IV. ENVIRONMENTAL DATA

Sampling

A variety of common methods have been used over the years to sample airborne ketones in the workplace. These have included the use of impingers, bubblers, gas bags, and silica gel tubes. Currently, most ketone collection is done with charcoal tubes.

Impingers or bubblers containing absorbing liquids were the most common early methods used to collect ketone vapor. Smith and Wood [100] determined that a single absorber with water as the absorbent was 70 to 100% efficient in collecting acetone, methyl ethyl ketone, methyl isobutyl ketone, diacetone alcohol, mesityl oxide, and cyclohexanone in small air samples (125-1,625 ml). Kacy and Cope [101] recommended a fritted-glass bubbler for collecting airborne isophorone. Glacial acetic acid was the absorbent, and a sampling rate of 1 liter/minute for 5 minutes was used. No data on collection efficiency were presented. Andrew and Wood [102] used water as an absorbent in an impinger for isophorone sampling. Smith and Wood [99] used sodium nitroprusside and ammonium acetate in a bubbler to absorb acetone. A color complex was formed on the addition of ammonium solution, and the concentration was determined rapidly by visual comparison with standards. No efficiency data were presented. Acetone has also been collected in a series of two fritted bubblers with water as the absorbent [103].

Ketones have also been collected by the grab sample method using gas bags [104] or sample or prescription bottles [104,105]. Van Houten and Lee [105] found that the recovery of methyl isobutyl ketone was 95% after 30 days of storage in sample bottles and was 94% when samples were subjected to one week's storage over a temperature range of 0-175 F. The 1-week storage was used to simulate shipment by aircraft. Maykoski and Jacks [104] found recoveries of 91, 84, and 91% for collection of methyl ethyl ketone with a Scotchpac bag, Tedlar bag, and prescription bottle, respectively.

Using impingers, bubblers, and grab sample methods can be efficient ways to collect ketones, but such methods are undesirable for personal monitoring. Grab samples generally limit sample size; therefore, collection time is short. Impingers, bubblers, and other collection devices containing liquids may hamper the free movement of the worker. Spillproof impingers are commercially available, but these still have the problem of absorbent losses through evaporation and interference with movement.

More recently, solid sorbents in tubes, including silica gel, activated charcoal, and some chromatographic column packings have been used to collect ketones. The advantages of collection with a solid sorbent include the ability to collect samples over a wide range of sampling times, ease of transportation over that of air bags and impingers, minimal restriction on workers' movements, and collection efficiency. Some disadvantages are loss of the sample if the concentration of the ketone exceeds the adsorption capacity of the sorbent, the decrease in adsorption capacity with increasing humidity, and the need to determine or predict desorption efficiency.

Erley [106] reported 100% recovery of acetone from silica gel using thermal desorption at 400 C. A sampling rate of 1-3 liters/minute was used. Buchwald [107] has stated that acetone can be removed from silica gel by desorbing with 1 N sodium hydroxide. In a review, Buchwald [108] recommended 20/40 mesh silica gel and stated, without providing data, that variations in humidity did not interfere with the sampling. Feldstein et al [109] used silica gel to collect methyl ethyl ketone and methyl isobutyl ketone.

In 1976, Parkes et al [110] reported results showing 96-99% primary tube collection efficiency on preconditioned 80/100 mesh Chromosorb 101 for a variety of ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone, methyl n-amyl ketone, and cyclohexanone when they were removed from the sorbent by thermal desorption.

Activated charcoal is the most widely used and tested of the solid sorbents. Fraust and Hermann [111] determined that 0.7 g of 10/30 mesh charcoal and a sampling rate of 100-200 ml/minute were most efficient for sampling methyl ethyl ketone. The volume of air sampled did not affect efficiency except in the case of methyl ethyl ketone, but efficiency decreased as the contaminant concentration in the air increased. Charcoal tubes also have good storage characteristics when stored at or below room temperatures. Sadenwasser [112] found no loss of acetone (472 ppm) or methyl ethyl ketone (189 ppm) when the substances were stored for 6 days on a 2-inch section of 10/20 mesh charcoal. When White et al [113] used a 1-inch section of charcoal for collection and carbon disulfide for desorption, methyl ethyl ketone recoveries were over 90%, even when 13 other solvents were simultaneously collected.

NIOSH has investigated and validated charcoal tube sampling for many ketones [114,115]. Experimental results on breakthrough for these ketones are presented in Table IX-2. These data show that the efficiency of charcoal tube collection is adequate at the recommended concentration limits. For the selected ketones in this document, breakthrough from overloading the charcoal should not be a problem except at unusually high ketone concentrations, and it can be avoided by decreasing the sample volume.

Charcoal tube collection has many advantages. The tubes are inexpensive and readily available. They do not interfere with the workers' movements, and methods including charcoal tube collection have been validated; however, the sample volume is limited by the amount of the ketone which can be adsorbed on a given amount of charcoal, and there is the possibility of breakthrough. For these reasons, charcoal sampling is recommended for these ketones; details of the recommended sampling method are given in Appendix I. The presence of ketone aerosols does not seem likely because of the volatility of these substances. However, should such aerosol formation occur, it will probably be sorbed on charcoal if the airborne concentration is not too high. If any such aerosols are formed, possible breakthrough should be investigated.

The pump used to pull air through the collecting device should be a personal sampling pump capable of maintaining a constant flowrate of about 0.2 liters/minute (within 5%) across the pressure drop of the charcoal tube. Because the ketones exhibit various degrees of flammability, only pumps that are certified explosion-proof should be used, especially where the concentrations of airborne ketones are suspected or known to be high.

The recommended sampling method, as well as other methods discussed above, does not allow for continuous 10-hour sampling. Therefore, several samples may be required to accurately determine the TWA exposure of any given employee. For a discussion of the estimation and calculation of TWA exposure concentrations from less than full-shift samples, refer to the NIOSH report, Occupational Exposure Sampling Strategy Manual [116].

Analysis

There are many methods available for the analysis of ketones in environmental samples. Colorimetry using detector tubes, gas-liquid chromatography, titration of iodoform, and ultraviolet absorption spectroscopy are the most common analytical methods.

Methyl ketones have been analyzed for many years by the iodoform test [103,117,118]. In this test, iodine in the presence of a base, which is often the sampling medium, reacts with the methyl group of the ketone to yield iodoform. Excess iodine is determined by titration with an indicator, such as thiosulfate, and the concentration of ketone is then calculated. This method can be used to measure ketones at low concentrations. For example, acetone can be measured at a concentration of 10 ppm in a 1-cu ft air sample, approximately 23.7 mg/cu m, [103], and 1 mg of mesityl oxide [119] and 0.73 mg of methyl ethyl ketone [120] can be measured in a 25-liter sample. However, any compound that reacts with iodine to form iodoform, eg, many alcohols, aldehydes, and other ketones, will interfere.

The formation of colored complexes has also been used to analyze ketones. In a field test method, Smith and Wood [100] collected acetone, methyl ethyl ketone, methyl iso-butyl ketone, diacetone alcohol, and mesityl oxide in water and reacted them with 2,4-dinitrophenylhydrazine.

When potassium hydroxide in methanol was added, a red color developed, which was compared visually to standards, allowing a rough determination to the nearest 500 ppm. Haidle and Knight [121] reported that methyl n-amyl ketone could be measured by the 2,4-dinitrophenylhydrazine method over the range of 0.25-3.0 μmol when a spectrophotometer was used rather than visual comparison to standards. Isophorone has been measured colorimetrically by its reaction with phosphomolybdic acid in glacial acetic acid. Over the range of 12-93 μg, isophorone was measured with a standard deviation of 40 μg. Andrew and Wood [102] used dodecamolybdophosphoric acid with perchloric acid to analyze isophorone in a range-finding field test method. Concentrations were determined to the nearest 35 mg/cu m over the range of 0-140 mg/cu m. When they are performed carefully, most colorimetric methods can provide accurate and precise results. Field test methods are also available for range-finding purposes. However, these rapid methods tend to be inaccurate. Accurate results are time consuming, and quick tests are usually not accurate [100,102].

Ultraviolet spectrophotometry has also been used to measure ketones. Isophorone in isopropanol absorbs ultraviolet light at 235 nm, and concentrations down to about 14 μg of isophorone can be detected in a 25-liter air sample by this method [122]. Acetone concentrations of about 4.5 mg in a 25-liter sample can also be measured [103]. Interference can occur whenever two or more compounds are present, including aromatic and unsaturated compounds that absorb ultraviolet light at similar wavelengths.

Direct reading instrumentation is available for real time and continuous monitoring of the ketones. Infrared spectrophotometers, equipped with adjustable, long pathlength gas cells, can be used and provide quick, accurate measurement of the workplace concentrations. Analytical wavelengths of 8.2 μm (acetone), 8.3 μm (cyclohexanone), 8.5 μm (methyl ethyl ketone, methyl isobutyl ketone, and diacetone alcohol), and 8.6 μm (methyl isoamyl ketone, diisobutyl ketone, methyl n-butyl ketone, and methyl n-amyl ketone) have been used and have a minimum detectable concentration with a 20-meter cell of less than 1 ppm for each ketone [123]. The ketone wavelengths overlap and, therefore, where more than one ketone is present, the result may indicate the total amount present without allowing for separate determinations for each ketone. Combustible-gas meters and hydrocarbon meters are also available and, although nonspecific, can be useful for leak determinations.

Detector tubes or indicator tubes are being used more frequently since personnel require little specialized training to use them; they are inexpensive; and they give rapid estimations of exposure concentration. Indicator tubes are available for acetone (Draeger 100B, MSA 460423, and Kitagawa 102A) and methyl ethyl ketone (Kitagawa 139 B) according to a study of a working group of the British Occupational Hygiene Society [124]. Only the MSA acetone tube had been certified by NIOSH as of June 1976. The certified range of use was 500-5,000 ppm.

Gas-liquid chromatography (GLC) is widely applicable to the analysis of ketones. NIOSH has validated a GLC method for 11 of the 12 ketones, and the 12th, methyl isoamyl ketone, should be readily adaptable to this method [114,115]. In April 1977, documentation of the various validation tests of many of the methods was published by NIOSH [125]. Other investigators have also tested GLC methods for many of the ketones. McDonald et al [126] noted a retention time for acetone with a Porapak Q column of 0.88 minute and 0.65 minute relative to n-propanol. Cooper et al [127] were able to detect as little as 2.6 μg of methyl ethyl ketone in a 10-liter air sample when the GLC method was used with a mass spectrophotometric detector. The limits of detection achievable with a mass spectrophotometer are not necessary for routine industrial hygiene monitoring; sufficient results are attainable with a flame-ionization detector. White et al [113] reported measuring methyl ethyl ketone by means of GLC analysis in the presence of 13 other solvents.

For these reasons, GLC is recommended for quantitation of these ketones; details of the analysis and a general method applicable to all 12 ketones are given in Appendix I. Methods for many of the individual ketones have been published in the latest edition of the NIOSH Manual of Analytical Methods [114,115]. The GLC operating conditions, validated ranges, coefficients of variation, and standard deviations have been determined and are listed in Tables IX-1 and IX-3.

An important step in the use of GLC for ketone analysis is the desorption of the compound(s) from the solid sorbent used to collect the ketones from the sampled air. Charcoal or silica gel tubes are the most commonly used collection methods, and the validated charcoal tube procedure has been recommended as described in Appendix I. Feldstein et al [109] used dimethyl sulfoxide, carbon disulfide, and a carbon disulfide-water mixture as a solvent to desorb methyl ethyl ketone or methyl isobutyl ketone from silica gel. Carbon disulfide and the carbon disulfide-water mixture gave unacceptable recoveries of 4-75%; dimethyl sulfoxide desorption was 97-98% efficient. NIOSH [114,115,125] has tested and validated the use of carbon disulfide as the desorbing solvent for use with ketones collected on charcoal tubes. Regardless of the solid sorbent and desorbing solvent used, it is necessary to determine the desorption efficiency for each batch of analyses. Directions for this determination are included in Appendix I.

Environmental Data

Data on current and past occupational exposures to the ketones in this document are found only infrequently. Acetone and methyl ethyl ketone have been the most frequently monitored ketones.

Many NIOSH reports of health hazard evaluations [128-136] contain data on exposures to ketones in many different industries, but sampling of airborne ketones was performed primarily where the ketones have been used as solvents. The NIOSH method validated for the particular compound was used to obtain the data. Data from many such reports are briefly summarized in Table IV-1.

Data on methyl n-butyl ketone exposures during its manufacture have been reported to NIOSH [145]. Monitoring was performed during the summer of 1977. Operator breathing zone samples, collected during process sampling and laboratory analysis, averaged 41 mg/cu m with a range of from less than 0.01 up to 746 mg/cu m for 28 samples. Three samples taken in the operators' breathing zone during rail tank car loading were reported as containing a high of 187 mg/cu m and a low of 8 mg/cu m. Six samples taken during drum loading had methyl n-butyl ketone concentrations ranging from less than 4 to 27 mg/cu m.

Results from recent (April 1977) monitoring at the coated-fabric plant in Ohio have shown a reduction in environmental concentrations of

TABLE IV-1

ENVIRONMENTAL DATA FROM HEALTH HAZARD EVALUATION REPORTS

Compound	Use or Operation	Concentrations		Number of Samples	Reference
		Mean (mg/cu m)	Range (mg/cu m)		
Acetone	Acryloid	620	-	1	129
"	Injection molding	<2	-	-	130
"	Plastics cleaning	-	<118-493	5	131
"	Solvent	17	5-40	8	132
"	Fiberglass plant	76	15-324	26	133
"	Rifle scope production	982-summer	625-1550	44	134
		444-fall	94-1677	29	
"	Vinyl installation	185	128-216	3	136
"	Spray painting	40	-	-	136
Methyl ethyl ketone	Label printing	<1	-	8	135
"	Baseball bat manufacturing	9	3-15	11	137
"	Painting	4	ND-35	11	138
"	Parts cleaning	196	44-413	7	138
"	Ski plant	209	18-968	12	139
		55	<1-230	5	139
		79	ND-162	4	139
"	Painting	6	ND-21	-	140
"	Cementing	26	6-68	8	132
"	Spray painting	<30	-	-	136
"	Reinforced plastics plant	0.8	ND-33	47	141
"	Gasket cleaning	339	233-395	3	142
"	Paint plant	182	38-1441	21	143
Methyl butyl ketone	"	54	46-66	3	143
Methyl isobutyl ketone	Television cabinet manufacturing	4	<4-45	30	128
"	Spray painting	<40	-	-	136
"	Paint plant	104	39-197	12	143
Diacetone alcohol	Aerosol can production	114	18.5-265	30	144

*ND=non-detected

ketones from those present when cases of peripheral neuropathy were found in 1973 [146]. Methyl n-butyl ketone concentrations (84 samples) were all below the detection limit (0.01 mg/cu m) of the analytical method. Methyl ethyl ketone concentrations averaged 99 mg/cu m for 84 samples with a range from 7 to 388 mg/cu m. Methyl isobutyl ketone concentrations averaged 18 mg/cu m for 84 samples with a range of less than 0.01 mg/cu m to 108 mg/cu m. Methyl n-butyl ketone use had been discontinued following the episode of peripheral neuropathy, and methyl ethyl and methyl isobutyl ketones were substituted. All methyl ethyl ketone and methyl isobutyl ketone concentrations reported in April 1977 were below 388 and 108 mg/cu m, respectively.

Engineering Controls

Engineering controls should be designed to keep airborne ketones at concentrations at or below the permissible exposure limits. Closed systems, preferably under lower pressure than uncontaminated areas and properly operated and maintained, should be used wherever appropriate, for example, in the manufacture of the ketones and in their use as intermediate chemicals. Frequent tests must be conducted for leaks in such a closed system. Where closed systems are not feasible, well-designed local exhaust ventilation systems should be used. Guidance for design of ventilation systems can be found in *Industrial Ventilation--A Manual of Recommended Practice* [147] and in *Fundamentals Governing the Design and Operation of Local Exhaust Systems, ANSI Z9.2-1971* [148]. Continuous local exhaust ventilation or some means of ketone containment (such as cooling coils) should be used when ketones are used in open tanks and during their charging or discharging.

Ventilation systems require regular inspection to provide the necessary level of employee protection. Airflow should be measured on a frequent, regular basis, at least every 3 months. Continuous monitoring can be provided by the installation of oil or water manometers. The desired airflow can be indicated on the manometer to provide ready reference for a quick determination of optimum performance.

Electrical systems used in processes in which ketones are used, handled, or processed should conform to the National Electrical Code [149]. Motors used for ventilation systems or material transfer must be explosion-proof when ketones classified as flammable liquids (mesityl oxide, acetone, methyl n-butyl ketone, methyl ethyl ketone, methyl isobutyl ketone, and methyl n-propyl ketone) are present. Explosion-proof motors should also be used with the other ketones, which are all classified as combustible liquids. Concentrations of ketones in the exhaust system must be kept below the lower flammable limit for the particular ketone. Airmovers in exhaust systems where ketone concentrations may exceed one fourth of the lower explosive limit must be of sparkproof construction. Data on flashpoints and lower explosive limits are included in Table XI-2.

Storage facilities for the ketones must conform to the requirements for storing flammable and combustible liquids as stated in 29 CFR 1910.106. Many of the lower boiling ketones form flammable air-vapor mixtures in the spaces of a storage tank at normal temperatures unless air is excluded. Inert gas can be used to exclude air. If air is not excluded, a flame arrestor should be installed on the tank vent [150]. Storage tanks should be electrically bonded and grounded and should be diked to contain leaks. Diked areas should be equipped with a sump pump (non-sparking) to remove any spilled ketone. Steel piping and tanks are adequate for storing most ketones up to 2 months and when product quality is not unusually critical. For longer storage or critical purity, a steel tank may have to be lined, eg, with an inorganic zinc silicate coating [150].

V. WORK PRACTICES

The 12 ketones included in this document present different toxicologic problems; however, they also have many common properties that require similar work practices. Although all 12 ketones are liquids at room temperature (Table XI-2), some have high vapor pressure, and, therefore, employees may contact ketones by inhaling vapor or mist as well as by having their skin or eyes come in contact with the liquid. There is some evidence that skin absorption, at least of some ketones, may also occur [43,45]. All ketones are good lipid solvents and thus cause dermatitis whether or not they can penetrate the skin. Engineering controls and work practices should be designed and implemented to maintain concentrations of airborne ketones at or below permissible exposure limits, minimize excursions, prevent skin and eye contact, and reduce fire and explosion hazards.

The ketones have been shown to be a significant fire hazard. All of them have flashpoints below 200 F (Table XI-2) and are therefore classified as combustible or flammable liquids of Classes IA, IB, IC, II, and IIIA according to the criteria in 29 CFR 1910.106a. Boiling points and flashpoints for the 12 ketones are listed in Table XI-2.

A flammable liquid has a flashpoint below 100 F (37.8 C). The classes of flammable liquids are IA, liquids with a flashpoint below 73 F (22.8 C) and boiling point below 100 F; IB those with a flashpoint below 73 F and boiling point at or above 100 F; and IC, those with a flashpoint at or above 73 F (22.8 C) and below 100 F (37.8 C). Combustible liquids have flashpoints above 100 F and are divided into two classes. Those in Class

II have a flashpoint at or above 100 F and below 140 F, and those in Class III have a flashpoint above 140 F. Combustible liquids in Class IIIA have flashpoints at or above 140 F and below 200 F, and those in IIIB have flashpoints at or above 200 F. If ventilation is adequate to maintain the concentrations of ketones at or near their permissible exposure limits, which are based on toxicologic considerations, the potential for fire and explosion will be eliminated. However, elevated concentrations can be caused by vapor accumulation above a liquid surface, in depressions, at container openings, and at vent openings. The employer should be familiar with the particular properties of the ketone in use and should provide instructions for safely handling that ketone. All ignition sources, such as fire, sparks, and smoking, must be prohibited when and where ketones are handled, used, or stored. The National Fire Protection Association (NFPA) Standard #77, "Static Electricity," lists precautions to be taken to prevent the accumulation of static electricity which may be a source of ignition. Precautions include bonding, grounding, and humidity control.

Equipment for handling ketones should be properly bonded, grounded, and installed according to local and state building codes. Only sparkproof tools may be used with the ketones that are classified as flammable liquids, and it is a good practice to use them with all ketones. Outside storage areas are preferred to inside areas, but storage containers should always be protected from direct sunlight and from other sources of heat. Only containers and tanks designed to contain flammable or combustible liquids should be used for transporting or storing large amounts of ketones.

Detailed regulations for handling flammable and combustible liquids are found in 29 CFR 1910.106. These rules have been adapted from the NFPA. Areas covered include tank storage; piping, valves, and fittings; containers and portable tank storage; and industrial uses.

When fighting fires involving ketones, personnel must use protective equipment similar to that worn whenever there may be the danger of breathing hazardous products of combustion. Carbon dioxide or dry chemical extinguishers are most effective for extinguishing ketone fires. Water spray may also be used, but a water hose stream which can scatter the burning liquid should not. Larger spills or tank fires are best controlled with "alcohol type" foam [151,152]. When entering an area for firefighting, personnel should wear a self-contained breathing apparatus operated in the positive-pressure mode.

Closed system operations, when compatible with the use of the ketone, present the best means of protecting the worker from ketone exposure. When workers carefully observe good, preventive maintenance and frequently inspect systems for leaks, spills, and worn parts, closed systems are effective in minimizing exposure to ketones. When leaks do occur, they must promptly be repaired by trained workers wearing the appropriate protective clothing and respiratory protection.

Ketones are powerful degreasing agents and are capable of causing or aggravating skin irritation after prolonged or repeated exposure. Although the use of personal protective equipment is not an adequate substitute for good work practices and ventilation, in some cases it is necessary. Resistant gloves and clothing, safety goggles (with 20-cm minimum face shields if full-face protection is necessary), aprons, coats, and boots should be worn when needed to prevent prolonged or repeated skin contact with ketones. If clothing becomes soaked with a ketone, it is important that the clothing be removed immediately and not be reused until it is free of contamination. The prompt removal of clothing will not only lessen the chance for skin irritation but will also minimize the risk of burns, since clothing contaminated with ketones is readily flammable. Clothing may be decontaminated by laundering or by allowing the clothing to dry. (Clothing must be dried in a suitably ventilated area.) Laundry personnel must also be informed of any hazards to them and must be protected from ketone exposure. Foot burns may result if some ketones (acetone, for example [151]) with high vapor pressures are spilled into shoes and the shoes are not thoroughly cleaned and ventilated after contamination.

The employer should be aware that not all rubber or plasticized gloves are adequate protection from ketones. McFee [153] and Sansone and Tewari [154] have investigated gloves' resistance to acetone and methyl ethyl ketone penetration. The data, as shown in Table V-1, indicate that only milled butyl gloves offer protection for long periods and several (neoprene, polyvinyl chloride, and nitrile) may not be adequate even for short, half-hour usage. Employers must determine that gloves supplied for skin protection are adequate and provide the necessary protection for the particular ketone.

Although engineering controls are required to prevent or contain major spills, minor spills may also present a hazard and should be promptly cleaned up by personnel properly protected against the inhalation of and prolonged skin contact with ketones. These precautions will minimize the risk of fire and also reduce the spread of vapors into confined spaces or

TABLE V-1

EXTENT OF SOLVENT PENETRATION (%) THROUGH GLOVE MATERIALS

Glove Material	Glove Thickness (mm)	Penetration after 30 minutes		Penetration after 24 hours	Reference
		Acetone	Methyl ethyl ketone	Acetone	
Natural rubber	0.4	0.1-1	1-10	-	154
	0.18	-	-	41	153
Neoprene	0.4	1-10	>10	-	154
	0.18	-	-	83.4	153
Natural rubber and neoprene	0.5	0.1-1	1-10	-	154
	0.30	-	-	50	153
Polyvinyl chloride	0.2	>10	>10	-	154
	0.51-0.69	-	-	90	153
Polyvinyl alcohol	0.4	<0.1	<0.1	-	154
	0.74	-	-	3.6	153
Nitrile	0.4	>10	>10	-	154
Milled butyl	0.48	-	-	<0.3	153

into those located below ground level. Rags, mops, and other materials contaminated with a ketone or used to clean up a spill must be stored in a closed metal container until they can be removed from the work area and properly cleaned or disposed of.

Ketones and materials contaminated with ketones must be disposed of according to applicable Federal, state, and local regulations. The preferred method is to recover and reuse the ketone if possible. Incineration or burial in a proper land fill are other methods of disposal. Ketone disposal in sewers should be prohibited since vapors may still be ignited.

Under some conditions, ketones may collect in low and confined spaces. Confined-space entry procedures must be developed and enforced to prevent exposure from exceeding the permissible exposure limit in an enclosed or confined space. The atmosphere should be checked for the presence of ketones, sufficient oxygen, and toxic materials as may be necessary. Where ketones are present or where their absence cannot be assured, workers should wear proper equipment when entering an enclosed or confined space. The following protective measures are also required: use of a lifeline and harness, communication with an observer properly equipped to rescue, and the presence of a third party ready to lend assistance. Before entering a tank or confined space, every worker must obtain a permit signed by an authorized person stating that the atmosphere has been checked and found safe or stating that all necessary safety precautions have been observed.

Employees should never use ketones to remove grease and dirt from their hands. Employers should provide washrooms and showers where mild soap can be used to remove dirt and grease. If soap and water are not effective, the employer should provide an alternative means of removal, such as a waterless cleanser. The employees should also wash their hands following contact with any ketone; this procedure will minimize the risk of irritation. The requirements for sanitation facilities are listed in 29 CFR 1910.141.

Eyewash fountains and emergency showers must be provided for immediate emergency use in work areas where employees may come in contact with ketones at excessive concentrations. The requirements for emergency eyewash fountains and showers, as well as for medical and first aid, are detailed in 29 CFR 1910.151. Emergency equipment must be useable and sanitary at all times.

Engineering controls are the first choice in reducing exposure to ketone vapors. Work practices, such as those discussed in this chapter, may also significantly reduce exposure. Respirators are the least satisfactory means of preventing inhalation exposure to ketones, but there are situations, such as during the installation or testing of new exhaust systems, during performance of nonroutine maintenance or repair, during single operations, or during emergencies, when they represent the only feasible and adequate source of protection. When respirators are required, the employer should ensure that only respirators approved by NIOSH or MSHA are used. Respirator selection should follow the guidelines indicated in Table I-2. Respirators certified for use at higher concentrations may always be used at lower concentrations. Dust respirators are not suitable for protection against ketone vapors and offer only poor protection. Compressed oxygen should not be used when there is danger of contact with flammable liquids, vapors, or sources of ignition, especially in confined spaces [151].

Since some ketones can cause eye irritation, the use of half-mask facepiece respirators has been restricted. Data presented in Tables III-1 and III-8 suggest that eye irritation will occur at concentrations less than 10 times the proposed limit of each ketone except methyl n-butyl ketone and isophorone.

Evidence to support the use of air purifying (cartridge or canister) respirators was not found. Air purifying respirators can only be safely used when knowledge of the absorbent's capacity for the ketone is available and where an indication of breakthrough (end-of-service-life indicators or smell and taste properties) is available at non-hazardous concentrations. Nelson and Harder [155] have conducted respirator cartridge efficiency studies. The test concentration was 1,000 ppm, the flowrate 53.3 liters/minute, humidity 50%, and the temperature 20-22 C. These data show that the useful life of cartridges is limited to 1-2 hours, and they highlight the need to get more definitive data for breakthrough at other concentrations. End-of-service-life indicators for cartridges do not yet exist for the ketones, and, therefore, warnings of breakthrough are dependent on odor or taste. Odor threshold values, to provide an adequate margin of safety, must be no more than three times the recommended environmental limit. It seems probable that the odor of some of these ketones can be detected at such concentrations, but the reliability of detection, the rapidity of odor fatigue, and the variation in the population are not known.

In all workplaces where ketones or ketone-containing substances must be handled, written instructions informing employees of the particular hazards involved, the method of handling, procedures for cleaning up spilled material, personal protective equipment to be worn, and procedures for emergencies must be posted, on file, and available to employees. The employer must establish a program of instruction that will ensure that all potentially exposed employees are familiar with the procedures. The Material Safety Data Sheet described in Appendix II may be used as a guide for employers in providing the necessary information. The duties of employees involved in maintenance and repair activities pose special problems of potential contact and exposure, especially in work on enclosed systems or in operations involving ventilation-system repair and maintenance. The nature of this type of work increases the potential for exposure. Maintenance employees may not be sufficiently familiar with the hazardous materials with which they are involved. Therefore, special supervisory control and work practice precautions are required to prevent exposure of these employees.