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## IX. APPENDIX I

### BENZENE HAZARD

Benzene, an aromatic hydrocarbon derived primarily through the refinement and fractionation of crude petroleum, has a boiling point of 80.1 C (176 F) at 760 mmHg, and it may be a contaminant of some samples of refined petroleum solvents, especially if the solvent has a boiling range near or encompassing the boiling point of benzene. The extent of this contamination will also vary depending on the inherent chemical composition of the crude oil and the method of distillation in the refinery [155].

It has been shown by Elkins et al [156] that the vapor pressure of benzene in mixtures deviates from Raoult's Law and, therefore, the benzene vapor concentration resulting from handling such mixtures will frequently be higher than would be expected from the composition of the solvent.

Elkins and Pagnotto [157] felt that, if the benzene content of a solvent ranged from 1-4% in volume, ordinary use of the solvent would not produce benzene vapor hazards, but, if the concentration of benzene was greater than 5%, the possibility of "substantial" exposure to benzene vapors resulting from the "free" use of the solvent must be considered.

Benzene has been recognized as causing serious deleterious effects such as blood dyscrasias in humans and experimental animals, and, in 1974, NIOSH issued criteria and recommendations for occupational exposure to this compound [158]. Acute poisoning by benzene results primarily from its narcotic action. The inhalation of a high concentration of benzene (ie, 3,000 ppm for 0.1-1 hour) may cause a state of excitation and euphoria

(benzol jag) followed by drowsiness, fatigue, vertigo, nausea, and vomiting. With higher concentrations (ie, 7,500 ppm for 0.5-1 hour) or longer exposure times, convulsions followed by paralysis, loss of consciousness, and death from respiratory failure may result. The inhalation of small amounts of benzene over long periods have caused blood dyscrasias including aplastic anemia, leukopenia, and thrombocytopenia. Additional signs and symptoms of chronic toxicity may include headache, dizziness, fatigue, loss of appetite, irritability, nervousness, and nosebleed and other hemorrhagic manifestations. When Criteria for a Recommended Standard...Occupational Exposure to Benzene [158] was published, NIOSH recognized that there were data which suggested a relationship between the exposure to benzene and the occurrence of leukemia. However, at that time, there were insufficient epidemiologic investigations of the long-term relations of mortality and morbidity due to leukemia in the population at large and in those who work with benzene to classify it as a carcinogen.

In 1976, NIOSH issued an Update Criteria and Recommendations for a Revised Benzene Standard [159] and recognized that there was now sufficient evidence to conclude that benzene is leukemogenic. Since benzene causes progressive, malignant diseases of the hematopoietic system, NIOSH recommended that, for regulatory purposes, benzene should be considered carcinogenic in man. It was also recommended that the use of benzene as a solvent or diluent in open operations should be prohibited. NIOSH recommended that occupational exposure be controlled so that no worker will be exposed to benzene in excess of 3.2 mg/cu m (1 ppm) in air as determined by an air sample collected at 1 liter/minute for 2 hours.

As a consequence of the toxicity and carcinogenic potential of benzene, the benzene content of a solvent should be determined, and, if it is found to be present, air monitoring should be instituted to ensure compliance to the federal standard. When occupational exposure to benzene occurs, work practices like those described in Criteria for a Recommended Standard....Occupational Exposure to Benzene [158] should be instituted.

## X. APPENDIX II

### METHOD FOR THE SAMPLING AND ANALYSIS OF PETROLEUM ETHER

#### Atmospheric Sampling

A combustible gas meter should be used to determine petroleum ether concentrations in areas where exposure is suspected. Instruments used for this purpose must be approved as intrinsically safe by the Mining Enforcement and Safety Administration. When a combustible gas meter is used to evaluate conformance with the recommended environmental limits, a sufficient number of samples must be taken so that representative TWA and ceiling concentrations may be determined.

#### Sampling Procedure

Follow the instructions which are given in the manual for each combustible gas meter type. Typically, the sampling procedure will require the following steps:

- (a) Sweep the combustion chamber free of combustible gases and fill it with fresh air.
- (b) Turn on the batteries and apply the proper voltage to the bridge.
- (c) Balance the bridge to zero deflection on the meter while the fresh air is in the open chamber.
- (d) Draw the air sample into the meter and record the meter reading. Repeat this at least three times; calculate and record the average of the readings.



(e) Determine the concentration of petroleum ether samples from a calibration curve.

(f) Record a description of sampling location and conditions such as temperature, pressure, equipment used, time, rate of sampling, and any other pertinent information.

## XI. APPENDIX III

### METHOD FOR SAMPLING REFINED PETROLEUM SOLVENTS IN AIR

In order to evaluate conformance with the recommended environmental limits, air concentrations of rubber solvent, varnish makers' and painters' naphtha, mineral spirits, Stoddard solvents, and kerosene must be measured within the individual worker's breathing zone. Sampling procedures must conform with the following criteria.

#### Atmospheric Sampling

Collect breathing zone or personal samples representative of the individual employee's exposure. At the time of sample collection, record a description of sampling location and conditions, equipment used, time and rate of sampling, and any other pertinent information. Collect enough samples to permit calculation of a TWA exposure for every operation or location in which there is exposure to any refined petroleum solvents.

#### (a) Equipment

The sampling train consists of a charcoal tube and a vacuum pump.

(1) Charcoal tubes: Glass tubes, with both ends flame-sealed, 7-cm long with a 6-mm OD and a 4-mm ID, containing two sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The primary section contains 100 mg of charcoal, the backup section, 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of glass wool is placed in front of the primary section. Tubes with the above specifications are commercially

available. It should be noted that when conditions of very high humidity exist, evident by the visible condensation within the tube, the collection efficiency of the sampling tube will be seriously reduced.

(2) Pump: A battery-operated pump, complete with clip for attachment to the employee's belt, capable of operating at 200 ml/minute or less.

(b) Calibration

The accurate calibration of a sampling pump is essential for the correct interpretation of the volume sampled. The frequency of calibration is dependent on the use, care, and handling to which the pump is subjected. Pumps should also be recalibrated if they have been misused or if they have just been repaired or received from a manufacturer. If the pump receives hard usage, more frequent calibration may be necessary. Maintenance and calibration should be performed on a regular schedule and records of these should be kept.

Ordinarily, pumps should be calibrated in the laboratory both before they are used in the field and after they have been used to collect a large number of field samples. The accuracy of calibration is dependent on the type of instrument used as a reference. The choice of calibration instrument will depend largely on where the calibration is to be performed. For laboratory testing, a soapbubble meter is recommended, although other standard calibrating instruments can be used. The actual setups will be similar for all instruments.

Instructions for calibration with the soapbubble meter follow. If another calibration device is selected, equivalent procedures should be used. The calibration setup for personal sampling pumps with a charcoal

tube is shown in Figure XIV-1. Since the flowrate given by a pump is dependent on the pressure drop across the sampling device, in this case a charcoal tube, the pump must be calibrated while operating with a representative charcoal tube in line.

(1) Check the voltage of the pump battery with a voltmeter to ensure adequate voltage for calibration. Charge the battery if necessary.

(2) Break the tips of a charcoal tube to produce openings of at least 2 mm in diameter.

(3) Assemble the sampling train as shown in Figure XIV-1.

(4) Turn on the pump and moisten the inside of the soapbubble meter by immersing the buret in the soap solution. Draw bubbles up the inside until they are able to travel the entire buret length without bursting.

(5) Adjust the pump flowmeter to provide the desired flowrate.

(6) Check the mercury manometer to ensure that the pressure drop across the sampling train does not exceed 1 inch of mercury at 1 liter/minute or less.

(7) Start a soapbubble up the buret and measure with a stopwatch the time it takes the bubble to move from one calibration mark to another.

(8) Repeat the procedure in (7) above at least three times, average the results, and calculate the flowrate by dividing the volume between the preselected marks by the time required for the soapbubble to traverse the distance. If, for the pump being calibrated, the volume of

air sampled is calculated as the product of the number of strokes times a stroke factor (given in units of volume/stroke), the stroke factor is the quotient of the volume between the two preselected marks divided by the number of strokes.

(9) Data for the calibration include the volume measured, elapsed time or number of strokes of the pump, pressure drop, air temperature, atmospheric pressure, serial number of the pump, date, and name of the person performing the calibration.

(c) Sampling Procedure

(1) Break both ends of the charcoal tube to provide openings of at least 2 mm, which is half the ID of the tube. A smaller opening causes a limiting orifice effect which reduces the flow through the tube. The smaller section of charcoal in the tube is used as a backup section and therefore is placed nearest the sampling pump. Use tubing to connect the back of the tube to the pump, but tubing must never be put in front of the charcoal tube. The tube is supported in a vertical position within the employee's breathing zone.

(2) Sample a maximum of 10 liters of air at a flowrate not in excess of 200 ml/minute. A sampling rate of 20 ml/minute would collect a volume of 9.6 liters in an 8-hour period. For the determination of ceiling concentrations the sampling time is 15 minutes at a sampling rate of 200 ml/minute. In addition to the personal and ceiling samples, a bulk air sample may also be collected. This air sample should be taken by drawing air through a charcoal tube at 200 ml/minute for 4-6 hours.

(3) Measure and record the temperature and pressure of the atmosphere being sampled.

(4) Treat at least one charcoal tube in the same manner as the sample tubes (break, seal, and ship), except do not draw air through it. This tube serves as a blank.

(5) Immediately after samples are collected, cap the charcoal tubes with plastic caps. Do not use rubber caps. To minimize breakage during transport, pack capped tubes tightly in a shipping container.

#### Shipping Samples

Prior to shipping, the charcoal tubes should be packed tightly and padded to minimize breakage during shipping. A sample of the bulk material (approximately 20 ml), of the same batch of material which was being used in the plant at the time of the sampling, should be submitted to the laboratory in a glass container with a polymer-lined cap. This sample should not be transported in the same container as the charcoal tubes.