

## XI. APPENDIX III

### SAMPLING AND ANALYTICAL METHOD FOR DGE

This sampling and analytical method is adapted from a method tested by NIOSH [79]. It was found unsuitable for determining DGE at the current Federal standard of 2.8 mg/cu m because recovery of DGE from the sampling tubes was unacceptably low. However, it is believed that, with immediate desorption of samples as described below, this method can be used to measure DGE in air at the recommended concentration limit of 1.0 mg/cu m.

#### Principle of the Method

A known volume of air is drawn through a charcoal tube to collect organic vapors. The sample is immediately desorbed with methylene chloride and analyzed by gas chromatography. The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

#### Range and Sensitivity

The range and sensitivity of this method is dependent on the decomposition of the DGE on the charcoal prior to analysis. If decomposition time is minimized, the recovery of DGE from the samples should be adequate to analyze for the compound at the recommended standard.

### Interferences

When the amount of water in the air is so great that condensation actually occurs in the charcoal tube, organic vapors will not be trapped efficiently. When two or more compounds are known or suspected to be present in the air, such information, including the suspected identities of the compounds, should be transmitted with the sample. It must be emphasized that any compound that has the same retention time as DGE at the operating conditions described in this method is an interference. Retention-time data on a single column cannot be considered proof of chemical identity. If the possibility of interference exists, separation conditions (column packing, temperature, etc) must be changed to circumvent the problem.

### Precision and Accuracy

The Coefficient of Variation (CVT) and standard deviation at half the current Federal standard (1.5 mg/cu m) for DGE using this method were 0.081 and 0.090, respectively [79]. While the CVT and standard deviation for this method have not been determined at the recommended limit of 1.0 mg/cu m, it is likely that the method as modified will be able to detect DGE at this limit given a standard deviation of 0.1.

### Advantages and Disadvantages of the Method

The sampling method uses a small, portable sampling device that involves no liquids. Interferences are minimal, and most of those that do occur can be eliminated by altering chromatographic conditions. The tubes

are analyzed by means of a quick instrumental method. The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample simply by changing gas-chromatographic conditions from isothermal to a temperature-programmed mode of operation.

The major disadvantage of this method is the necessity for immediate desorption of samples and the attendant problems of breakage, spillage, and evaporation associated with transporting liquid samples to the analytical laboratory.

Another disadvantage is that the amount of sample that can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained from the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists. The precision of the method is affected by the reproducibility of the pressure drop across the tubes. This drop will affect the flowrate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

### Apparatus

(a) An approved and calibrated personal sampling pump whose flow can be determined within  $\pm 5\%$  at the recommended flowrate.

(b) Charcoal tubes: glass tube with both ends flame sealed, 7-cm-long with a 6-mm outer diameter and a 4-mm inner diameter, containing two sections of 20/40-mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600 C prior to packing. The adsorbing 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 silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than 1 inch of mercury at a flowrate of 1 liter/minute.

(c) Glass vials with Teflon-lined screw caps, for desorbing and shipping samples.

(d) Gas chromatograph equipped with a flame ionization detector.

(e) Column (10-foot x 1/8-inch stainless steel) packed with 5% Carbowax 20M on 80/100-mesh acid-washed DMCS Chromosorb W.

(f) An electronic integrator or some other suitable method for measuring.

(g) Microliter syringes: 10- $\mu$ l, and other convenient sizes for making standards.

(h) Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

(i) Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

#### Reagents

(a) DGE, reagent grade.

(b) Methylene chloride, chromatographic quality.

(c) Nitrogen, purified.

(d) Hydrogen, prepurified.

(e) Filtered compressed air.

### Sampling Procedure

(a) Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line, as shown in Figure XIV-1. This will minimize errors associated with uncertainties in the sample volume collected.

(b) Collection and Shipping of Samples.

(1) Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

(2) The smaller section of charcoal is used as a backup and should be positioned nearest the sampling pump.

(3) The charcoal tube should be placed in a vertical position during sampling to minimize channeling through the charcoal.

(4) Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

(5) The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

(6) The charcoal in the front and back section of the tube should be transferred to separate glass vials immediately after sampling. One milliliter of methylene chloride should be added to each vial, and they should be capped with Teflon-lined screw caps.

(7) One tube should be handled in the same manner as the sample tube (break, desorb, and transport), except that no air is drawn through this tube. An intact charcoal tube should also be shipped to the laboratory with the samples.

(8) Capped vials should be packed tightly and padded before they are shipped to minimize breakage during shipping.

#### Analysis of Samples

(a) Gas-chromatographic Conditions. The typical operating conditions for the gas chromatograph are:

- (1) Nitrogen carrier gas flow, 50 ml/minute (60 psig).
- (2) Hydrogen gas flow to detector, 65 ml/minute (24 psig).
- (3) Air flow to detector, 500 ml/minute (50 psig).
- (4) Injector temperature, 220 C.
- (5) Manifold temperature (detector), 275 C.
- (6) Column temperature, 205 C

(b) Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blowback or distillation within the syringe needle, one should employ the solvent-flush injection technique. The 10- $\mu$ l syringe is first flushed with solvent several times to wet the barrel and plunger. Draw 3  $\mu$ l of solvent into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2  $\mu$ l to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5- $\mu$ l aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2  $\mu$ l to minimize evaporation of the sample from the tip of the needle. Observe that the

sample occupies 4.9-5.0  $\mu$ l in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

(c) Area Measurement. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

#### Determination of Desorption Efficiency

(a) Importance of Determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

(b) Procedure for Determination. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5-inch, 4-mm inner diameter glass tube, flame-sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of DGE is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. The amount injected is equivalent to that present in an air sample at the selected level. Six tubes at each of three levels (0.5, 1, and 2 times the standard) are prepared in this manner and allowed to stand at least overnight to assure complete adsorption of the DGE onto the

charcoal. These tubes are referred to as the samples. A parallel blank tube is also prepared. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube. Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of methylene chloride with the same syringe used in the preparation of the samples. These are analyzed with the samples. The desorption efficiency (DE) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or:

$$DE = \frac{\text{Average weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of DGE collected on the charcoal. The desorption efficiency is plotted against the weight of DGE found.

#### Calibrations and Standards

It is convenient to express concentrations of standards in terms of mg/ml of methylene chloride, because samples are desorbed in this amount of methylene chloride. The density of DGE is used to convert mg into  $\mu$ l for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same gas-chromatographic conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the analysis of samples is done. This will minimize the effect of known day-to-day variations and variations during the same day in the gas-chromatographic detector response.



### Calculations

The weight in mg corresponding to each peak area is read from the standard curve. No volume corrections are needed, because the standard curve is based on mg/ml of methylene chloride and the volume of sample injected is identical to the volume of the standards injected.

Corrections for the blank must be made for each sample:

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

Add the weights found in the front and backup sections to get the total weight in the sample.

Read the desorption efficiency from the curve for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{DE}}$$

Determine the volume (in liters) of air sampled at ambient conditions based on the appropriate information, such as flowrate in liters/minute multiplied by sampling time. If a pump using a rotameter for flowrate control was used for sample collection, a pressure and temperature correction must be made for the indicated flowrate when the pump was

calibrated under substantially different conditions than those that exist during sampling. The expression for the correction is:

$$\text{Corrected volume} = f \times t \left( \sqrt{\frac{P_1 \times T_2}{P_2 \times T_1}} \right)$$

where:

- f = flowrate during sampling
- t = sampling time
- P<sub>1</sub> = pressure during calibration of sampling (mmHg)
- P<sub>2</sub> = pressure of air sampled (mmHg)
- T<sub>1</sub> = temperature during calibration of sampling pump (K)
- T<sub>2</sub> = temperature of air sampled (K)

The concentration of DGE in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg} \times 1,000 \text{ (liters/cu m)}}{\text{Air volume sampled (liters)}}$$

Another method of expressing concentration is ppm:

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{130} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

- P = pressure (mmHg) of air sampled
- T = temperature (C) of air sampled
- 24.45 = molar volume (liters/mole) at 25 C and 760 mmHg
- 130 = molecular weight (g/mole) of DGE
- 760 = standard pressure (mmHg)
- 298 = standard temperature (K)

XII. APPENDIX IV  
MATERIAL SAFETY DATA SHEET

The following items of information which are applicable to a specific product or material shall be provided in the appropriate block of the Material Safety Data Sheet (MSDS).

The product designation is inserted in the block in the upper left corner of the first page to facilitate filing and retrieval. Print in upper case letters as large as possible. It should be printed to read upright with the sheet turned sideways. The product designation is that name or code designation which appears on the label, or by which the product is sold or known by employees. The relative numerical hazard ratings and key statements are those determined by the rules in Chapter V, Part B, of the NIOSH publication, An Identification System for Occupationally Hazardous Materials. The company identification may be printed in the upper right corner if desired.

(a) Section I. Product Identification

The manufacturer's name, address, and regular and emergency telephone numbers (including area code) are inserted in the appropriate blocks of Section I. The company listed should be a source of detailed backup information on the hazards of the material(s) covered by the MSDS. The listing of suppliers or wholesale distributors is discouraged. The trade name should be the product designation or common name associated with the material. The synonyms are those commonly used for the product, especially

formal chemical nomenclature. Every known chemical designation or competitor's trade name need not be listed.

(b) Section II. Hazardous Ingredients

The "materials" listed in Section II shall be those substances which are part of the hazardous product covered by the MSDS and individually meet any of the criteria defining a hazardous material. Thus, one component of a multicomponent product might be listed because of its toxicity, another component because of its flammability, while a third component could be included both for its toxicity and its reactivity. Note that a MSDS for a single component product must have the name of the material repeated in this section to avoid giving the impression that there are no hazardous ingredients.

Chemical substances should be listed according to their complete name derived from a recognized system of nomenclature. Where possible, avoid using common names and general class names such as "aromatic amine," "safety solvent," or "aliphatic hydrocarbon" when the specific name is known.

The "%" may be the approximate percentage by weight or volume (indicate basis) which each hazardous ingredient of the mixture bears to the whole mixture. This may be indicated as a range or maximum amount, ie, "10-40% vol" or "10% max wt" to avoid disclosure of trade secrets.

Toxic hazard data shall be stated in terms of concentration, mode of exposure or test, and animal used, eg, "100 ppm LC50-rat," "25 mg/kg LD50-skin-rabbit," "75 ppm LC man," or "permissible exposure from 29 CFR 1910.1000," or, if not available, from other sources of publications such as the American Conference of Governmental Industrial Hygienists or the

American National Standards Institute Inc. Flashpoint, shock sensitivity, or similar descriptive data may be used to indicate flammability, reactivity, or similar hazardous properties of the material.

(c) Section III. Physical Data

The data in Section III should be for the total mixture and should include the boiling point and melting point in degrees Fahrenheit (Celsius in parentheses); vapor pressure, in conventional millimeters of mercury (mmHg); vapor density of gas or vapor (air = 1); solubility in water, in parts/hundred parts of water by weight; specific gravity (water = 1); percent volatiles (indicated if by weight or volume) at 70 F (21.1 C); evaporation rate for liquids or sublimable solids, relative to butyl acetate; and appearance and odor. These data are useful for the control of toxic substances. Boiling point, vapor density, percent volatiles, vapor pressure, and evaporation are useful for designing proper ventilation equipment. This information is also useful for design and deployment of adequate fire and spill containment equipment. The appearance and odor may facilitate identification of substances stored in improperly marked containers, or when spilled.

(d) Section IV. Fire and Explosion Data

Section IV should contain complete fire and explosion data for the product, including flashpoint and autoignition temperature in degrees Fahrenheit (Celsius in parentheses); flammable limits, in percent by volume in air; suitable extinguishing media or materials; special firefighting procedures; and unusual fire and explosion hazard information. If the product presents no fire hazard, insert "NO FIRE HAZARD" on the line labeled "Extinguishing Media."

(e) Section V. Health Hazard Information

The "Health Hazard Data" should be a combined estimate of the hazard of the total product. This can be expressed as a TWA concentration, as a permissible exposure, or by some other indication of an acceptable standard. Other data are acceptable, such as lowest LD50 if multiple components are involved.

Under "Routes of Exposure," comments in each category should reflect the potential hazard from absorption by the route in question. Comments should indicate the severity of the effect and the basis for the statement if possible. The basis might be animal studies, analogy with similar products, or human experiences. Comments such as "yes" or "possible" are not helpful. Typical comments might be:

Skin Contact--single short contact, no adverse effects likely; prolonged or repeated contact, possibly mild irritation.

Eye Contact--some pain and mild transient irritation; no corneal scarring.

"Emergency and First Aid Procedures" should be written in lay language and should primarily represent first-aid treatment that could be provided by paramedical personnel or individuals trained in first aid.

Information in the "Notes to Physician" section should include any special medical information which would be of assistance to an attending physician including required or recommended preplacement and periodic medical examinations, diagnostic procedures, and medical management of overexposed employees.

(f) Section VI. Reactivity Data

The comments in Section VI relate to safe storage and handling of hazardous, unstable substances. It is particularly important to highlight instability or incompatibility to common substances or circumstances, such as water, direct sunlight, steel or copper piping, acids, alkalies, etc. "Hazardous Decomposition Products" shall include those products released under fire conditions. It must also include dangerous products produced by aging, such as peroxides in the case of some ethers. Where applicable, shelf life should also be indicated.

(g) Section VII. Spill or Leak Procedures

Detailed procedures for cleanup and disposal should be listed with emphasis on precautions to be taken to protect employees assigned to cleanup detail. Specific neutralizing chemicals or procedures should be described in detail. Disposal methods should be explicit including proper labeling of containers holding residues and ultimate disposal methods such as "sanitary landfill" or "incineration." Warnings such as "comply with local, state, and Federal antipollution ordinances" are proper but not sufficient. Specific procedures shall be identified.

(h) Section VIII. Special Protection Information

Section VIII requires specific information. Statements such as "Yes," "No," or "If necessary" are not informative. Ventilation requirements should be specific as to type and preferred methods. Respirators shall be specified as to type and NIOSH or US Bureau of Mines approval class, ie, "Supplied air," "Organic vapor canister," etc. Protective equipment must be specified as to type and materials of construction.

(i) Section IX. Special Precautions

"Precautionary Statements" shall consist of the label statements selected for use on the container or placard. Additional information on any aspect of safety or health not covered in other sections should be inserted in Section IX. The lower block can contain references to published guides or in-house procedures for handling and storage. Department of Transportation markings and classifications and other freight, handling, or storage requirements and environmental controls can be noted.

(j) Signature and Filing

Finally, the name and address of the responsible person who completed the MSDS and the date of completion are entered. This will facilitate correction of errors and identify a source of additional information.

The MSDS shall be filed in a location readily accessible to employees exposed to the hazardous substance. The MSDS can be used as a training aid and basis for discussion during safety meetings and training of new employees. It should assist management by directing attention to the need for specific control engineering, work practices, and protective measures to ensure safe handling and use of the material. It will aid the safety and health staff in planning a safe and healthful work environment and in suggesting appropriate emergency procedures and sources of help in the event of harmful exposure of employees.



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## MATERIAL SAFETY DATA SHEET

I PRODUCT IDENTIFICATION		
MANUFACTURER'S NAME	REGULAR TELEPHONE NO. EMERGENCY TELEPHONE NO.	
ADDRESS		
<b>TRADE NAME</b>		
<b>SYNONYMS</b>		
II HAZARDOUS INGREDIENTS		
MATERIAL OR COMPONENT	%	HAZARD DATA
III PHYSICAL DATA		
BOILING POINT, 760 MM HG		MELTING POINT
SPECIFIC GRAVITY (H <sub>2</sub> O = 1)		VAPOR PRESSURE
VAPOR DENSITY (AIR = 1)		SOLUBILITY IN H <sub>2</sub> O, % BY WT
% VOLATILES BY VOL		EVAPORATION RATE (BUTYL ACETATE = 1)
APPEARANCE AND ODOR		

<b>IV FIRE AND EXPLOSION DATA</b>				
FLASH POINT (TEST METHOD)		AUTOIGNITION TEMPERATURE		
FLAMMABLE LIMITS IN AIR, % BY VOL.		LOWER		UPPER
EXTINGUISHING MEDIA				
SPECIAL FIRE FIGHTING PROCEDURES				
UNUSUAL FIRE AND EXPLOSION HAZARD				
<b>V HEALTH HAZARD INFORMATION</b>				
HEALTH HAZARD DATA				
ROUTES OF EXPOSURE				
INHALATION				
SKIN CONTACT				
SKIN ABSORPTION				
EYE CONTACT				
INGESTION				
EFFECTS OF OVEREXPOSURE				
ACUTE OVEREXPOSURE				
CHRONIC OVEREXPOSURE				
EMERGENCY AND FIRST AID PROCEDURES				
EYES				
SKIN				
INHALATION				
INGESTION				
NOTES TO PHYSICIAN				

<b>VI REACTIVITY DATA</b>	
CONDITIONS CONTRIBUTING TO INSTABILITY	
INCOMPATIBILITY	
HAZARDOUS DECOMPOSITION PRODUCTS	
CONDITIONS CONTRIBUTING TO HAZARDOUS POLYMERIZATION	
<b>VII SPILL OR LEAK PROCEDURES</b>	
STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED	
NEUTRALIZING CHEMICALS	
WASTE DISPOSAL METHOD	
<b>VIII SPECIAL PROTECTION INFORMATION</b>	
VENTILATION REQUIREMENTS	
SPECIFIC PERSONAL PROTECTIVE EQUIPMENT	
RESPIRATORY (SPECIFY IN DETAIL)	
EYE	
GLOVES	
OTHER CLOTHING AND EQUIPMENT	

**IX SPECIAL PRECAUTIONS**

PRECAUTIONARY  
STATEMENTS

OTHER HANDLING AND  
STORAGE REQUIREMENTS

PREPARED BY \_\_\_\_\_

ADDRESS \_\_\_\_\_

DATE \_\_\_\_\_