

#### IV. ENVIRONMENTAL DATA AND ENGINEERING CONTROLS

##### Sampling and Analysis

There are many general methods of sampling and analysis for alkanes and for various hydrocarbon mixtures containing alkanes. Many of these methods were developed for specific purposes, such as analyses of ambient air [60,61], petroleum distillates [62-64], gasoline components [63-65], crude oil [66], automobile exhausts [67], polluted atmospheres [68-70], and polluted water samples [71].

Sampling with plastic bags [72-75] or with glass bottles [76] involves drawing a volume of environmental air at a known temperature and pressure into a container of known volume. This type of "grab" sample is collected from a few seconds to several hours depending on flowrate. Although plastic bags are lightweight and inexpensive, and no correction is necessary for dilution of the sample during analysis, the rate of sample decay within the bags may vary as a function of storage time [75], and sample transport may be inconvenient because of the bulkiness of the containers. The rate of loss of alkane vapors from plastic bags is also a function of the type of plastic used, adsorption and diffusion characteristics for the specific plastic, the concentration of alkanes present, temperatures, and pressure [73]. No reports were found on the specific use of plastic bags and glass bottles for sampling alkanes.

Another type of collection device involves the passage of a known volume of air through an absorbing or adsorbing medium to retain the alkanes [77-80]. With such devices, samples can be collected over recorded periods of time, and the resultant data can be analyzed to calculate the

TWA concentration of the alkanes present. Impingers and bubblers can be used to collect alkane vapors in carbon disulfide, although caution should be exercised with carbon disulfide because of its high toxicity [61]. Direct-feed sampling can also be done where air samples containing alkanes are flushed directly into a gas chromatograph with helium [68,70] or alkane samples are collected in freeze-traps at low temperatures [60,69]. No efficiency data have been determined, but, where adsorbing or absorbing media are used to collect samples, it might be necessary to use more than one impinger, bubbler, or freeze-trap in series.

Of the various techniques, adsorption offers the greatest ease of collection. Activated charcoal [61,79,80,81], silica gel [77,78], and bonded stationary phases [60] have been used to adsorb hydrocarbon vapors. The method of Otterson and Guy [79] provides a simple means of sample collection: alkane vapors are adsorbed on activated charcoal and then desorbed with carbon disulfide. Liquid desorption offers the advantage of permitting multiple analyses of each sample.

The efficiency of the adsorption on activated charcoal is not affected by small variations in mesh size or type of charcoal used [79,82]. In this charcoal sampling system, a pump capable of drawing a measured quantity of air through a charcoal tube is used. Once the sampling is completed, charcoal tubes are easy to seal, handle, transport, and store. One disadvantage of charcoal tubes is that the amount of sample that can be collected is limited by the weight of charcoal in a given tube. If too much sample is drawn through the charcoal, overloading occurs and the possibility of sample loss (breakthrough) exists. When the sample in the backup section of the charcoal trap exceeds 25% of that found in the front

section, either the charcoal section length in the front section should be increased to prevent loss of the sample or the size of the sample should be decreased. The precision of the charcoal tube method is limited by the reproducibility of the pressure drop across the charcoal tubes. Because the sampling pump is usually calibrated for one tube for each batch, variation in tubes may affect the flow rate and cause the volume calculation to be imprecise.

The charcoal tube method is nevertheless recommended as the method of choice. Details concerning its use are presented in Appendix I. Because the charcoal tube collects a large number of organic vapors, the use of a specific analytical method is necessary.

A number of analytical methods have been developed that, when coupled with gas chromatography, can be used for the detection of alkanes. These various methods use infrared spectrometry [67,83], nuclear magnetic resonance spectrometry [66], and mass spectrometry [66] as gas-chromatographic detectors instead of a flame ionization detector which is employed often in alkane analysis [61,65,68].

Indicator-type detector tubes are used frequently for a quick, direct detection of the concentrations of alkanes in air [84]. They have been shown to detect n-pentane at concentrations ranging from 290 to 4,400 mg/cu m and hexane, heptane, and octane at concentrations ranging from 2,000 to 25,000 mg/cu m [84]. Currently, no alkane detector tubes have been certified for use by NIOSH.

In addition to the previously described detection apparatus, there are various types of combustion detectors [85]. The most common types use a Wheatstone bridge and a balanced electrical circuit. When a combustible

gas is drawn over an arm of the Wheatstone bridge, there is an increase in resistance due to the effect of the gas in one section of the circuit and the imbalance over the total circuit is measured. The Wheatstone bridge is not very sensitive to the presence of low concentrations of various combustible vapors; it is also affected by environmental conditions and by the presence of other substances in the atmosphere. These detectors are useful for locating leaks in closed systems and testing for the presence of alkane vapor in confined spaces. They may also be used to make rough estimates of airborne alkane concentrations.

The method recommended for the analysis of alkanes was adapted from the NIOSH/OSHA Standards Completion Program [61] and is described in Appendix II. In the method, a charcoal tube is used to adsorb the alkanes from the air drawn through the tube, the alkanes are desorbed from the charcoal with carbon disulfide solution, and then the carbon disulfide solution is analyzed with a gas chromatograph. The gas-chromatographic separation is performed on a column packed with 10% FFAP on 80/100 mesh Chromosorb W-AW. This method provides for a quick, accurate means of analysis and for the analysis of two or more compounds suspected to be present in a mixture. In conjunction with this method, mass spectrometry can be used to determine the identities of compounds in complex mixtures.

### Engineering Controls

Alkanes are used primarily as solvents in operations involving extraction, spraying, pouring, mixing, and oven-drying [86-88]. Some of these operations are not enclosed and alkane vapor may be released into the atmosphere. The principles set forth in Industrial Ventilation--A Manual

of Recommended Practices, published by the American Conference of Governmental Industrial Hygienists Committee on Industrial Ventilation [89], and Fundamentals Governing the Design and Operation of Local Exhaust Systems, Z9.2-1971 [90], published by the American National Standards Institute, should be applied to the control of atmospheric releases of alkanes. Seed-oil extraction with alkanes is normally performed in closed systems so that only small amounts of vapor are released to the atmosphere [87,88]. However, when closed systems are opened for maintenance, the possibility of concentrations existing which may exceed 10% of the lower explosive limit should be considered. Such operations should always be ventilated, preferably by blowers and correctly positioned ducts. Where possible, the release of alkane vapors should be controlled by local ventilation at the source of emission. Operations such as extraction, drying, and evaporation which involve the use of alkanes at elevated temperatures may require special placement of local ventilation controls. Such controls must be explosion-proof [87]. Special care must be taken to make sure that substances that form explosive mixtures are not vented into the same system. Frequent tests should be conducted to ensure that leaks do not occur in closed systems containing alkanes. The major alkane-manufacturing processes in use in the United States are currently closed processes [88].

## V. DEVELOPMENT OF A STANDARD

### Basis for Previous Standards

#### (a) ACGIH Threshold Limit Values

##### (1) Pentane

In 1929, Patty and Yant [41] reported that pentane at 5,000 ppm produced no sensory effects on human subjects after 10 minutes of exposure. Fuhner [12] found that mice exposed to pentane at air concentrations of approximately 270,000 mg/cu m in air showed no loss of reflexes after 116 minutes of exposure. In 1945, based on the Patty and Yant report [41], Cook [91] suggested a maximum allowable concentration (MAC) of 5,000 ppm (14,750 mg/cu m) for pentane. It was this 5,000-ppm MAC value that the Committee on Threshold Limits of the American Conference of Governmental Industrial Hygienists (ACGIH) adopted as the recommended environmental limit in 1946 [92].

In 1947, the ACGIH Committee [93] changed the MAC for pentane to 1,000 ppm (2,950 mg/cu m). The reason for this change was not specified, and whether this MAC was intended as a ceiling value or as a TWA concentration was not indicated.

In 1948, the ACGIH [94] still designated 1,000 ppm as the recommended limit for pentane but called the limit a Threshold Limit Value (TLV). The TLV for pentane remained at 1,000 ppm until 1970 when the ACGIH [95] lowered it to 500 ppm (1,500 mg/cu m). A notice of intended change, calling for a revision of the TLV for pentane from 500 to 600 ppm (1,800 mg/cu m), was published by the ACGIH [96] in 1974; 600 ppm was adopted as the TLV in 1976 [97]. The ACGIH [98] stated that a TLV for pentane of 600

ppm, as a TWA concentration, was at a level "where the odor and irritation did not constitute a nuisance during prolonged exposure" and that this was also consistent with the findings of Swann et al [44] and others [12,41] that the shorter the carbon chain in a homologous series, the less the toxic effect.

(2) Hexane

In 1943, Drinker et al [32] had two groups of volunteers inhale petroleum distillate for 8 hours. Ninety percent of the distillate boiled between 42 and 127 C, a range which would include hexane. The wide boiling range indicates that the distillate contained a number of aliphatic and possibly aromatic hydrocarbon components in addition to hexane. Volunteers in one group were exposed to the distillate vapor at 150 ppm, and those in the other group were exposed at 140 ppm. At both concentrations, nausea, headache, and throat and eye irritation were the common complaints, but the authors [32] stated that none of the volunteers considered the exposure sufficiently disagreeable to preclude working in the exposure area. Nelson et al [33], in 1942, exposed volunteers to n-hexane at 500 ppm for 3-5 minutes; the subjects described this exposure as being quite innocuous. Although the effects of higher concentrations were not evaluated, the volunteers felt that higher concentrations could be tolerated in the workplace.

In 1948, the ACGIH [94] designated 500 ppm as a TLV for hexane. The TLV remained at 500 ppm until 1974 when a notice [96] of intended change, calling for a revision of the TLV for n-hexane from 500 to 100 ppm (360 mg/cu m), was published. In 1976, the ACGIH [97] adopted a new TLV, 100 ppm for n-hexane. The decision [99] to lower the TLV of n-hexane from 500

to 100 ppm was based on reports [13,17,18] of polyneuropathy in workers who used hexane as a solvent in various industrial applications. Yamada [17] described the occurrence of polyneuropathy in 17 workers in Japan, 6 of whom were exposed to hexane vapor in a polyethylene-laminating plant and 11 to hexane in a pharmaceutical plant. Inoue et al [18] reported an outbreak of polyneuropathy from exposure to the vapor of hexane from glue used in sandal making in Japan. Herskowitz et al [13] described sensorimotor polyneuropathy in three employees in a furniture factory in the United States. Inoue et al [100] showed that inhalation of hexane at 250 ppm caused peripheral nerve disturbances in mice, but no disturbances were observed at 100 ppm. Based on these and another report [101] of polyneuropathy, the ACGIH lowered the TLV for n-hexane from 500 ppm to 100 ppm.

### (3) Heptane

In 1929, Patty and Yant [41] reported that exposure of humans to heptane at a concentration of 1,000 ppm (4,000 mg/cu m) for 6 minutes resulted in only slight dizziness. Based on this report, Cook [91], in 1943, suggested an MAC for heptane of 500 ppm (2,000 mg/cu m), although he stated, "exposures somewhat in excess of this concentration are not considered toxic." In 1946, the ACGIH adopted an MAC for heptane of 500 ppm. In 1948, the ACGIH designated 500 ppm as the limit for heptane and changed the name to a TLV, specified as a TWA concentration. The TLV remained at 500 ppm until 1974 when a notice [96] of intended change, calling for a lowering of the TLV for n-heptane from 500 ppm to 400 ppm (1,600 mg/cu m), was published. In 1976, the ACGIH [97] adopted 400 ppm as the TLV for n-heptane. The ACGIH [102] based this revision on the



possibility that heptane could cause polyneuropathy since it probably had been in the mixtures of hydrocarbon solvents implicated in numerous cases of polyneuropathy [13,17,101], although no nervous system disturbances had been directly attributed to heptane.

#### (4) Octane

In 1945, Cook [91] suggested an MAC value of 500 ppm (2,350 mg/cu m) for octane, based on the investigation by Patty and Yant [41] whose report stated that heptane at 1,000 ppm caused slight dizziness in humans. The MAC value of 500 ppm was suggested by Cook [91] because he felt that octane was a more potent narcotic agent than heptane.

In 1946, the ACGIH [92] adopted an MAC for octane of 500 ppm. In 1948, the ACGIH [94] designated 500 ppm as the TLV for octane. The TLV for octane remained at 500 ppm until 1970 when the ACGIH [95] lowered it to 400 ppm (1,900 mg/cu m). A notice [96] of intended change, calling for a reduction of the TLV for octane from 400 to 300 ppm (1,450 mg/cu m), was published in 1974. The change was adopted [97] in 1976. The ACGIH [103] reasoned that since, according to several studies [12,44,104], octane was more toxic than heptane and had a greater molecular weight than heptane, octane should have a lower TLV than heptane to avoid narcosis or irritation. Since a TLV for heptane of 400 ppm had been chosen, the TLV for octane was lowered to 300 ppm.

#### (b) Other Workplace Limits

In 1971, the Pennsylvania Department of Environmental Resources [105] adopted 500-ppm TLV's for pentane (1,475 mg/cu m), n-hexane (1,770 mg/cu m), and n-heptane (2,050 mg/cu m), and a 400-ppm TLV for octane (1,870 mg/cu m). These values were specified as TWA concentrations. The

department also adopted Short-Term Limits (STL) of 500 ppm for a 30-minute exposure to hexane, heptane, and octane.

In 1976, the ACGIH [97] set tentative Threshold Limit Value-Short Term Exposure Limits (TLV-STEL) of 750 ppm (2,250 mg/cu m) for pentane, 125 ppm (450 mg/cu m) for n-hexane, 500 ppm (2,000 mg/cu m) for n-heptane, and 375 ppm (1,800 mg/cu m) for octane. These limits were described as maximal concentrations to which employees could be exposed for a period up to 15 minutes continuously without suffering from intolerable irritation, chronic or irreversible tissue change, or narcosis of sufficient degree to increase accident proneness, impair self-rescue, or reduce work efficiency. A provision that limited the number of excursions to no more than four each day, with at least 60 minutes between exposure periods, was also included.

The MAC values for pentane, hexane, heptane, and octane that have been established in various foreign countries are shown in Table V-1.

In 1971, the Japanese Subcommittee on Permissible Concentrations of Hazardous Substances [109] recommended the continued acceptance of the 1966 TWA concentration of 100 ppm (360 mg/cu m) for n-hexane. The recommendation was based on reports and data from human and animal experiments as well as from experience in industry. No documentation was provided.

The present federal workplace environmental limit (29 CFR 1910.1000) for pentane is an 8-hour TWA concentration of 1,000 ppm (2,950 mg/cu) for a 40-hour workweek. For n-hexane, n-heptane, and octane, the limits are 8-hour TWA concentrations of 500 ppm (1,800 mg/cu m, 2,000 mg/cu m, and 2,350 mg/cu m, respectively) for a 40-hour workweek. These limits are based on the ACGIH TLV concentrations for 1968 [110].

TABLE V-1

MAXIMUM ALLOWABLE ALKANE CONCENTRATION VALUES  
FOR VARIOUS FOREIGN COUNTRIES

Country	Pentane		Hexane		Heptane		Octane	
	ppm	mg/cu m	ppm	mg/cu m	ppm	mg/cu m	ppm	mg/cu m
Japan	-	-	100*	360	-	-	-	-
Finland	1,000	2,950	500*	1,800	500*	2,000	500	2,350
Germany (Federal Republic)	1,000	2,950	100*	360	500*	2,000	500	2,350
Poland	-	1,000	-	400	-	200	-	200
Rumania	-	2,400	-	1,500*	-	1,500*	-	1,500
Yugoslavia	1,000	2,950	500*	1,800	500*	2,000	-	2,350
Sweden	-	-	-	-	-	-	300	1,400

\*Values for straight chain isomers

Adapted from references 106-108

Basis for the Recommended Standard

(a) Workplace Environmental Limits

Toxicologic data suitable for establishing a standard for the alkanes in the occupational environment are limited. Data have been reported that indicate that exposure to hexane can result in the development of polyneuropathy [13,17,18,36-39]. Yamamura [37] reported that workers exposed to hexane used in glue for sandal production in Japan had developed polyneuropathy. Of 296 sandal workers examined, 93 were classified as

having polyneuropathy. All 93 had been engaged in the gluing operation that took place in the workers' poorly ventilated dwellings. The airborne hexane concentration in the pasting rooms of the dwellings ranged from 500 to 2,500 ppm with exposure durations exceeding 8 hours/day for 6-7 days/week. Inoue and his coworkers [18], reporting on the same study, indicated that some workers who developed polyneuropathy had been exposed to concentrations of n-hexane below 500 ppm.

Yamada [17] described the conditions under which 17 workers who developed polyneuropathy were exposed to hexane vapor in Japan. Six of the patients worked in small laminating plants for an average of 10 hours/day, 6 days/week. During the laminating process, airborne concentrations of hexane vapor ranged from 1,000 to 2,500 ppm. The hexane solvent used in these plants contained 16% methyl pentane, 20% methyl cyclopentane, and 64% n-hexane. Eleven of the 17 cases of polyneuropathy occurred in a pharmaceutical plant where a 95% n-hexane solution was used to remove oil from the surfaces of tablets. The workers lived and worked in the factory, where the concentration of airborne hexane was 500-1,000 ppm. Herskowitz et al [13] described three cases of sensorimotor polyneuropathy in employees of a furniture factory in New York. Air sampling indicated that the employees were exposed to n-hexane at concentrations which averaged 650 ppm.

Miyagaki [46] exposed mice to n-hexane at various concentrations for 24 hours/day, 6 days/week, for 1 year. After the 1-year exposure, examinations of the lower extremities of the mice for neurotoxic effects were performed. The author [46] determined that the toxic concentration of hexane in mice was 250 ppm. At a concentration of 100 ppm, he found no

clear neurotoxic effects.

In view of the evidence that exposure to hexane at concentrations below 500 ppm [18,46] has been associated with the development of polyneuropathy, an environmental limit well below 1,800 mg/cu m (500 ppm) of hexane is needed. The absence of definitive epidemiologic or toxicologic evidence makes it difficult to determine how much lower the environmental limit should be. Professional judgment suggests that a TWA concentration of 350 mg/cu m (100 ppm) offers a sufficient margin of safety to protect against the development of chronic nerve disorders in workers. Further research should be conducted to better define this limit. It is noted that the German Research Association and the Japanese Association of Occupational Health have come to a similar conclusion regarding hexane.

Although polyneuropathy in humans has not been attributed to exposure to pentane, heptane, or octane, evidence exists which suggests that these alkanes are similar in toxicity to hexane. Five workers in a belt-manufacturing shop in Paris developed polyneuropathy as a result of exposure to a solvent which contained 80% pentane, 14% heptane, and only 5% hexane [36]. Although neither the duration of exposure to the solvent nor the concentration of the solvent in the environment was described, the authors [36] concluded that pentane and heptane might also cause polyneuropathy. It was experimentally shown [41,44] that the concentration of an alkane required to cause the development of acute toxic effects decreases as the carbon number of an alkane increases. It is reasonable to conclude that this trend applies to the effects of long-term exposures to these compounds.

Truhaut et al [20] exposed rats to technical grade hexane, which contained pentane, hexane, heptane, cycloalkanes, and benzene, and to technical grade heptane, which contained heptane, octane, cycloalkanes, toluene, and benzene. Exposure to the two grades of alkanes resulted in the development of similar signs of neurologic disorder in two groups of rats. The authors noted that components other than straight-chain alkanes might have been responsible for some of the results observed.

On the basis of these studies [20,36,41,44], TWA concentrations of 350 mg/cu m are also recommended as the environmental limits for pentane, heptane, and octane. On a volume/volume basis, these concentrations are equal to about 120 ppm pentane, 100 ppm hexane, 85 ppm heptane, and 75 ppm octane. The recommended limits decrease slightly with increasing carbon number. In addition, ceiling concentration limits of 1,800 mg/cu m (about 610 ppm pentane, 510 ppm hexane, 440 ppm heptane, and 385 ppm octane), based on a sample collection period of 15 minutes, are recommended to protect workers from acute exposures which might cause effects such as vertigo or other adverse reactions which could result in accident-proneness.

In most workplace situations, workers will be exposed to a mixture of alkanes rather than to a single alkane isomer. Because similar effects result from acute exposures to hexane and to heptane [41], and adverse effects produced by the alkanes tend to increase as the carbon number of the alkane increases [12,41], it seems likely that components of an alkane mixture may exert additive toxic effects.

In the absence of more substantial data on mixtures and on the metabolism of individual alkanes, environmental limits of 350 mg/cu m of

total alkanes as a TWA concentration and 1,800 mg/cu m of total alkanes as a 15-minute ceiling concentration are recommended.

(b) Sampling and Analysis

Sampling and analytical methods were reviewed in Chapter IV. According to the recommended sampling method, airborne alkane vapors are collected in charcoal-filled tubes and then desorbed from the charcoal with carbon disulfide. An aliquot of the solution of desorbed alkanes and carbon disulfide is analyzed with a gas chromatograph. The areas of the resulting peaks are determined and compared with those of injected standards. The sampling method was chosen because it is thought to be the best available at the present time and is expected to provide adequate collection efficiency for airborne alkanes. The gas-chromatographic method of analysis was selected because it is sensitive and relatively simple to perform. The method is not entirely specific for alkanes. Other compounds having the same retention times as the alkanes being analyzed will interfere with the analysis; however, mass spectrometry can be used to identify some of the eluted compounds (see Appendix II). To ensure that sampling and analysis information is available for later reference, the employer should keep records of environmental monitoring for at least 30 years.

(c) Medical Surveillance

The neurotoxicity of hexane and the possible neurotoxicity of pentane, heptane, and octane have been discussed in Chapter III. The possibility of the development of polyneuropathy from exposure to alkanes warrants a requirement for preplacement physical examinations directed towards the nervous system. In addition, similar physical examinations

giving particular attention to the skin and to the nervous system should be made on an annual basis. Preplacement examinations can serve as a useful basis for comparison in the event that overexposure to alkanes occurs. To ensure that these records are available if needed, the employer should keep them for 30 years after termination of a worker's employment.

(d) Labeling and Posting

Containers holding 10% or more alkanes should bear labels which provide a brief description of the hazards associated with the alkanes and the precautions necessary for safe use and minimal exposure. Signs containing similar information should be posted in areas where alkanes are stored in bulk quantities or where there is occupational exposure to alkanes.

(e) Personal Protective Equipment

Alkanes are moderate eye irritants; the use of safety glasses or goggles is recommended when contact of alkanes with the eyes is likely. Other personal protective equipment should include respirators, gloves, and other protective clothing when necessary. The types of respiratory protective devices described in Table I-1 are those approved under the provisions of 30 CFR 11 for the concentrations specified. In conjunction with this approval, other factors have been considered for each class of alkanes [111].

(f) Information and Education

The employer should institute a continuing education program to ensure that all employees occupationally exposed to alkanes have current knowledge of job hazards, signs and symptoms of overexposure, proper maintenance and emergency procedures, proper use of protective clothing and



equipment, and precautions to take to ensure safe use of, and minimal exposure to, alkanes. Where a potential for emergencies exists, periodic drills should be held to provide employees with an opportunity to develop skill in dealing with emergency situations.

(g) Work Practices

Work practices are discussed in Chapter VI. Precautions against fire and explosion hazards are emphasized to ensure that flammable substances are handled properly and that their vapors do not build up to explosive levels in the work environment.

(h) Action Level

It is recognized that many workers handle small amounts of either pentane, hexane, heptane, or octane or work in situations where, regardless of the amount used, there is only negligible contact with these substances. Under these conditions, compliance with only a limited number of the provisions of this recommended standard, which has been prepared primarily to protect the workers' health under more hazardous circumstances, should be necessary. Concern for the workers' health requires that protective measures be instituted below the enforceable limits to ensure that exposures stay below those limits. A TWA concentration of 200 mg/cu m has been chosen as an action level on the basis of professional judgment rather than on quantitative data that delineate nonhazardous areas from areas in which a hazard may exist. Occupational exposure to alkanes has been defined as worker exposure above the action level, thereby delineating those work situations which do not require the expenditure of health resources for environmental and medical monitoring and associated recordkeeping. However, because of nonrespiratory hazards such as those

resulting from skin or eye contact or from ingestion, it is recommended that appropriate work practices and protective measures to prevent topical contact or ingestion be required regardless of the air concentration.