IV. ENVIRONMENTAL DATA AND ENGINEERING CONTROLS

Hydrazines are generally handled and used in enclosed systems; thus, the concentrations of hydrazines present in workroom air should be very low. Higher concentrations may be expected during the transfer of the hydrazines from one container to another, when the containers are open, or during an accidental spill, since vapors or aerosols of these hydrazines may escape into the air. However, insufficient information has been found on the concentrations of hydrazines in workroom air to reach any conclusions on typical worker exposures. Many analytical methods have been developed, but most were not designed for air monitoring. Some methods were developed for this purpose, but few reports were found concerning their application to actual monitoring. The available methods will be reviewed, and appropriate sampling and analytical methods will be recommended. Engineering control techniques will also be discussed.

Air Sampling

Air sampling techniques used for collecting gases or vapors can be used to collect hydrazine bases in air. These techniques include absorption in a liquid medium and adsorption on a solid sorbent. Generally, the latter is favored because a solid is easier to handle than a liquid. However, other factors, such as collection efficiency, stability, and subsequent analysis, should also be considered in the selection of a sampling method. A reactive medium should be used so that only a 10- to 20-ml volume of a liquid medium or a few hundred milligrams of a solid

sorbent can collect the hydrazines at concentrations several times the recommended exposure limits. The collection efficiency for either medium should also be independent of the concentrations of the hydrazines. For solid sorbents, a solvent capable of desorbing the collected hydrazines with a constant efficiency should be available.

Because of their alkalinity, the hydrazine bases have been collected in midget bubblers containing an acid medium such as dilute sulfuric or hydrochloric acid [154,155]. At a flowrate of 1 liter/minute, the collection efficiency was nearly 100% in 10-15 ml of hydrochloric acid for known concentrations of up to 3.44, 0.78, 2.22, and 44.8 mg/cu m of hydrazine, methylhydrazine, 1,1-dimethylhydrazine, and phenylhydrazine, respectively [155]. In these studies, the collected samples were also found to be stable for at least 5 days. No report has been found on the collection efficiency of hydrazines in sulfuric acid. Pinkerton et al [156] used 20 ml of a buffered solution containing citric acid and disodium acid phosphate to collect 1,1-dimethylhydrazine at 1 liter/minute and found a collection efficiency of 91.6% for amounts up to 0.24 mg.

Hydrazines have been collected on a sulfuric acid-coated silica gel sorbent for subsequent gas-chromatographic analysis [157-160]. At a flowrate of 1 liter/minute, 400 mg of sulfuric acid-coated silica gel equally divided in two sections in a glass tube was found to collect 32 mg of 1,1-dimethylhydrazine, which was considered to be less reactive than hydrazine, methylhydrazine, or phenylhydrazine [157]. Sorption efficiency was independent of vapor concentration and humidity.

Only a few reports were found on the application of the above-mentioned methods in actual air sampling; therefore, the results of

laboratory studies are used as the basis for a recommended method for sampling. Since the concentrations of hydrazines to be expected in workroom air are much lower than the concentrations tested for hydrochloric acid or silica gel media, either one can be used to collect airborne hydrazines. Other collection media are not recommended because of their lower efficiency or the lack of information on their performance. At a flowrate of 0.2-1.0 liter/minute with 200 mg of sulfuric acid-coated silica gel packed in a 6-mm internal diameter, 8-cm long glass tube, virtually 100% of the hydrazines that pass through the sorbent will be collected. At 0.2 liter/minute, the pressure drop across sampling tubes is 6 mmHg; at 1 liter/minute, it is 33 mmHg [159]. Thus, at 0.2 liter/minute, sampling can be continued for a full workshift, but at 1 liter/minute, sampling should last no more than 2 hours. Sorbent tubes are convenient to use, but the sorbent and the tube used for sampling may need to be prepared by the person responsible for measurement pending commercial availability. Details of the recommended method of sampling and preparation of silica gel tubes are given in Appendix I [161]. Salts of hydrazines would be present in air as aerosols. A particulate collecting filter, such as a glass-fiber filter, should be used for their collection. How efficient the sampling method in Appendix I is when both vapor and particulate forms of the hydrazines are present is not known. A modification involving a filter and a silica gel adsorber should be efficient for the collection of both, but the ability of the pump to cope with the greater resistance to flow needs checking. Also, combining of two samples for analysis or the separate analyses of two samples probably involves more error than collection of a single sample for analysis.

Chemical Analysis

In considering an analytical method, the sensitivity of the method is an important factor. Since there are instances when hydrazine, methylhydrazine, and 1,1-dimethylhydrazine are used simultaneously, the analytical method also should be either specific for individual hydrazines or capable of measuring all with equal sensitivity. Titration with acids and oxidants and reaction with color-forming reagents have been used to analyze hydrazines. Generally, these methods do not distinguish different hydrazines, although some methods are very sensitive. More specific techniques, such as gas-chromatographic or other separation methods, have to be used to analyze mixtures of hydrazines. Many analytical methods have been developed and tested under controlled conditions, but only a few reports are available on the actual analysis of workroom air samples for the hydrazines. Again, laboratory studies provide the basis for recommendations.

Kolthoff [162], in a 1924 report, found that the rate of reaction of iodine with hydrazine sulfate in a buffered solution decreased with increasing hydrogen ion concentration, which made the titration end point difficult to determine. When sodium bicarbonate was used as a buffer, 100% accuracy was reported for a sample containing 162.5 mg of hydrazine sulfate. Titration of hydrazine sulfate with iodate, bromate, or permanganate was also examined by Kolthoff, who found that accurate results were obtained when 81-163 mg of hydrazine sulfate were tested using a sufficient amount of hydrochloric acid. The permanganate titration had to be carried out with a boiling sample solution.

Feinsilver et al [154], in 1959, reported on the iodate and bromate methods to determine the concentration of salts of hydrazine, methylhydrazine, 1,1-dimethylhydrazine, or 1,2-dimethylhydrazine in aqueous solution. The acidified solution of hydrazines was titrated with potassium iodate to a visual end point or with potassium bromate to a potentiometric end point. The iodate method was tested to analyze samples containing 14 mg or more of each of the four hydrazines, and recoveries of at least 96% were found. Potassium iodate titration has been used to determine exposure chamber concentrations of 0.1-5 ppm for methylhydrazine [93,95] and 5-140 ppm for 1,1-dimethylhydrazine [110]. The potassium bromate method was tested to detect 3 mg of each of the four compounds, and recoveries were at least 92.5% for all except 1,1-dimethylhydrazine, for which the results were not reproducible. No detection limits for these titration methods were reported.

Manometric methods, which measure the amount of nitrogen evolved from the oxidation of hydrazine, have also been used to determine the concentrations of several hydrazine compounds in aqueous solution [163]. Nitrogen was released almost instantaneously when hydrazine and methylhydrazine were reacted with iodate. The reaction of iodate with 1,2-dimethylhydrazine required 15 minutes, but the reaction with phenylhydrazine required almost 5 hours. Of the 1.28 and 1.84 mg of hydrazine and methylhydrazine tested in samples, respectively, almost 100% was recovered. However, only 88% of 5.1 mg of phenylhydrazine in a sample could be detected after 5 hours of reaction. A recovery of 93% of 2.4 mg of 1,2-dimethylhydrazine in a sample was determined. This procedure was rather cumbersome, and the sensitivity was not optimal.

Several colorimetric methods have also been developed and widely used. In one method [154], phosphomolybdic acid added to the sample was reduced by the hydrazines, including 1,2-dimethylhydrazine, to form a molybdenum blue complex, whose color intensity could then be measured. NIOSH has validated this method for methylhydrazine over a range of 0.169-0.78 mg/cu m for a 15-minute sample at a flowrate of 1.5 liters/minute, 1,1-dimethylhydrazine at 0.566-2.22 mg/cu m for a 100-liter air sample, and phenylhydrazine at 10.37-44.8 mg/cu m also for a 100-liter air sample, the last two collected at 1 liter/minute [155]. Because the absorbance of these three compounds was measured at the same wavelength, this method was not specific. For methylhydrazine and 1,1-dimethylhydrazine, there may be positive interference from agents such as stannous ion, ferrous ion, zinc, sulfur dioxide, and hydrogen sulfide. Oxidizing agents such as halogens and oxygen will cause negative interferences. Because phenylhydrazones may form in an acid medium, aldehydes and ketones in air may interfere with the analysis of phenylhydrazine.

Another colorimetric method has been used to determine the concentration of hydrazine or methylhydrazine in aqueous solutions [164-168] and to determine hydrazine concentrations in test air samples [155,169]. This method was based on the formation of a yellow-orange complex in acid solution following the reaction of hydrazine or methylhydrazine with para-dimethylaminobenzaldehyde. Peak absorbance was measured at 460-480 nm for methylhydrazine [164,165] and 460 nm [166] or 480-490 nm for hydrazine [164,167]. Since the absorbance bands for hydrazine and methylhydrazine overlap, this method cannot be used to distinguish the two compounds. McKennis and Witkin [169] tested this

method with a prepared air sample containing hydrazine at a concentration of 4-5 mg/cu m. In other studies, 0.5-0.75 μg of hydrazine [164,168] or 1.5 μg of methylhydrazine [164] in a sample was detected. NIOSH has validated this method over a range of 0.589-3.44 mg/cu m for a 100-liter air sample [155].

In addition to the molybdenum blue and the potassium iodate methods, 1,1-dimethylhydrazine concentrations in air, water, or biologic samples were also measured colorimetrically with trisodium pentacyanoamino ferrate as a reagent. The reaction produced a red complex that could be measured with a spectrophotometer at 480 nm [170] or 500 nm [156]. Pinkerton et al [156] tested this method at a concentration of 6 mg/cu m. Nitrogen dioxide was found to inhibit the colored-complex formation, while hydrazine had no effect on it.

Continuous monitoring methods have been developed to evaluate the exposure of rocket fuel workers and to determine the concentrations in animal exposure chambers. Buck and Eldridge [171] developed a continuous coulometric titration method for determining 1,1-dimethylhydrazine concentrations in the air in the vicinity of rocket launching areas. Air samples were drawn though the inner chamber of a four-electrode potentiostat titration cell. The electrolyte used was potassium bromide buffered to pH 8. Bromine was evolved in the outer chamber of the titration cell when 1,1-dimethylhydrazine was introduced. Production continued until the reaction was complete and a null point was again attained. At a flowrate of 835 ml/minute, a current of 42 microamperes for 0.2 mg/cu m was reported, as compared to a background noise level of ±3

microamperes. No interference from nitrogen dioxide, unsaturated hydrocarbons, or acid gases was found.

Geiger and Vernot [172] used the reaction of iodine with methylhydrazine to continuously determine methylhydrazine concentrations in an exposure chamber. Air was drawn through a reaction cell, where iodine reacted with methylhydrazine stoichiometrically in a buffered potassium iodate solution, and the absorbance of iodine was monitored by a colorimeter. At a flowrate of 200 ml/minute, the collection efficiency was virtually 100% at a concentration of 300 ppm (560 mg/cu m). However, the response time was 10 minutes.

In 1976, Saunders and Larkins [18] described a direct-reading instrumental method that used paper tapes impregnated with phosphomolybdic acid to detect hydrazine. The stain developed on exposure to hydrazine gave a photomultiplier reading proportional to the hydrazine concentration. An instrument based on this principle and marketed in the United States reportedly has a lower limit of detection for hydrazine of 50 ppb with a response time of 2-3 minutes. The detection limit for methylhydrazine or other hydrazines was not described. Although the method appears to be rather sensitive, the specificity is poor, since phosphomolybdic acid will respond to all the hydrazines and some other nitrogen compounds.

Saunders and Larkins [18] also reported on two sensitive methods for continuous monitoring of hydrazine and methylhydrazine concentrations in air. The hydrazine compound was catalytically converted to nitric oxide and measured at very low concentrations by a chemiluminescent method. The method was able to detect 10 ppb of nitric oxide, the equivalent of 5 ppb of hydrazine. However, nitric oxide and nitrogen dioxide, frequently found

in the air at concentrations of 50-100 ppb, were interferences. Therefore, this method is not suitable in an industrial hygiene survey for measuring hydrazines in the ppb range. The second method also involved conversion of hydrazine compounds to nitric oxide, but the detection of nitric oxide was based on electrochemical oxidation-reduction. An instrument was available to measure 10 ppb of nitric oxide, which was equal to 5 ppb of hydrazine or methylhydrazine. Since nitric oxide and nitrogen dioxide concentrations in the air could be determined separately from the hydrazines with this instrument, the interferences were eliminated. This method cannot differentiate between hydrazine compounds, and the instrument used is not commercially available.

Direct-reading detector tubes have also been used to detect hydrazines in air. Glass tubes, packed with an acid-base indicating solid, changed color when a measured and controlled flow of air containing hydrazine was passed through the packing. The length of the color zone was proportional to the concentration for a given sample volume, and a detection range of 0.25-3 ppm for hydrazine, 1,1-dimethylhydrazine, and methylhydrazine tubes was reported [173,174]. Since the tubes react to bases, any other substance with the same property, such as hydrazine derivatives, ammonia, or amines, would cause interferences. Although detector tubes are widely used for on-the-spot checking [28], they lack specificity and have low sensitivity, so they are not recommended for measuring the concentrations of hydrazines in air for the purpose of compliance.

Since some rocket fuels contain more than one of the hydrazines, methods are needed to analyze the composition of a mixture.

Salicylaldehyde has been used as a reagent to determine the concentration of hydrazine and 1,1-dimethylhydrazine in a mixture [175-177], because it reacts with hydrazine to form a neutral crystalline azine and with 1,1-dimethylhydrazine to form a basic hydrazone. Malone [175] used perchloric acid titration to determine the total amount of the two hydrazines in the mixture; hydrazine was then precipitated from solution as salicylaldazine, and the 1,1-dimethylhydrazine in solution was determined. The maximum absolute error for either component of the mixture was 0.36%. The titration end point of this method was rather ill defined, and Burns and Lawler [176] used potentiometric or spectrophotometric titration to reduce human error. The potentiometric method was preferred because it was relatively simple and gave more reproducible results, although there was no decrease in average error. Bailey and Medwick [177] used ultraviolet spectral absorbance to determine the amount of the compounds produced from the reaction of salicylaldehyde and the hydrazine/1,1-dimethylhydrazine mixture. Although absorption spectra overlapped, simultaneous equations could be used to calculate individual absorbance. Tests with a single compound had shown that the method was sensitive to hydrazine at a concentration of 0.3 μg/ml and to 1,1-dimethylhydrazine at 0.25 μg/ml. A test mixture containing 0.2109-0.5454 g of hydrazine and 0.7292-0.2421 g of 1,1-dimethylhydrazine was separated and showed a standard deviation of 0.8% in the recovery of hydrazine and 1.6% for 1,1-dimethylhydrazine. The applicable limits of detection for other separation methods were not reported.

Previous studies [175,176] have shown that the reaction of salicylaldehyde and methylhydrazine did not produce a stable hydrazone that

could be titrated with perchloric acid. Serencha et al [178] found that, with excess perchloric acid, the hydrazone formed from methylhydrazine was hydrolyzed back to salicylaldehyde and methylhydrazine. With hydrazine precipitated out as salicylaldazine, the hydrolyzed methylhydrazone could be titrated; thus, a mixture of the hydrazine and methylhydrazine was separated. Clark and Smith [179] used Chloramine-T solution and sodium hypochlorite to separate hydrazine and methylhydrazine in mixtures based on different rates of oxidation of methylhydrazine.

1,1-Dimethylhydrazine can be analyzed in the presence of methylhydrazine by using the differential acetylation of the two compounds [180]. In an acetic acid medium, methylhydrazine and acetic anhydride reacted immediately to form a neutral compound, while the reaction between 1,1-dimethylhydrazine and acetic anhydride was slow, forming a basic compound. 1,1-Dimethylhydrazine was determined by perchloric acid titration after neutralization of methylhydrazine. Hydrazine has the same acetylation property as methylhydrazine; therefore, a mixture of hydrazine and 1,1-dimethylhydrazine could be similarly analyzed.

These separation methods can only be used in a binary mixture; in mixtures containing three or more hydrazines, gas-chromatographic methods can be used. A chromatographic column containing Celite C22 as the support phase and Carbowax 400 as the stationary phase has been used to separate a mixture of hydrazine, methylhydrazine, and 1,1-dimethylhydrazine [181,182]. The peak in the chromatogram of each component was well defined, separated by at least a 5-minute retention time difference. With a thermal conductivity cell, detection limits of 8, 12, and 2 μg of hydrazine, methylhydrazine, and 1,1-dimethylhydrazine, respectively, in a sample were

reported. Dee [183] used the quantitative formation of each hydrazine to its corresponding substituted pyrazole by reaction with 2,4-pentanedione to enhance the sensitivity of separation of hydrazine and methylhydrazine by gas chromatography. With a dual flame ionization detector, a range of 0.5-250 ng of either hydrazine or methylhydrazine in a sample was tested. No interference from 1,1-dimethylhydrazine, urea, aluminum, iron, copper, or alanine was found. The sensitivity of this method was very high, but the method was designed to analyze aqueous solutions.

Liu et al [184] described a chromatographic method for determining hydrazine concentrations in cigarette smoke. Hydrazine was trapped with pentafluorobenzaldehyde. The resulting stable derivative was detected chromatographically with an electron capture detector. A limit of 0.1 ng of hydrazine in a sample was reported.

Wood and Anderson [157-159] studied the sampling and analysis of hydrazine compounds in air to monitor work environments. Test air samples were collected in a sulfuric acid-coated silica gel sorbent. The hydrazinium hydrogen sulfates were desorbed from the silica gel with water. The resulting solution was neutralized with sodium acetate and reacted with 2-furaldehyde to form 2-furaldazine or the methylhydrazone, dimethylhydrazone, or phenylhydrazone from hydrazine, methylhydrazine, 1,1-dimethylhydrazine, or phenylhydrazine, respectively. These derivatives were extracted into ethyl acetate and determined by gas chromatography, using flame ionization detection. Single peaks of hydrazine, methylhydrazine, and 1,1-dimethylhydrazine and double peaks of phenylhydrazine were obtained in the chromatogram. This method was very sensitive, detecting as little as 2 ng/injection for hydrazine and 35

ng/injection for methylhydrazine. In a 15-minute, 15-liter air sample, the limits of sensitivity correspond to concentrations of 0.0065 mg/cu m (0.005 ppm) of hydrazine, 0.14 mg/cu m (0.08 ppm) of methylhydrazine, 0.06 mg/cu m (0.03 ppm) of 1,1-dimethylhydrazine, and 0.022 mg/cu m (0.005 ppm) of phenylhydrazine. However, the reaction time of methylhydrazine with 2-furaldehyde needs to be carefully controlled to prevent the formation of a secondary product that cannot be eluted from the gas-chromatographic column. The desorption efficiency for methylhydrazine was 75%, while it was close to 100% for the other hydrazines. However, it has been found (V Carter, written communication, November 1977) that 100% recovery for hydrazine and 1,1-dimethylhydrazine at low concentrations was difficult to achieve. This same investigator has also found that hydrazine adsorbed on an acidified silica gel sorbent was stable for only 24 hours. 1,1-Dimethylhydrazine was stable for 5 days [157].

Of the analytical methods reviewed, the gas-chromatographic method described by Wood and Anderson [157-159] has the best sensitivity and specificity for hydrazine, methylhydrazine, 1,1-dimethylhydrazine, and phenylhydrazine. Therefore, this method is recommended for analyzing concentrations of these four hydrazines in workroom air. The lowest amounts of hydrazines in a sample that can be detected with an analytical precision of about 15% relative standard deviation were 4 μg for hydrazine, 9 μg for methylhydrazine, 15 μg for 1,1-dimethylhydrazine, and 66 μg for phenylhydrazine [159]. Since short-term sampling is preferable for carcinogens, a flowrate of 1 liter/minute is recommended. For a 2-hour sample collected at this flowrate, a concentration of 0.04 mg/cu m (0.03 ppm) for hydrazine, 0.08 mg/cu m (0.04 ppm) for methylhydrazine, 0.15 mg/cu m (0.06

ppm) for 1,1-dimethylhydrazine, and 0.6 mg/cu m (0.14 ppm) for phenylhydrazine can be accurately determined. Details of the recommended method for sampling and analysis are given in Appendix I [161].

The colorimetric para-dimethylaminobenzaldehyde method for hydrazine and the molybdenum blue method for methylhydrazine, 1,1-dimethylhydrazine, and phenylhydrazine are at least as sensitive as the recommended gas-chromatographic method, although they are not specific. When no interfering substances are present, these colorimetric methods can be considered as a reasonable alternative. The method described by Dee [183] might also be an acceptable alternative, especially for methylhydrazine. However, air sampling was not performed, and the applicability of this method [183] for samples collected from air needs to be established before it can be recommended.

There is insufficient information to recommend a sampling and analytical method for 1,2-dimethylhydrazine for compliance purposes. The method recommended in Appendix I is not applicable, since the complex with 2-furaldehyde would not form. The titration method of Feinsilver et al [154] lacks adequate sensitivity to measure a concentration that could afford protection to workers. The colorimetric method of NIOSH using phosphomolybdic acid [155] should be applicable to 1,2-dimethylhydrazine, since it is essentially the same as that tested by Feinsilver et al [154]. However, no limit of sensitivity is available for 1,2-dimethylhydrazine. para-Dimethylaminobenzaldehyde is probably not a suitable reagent for colorimetric determination of 1,2-dimethylhydrazine, since it was not adequate as a spray reagent for thin-layer chromatography [185].

Gas chromatography using a technique different from that recommended for other hydrazines has been tested for 1,2-dimethylhydrazine (E Sowinski, written communication, November 1977). In this method, a 19-foot x 1/8-inch stainless steel column containing 10% Carbowax 20 M and 2% Igepal CO-880 and a nitrogen detector were used. A peak was observed at the 0.1-μg level in 13.5 minutes when the temperature was programmed from 70-170 C at 4 C/minute with a helium flow of 20 ml/minute. Acetone, methanol, and tetrahydrofuran were suitable solvents. The applicability of this method to the analysis of air samples and the range of detection would have to be established before it can be recommended as an appropriate analytical method. Therefore, no sampling and analytical methods for 1,2-dimethylhydrazine are recommended at this time.

Environmental Levels

From July 1972 to June 1977, the Occupational Safety and Health Administration [186] conducted three investigations of workplaces in which air samples were collected to determine concentrations of hydrazines. Measurements of phenylhydrazine were taken in a paint shop and a produce warehouse, and samples for hydrazine were taken in a chemical company. No place inspected was found to be in violation of the Federal standards, which were 1.3 mg/cu m for hydrazine and 22 mg/cu m for phenylhydrazine.

The US Army Environmental Hygiene Agency [187] conducted two surveys to evaluate worker exposure to hydrazine and 1,1-dimethylhydrazine at the Rocky Mountain Arsenal hydrazine facility in October 1976 and January 1977. The gas-chromatographic method as described by Wood and Anderson [157-159] was used to determine concentrations of hydrazine and 1,1-dimethylhydrazine

during various phases of drum filling and tank car loading operations. Depending on the location of sampling sites, phase of operation, and wind direction, the concentration determined from area monitoring varied over a wide range. During the first survey, 32 samples were analyzed for hydrazine and 12 samples had no detectable concentration. The lowest detected concentration reported was 0.002 ppm, and the highest, 0.64 ppm, was found in a metering house for tank car loading during the cleaning of filters on feedlines. Of the 52 samples analyzed for 1,1-dimethylhydrazine, 13 had no detectable concentration. The lowest reported concentration was 0.0004 ppm, and the highest concentration, 1.66 ppm, occurred 3 feet away from the loading station during drum filling operations. There were some leaks in the transfer pumps during this survey; when the leaks were repaired and air samples retaken in January 1977, the concentrations at the same locations were generally lower than those determined before. The highest concentrations found were 0.39 ppm for hydrazine 7 feet from the loading station during the drum filling operation, and 0.35 ppm for 1,1-dimethylhydrazine 60 feet from a blend metering house during an equipment maintenance operation. All personnel performing the drumming and loading operations were required to wear respirators, and personal air samples were collected both outside and inside the masks during various operations. Although rather high concentrations were found outside the mask, 0.22-1.98 ppm for hydrazine and 0.14-4.61 ppm for 1,1-dimethylhydrazine in both surveys, the concentrations of these two compounds inside the mask were usually not detectable or less than 0.001 ppm. On one occasion, 0.03 ppm of 1,1-dimethylhydrazine was detected inside a mask during a drumming operation. This reading was

considered to be caused by a leak in the face seal of the mask. It was concluded that both hydrazine and 1,1-dimethylhydrazine were present around the hydrazine facility, but adequate protection to the workers was afforded by the use of respirators. The report [187] also indicated that nitrosodimethylamine was present in the ambient air near 1,1-dimethylhydrazine storage and tank car unloading areas, although the concentrations were not determined because of the lack of a suitable method.

Engineering Controls

Engineering design for controlling exposure to the hydrazines and their salts should accomplish the purpose of maintaining concentrations in workroom air at or below the recommended environmental limits and of minimizing skin and eye contact.

In manufacturing and formulating plants, laboratories, and other places where it is suitable and practicable, closed systems, properly operated and maintained, should be used to reduce the possibility of vapors or aerosols escaping into the workroom air and to minimize the likelihood of skin and eye contact. Where closed systems are not feasible, well-designed local exhaust ventilation should be provided. Such systems should be designed, if possible, to operate under negative pressure to prevent leaks into the workroom atmosphere. Guidance for design can be found in Industrial Ventilation--A Manual of Recommended Practice [188], in Fundamentals Governing the Design and Operation of Local Exhaust Systems Z9.2-1971 [189], and in NIOSH's Recommended Industrial Ventilation Guidelines [190]. Specifically, when a fire hazard exists, particular

attention must be given to the need for sparkproof fans and explosion proof motors in ventilation systems. An average face velocity of 150 feet/minute should be maintained when handling hydrazines or other suspected carcinogens in a hood [191]. Where a fire hazard could exist, all electrical fixtures used in the ventilation system or in the work area should be sparkproof, and all wiring should be enclosed in rigid metal conduits [192]. Exhaust air containing hydrazines should not be recirculated, and applicable Federal, state, and local regulations should be adhered to when exhaust air is released to the outside. Where exhaust ventilation is required, adequate makeup air, conditioned as needed for comfort, must be provided. Connections between exhaust air vents from a regulated area and those from other areas are prohibited, but a common makeup air inlet may be used. Exhaust ventilators must be located away from intake manifolds to prevent short circuiting. Respiratory protective equipment is not an acceptable substitute for proper engineering controls, but it should be available for emergencies, for nonroutine maintenance and repair situations, and for entry into confined spaces.

An enclosed system for the materials, processes, and operations is effective only if the integrity of the system is maintained. Such systems must be inspected regularly by qualified persons, and any leaks or worn parts must be repaired promptly. The conditions of seals, joints, access ports, and other such potential release points should be given special attention. Scheduled preventive maintenance, which offers more protection to the employee than nonroutine maintenance, should be practiced.