chromatograph—Perkin-Elmer Corporation Model F-40 head-space analyzer, No. 104-0001, or equivalent.

5.3.2 Chromatographic column—Stainless steel, 2 m<sup>2</sup> × 3.2 mm, containing 0.4% Carbowax 1500 on Carbobak A, Perkin-Elmer Corporation No. 105-0133, or equivalent. Carbobak C can be used in place of Carbobak A.

5.3.3 Thermometer—0 to 100° C, accurate to ±0.1° C, Perkin-Elmer No. 105-0109 or equivalent.

5.3.4 Sample tray thermostat system—Perkin-Elmer No. 105-0103, or equivalent.

5.3.5 Septa—Sandwich type, for automatic dosing, 13 mm, Perkin-Elmer No. 105-1008, or equivalent.

5.3.6 Integrator - recorder — Hewlett Packard Model 3380A, or equivalent.

5.3.7 Filter drier assembly (3)—Perkin-Elmer No. 2230117, or equivalent.

5.3.8 Soap film flowmeter—Hewlett Packard No. 0101-0113, or equivalent.

5.4 Calibration.

5.4.1 Regulators—for required gas cylinders.

6. Reagents.

6.1 Analysis.

6.1.1 Hydrogen gas—zero grade.

6.1.2 Nitrogen gas—zero grade.

6.1.3 Air—zero grade.

6.2 Calibration.

6.2.1 Standard cylinders (4)—one each of 50, 500, 2000, and 4000 ppm vinyl chloride in nitrogen, with certified analysis.

7. Procedure.

7.1 Sampling.

7.1.1 PVC sampling—Allow the resin or slurry to flow from a tap on the tank or silo until the tap line has been well purged. Extend a 60 ml sample bottle under the tap, fill, and immediately tightly cap the bottle. Wrap electrical tape around the cap and bottle to prevent the top from loosening. Place an identifying label on each bottle, and record the date, time, and sample location both on the bottles and in a log book.

7.1.2 Water sampling—Prior to use, the 50 ml vials (without the discs) must be capped with aluminum foil and muffed at 400°C for at least one hour to destroy or remove any organic matter that could interfere with analysis. At the sampling location fill the vials bubble-free, to overflowing so that a convex meniscus forms at the top. The excess water is displaced as the sealing disc is carefully placed, Teflon side down, on the opening of the vial. Place the aluminum seal over the disc and the neck of the vial and crimp into place. Affix an identifying label on the bottle, and record the date, time, and sample location both on the vials and in a log book. All samples must be kept refrigerated until analyzed.

7.2 Sample recovery. Samples must be run within 24 hours.

7.2.1 Resin samples—The weight of the resin used must be between 0.1 and 4.5 grams. An exact weight must be obtained ( $\pm 0.001$  gram) for each sample. In the case of suspension resins a volumetric cup can be prepared which will hold the required amount of sample. The sample bottle is opened, and the cup volume of resin is added to the tared sample vial (including septum and aluminum cap). The vial is immediately sealed and the exact sample weight is then obtained. Report this value on the data sheet as it is required for calculation of RVCM. In the case of relatively dry resin samples (water content <0.3 weight %), 100  $\mu$ l of distilled water must be injected into the vial, after

sealing and weighing, using a 100  $\mu$ l syringe. In the case of dispersion resins, the cup cannot be used. The sample is instead weighed approximately in an aluminum dish, transferred to the tared vial and weighed accurately in the vial. The sample is then placed in the Perkin-Elmer head space analyzer (or equivalent) and conditioned for one hour at 90°C.

NOTE: Some aluminum vial caps have a center section which must be removed prior to placing into sample tray. If not removed, serious damage to the injection needle will occur.

7.2.2 Suspension resin slurry and wet cake samples—Slurry must be filtered using a small Buchner funnel with vacuum to yield wet cake. The filtering process must be continued only as long as a steady stream of water is exiting from the funnel. Excessive filtration time could result in some loss of VCM. The wet cake sample (0.10 to 4.5 grams) is added to a tared vial (including septum and aluminum cap) and immediately sealed. Sample weight is then determined to 3 decimal places. The sample is then placed in the Perkin-Elmer head space analyzer (or equivalent) and conditioned for one hour at 90°C. A sample of wet cake is used to determine TS (total solids). This is required for calculating the RVCM.

7.2.3 Dispersion resin slurry samples.—This material should not be filtered. Sample must be thoroughly mixed. Using a tared vial (including septum and aluminum cap) add approximately 8 drops (0.25 to 0.35 grams) of slurry or latex using a medicine dropper. This should be done immediately after mixing. Seal the vial as soon as possible. Determine sample weight accurate to 0.001 grams. Total sample weight must not exceed 0.50 grams. Condition the vial for one hour at 90°C in the analyzer. Determine the TS on the slurry sample (Section 7.3.5).

7.2.4 Inprocess wastewater samples—Using a tared vial (including septum and aluminum cap) quickly add approximately 1 cc of water using a medicine dropper. Seal the vial as soon as possible. Determine sample weight accurate to 0.001 gram. Condition the vial for two hours at 90°C in the analyzer.

7.3 Analysis.

7.3.1 Preparation of gas chromatograph—Install the chromatographic column and condition overnight at 150°C. Do not connect the exit end of the column to the detector while conditioning.

7.3.1.1 Flow rate adjustments—Adjust flow rates as follows:

a. Nitrogen carrier gas—Set regulator on cylinder to read 50 psig. Set regulator on chromatograph to 1.3 kg/cm<sup>2</sup>. Normal flows at this pressure should be 25 to 40 cc/minute. Check with bubble flow meter.

b. Burner air supply—Set regulator on cylinder to read 50 psig. Set regulator on chromatograph to supply air to burner at a rate between 250 and 300 cc/minute. Check with bubble flowmeter.

c. Hydrogen supply—Set regulator on cylinder to read 30 psig. Set regulator on chromatograph to supply approximately 35±5 cc/minute. Optimize hydrogen flow to yield the most sensitive detector response without extinguishing the flame. Check flow with bubble meter and record this flow.

7.3.1.2 Temperature adjustments—Set temperatures as follows:

a. Oven (chromatographic column), 50° C.

b. Dosing line, 140° C.

c. Injection block, 140° C.

d. Sample chamber, water temperature, 90° C±1.0° C.

7.3.1.3 Ignition of flame ionization detector—Ignite the detector according to the manufacturer's instructions.

7.3.1.4 Amplifier balance—Balance the amplifier according to the manufacturer's instructions.

7.3.2 Programming the chromatograph—Program the chromatograph as follows:

a. I—Dosing time—The normal setting is 2 seconds.

b. A—Analysis time—The normal setting is 8 minutes. Certain types of samples contain high boiling materials which can cause interference with the vinyl chloride peak on subsequent analyses. In these cases the analysis time must be adjusted to eliminate the interference. An automated backflush system can also be used to solve this problem.

c. B—Flushing—The normal setting is 0.2 minutes.

d. W—Stabilization time—The normal setting is 0.2 minutes.

e. X—Number of analyses per sample—The normal setting is 1.

7.3.3 Preparation of sample turntable—Before placing any sample into turntable, be certain that the center section of the aluminum cap has been removed. The numbered sample bottles should be placed in the corresponding numbered positions in the turntable. Insert samples in the following order:

Positions 1 & 2—Old 2000 ppm standards for conditioning. These are necessary only after the analyzer has not been used for 24 hours or longer.

Position 3—50 ppm standard, freshly prepared.

Position 4—500 ppm standard, freshly prepared.

Position 5—2000 ppm standard, freshly prepared.

Position 6—4000 ppm standard, freshly prepared.

Position 7—Sample No. 7 (This is the first sample of the day, but is given as 7 to be consistent with the turntable and the integrator printout.)

After all samples have been positioned, insert the second set of 50, 500, 2000, and 4000 ppm standards. Samples, including standards must be conditioned in the bath of 90° C for 1 hour (not to exceed 5 hours).

7.3.4 Start chromatograph program—When all samples, including standards, have been conditioned at 90° C for 1 hour, start the analysis program according to the manufacturers' instructions. These instructions must be carefully followed when starting and stopping program to prevent damage to the dosing assembly.

7.3.5 Determination of total solids (TS).

For wet cake, slurry, resin solution, and PVC latex samples, determine TS for each sample by accurately weighing approximately 3 to 4 grams of sample in an aluminum pan before and after placing in a draft oven (105 to 110° C). Samples must be dried to constant weight. After first weighing return the pan to the oven for a short period of time and then reweigh to verify complete dryness. TS is then calculated as the final sample weight divided by initial sample weight.

8. Calibration.

Calibration is to be performed each eight-hour period when the instrument is used. Each day, prior to running samples, the column should be conditioned by running two of the previous days 2000 ppm standards.

8.1 Preparation of Standards.

Calibration standards are prepared by filling the vials with the vinyl chloride/nitrogen standards, rapidly sealing the septum and sealing with the aluminum cap. Use a stainless steel line from the cylinder to the vial. Do not use rubber or tygon tubing. The sample line from the cylinder must be

purged (into hood) for several minutes prior to filling vials. After purging, reduce the flow rate to approximately 500-1000 cc/min. Place end of tubing into vial (near bottom) and after one minute slowly remove tubing. Place septum in vial as soon as possible to minimize mixing air with sample. After the standard vials are sealed, inject 100  $\mu$ l of distilled water.

### 3.2 Preparation of chromatograph calibration curve.

Prepare two 50 ppm, two 500 ppm, two 2000 ppm, and two 4000 ppm standard samples. Run the calibration samples in exactly the same manner as regular samples. Plot  $A_s$ , the integrator area counts for each standard sample vs  $C_e$ , the concentration of vinyl chloride in each standard sample. Draw a line of best fit through the points.

#### 9. Calculations.

##### 9.1 Response factor.

From the calibration curve described in Section 8.2, above, select the value of  $C_e$  that corresponds to  $A_s$  for each sample. Compute the response factor,  $R_f$ , for each sample, as follows:

$$R_f = \frac{A_s}{C_e} \quad \text{Equation 107-1}$$

##### 9.2 Residual vinyl chloride monomer concentration, or vinyl chloride monomer concentration.

Calculate  $C_{rvc}$  as follows:

$$C_{rvc} = \frac{A_s P_a}{R_f T_1} \left( \frac{M_r V_r}{m_t R} + K T_2 \right)$$

$$\text{Equation 107-2}$$

where:

$C_{rvc}$ =Concentration of vinyl chloride in the sample, in ppm.

$P_a$ =Laboratory atmosphere pressure, mm Hg.

$T_1$ =Room temperature, °K.

$M_r$ =Molecular weight of VCM (62.5).

$V_r$ =Volume of vapor phase (vial volume less sample volume).

$m_t$ =Weight of sample, grams.

$R$ =Gas constant (62,360).

$K$ =Henry's Law constant for VCM in PVC at 90°C,  $K=6.52 \times 10^{-4}=K_1$  for VCM in 1 cc (approximate) wastewater sample at 00°C,  $K=5.0 \times 10^{-4}=K_2$ .

$T_2$ =Equilibrium temperature, °K.

If the following conditions are met, Equation 107-2 can be simplified as follows:

1.  $T_1=22^{\circ}\text{C}$  ( $295^{\circ}\text{K}$ ).
2.  $T_2=90^{\circ}\text{C}$  ( $363^{\circ}\text{K}$ ).
3.  $P_a=750$  mm. Hg.

$$4. V_r = V_v - \frac{m_t}{1.4} = 21.5 - \frac{m_t}{1.4}$$

where

$V_v$ =Vial volume, cc (23.0).

5. Sample contains less than 0.5% water.

$$C_{rvc} = \frac{A_s}{R_f} \left( 4.107 \times 10^{-3} + \frac{5.988 \times 10^{-3}}{m_t} \right)$$

$$\text{Equation 107-3}$$

The following general equation can be used for any sample which contains VCM, PVC and/or water.

$$C_{rvc} = \frac{A_s P_a}{R_f T_1}$$

$$\times \left[ \frac{M_r V_r}{R m_t} + K_1 (T_2) T_2 + K_2 (1 - T_2) T_2 \right]$$

$$\text{Equation 107-4}$$

where:

$T_2$ =Total solids.

Note:  $K_2$  must be determined.

Results calculated using Equation 107-4 represent concentration based on the total sample. To obtain results based on dry PVC content, divide by TS.

For a 1 cc (approximate) wastewater sample, Equation 107-4 can be simplified to the following:

$$C_{rvc} = \frac{A_s}{R_f} \left[ \frac{5.988 \times 10^{-3}}{m_t} + (2.066 \times 10^{-3}) \right]$$

$$\text{Equation 107-5}$$

#### 10. References.

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