IV. ENVIRONMENTAL DATA

Sampling and Analytical Methods

Most of the sampling and analytical procedures for airborne vinyls in occupational environments have been developed and tested for vinyl chloride. While these procedures may provide some guidance for choosing sampling and analytical conditions for the other vinyl halides, caution must be exercised in extrapolating or interpolating from vinyl chloride to vinylidene chloride, vinyl bromide, vinyl fluoride, and vinylidene fluoride. Certain physical and chemical properties of the latter compounds are quite different from those of vinyl chloride at ambient temperatures and pressures (see Table XVII-1). The collection media used for sampling the various vinyls should be selected to permit reproducible air sampling, adequate collection efficiency, storage stability, retention, and minimum breakthrough of the specific compounds.

(a) Sampling

(1) Vinyl Chloride

Denenberg and Miller [234] reported on several types of sampling equipment that can be used for the collection of workplace samples of vinyl chloride. These included evacuated glass flasks, glass syringes, and evacuated bottles for the collection of grab samples, and inflatable sampling bags (Saran, Mylar, or Teflon) and charcoal tubes for the collection of integrated samples.

Murdoch and Hammond [235] used evacuated glass bottles to collect grab samples for the determination of vinyl chloride concentrations in polyvinyl chloride work areas. After the samples were collected, the bottles were sealed with silicone rubber septa. Aliquots were later removed by syringe for analysis by gas chromatography.

Williams et al [236] also reported using evacuated stainless-steel containers equipped with critical orifices for collecting grab or integrated samples of air that contained mixtures of vinyl chloride, vinylidene chloride, and other compounds under laboratory conditions. Identical results were obtained for samples collected in steel containers from a chamber and for samples taken directly from the chamber.

Stainless steel canisters and Tedlar bags have both been used for sampling for vinyl chloride. Losses of 0-10% vinyl chloride/day were reported for samples stored in Tedlar bags [10]. The losses were attributed either to leakage from the bags or to reactions of vinyl chloride with other air contaminants, such as nitrogen dioxide and ozone.

Levine et al [237] compared the storage stability of vinyl chloride collected in Teflon and aluminized Scotchpak gas sampling bags. The comparison showed the loss from Teflon bags to be about 20%/day, but it was not determined whether the loss resulted from the permeability of the Teflon, from chemical reaction, or from mechanical problems. No detectable loss occurred during a 1-week period from aluminized Scotchpak bags that contained samples of vinyl chloride at concentrations of 0.1-1.1 ppm (0.256-2.8 mg/cu m).

Ketterer [238] found Teflon bags to be satisfactory for holding samples that would be analyzed for vinyl chloride soon after collection but did not report the time between sample collection and analysis. The relative standard deviations for seven samples of vinyl chloride at a concentration of 25 ppm (64 mg/cu m) and for eight samples at a concentration of 52.2 ppm (133.6 mg/cu m) were 2.24 and 1.77%, respectively, and the reported accuracy at both concentrations was 95%. The author concluded that this degree of accuracy and reproducibility should be readily attainable in field use, since fluctuations in temperature and humidity and the presence of other volatile organic materials had little effect [238].

The major advantage of bag sampling is that it permits direct analysis of the sampled air, ie, without the adsorption and desorption steps required for collection on solid sorbents [239]. Its disadvantages include the bulky equipment required for personal sampling and the relatively high detection limit, approximately 50 ppb (0.13 mg/cu m) that results from the sample not being concentrated. Another disadvantage of bag sampling is that the sample volume is limited.

The most widely used sampling technique involves adsorption on solid sorbents such as Tenax-GC resin and activated charcoal. The major sampling problem in collecting vinyls on solid media is that vinyls have appreciable vapor pressures, which can result in sample migration or loss.

Tenax-GC resin was used by Ives [240] to concentrate grab samples of contaminated air. Average recoveries of 90% for vinyl chloride at 6 ppb (0.015 mg/cu m) and 100% at 60 ppb (0.15 mg/cu m) were reported when contaminated air in a 500-ml gas sampling tube was flushed with nitrogen through the Tenax-GC resin trap at a flowrate of 85 ml/minute for 35 minutes. The trap was cooled in dry ice. Ahlstrom et al [241] reported that Tenax-GC resin did not quantitatively adsorb vinyl chloride from the atmosphere, but they presented no data supporting this conclusion. Zado and Rasmuson [242] reported that the breakthrough volume for vinyl chloride on Tenax-GC resin was 170 ml at a flowrate of 50 ml/minute, but they did not specify the concentration sampled nor the dimensions of the resin bed. They stated that Tenax-GC resin had the next to the poorest breakthrough performance of 10 adsorbents tested.

Nelms et al [243] described a permeation sampling technique using a charcoal badge, 41 x 48 mm and 7 mm thick, pinned to the worker's clothing for

monitoring 8-hour exposures of vinyl chloride at concentrations of 5 ppb to 50 ppm (0.01-128 mg/cu m). Vinyl chloride passed through a permeable membrane and was adsorbed on activated charcoal. The vinyl chloride concentration was later determined by gas chromatography. The authors stated that temperature and humidity had no measurable effect on the determination of vinyl chloride. Of the compounds tested (including sulfur dioxide, nitrogen dioxide, and ozone) only ethylene chloride was reported to cause positive interference during analysis.

Hill et al [244] evaluated breakthrough volumes for vinyl chloride on 20 sorbents, 6 activated charcoals and 14 gas-chromatographic column packings, each contained in 1.5-cm sections of glass tubing with inner diameters of 4 mm. Breakthrough volume was defined as the air volume sampled when 5% of the synthetic atmospheric concentration of vinyl chloride was detected in the tube effluent. Vinyl chloride was measured using a portable gas chromatograph with a flame ionization detector. The results are shown in Table XVII-5. Breakthrough volume for Dow carbon XF 4175 L and MSA-6 coconut charcoal increased with decreasing flowrate, and the amount of vinyl chloride adsorbed increased with increasing concentrations of vinyl chloride in the air. The authors concluded that the MSA-6 coconut charcoal was suitable for collecting vinyl chloride at concentrations of about 1 ppm (2.56 mg/cu m) or lower, at flowrates of 50-100 ml/minute. High humidity or high concentrations of other organic contaminants could reduce the breakthrough volume, but this was not investigated [244]. The authors suggested that maximum sample volumes of 5 liters at a flowrate of 50 ml/minute would not result in significant breakthrough. These suggested values have been adopted for the NIOSH-accepted method [245].

Cuddeback . al [246] tested commercially available charcoal tubes from two manufacturers. By examining the packings of the front sections of the tubes, they determined that MSA tubes averaged 99.7 mg of charcoal (±6%) for three samples in 16.5 mm (±10.9%) tubes, and SKC tubes averaged 86.2 mg (±3.1%) for six samples in 15.9 mm (±7.8%) tubes. Breakthrough volumes, defined as those at which the effluent concentration of vinyl chloride was 10% of the inlet concentration, were measured using the front sections of the MSA tubes. As shown in Table XVII-6, there was no consistent correlation between breakthrough volume and sampling rate.

Several activated charcoals were evaluated for vinyl chloride collection and breakthrough by Severs and Skory [247]. They concluded that the Pittsburgh PCB had superior breakthrough characteristics for vinyl chloride sampling. Breakthrough volumes for commercial tubes with different packings were also compared. Tubes packed with 600 mg of SKC (Lot 105) charcoal or 700 mg of Pittsburgh PCB carbon had a breakthrough of less than 2% for vinyl chloride at 25 ppm (64 mg/cu m) at a flowrate of 1 liter/minute for 30 minutes. The same tubes packed with 150 mg of the SKC charcoal had breakthrough of 2% within 2 minutes for vinyl chloride at 1 ppm (2.56 mg/cu m) sampled at 1 liter/minute.

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(2) Vinylidene Chloride

Severs and Skory [247] used charcoal tubes for collecting vinylidene chloride in workplace samples. No data on collection efficiency or storage stability were reported. Tubes packed with 600 mg of SKC charcoal had "good" retention capacity for vinylidene chloride. At 31 ppm (123 mg/cu m) of vinylidene chloride, samples collected at a flowrate of 1 liter/minute had a breakthrough below 0.08% after 75 minutes. Russell [248] reported that the breakthrough volume of vinylidene chloride on Carbosieve B was greater than 10 liters of air.

(3) Vinyl Bromide

Russell [248] collected vinyl bromide on Porapak N porous polymer in a 4-inch by 0.19-inch inner diameter stainless steel sampling tube. The breakthrough volume was 1 liter at a sampling flowrate of 100 ml/minute of air that was nearly saturated with water and that contained 1-5 ppm (4.38-21.9 mg/cu m) of vinyl bromide. Bales [249] used a charcoal tube to collect vinyl bromide in a production facility. No data on breakthrough volume, collection efficiency, or storage stability were reported.

(4) Vinyl Fluoride

Bales [250] used Teflon bags for collecting air samples to be analyzed for vinyl fluoride. DW Yeager (written communication, August 1977) stated that there was no measurable leakage of vinyl fluoride from Teflon bags in a 4-day period; however, within 2 weeks a 50% loss had occurred. Only a limited number of samples were analyzed for this study.

(5) Vinylidene Fluoride

Pennwalt Corporation [251] recommended that charcoal tubes be used to collect vinylidene fluoride. No data regarding efficiency and stability were reported.

NIOSH recommends using the sampling methods as outlined in Appendices II-V. Charcoal tubes are recommended for sampling vinyl chloride in the NIOSH-accepted method (Appendix II) and for sampling vinylidene chloride in the NIOSH-proposed method (Appendix III). There are no validated methods for vinyl bromide, vinyl fluoride, or vinylidene fluoride; however, NIOSH recommends that charcoal tubes be used for vinyl bromide (Appendix IV) and vinylidene fluoride (Appendix VI). Teflon air bags, as used by Bales [250], are recommended for sampling vinyl fluoride in the proposed method (Appendix V).

(b) Analysis

The available methods for determination of vinyls in the workplace include gas-chromatographic and infrared techniques, among others, but vinyl chloride

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has most often been analyzed by gas chromatography. This method has the advantages of being more specific and less expensive than infrared analysis.

(1) Gas Chromatography

Analysis by gas chromatography generally involves direct injection of a portion of the air sample taken from a sampling bag or canister or injection of an aliquot of sample desorbed from a suitable adsorption material through which ambient air has been drawn. Ives [240] used both procedures in series to sample and analyze for vinyl chloride. Grab samples in a 500-ml gas sampling tube were flushed with nitrogen through a Tenax-GC cold trap. Vinyl chloride was subsequently thermally desorbed directly onto a gas chromatographic column. Severs and Skory [247], on the other hand, thermally desorbed vinyl chloride from charcoal into a gas sampling bag. While the injection of contaminated air obtained from a bag or canister is straightforward, samples from activated carbon or gas-chromatographic packings must be desorbed before analysis.

(A) Desorption

Desorption from sampling tubes is accomplished thermally or by solvent extraction. A variety of operating conditions for these two techniques have been investigated.

Three variations of thermal desorption have been applied to vinyl chloride. The first variation involved heating charcoal in a flow of prepurified nitrogen and collecting the vinyl chloride containing effluent in a bag [247]. Heating the charcoal to 430 C eliminated low and erratic recoveries. The nitrogen flow was maintained at 500-800 ml/minute.

In the second variation [239,241,248], activated charcoal or gas-chromatographic packing was heated, and the vinyl chloride-laden effluent was flushed directly onto the analytical column with carrier gas. Purcell [239] maintained the desorption chamber at 260-300 C and the column at 25 C for 4 minutes during desorption. After desorption, the column temperature was raised to 70 C, and the vinyl chloride was eluted. When this technique was used to analyze the front section (100 mg) of the charcoal tube, an overall recovery of 90% was determined for a 278-ml sample spiked with vinyl chloride at 1 ppm (2.56 mg/cu m). Good reproducibility was demonstrated by obtaining a relative standard deviation of 4.1% in the analysis of 11 sampling tubes, each containing a 278-ml sample spiked with vinyl chloride at 1 ppm.

Ahlstrom et al [241] also thermally desorbed vinyl chloride directly onto a gas-chromatographic column. The sample, collected on 150 mg of petroleum-derived charcoal (SKC Lot 104) packed in a 5- x 3/16-inch U-shaped stainless steel tube, was desorbed by pulse heating the tube for 2 minutes at 400 C. The desorbed vinyl chloride was swept by the helium carrier gas onto the column, which was maintained at 90 C. The carrier gas flow was 20 ml/minute. Recovery of a 45-ppm vinyl chloride synthetic atmosphere sampled at 50

ml/minute for 1, 2, and 3 minutes averaged 99 ±2%. For four runs of a 1-ppm vinyl chloride standard, the relative standard deviation was 1.2%.

Russell [248] thermally desorbed vinyl bromide from Porapak N and vinyl chloride and vinylidene chloride from Carbosieve B adsorbents. In each case, the recovery was 100 ±3%. Samples were collected at a flowrate of 100 ml/minute, but specific concentrations and sample volumes were not reported. Desorption from Porapak N was performed by heating for 5 minutes at 200 C, and desorption from Carbosieve B was accomplished by heating for 5 minutes at 270 C. The adsorbent column was maintained at 60 C for desorption from Porapak N and at 80 C for desorption from Carbosieve B.

The third thermal desorption variation [240,252] is similar to that of Ahlstrom et al [241]. It differs from that of Russell [248] in that the sample is injected into the analytical column only after desorption is complete, rather than being continuously flushed into the column during desorption while elutriation is retarded by a relatively low column temperature.

Ives [240] used Tenax-GC sorbent cooled to dry ice temperature to concentrate air bag samples, with thermal desorption directly onto the chromatography column. Ives heated the Tenax for 5 minutes at 150-180 C before flushing it with carrier gas through the gas-chromatographic column. Recovery was 100% for a 579-ml sample spiked with vinyl chloride at 60 ppb and 90% for a similar sample spiked with vinyl chloride at 6 ppb.

Myers et al [252] collected vinyl chloride on activated charcoal (GC grade, 60/80 mesh, Coast Engineering Laboratory) packed in glass columns 6.5 cm long and 5-mm outside diameter. For desorption, the tubes were heated for 30 seconds at 300 C. The analytical column, 6-feet x 1/8-inch Chromosorb 101, was maintained at 100 C. Replicate analysis of 13 samples of a standard atmosphere containing vinyl chloride at approximately 1 ppm indicated an average of 1.25 ±0.037 ppm (3.2 ±0.09 mg/cu m). The authors concluded that vinyl chloride could be detected at 100 ppb (0.256 mg/cu m), in a 1-liter sample and at 20 ppb (0.05 mg/cu m) in a 5-liter sample. They speculated that 1 ppb (0.003 mg/cu m) could be detected by increasing the instrument's operating sensitivity.

The advantages of the thermal technique for desorption of vinyl chloride, according to Zado and Fastuson [242], are that it is simple to handle, free of interferences, and highly sensitive. The authors noted that its disadvantages include the requirement of expensive equipment and the inability to make repeated injections of the sample. They suggested using the less expensive Porapak N instead of Carbosieve B. However, the disadvantage of Porapak N is its low breakthrough volume of 976 ml, compared with greater than 2,000 ml for Carbosieve B, at a flowrate of 50 ml/minute.

For solvent desorption of vinyl chloride and other vinyls, carbon disulfide has generally been used. However, tetrahydrofluran and a bromine-hexane mixture have also been used.

Hill et al [244] reported using a 2-ml vial containing 0.5 or 1.0 ml of carbon disulfide for desorption of vinyl chloride from the front section of a charcoal tube (100 mg of charcoal). The 13-μg samples were analyzed after desorption periods of 10-30 minutes at ambient temperature. The authors found that desorption efficiencies were generally in the 80-90% range. Hill et al also determined that the addition of the charcoal to the carbon disulfide enabled more precise analyses at ambient temperatures than if the solvent were added to the charcoal. They concluded that solvent temperature and volume had little effect on precision, although only one set of tests was performed at other than ambient temperature (0 C). Studies of the stability of vinyl chloride samples by the same authors [244] demonstrated that vinyl chloride was stable on charcoal for periods of over 2 weeks, but that migration from the front to the back section occurred when the tubes were stored at ambient temperatures. Cooling to -20 C retarded this effect. The authors suggested using two tubes in series as the front and backup sections to obviate the need for storage at low temperatures.

Severs and Skory [247] studied a desorption technique by which 1 g of PCB 12/30 charcoal was added slowly to 10 ml of carbon disulfide, the mixture was cooled in a dry ice/acetone slurry and agitated for 30 minutes. Samples were stored under refrigeration and held in a wet ice bath while they were analyzed. An average recovery of 98% (93-101%) was reported. When the same procedure was applied to the desorption of vinylidene chloride, recovery ranged from 95 to 100%. In neither case was sample loading specified.

Lao et al [253] added 15 ml of carbon disulfide, cooled to -15 C, to 1-g aliquots of 20/50 carbon in a 25-ml flask fitted with mini-inert valves. The system was allowed to equilibrate for 15 minutes at 15 C before samples were withdrawn for analysis. Recovery was 88% for 2.7 ng of vinyl chloride, 95% for 14.1 ng, 98% for 54 ng, and 97% for 126 ng. The concentration of vinyl chloride in the headspace of the flasks never exceeded 2% of its concentration in the liquid.

Still another desorption technique was used by Cuddeback et al [254]. The charcoal (100 mg) was placed in a 2-ml glass vial, which was sealed with a silicone rubber septum. The vial was cooled to dry ice temperature, and 0.5 ml of carbon disulfide at room temperature was injected through the septum. When bubbling produced by the mixing ceased, the vial was removed from the dry ice and allowed to stand at room temperature for 5 minutes before samples were withdrawn for analysis. Recoveries from a 2.55-μg sample were 85% for immediate analysis, 83% after 7 days, and 71% after 14 days. For a 31.9-μg sample, respective recoveries for these intervals were 89, 79, and 81%.

Hoffmann et al [255] used a mixture of 0.5 ml of bromine and 11 ml of n-hexane, cooled to -30 C in a Reacti-flask, to desorb vinyl chloride from 1 g

of charcoal. After the charcoal was added, the flask was sealed and covered with dark paper, and the contents were stirred magnetically for 7 minutes. During this procedure, vinyl chloride is converted to 1,2-dibromo-1-chloroethane, which has a much greater sensitivity to electron-capture detection than vinyl chloride. For samples enriched by column chromatography and determined by gas chromatography using an electron-capture detector, the authors reported a recovery of at least 85%.

Desorption of vinyl chloride with tetrahydrofuran was reported in an Environmental Protection Agency (EPA) publication [10]. Recovery was 88%, and there was less diffusion into the headspace than was evident with carbon disulfide desorption; however, the solvent volume and the desorption conditions were not reported.

Ethyl Corporation [14] reported that a carbon disulfide-pentane mixture was used to desorb vinyl bromide from about 14 g of Pittsburgh 20x50 activated carbon.

No data were located on the desorbing agent for vinyl fluoride and vinylidene fluoride samples.

(B) Chromatographic Columns

The choice of column materials and operating parameters for analysis of vinyls will depend on the interfering compounds that may be present and their relative retention times. For vinyl chloride analysis, potential interferences include light hydrocarbons, other halocarbons, Freons, and sulfur dioxide [240,247,256,257]. Contaminants often found during analyses for vinyl chloride include acetylene, methyl chloride, 1,3-butadiene, and vinylidene chloride [253]. Table XVII-7 shows the retention times relative to vinyl chloride for a number of interfering compounds on various column materials. Foris and Lehman [258] listed the Kovats retention indices for four vinyl halides on Poropak Q.

Severs and Skory [247] separated vinyl chloride and vinylidene chloride on a 20-foot x 1/8-inch stainless steel column containing Carbowax 4,000 on 80/100-mesh Supelcoport and with a 6-foot x 1/8-inch column of 20% DC 200 on 80/100-mesh Chromosorb W.

For vinylidene chloride separation, the NIOSH-proposed method [259] recommends that a silanized glass column (10-foot x 1/4-inch outer diameter) packed with 100/120-mesh Durapak OPN be used. The Manufacturing Chemists' Association (MCA) reported use of a stainless-steel column (10 feet x 1/8 inch) packed with 100/120-mesh Durapak OPN chemically bonded to Porasil C [260].

Rein et al [261] reported using a 50-foot x 1/4-inch column packed with 33.5% DC-200 oil on 30/60-mesh Chromosorb P to analyze for vinyl fluoride and vinylidene fluoride at about 30 C. The packed column was conditioned for 8-12

hours in the instrument under operating conditions. The authors noted that the column was excellent for separating compounds with low boiling points at ambient temperatures. The retention times for vinyl fluoride and vinylidene fluoride were 16.4 and 12.4 minutes, respectively. Rein et al [261] also reported analyzing for vinyl fluoride and vinylidene fluoride on combined 6-foot and 12-foot columns packed with 33.5% DC-200 oil on 30/60-mesh Chromosorb P, but they found that resolution of any low-boiling fractions that were present was poor at ambient temperatures.

The Ethyl Corporation [14] has analyzed for vinyl bromide using a 25-foot x 1/8-inch stainless steel column packed with 30% SE-52 on 80/100-mesh Gas Chrom Q conditioned for 16 hours at 200 C; Lao et al [253] have used a 6-foot x 1/8-inch column of Chromosorb 102, similarly conditioned. The Ethyl Corporation report [14] noted that isopentane interfered with the determination of vinyl bromide on an SE-52 column, and suggested that a combined column of 12 feet of SE-52 and 6 feet of 10% Carbowax 20M gave a good separation of vinyl bromide from isopentane. The SE-52 on Gas Chrom Q column was used to determine vinyl bromide at concentrations of less than 1 ppm.

(C) Chromatographic Detectors

Detection methods used in gas chromatography to quantitate vinyls, particularly vinyl chloride, include electron capture [10,255], microcoulometry and electroconductivity [256], chemiluminescence [262], mass spectroscopy [257,263], and flame-ionization [238,239,242,247,253,264]. Table XVII-8 shows the specificity and approximate detection limit of each of these detectors for vinyl chloride.

Electron-capture detectors belong to the general class of direct-current ion chambers. Nitrogen or argon is used as the carrier gas, and 3H or 63Ni is used as the radioactive source to excite the gas. As compounds are eluted from the gas chromatographic column, they become ionized by the excited carrier gas and produce an increased current flow across parallel electrodes. The current flow is proportional to the amount of compound present. Electron-capture detection is more selective than flame-ionization detection, but it is less reliable and has a smaller dynamic range [10]. A further disadvantage of electron-capture detection with respect to vinyl chloride analysis is that response to aromatic halides and polychlorinated hydrocarbons is relatively low [264]. Hoffmann et al [255] have extended the electron-capture detection limit for vinyl chloride by brominating vinyl chloride to produce 1,2-dibromo-1-chloroethane. The detection limit for this compound was 15 pg/injection, and the response was linear between 50 and 300 pg [255].

Microcoulometric detection is highly sensitive and accurate for chloride ions [10]. As chlorinated hydrocarbons are eluted from the gas chromatograph column, they are pyrolyzed to form hydrogen chloride gas. The hydrogen chloride causes silver chloride to precipitate, and to disturb the electrical balance at the positive silver electrode. The coulometer regenerates silver ions until the electrical balance is restored, and the current generated to

restore the balance is proportional to the number of chloride ions generated. Ernst and Van Lierop [256] used a Hall detector (microcoulometer) for the analysis of vinyl chloride; the vinyl chloride was pyrolyzed in a quartz tube in the presence of hydrogen and the hydrogen chloride formed was detected as a function of the increased conductivity of an aqueous reservoir. A detection limit of 0.07 ng, slightly better than the flame-ionization detection limit, has been reported [264]. The major advantage of microcoulometry is its sensitivity to organohalides [264]. Its disadvantage is its electrical power requirements, which make the detector impractical for field use [10].

Chemiluminescence detection of vinyl chloride has been used by McClenny et al [262]. This method is based on light emission from the products of the gas phase reaction of vinyl chloride with ozone. The authors determined the lower detection limit to be 50 ppb (0.13 mg/cu m), and response was linear from 50 ppb to 10 ppm (0.13-25.6 mg/cu m).

Mass spectroscopy specific ion monitoring is a highly sensitive and selective detection method, but it is relatively expensive to install. According to Rosen et al [257], it offers a detection limit for vinyl chloride of 8.7 pg/10 ml injection. Detection depends on the response of the instrument to the vinyl chloride molecular ion (m/e 62) and the 37Cl ion (m/e 64) [257,263]. For qualitative confirmation of vinyl chloride, the ratio of the m/e 62 and m/e 64 peaks should be about 3:1, conforming to the natural abundance ratio of 35Cl and 37Cl [253,257].

The flame-ionization detector is perhaps the most commonly used instrument for the analysis of vinyls. This detector responds to most organic compounds and is insensitive to almost all inorganic compounds [10]. It has a wide linear range covering several orders of magnitude, and it can detect vinyls in the ppb range. According to reports of the NIOSH-accepted method for the analysis of vinyl chloride [245], and the MCA method for vinylidene chloride [260], a sample of 0.2 ng/injection of vinyl chloride and vinylidene chloride, respectively, can be detected by flame-ionization. However, the conditions under which the MCA method was tested were not specified. For vinylidene chloride analysis, the NIOSH-proposed method [259] reports that a sample loading of 7 µg (about 35 ng/injection) had a desorption efficiency of greater than 80%. Detector response is generally a function of the number of carbon atoms in a molecule of a compound, although a reduced response or no response may occur when the carbon atom is attached to atoms other than hydrogen, such as chlorine, oxygen, or sulfur. A lower detection limit of 0.01 ppm (0.03 mg/cu m) for vinyl chloride in a 10-ml sample of air has been reported for the flame-ionization detector [10]. The major disadvantage of the flame-ionization detector is its relatively nonselective response [264].

(2) Infrared and Other Analytical Methods

According to a personal communication by Keenan cited in an EPA publication [10], the analysis for vinyl chloride by infrared spectrophotometry has one major problem: several substances that are present

in ambient air act as interferences, and thus the method is not specific for vinyl chloride. The EPA report [10] noted that vinyl chloride is detectable at an absorption frequency of 941 or 917 1/cm. The authors pointed out that these major problems could be circumvented by additional instrumentation, but they cautioned that the cost would be high. Effective optical paths of 20 meters are required in order for infrared analyzers to achieve a detection limit of 1 ppm (2.56 mg/cu m).

Other methods that have been used to determine vinyl chloride concentrations include colorimetry and polarography [10]. The sensitivities of the colorimetric methods are very much affected by such interferences as ethylene and methanol, and the sensitivity of the polarographic method is affected by any other volatile materials that may be present.

Gronsberg [265] used a photometric method to determine concentrations of vinylidene chloride in air. His method is based on the reaction of vinylidene chloride with pyridine and on subsequent condensation of the reaction products with aniline or barbituric acid. After the reaction, a polymethine dye complex is formed. The method has a sensitivity of 2 μg/photometric cuvette volume and is capable of determining vinylidene chloride in air at concentrations of 10 mg/cu m (2.5 ppm). The author reported that vinyl chloride, acrylonitrile, dichloroethane, and hydrogen chloride had no effect on the analysis for vinylidene chloride but noted that trichloroethylene and 1,1,2-trichloroethane produced analogous reactions.

Color-specific detector tubes are available for the determination of vinyl chloride or vinylidene chloride in the work environment. Two types of color reactions, one using chromate and bromophenol blue, and the other using permanganate and o-tolidine, were used for analyzing for vinyl chloride [266]. Their ranges of linearity were 0.5-3 ppm (1.28-7.68 mg/cu m) and 1-50 ppm (2.55-128 mg/cu m), respectively. Vinylidene chloride can be determined with twice the sensitivity with which vinyl chloride can be determined. No detector tubes for vinyl bromide, vinyl fluoride, or vinylidene fluoride are known to be available.

Murdoch and Hammond [235] reported using detector tubes to determine concentrations of vinyl chloride in polyvinyl resin production environments. Vinyl chloride was determined at concentrations of 0-3 ppm (0-7.68 mg/cu m). The tubes had a lower detection limit of 0.5 ppm (1.28 mg/cu m).

Detector tubes have the advantages of being simple and inexpensive, and do not require that samples be transported for analysis. Their major disadvantages are their susceptibility to interferences and lack of sensitivity.

(3) Continuous Monitors

Continuous monitoring systems can be used to warn employees of overexposure to vinyl chloride at high concentrations, permit reduction of

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emissions by locating sources of leaks, and produce permanent records for areas where employees have been exposed to vinyl chloride.

Continuous systems with multiple sampling points have been reported to be effective for monitoring concentrations of vinyls in work area atmospheres [239,267-270]. The air samples were analyzed by infrared spectrometry or gas chromatography. Other continuous-analysis methods that have been used for vinyl chloride include impregnated paper tape [234,271], Stark spectroscopy with a carbon monoxide or carbon dioxide laser [272], and an ultraviolet (UV) conductivity system [273].

Portable infrared analyzers with 20- to 25-meter folded-path absorption cells have been used to detect vinyl chloride at a working lower detection limit of about 1 ppm (2.56 mg/cu m) [267,274]. Also, portable gas chromatographs with flame-ionization or electron-capture detectors have been used for "continuous" monitoring for vinyl chloride, and a sensitivity of 0.1 ppm has been reported for such systems [10]. Purcell [239] found lower detection limits for vinyl chloride of 50 ppb with gas-liquid chromatography and 1 ppm with infrared spectrometry.

Baker and Reiter [275] described an automatic monitoring system, based on a gas chromatograph equipped with a flame-ionization detector and an alarm device that has been used for the determination of vinyl chloride in workplace atmospheres. Each analyzer in the system could monitor 20 sample points, and each analysis required 2 minutes from collection to readout. An analytic range of 0.1-25 ppm (0.256-64 mg/cu m) was reported. The compounds found to interfere with the analysis of vinyl chloride included methyl chloride, isobutylene, n-butyl acrylate, and toluene, and the interference from the last two compounds occurred after approximately 40 minutes. The authors concluded that the monitoring system had the advantages of being very sensitive, very accurate, and relatively maintenance free.

Denenberg et al [234,271] reported the use of impregnated paper tape for monitoring vinyl chloride. With this method the intensity of light reflected from the tape surface is theoretically proportional to the concentration of analyte. The double bond in the vinyl chloride molecule is broken by means of an oxidant converter, releasing free chlorine. The chlorine reacts to darken the paper tape. A lower detection limit of between 0.05 and 0.1 ppm (0.13 and 0.256 mg/cu m) is claimed, and performance and sensitivity are unaffected over ranges of 0-100% relative humidity and 0-40 C [234]. Trichloroethylene, which produces a response three times as great as vinyl chloride, will interfere, and vinylidene chloride, with a double bond and two chlorine atoms, will produce twice as great a response as vinyl chloride [271].

Stark spectroscopy was used by Freund and Sweger [272] for the measurement of vinyl chloride concentrations. Carbon monoxide and carbon dioxide lasers were investigated and the extracavity absorption cell contained two 40-cm stainless steel Stark electrodes spaced 1 mm apart. The method is capable of detecting vinyl chloride at 1 ppm (2.56 mg/cu m).

A UV method for measuring vinyl chloride in air has been developed by Confer [273], in which vinyl chloride exposed to UV light decomposes to produce chlorine, hydrogen chloride, phosgene, and other products, and the concentrations of the decomposition materials are measured by changes in conductivity of deionized water. A 6-inch UV lamp with an output of 2.5 watts, 90% of which is at a wavelength of 253.7 nm, was positioned in a 600-ml gas washing flask directly upstream from the sensor of a conductivity analyzer. Air was passed over the lamp at 2 liters/minute, and the deionized-water absorber was set at a flowrate of 6 ml/minute. Degradation efficiency was 80%, and, with a 2.5-minute holdup time in the conductivity cell, response reached 90% of the final reading. A lower detection limit of 0.05 ppm (0.13 mg/cu m) was found. Response was linear for concentrations up to 25 ppm (64 mg/cu m). Interferences by sulfur dioxide, chlorine, and hydrogen sulfide can be removed by scrubbing in a 100-ml gas-washing bottle equipped with a fritted bubbler and containing 20 ml of deionized water. Interferences by nitric oxide, carbon disulfide, and trichloroethylene, however, are not removed by this scrubbing method.

(4) Recommendations

The analytical methods described in detail in Appendices II-VI offer the necessary quantitative sensitivity and precision. Their accuracy, technical requirements, and cost requirements are easily within the range of most analytical laboratories.

For the analysis of vinyl chloride and vinylidene chloride, NIOSH recommends desorption of samples with carbon disulfide and analysis by gas chromatography with flame-ionization detection. A stainless steel column (20 feet x 1/8 inch) packed with 10% SE 30 on 80/100-mesh Chromosorb W is recommended for vinyl chloride [245]. For analysis of vinylidene chloride, a silanized glass column (10 feet x 1/4 inch) packed with Durapak OPN (oxypropionitrile) chemically bonded to 100/120-mesh Porasil C is recommended [259].

There are no NIOSH-validated methods for the sampling and analysis of vinyl bromide, vinyl fluoride, or vinylidene fluoride. However, NIOSH recommends that samples of vinyl bromide and vinylidene fluoride, collected on charcoal tubes, be desorbed with carbon disulfide and that samples of vinyl fluoride, collected in Teflon bags, be injected directly into the chromatograph. For analysis of these compounds, gas chromatography with flame-ionization detection is recommended. The column recommended for vinyl bromide analysis is an SE-30 (20-ft) column, the column recommended for vinyl fluoride is also a 20-foot, SE-30 column (DW Yeager, written communication, February 1978), and the recommended column for vinylidene fluoride is a stainless steel (6 feet x 1/8 inch) column packed with 80/100-mesh Chromosorb 102 (JL Sadenwasser, written communication, March 1978). However, other columns with high separation efficiencies can also be used. All work with the desorbing agent should be performed in an exhaust hood because of the high toxicity of carbon disulfide.

NIOSH also recommends that a continuous monitoring system with alarm-indicator devices be installed to monitor area concentrations of vinyl chloride or vinylidene chloride in accordance with 29 CFR 1910.1017(g)(6)ii. Continuous monitors should be installed to monitor vinyl bromide, vinyl fluoride, or vinylidene fluoride as soon as systems sensitive enough become available. The system ideally should be highly sensitive and specific to the vinyl halides sampled and free of interferences.

Environmental Levels

In 1975, Barnhart et al [276] reported the results of NIOSH industrial hygiene surveys of vinyl chloride monomer producers and polyvinyl chloride processers. Three vinyl chloride manufacturing plants and seven polyvinyl chloride processing plants were included in the study. Workplace air samples were collected on charcoal tubes and analyzed by gas chromatograph after desorption with carbon disulfide. The survey found concentrations in the range of 0.1-9.20 ppm (0.256-23.55 mg/cu m) in the monomer plants and 0.01-0.85 ppm (0.03-2.18 mg/cu m) in the polyvinyl chloride processing plants. The authors concluded from these data that polyvinyl chloride processors were rarely exposed to vinyl chloride at concentrations greater than 0.5 ppm (1.28 mg/cu m), which was the Federal action level at that time. Monomer production workers, on the other hand, had a greater risk of vinyl chloride exposure. Polyvinyl chloride producers were not included in this study.

Results of other vinyl chloride monitoring surveys have also been reported [277-280] and the data are presented in Tables IV-1 and IV-2.

Baretta et al [269] monitored the concentrations of vinyl chloride in a vinyl chloride polymerization plant, apparently before and during 1967, continuously with an infrared spectrometer. Five sampling probes were placed in the work area for each of four job classifications, and mean vinyl chloride concentrations were calculated weekly. Mean area concentrations for the coagulator operator, dryer operator, blender-packager, and polymer operator declined steadily during the 7 months of the study. The authors attributed the decline to undescribed "actions undertaken to reduce the atmospheric concentration" of vinyl chloride. Weekly average vinyl chloride concentrations decreased from 205 to 40 ppm (524.8 to 102.4 mg/cu m) for coagulator operators and from 90 to 20 ppm (230 to 51 mg/cu m) for dryer operators. Blender-packagers and polymer operators were consistently exposed at concentrations below the target concentration of 50 ppm (128 mg/cu m) used in the plant at that time.

Kramer and Mutchler [76], in 1972, reported 8-hour TWA concentrations for vinyl chloride of from 0 to 300 ppm (0 to 768 mg/cu m) in a vinyl chloride polymerization plant. They stated that the mean TWA concentration was 155 ppm (396.8 mg/cu m) in 1950 and 30 ppm (76.8 mg/cu m) in 1965. Concentrations were estimated on the basis of area sampling data.

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TABLE IV-1

SUMMARY-VINYL CHLORIDE MONITORING

Operation	Year	Mean Concentration	Concentration Range	Reference
Ethyl Corporation				
Vinyl chloride unit (monthly averages–October to April)	1973	2.7 ppm (6.9 mg/cu m)	– –	279
	1973	2.3 ppm (5.9 mg/cu m)	– –	279
	1973	1.6 ppm (4.1 mg/cu m)	– –	279
	1974	1.7 ppm (4.4 mg/cu m)	– –	279
	1974	1.6 ppm (4.1 mg/cu m)	– –	279
	1974	1.4 ppm (3.6 mg/cu m)	– –	279
	1974	1.3 ppm (3.3 mg/cu m)	– –	279
Dow Chemical USA				
Loading area (TWA concentrations)	1975	0.5 ppm (1.28 mg/cu m)	0.1 – 6.2 ppm (0.256– 15.87 mg/cu m)	280
	1976	0.3 ppm (0.77 mg/cu m)	0.1 – 0.6 ppm (0.256– 1.54 mg/cu m)	280
Production unit (TWA concentrations) 378 samples	1975	0.3 ppm (0.77 mg/cu m)	0.1 –173 ppm (0.256–443 mg/cu m)	280
304 samples	1976	0.3 ppm (0.77 mg/cu m)	0.1 – 29 ppm (0.256– 74.24 mg/cu m)	280

TABLE IV-1 (CONTINUED)

SUMMARY-VINYL CHLORIDE MONITORING

Operation	Year	Mean Concentration		Concentration Range		Reference
Reactor operator (TWA concentrations)						
No. 1	1976-1977	0.8	ppm	-		280
		(2.0	mg/cu m)	-		
No. 2	1976-1977	0.2	ppm	-		280
		(0.5	mg/cu m)	-		
First operators	1976-1977	0.3	ppm	nd - 1.2	ppm	280
		(0.77	mg/cu m)	(nd - 3.1	mg/cu m)	
Utility operators	1976-1977	0.3	ppm	0.1 - 0.5	ppm	280
		(0.77	mg/cu m)	(0.256- 1.28	mg/cu m)	
Union Carbide Corp						
Solvent Process Area						
Personal samples	1974	-		0.6 - 8.1	ppm	277
		-		(1.5 - 20.7	mg/cu m)	
Area samples	1974	-		0.7 - 6.8	ppm	277
				(1.8 - 17.4	mg/cu m)	
Dynel Process Area						
Personal samples	1974	-		0.2 - 2.7	ppm	277
		-		(0.5 - 6.9	mg/cu m)	
Area samples Control room	1974	1.4 (3.58	ppm mg/cu m)	- -		277
Dispersion Process Area						
Personal samples	1974	-		3.0 - 43.7	ppm	277
		-		(7.68 -111.87	mg/cu m)	
Area samples Control room	1974	-		1.2 - 11.7 (3.1 - 30.0	ppm mg/cu m)	277

TABLE IV-2

SUMMARY–VINYL CHLORIDE MONITORING

Operation	Mean Concentration	Standard Deviation	Concentration Range
B.F. Goodrich Chemical Company 1974			
Mass Polymerization Process Area			
Office	1.0 ppm (2.56 mg/cu m)	1.4 ppm (3.6 mg/cu m)	nd– 3.8 ppm (nd– 9.7 mg/cu m)
Lead technician	4.4 ppm (11.2 mg/cu m)	7.0 ppm (17.9 mg/cu m)	nd– 22.6 ppm (nd– 57.8 mg/cu m)
Operating technician	3.6 ppm (9.2 mg/cu m)	3.9 ppm (10.0 mg/cu m)	nd– 13.7 ppm (nd– 35.0 mg/cu m)
Serviceman	6.4 ppm (16.4 mg/cu m)	12.9 ppm (33.0 mg/cu m)	nd– 71.4 ppm (nd–182.78 mg/cu m)
Bagger	nd	– –	– –
Suspension Resin Process Area			
Office	14.5 ppm (37.1 mg/cu m)	25.3 ppm (64.8 mg/cu m)	nd– 96.5 ppm (nd–247.0 mg/cu m)
Pearl technician	27.7 ppm (70.9 mg/cu m)	60.7 ppm (155.4 mg/cu m)	nd–245.0 ppm (nd–627.0 mg/cu m)
Paste technician	28.2 ppm (72.2 mg/cu m)	41.1 ppm (105.2 mg/cu m)	1.6–158.8 ppm (4.1–406.5 mg/cu m)
Rover technician	11.9 ppm (30.5 mg/cu m)	12.6 ppm (32.3 mg/cu m)	nd– 46.7 ppm (nd–119.6 mg/cu m)

TABLE IV-2 (CONTINUED)

SUMMARY-VINYL CHLORIDE MONITORING

Operation	Mean Concentration	Standard Deviation	Concentration Range
Suspension Resin Process Area			
Utility man	3.2 ppm (21.0 mg/cu m)	8.7 ppm (22.3 mg/cu m)	nd- 23.6 ppm (nd- 60.4 mg/cu m)
Bagger	0.2 ppm (0.5 mg/cu m)	0.4 ppm (1.0 mg/cu m)	nd- 0.9 ppm (nd- 2.30 mg/cu m)

Adapted from Jones [278]

Cook et al [75], in 1971, reported that concentrations of airborne vinyl chloride inside a reactor during scraping operations tended to be below 100 ppm (256 mg/cu m) and were usually about 50 ppm (128 mg/cu m). These estimates were developed from information supplied by a "small number" of unspecified plants, and the dates of the analyses were not reported.

In 1975, Ott et al [86] summarized 8-hour TWA concentrations of vinyl chloride measured by area sampling techniques from 1950 to 1966 in a polymerization facility. From 1950 to 1959, TWA concentrations ranged from 5 to 825 ppm (12.8 to 2,112 mg/cu m) with excursions to 4,000 ppm (10,240 mg/cu m). Large variations in the TWA concentrations were reported for different job classifications, and even within a single job classification, eg, dry end packer, 5-10 ppm (12.8-25.6 mg/cu m) and coagulator, 135-825 ppm (345.6-2112 mg/cu m). From 1960 to 1966, TWA concentrations ranged from 5 to 240 ppm with excursions to 500 ppm. The TWA concentration for the dry end packer during this period was listed as 5 ppm and that for the coagulator was 30-240 ppm (76.8-614 mg/cu m).

Ott et al [73], in 1976, also estimated TWA concentrations of vinylidene chloride from data gathered by area monitoring in production and polymerization facilities from 1956 through 1965. Estimated concentrations ranged from 5 to 70 ppm (19.85-277.9 mg/cu m) with excursions to 1,900 ppm (7,543 mg/cu m).

Dow Chemical USA [280] has provided NIOSH with vinylidene chloride monitoring data. These data are summarized in Table IV-3.

Bales [250], in 1977, provided NIOSH with the results of two industrial hygiene surveys conducted at a vinyl fluoride polymerization and monomer production plant. Samples were collected in 7.7-liter Teflon bags and were analyzed for vinyl fluoride by gas chromatography. TWA concentrations of vinyl fluoride ranged from 1 to 5 ppm (1.88 to 9.4 mg/cu m) for 11 samples collected from employees' breathing zones. Both personal and area samples collected in the monomer plant showed that concentrations of vinyl fluoride were less than 2 ppm (3.76 mg/cu m) for all but one (21 ppm or 39.5 mg/cu m) sample taken at the start of the operation.

Bales [249] also reported results from an industrial hygiene survey in a vinyl bromide monomer plant. The data are shown in Table IV-4.

Engineering Controls

Engineering controls should be used to eliminate the potential for exposure to vinyl halides in the workplace and to prevent fire and explosion. These goals can be achieved with properly constructed and maintained closed-system operations and appropriate safety precautions.

Closed-system operations provide the best means for eliminating employee exposures to vinyl halides. Closed-system operations are effective only when the integrity of the system is maintained by frequent inspection and by prompt repair of any leaks that are found. Closed-system operations should be performed under negative pressure.

Where closed systems cannot be adequately designed and effectively used, local exhaust ventilation systems should be provided to direct vapors and gases away from employees and to prevent the recirculation of contaminated exhaust air. Contaminated air should be directed to an incinerator equipped with scrubbers to remove any toxic combustion products. Exhaust ventilation systems for quality control laboratories or laboratory hoods where samples are prepared for analysis should be equipped with sorbers. Guidance for designing a local exhaust ventilation system can be found in Recommended Industrial Ventilation Guidelines [281], Industrial Ventilation--A Manual of Recommended Practice [282], or more recent revisions, and in Fundamentals Governing the Design and Operation of Local Exhaust Systems, ANSI Z9.2-1971 [283]. Ventilation systems of this type require regular inspection and maintenance for effective operation. These inspections should include face-velocity measurements of the collecting hood or duct, inspection of the air mover and collector, and measurements of vinyl concentrations in workroom air. Continuous airflow indicators, such as oil or water manometers, are recommended and should be properly mounted on collection hoods, ductwork, or laboratory hoods and marked to indicate the appropriate airflow.

TABLE IV-3

SUMMARY-VINYLIDENE CHLORIDE MONITORING

Operation	Year	Mean TWA Concentration	Mean TWA Concentration Range
Area samples Louisiana Division			
Loading area 6 samples	1975	0.4 ppm (1.59 mg/cu m)	0.1- 1.7 ppm (0.4- 6.75 mg/cu m)
7 samples	1976	0.6 ppm (2.38 mg/cu m)	0.1- 2.2 ppm (0.4- 3.7 mg/cu m)
Production unit			
30 samples	1974	1.5 ppm (5.96 mg/cu m)	0.1- 4.2 ppm (0.4-16.7 mg/cu m)
69 samples	1976	1.9 ppm (7.5 mg/cu m)	0.2- 9.5 ppm (0.8-33.7 mg/cu m)
Texas Division			
311 samples	1975	0.4 ppm (1.59 mg/cu m)	0.1- 9.5 ppm (0.4-37.7 mg/cu m)
600 samples	1976	0.5 ppm (1.99 mg/cu m)	0.1-10.0 ppm (0.4-31.7 mg/cu m)
Personal samples Reactor operators			
No. 1	1976-1977	0.2 ppm (0.8 mg/cu m)	– –
No. 2	1976-1977	0.2 ppm (0.8 mg/cu m)	– –
First operators (5)	1976-1977	6.7 ppm (26.6 mg/cu m)	–
Utility operators (4)	1976-1977	1.7 ppm (6.75 mg/cu m)	–

Adapted from reference 280

TABLE IV-4

SUMMARY-VINYL BROMIDE SURVEY

Operation	Year	Median TWA Concentration	TWA Concentration Range
Operators	1977	0.27 ppm (1.2 mg/cu m)	0.1 -0.43 ppm (0.44-1.88 mg/cu m)
Loading crewman	1977	1.2 ppm (5.3 mg/cu m)	- -
Lab technician	1977	0.4 ppm (1.8 mg/cu m)	0.29-0.51 ppm (1.27-2.23 mg/cu m)
Loading crewman (Observed during 61-min loading operation)	1977	6.3 ppm (27.6 mg/cu m)	- -

Adapted from Bales [249]

Although it may be unnecessary to ventilate monomer production equipment, since it is usually located outdoors, proper ventilation must be provided for the building from which the process is controlled [276]. The control building should be maintained under positive pressure, and its air intake should be positioned so as to provide clean fresh air.

The procedures developed for vinyl chloride as discussed in the following paragraphs can also be used to control exposure to the other vinyl compounds.

Vinyl chloride monomer is manufactured in closed systems. The maintenance of the integrity of such systems is dependent on careful inspection of seals, especially at joints, valves, and pumps. Generally, where seals are closely inspected and maintained, escape of vinyl chloride can be prevented during monomer production. Several reports, however, have mentioned processes, periods, or areas of potential exposure [279,280,284,285]. These include quality control sampling points [284], tank car loading [286], tank car gauging [285], storage and transfer systems [286], distillation areas [280], and leaks from other equipment [297,284]. These potential sources of exposure in monomer production should be avoided by the use of alternative methods of

tank car gauging [284] (slip-tube gauging has been a source of exposure and should be controlled and monitored [285]), by the use of purge gas in loading and storage operations, prior to maintenance entry, and in quality-control sample collection [284], by the careful collection and purification of purge gas, by the use of closed-loop systems for tank car loading and quality control sampling [276], and by the use of properly maintained laboratory hoods for quality control laboratory procedures.

Most of the cases of angiosarcoma of the liver found in vinyl chloride workers have occurred among employees of vinyl chloride polymerization plants. Controls are needed to reduce worker exposure to vinyl chloride during the opening and cleaning of reaction vessels, at discharge points from relief valves and piping joints, while monomer is being stripped from the polymer, and while tank cars are being loaded or unloaded. A reduction in the frequency of manual cleaning of reactor vessels is absolutely necessary. The crust on the vessel can contain up to 3-5% monomer, and 30-50% of this may be liberated during cleaning [287]. Automatic high-pressure water, steam, or organic solvent vessel-cleaning systems can reduce the frequency of worker entry into reactor vessels [286,288,289]. Organic solvents are also toxic to varying degrees, however, and their use should therefore be carefully controlled. A proposed proprietary system for lining reacto essels is claimed to eliminate resin buildup on the reactor vessel surfaces [286].

Because vinyl chloride polymerization reactions do not go to completion, polyvinyl chloride resins should be stripped of unreacted monomer. Stripping vessels, slurry tanks, centrifuges, and dryers must be enclosed and exhaust-ventilated [286].

If amount of residual monomers in polymers is reduced, the exposure of fabricating workers to vinyl chloride will be substantially reduced. The quantity of residual monomer that is released from a resin depends on the process temperature, the surface area of the resin, and the quantity of unreacted monomer in the resin [290]. Manufacturers should control their process to reduce these factors to the greatest extent consistent with the demands of the process. Fabricators should know the residual monomer content of the polyvinyl chloride resins that they use. Methods are available, eg, aspiration and air stripping [291], for reducing the residual monomer content of resins early in the fabricating cycle, preferably during the compounding and dry-blending stages. Oberg [292] found vinyl chloride concentrations of 0.04-1.5 ppm during laboratory blending operations.

Unless adequate ventilation is provided, the escape of residual vinyl chloride from bagged or boxed resin can result in buildup of the vinyl chloride concentration in warehouses and storerooms [293]. According to Oberg [292], vinyl chloride concentrations of 0.8-1.5 ppm have been found in storage areas. A manufacturer of vinylidene chloride reported that a latex containing 2,000 ppm of unreacted vinylidene chloride released 1,000 ppm of vinylidene chloride in 1 week of storage [294]. High storage or processing temperatures

may also accelerate the release of unreacted monomer. Oberg found ranges of vinyl chloride concentrations of 1.5-2.2 ppm at 46-68 C and 60-120 ppm at 71-110 C.

In vinyl production areas, employers should install automatic, multipoint continuous monitoring systems with alarm devices sensitive to airborne vinyls at the recommended exposure limits. Baker and Reiter [275] reported on a highly sensitive automatic monitoring system using a gas chromatograph equipped with a flame-ionization detector and an alarm device that activated when either the vinyl chloride concentration exceeded a preselected level, the check sample analysis was out of range, or the sample flow was insufficient. The system required 2 minutes for an analysis, and each analyzer could monitor up to 20 locations. Areas in which high vinyl concentrations are detected should immediately be monitored for gas leaks with a portable organic vapor analyzer. Also, entry into such areas should be limited to authorized personnel with proper protective clothing and equipment. As soon as a leak is located, properly equipped maintenance personnel familiar with emergency procedures should try to repair it.

Efforts should be made to minimize the extent to which vinyl vapors mix with air in confined or regulated areas and to prevent vapors from being exposed to any ignition source. A flexible hose ventilation unit and recovery system which can be moved to the source of the leakage should be available to control leaks which are not readily repaired.

Unloading vinyls from railroad tank cars is especially hazardous while lines and hoses are being coupled and uncoupled. Vinyl chloride vapor and vapor from other vinyl halides also remain in tank cars after the liquid is removed. If compressors and pumps are used to remove the vapor, care should be taken to avoid leaks from this equipment. It has been suggested that tank cars be emptied down to only the vinyl chloride vapor pressure, which eliminates the need to purge the car and reduces the use of pumps and compressors [286].

Storage and process areas where vinyl halides are stored as liquids should be diked to prevent the uncontrolled spread of any spilled material. The diked areas should be designed with drainage systems to carry spilled material into holding ponds or other areas where the product can be recovered or disposed of in a safe manner.

The flammability of some of these compounds mandates careful design and operation of all spark- or heat-producing equipment in vinyl halide work areas. Electric systems and motors must be spark- and explosion-proof. Sump pumps in diked areas must also be explosion-proof.

Achievement and maintenance of reduced concentrations of airborne vinyls in the workplace are dependent on the implementation of the engineering control recommendations. According to an unpublished report [295] submitted

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to NIOSH, the available data suggest that a combination of many control measures is required to keep vinyl chloride concentrations at or below the current Federal occupational limit of 1 ppm (2.56 mg/cu m). Since the promulgation of the vinyl chloride standard in 1974, many different types of control techniques have been employed in work areas, and employee vinyl chlorides to vinyl chloride have been greatly reduced. Table IV-5 shows the apparent reductions in vinyl chloride concentrations that have been achieved in typical vinyl chloride polymerization plants, especially during 1974-1975, when most of the controls were installed [295].

TABLE IV-5

8-HOUR TWA EXPOSURE OF WORKERS TO VINYL CHLORIDE, 1974-1977

Process-Year	Average Distribution of Vinyl Chloride Concentrations			
	<1	1-5	>5	ppm
PVC Mass Polymerization No. 1				
1974	2%	52%	46%	
1975	43%	45%	12%	
1976	73%	20%	7%	
PVC Mass Polymerization No. 2				
1974-1975	0%	45%	55%	
1977	80%	20%	0%	
PVC Suspension Polymerization				
1975	17%	66%	17%	
1976	83%	17%	0%	
PVC Dispersion Polymerization				
1975	50%	50%	0%	
1976	67%	33%	0%	
PVC Dispersion and Suspension Polymerization				
1974	0%	38%	62%	
1975	42%	44%	14%	
1976	55%	36%	9%	
1977(first half)	65%	30%	5%	

Adapted from reference 295