

Di(ethylene glycol) ethyl ether acrylate



Method no: PV2132

Target concentration: 1 mg/m³

Procedure: Samples are collected by drawing a known volume of air through glass sampling tubes containing Chromosorb 106. Samples are extracted with 99:1 carbon disulfide: *N,N*-dimethylformamide and analyzed by GC using a flame ionization detector.

Recommended sampling time and sampling rate: 240 min at 0.2 L/min (48 L)

Reliable quantitation limit: 43 µg/m³

Status of method: Partially evaluated method. This method has been subjected to established evaluation procedures of the Methods Development Team and is presented for information and trial use.

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Mary Eide

Methods Development Team
Industrial Hygiene Chemistry Division
OSHA Salt Lake Technical Center
Sandy UT 84070-6406

1. General Discussion

1.1 Background

1.1.1 History

Air samples were received at OSHA Salt Lake Technical Center collected on Chromosorb 106 tubes with an analysis request for di(ethylene glycol) ethyl ether acrylate (DEGEEA). Chromosorb 106 is a nonpolar collection medium, therefore, carbon disulfide was first selected for the extraction solvent. While the extraction efficiency of dry spiked samples was 98.2%, spiked samples exposed to humid air had a loss of the DEGEEA in solution as they sat after shaking, such that the recovery after 6 hours was 83.2%. This indicated that there was a need for a polar modifier in the extraction solvent. A mixture of 99:1 carbon disulfide: *N,N*-dimethylformamide (CS₂:DMF) was tried next as the extraction solvent. The average recovery was 98.6%, and there was no loss of DEGEEA, in humidified samples, as the samples sat on the autosampler. The analyte was found to be well retained on the Chromosorb 106 tubes, with a retention efficiency recovery of 98.6% and the storage stability recovery was 97.8% on day 14 of ambient storage.

1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.)¹

DEGEEA is a contact irritant affecting the skin, eyes, upper respiratory tract, and mucous membrane. DEGEEA may cause sensitization through skin contact. Prolonged skin exposure may cause defatting and dermatitis.

1.1.3 Workplace exposure²

DEGEEA is used as a reactive multifunctional monomer for UV curing of inks and coatings.

1.1.4 Physical properties and other descriptive information^{3,4}

synonyms:	acrylic acid, 2-(2-ethoxyethoxy)ethyl ester; carbitol acrylate; ethylcarbitol acrylate; ethyldiglycol acrylate; 2-(2-ethoxyethoxy)ethyl acrylate; ethyl acrylate ester monomer; 2-propenoic acid, 2-(2-ethoxy)ethyl ester; Reactomer RC-20
CAS number:	7328-17-8
IMIS: ⁵	D945
molecular weight:	188.22
density (g/mL):	1.016
melting point:	-66 °C
boiling point:	95 °C
appearance:	clear liquid
flash point:	113 °C (235 °F) (closed cup)
odor:	ester-like

¹ Material Safety Data Sheet: Di(ethylene glycol) ethyl ether acrylate, Aldrich Chemical Co., Milwaukee, WI, (accessed 10/3/03).

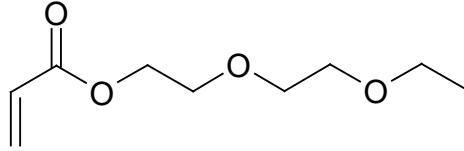
² Material Safety Data Sheet: Diethylene glycol ethyl ether acrylate, Chemwatch, Victoria, Australia, (accessed 12/17/03).

³ Material Safety Data Sheet: Di(ethylene glycol) ethyl ether acrylate, Aldrich Chemical Co., Milwaukee, WI, (accessed 10/3/03).

⁴ Material Safety Data Sheet: Ethyldiglycol acrylate, <http://www.corporate.BASF.com>, (accessed 12/17/03).

⁵ OSHA Chemical sampling Information, <http://www.osha.gov> (accessed 12/17/03).

molecular formula: C₉H₁₆O₄
solubility: soluble in most organic solvents
autoignition
temperature: 210 °C (410 °F)
structural formula:



This method was evaluated according to the OSHA SLTC "Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis".⁶ The Guidelines define analytical parameters, specify required laboratory tests, statistical calculations and acceptance criteria. The analyte air concentrations throughout this method are based on the recommended sampling and analytical parameters.

1.2 Detection limit of the overall procedure (DLOP) and reliable quantitation limit (RQL)

The DLOP is measured as mass per sample and expressed as equivalent air concentration, based on the recommended sampling parameters. Ten samplers were spiked with equal descending increments of analyte, such that the highest sampler loading was 9.41 µg of DEGEAA. This is the amount spiked on a sampler that would produce a peak at least 10 times the response for a sample blank. These spiked samplers were analyzed with the recommended analytical parameters, and the data obtained used to calculate the required parameters (standard error of estimate and slope) for the calculation of the DLOP. The slope was 715 and the SEE was 148. The RQL is considered the lower limit for precise quantitative measurements. It is determined from the regression line parameters obtained for the calculation of the DLOP, providing 75% to 125% of the analyte is recovered. The DLOP and RQL were 0.62 µg and 2.07 µg, respectively. The recovery at the RQL was 98.5%.

Table 1.2
Detection Limit of the Overall Procedure for DEGEAA

mass per sample (µg)	area counts (µV-s)
0.00	0
0.91	550
1.83	1021
2.74	1635
3.66	2216
4.57	2872
5.49	3640
6.40	4339
7.32	4939
8.23	5720
9.14	6859

⁶ Burreight, D.; Chan, Y.; Eide, M.; Elskamp, C.; Hendricks, W.; Rose, M. C. *Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis*; OSHA Salt Lake Technical Center, U.S. Department of Labor: Salt Lake City, UT, 1999.

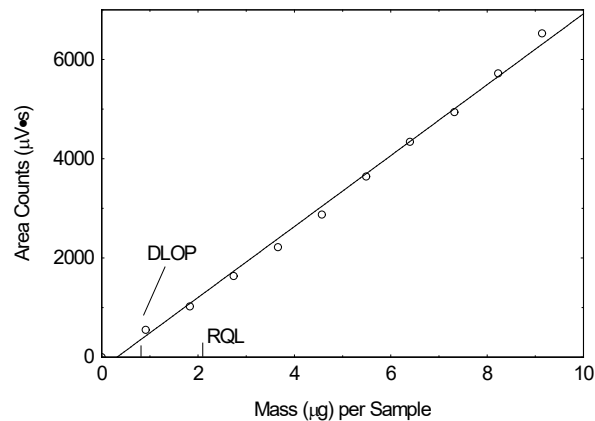


Figure 1.2.1 Plot of data to determine the DLOP/RQL for DEGEAA.
 $(y = 715x - 226)$

Below is a chromatogram of DEGEAA near the RQL. The recovery at the RQL was 98.5%.

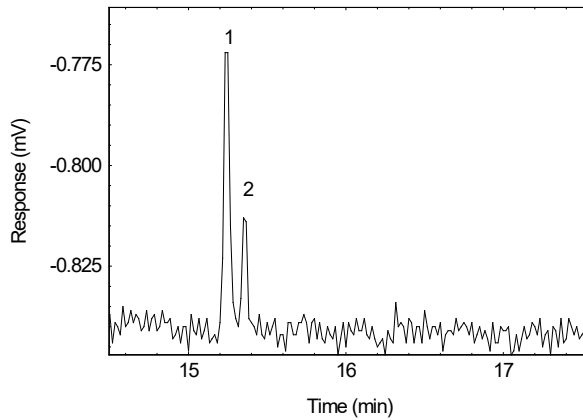


Figure 1.2.2 Chromatogram of the DEGEAA near the RQL.
 (Key: (1) DEGEAA, (2) interferant)

2. Sampling Procedure

All safety practices that apply to the work area being sampled should be followed. The sampling equipment should be attached to the worker in such a manner that it will not interfere with work performance or safety.

2.1 Apparatus

2.1.1 Samples are collected using a personal sampling pump calibrated, with the sampling device attached, to within $\pm 5\%$ of the recommended flow rate.

2.1.2 Samples are collected with 7-cm \times 4-mm i.d. \times 7-mm o.d. glass sampling tubes packed with two sections (100/50 mg) of Chromosorb 106. The sections are held in place with foam plugs and with a glass wool plug at the front. For this evaluation, commercially prepared sampling tubes were purchased from SKC, Inc. (Catalog no. 226-110, lot 2573).

2.2 Reagents

None required.

2.3 Technique

- 2.3.1 Immediately before sampling, break off the ends of the flame-sealed tube to provide an opening approximately half the internal diameter of the tube. Wear eye protection when breaking the tube. Use tube holders to minimize the hazard of broken glass. All tubes should be from the same lot.
- 2.3.2 The smaller section of the adsorbent tube is used as a back-up and is positioned nearest the sampling pump. Attach the tube holder to the sampling pump so that the adsorbent tube is in an approximately vertical position with the inlet facing down during sampling. Position the sampling pump, tube holder and tubing so they do not impede work performance or safety.
- 2.3.3 Draw the air to be sampled directly into the inlet of the tube holder. The air being sampled is not to be passed through any hose or tubing before entering the sampling tube.
- 2.3.4 After sampling for the appropriate time, remove the adsorbent tube and seal it with plastic end caps. Seal each sample end-to-end with an OSHA-21 form as soon as possible.
- 2.3.5 Submit at least one blank sample with each set of samples. Handle the blank sample in the same manner as the other samples except draw no air through it.
- 2.3.6 Record sample air volumes (liters), sampling time (minutes), and sampling rate (L/min) for each sample, along with any potential interferences on the OSHA-91A form.
- 2.3.7 Submit the samples to the laboratory for analysis as soon as possible after sampling. If delay is unavoidable, store the samples at refrigerator temperature. Ship any bulk samples separate from the air samples.

2.4 Extraction efficiency

The extraction efficiency was determined by spiking front sections of Chromosorb 106 tubes with DEGEEA at 0.1 to 2 times the target concentration, based on a 48-L air volume, for a loading of 4.57 to 91.4 µg/sample. These samples were stored overnight at ambient temperature and then extracted with 1 mL of extracting solvent for 30 minutes with shaking, and analyzed by GC-FID. The mean extraction efficiency over the studied range was 98.6%. The wet extraction efficiency was determined at 1 times the target concentration by liquid spiking the analyte onto Chromosorb 106 tubes which had 48-L humid air (absolute humidity of 15.9 mg/L of water, about 80% relative humidity at 22.2 °C) drawn through them immediately before spiking. The mean recovery for the wet samples was 98.9%.

Table 2.4
Extraction Efficiency (%) of DEGEEA

<u>level</u>		<u>sample number</u>						
<u>× target concn</u>	<u>µg per sample</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>mean</u>
0.1	4.57	97.4	97.2	98.2	98.3	97.0	97.6	97.6
0.5	22.9	99.1	99.3	98.5	98.4	98.8	99.0	98.9
1.0	45.7	99.1	98.5	98.9	98.6	99.2	98.8	98.9
1.5	68.6	99.0	98.3	99.3	98.7	99.4	97.9	98.8
2.0	91.4	98.9	99.0	99.1	99.0	99.4	98.8	99.0
1.0 (wet)	45.7	98.9	99.0	98.6	98.5	99.1	99.3	98.9

2.5 Retention efficiency

Six Chromosorb 106 tubes were spiked with 91.4 µg (1.9 mg/m³) of DEGEAA in the front sections, and allowed to equilibrate for 6 h. The tubes had 48-L humid air (absolute humidity of 15.9 mg/L of water, about 80% relative humidity at 22.2 °C) pulled through them at 0.2 L/min. The samples were extracted and analyzed. The mean recovery was 98.6%. There was no analyte found on the back-up section of any of the tubes.

Table 2.5
Retention Efficiency (%) of DEGEAA

section	sample number						mean
	1	2	3	4	5	6	
front of spiked tube	99.1	98.3	99.0	98.8	98.5	97.9	98.6
rear of spiked tube	0.0	0.0	0.0	0.0	0.0	0.0	0.0
total	99.1	98.3	99.0	98.8	98.5	97.9	98.6

2.6 Sample storage

Fifteen Chromosorb 106 tubes were each spiked with 45.7 µg (0.95 mg/m³) of DEGEAA. They were allowed to equilibrate for 6h, then they had 48 L of air, with an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 23 °C), drawn through them. Three samples were analyzed immediately, and the rest were sealed. Six were stored at room temperature (23°C), while the other six were stored at refrigerated temperature (4°C). Three samples stored at room temperature and three samples stored at refrigerated temperature were analyzed after 7 days and the remaining three of each set after 14 days. The amounts recovered indicate good storage stability for the time period studied.

Table 2.6
Storage Test for DEGEAA

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	99.5	98.3	98.9			
7	98.8	98.5	97.7	98.9	99.3	98.0
14	97.5	98.7	97.2	98.5	99.2	97.9

2.7 Recommended air volume and sampling rate

Based on the data collected in this evaluation, 48-L air samples should be collected at a sampling rate of 0.2 L/min for 240 minutes.

2.8 Interferences (sampling)

2.8.1 There are no known compounds which will severely interfere with the collection of DEGEAA.

2.8.2 Suspected interferences should be reported to the laboratory with submitted samples.

3. Analytical Procedure

Adhere to the rules set down in your Chemical Hygiene Plan. Avoid skin contact and inhalation of all chemicals and review all appropriate MSDSs.

3.1 Apparatus

- 3.1.1 A gas chromatograph equipped with an FID detector. For this evaluation, an Agilent 6890 GC was used.
- 3.1.2 A GC column capable of separating DEGEAA from the extraction solvent, internal standard, and any potential interferences. A 60-m × 0.32-mm i.d. DB-1 (1- μ m df) capillary column (J&W Scientific, Folsom, CA) was used in this evaluation.
- 3.1.3 An electronic integrator or some other suitable means of measuring peak areas. A Waters Millennium³² Data System and an Agilent integrator 3396 were used in this evaluation.
- 3.1.4 Glass vials with poly(tetrafluoroethylene)-lined caps. For this evaluation 2-mL vials were used.
- 3.1.5 A dispenser capable of delivering 1.0 mL of extraction solvent to prepare standards and samples. If a dispenser is not available, a 1.0-mL volumetric pipet may be used.
- 3.1.6 Volumetric flasks 10-mL and other convenient sizes for preparing standards.
- 3.1.7 Calibrated 10- μ L or 20- μ L syringe for preparing standards.
- 3.1.8 A mechanical shaker. An Eberbach mechanical shaker was used in this evaluation.

3.2 Reagents

- 3.2.1 Di(ethylene glycol) ethyl ether acrylate, technical grade. Aldrich 90% (lot 07619DF) was used in this evaluation.
- 3.2.2 Carbon disulfide, Reagent grade. EM Science Omni-Solv® 99.99% (lot 43279343), was used in this evaluation.
- 3.2.3 *N,N*-Dimethylformamide, anhydrous. Aldrich 99.8% (lot 04643LA) was used in this evaluation.
- 3.2.4 *p*-Cymene, reagent grade. Aldrich 99% (lot 11703TR) was used in this evaluation.
- 3.2.5 The extraction solvent solution was 99:1 carbon disulfide: DMF with 0.25 μ L/mL of *p*-cymene as internal standard.

3.3 Standard preparation

- 3.3.1 Prepare at least two stock standards by spiking microliter quantities of DEGEAA from a microliter syringe into volumetric flasks containing the extraction solution. Working analytical standards are prepared by serial dilutions of the stock standard with the extraction solvent. A stock standard of 5 μ L/10 mL (0.5 μ L/mL) is equivalent to 457 μ g/mL, based on the density and the purity of 90%. A 1:10 dilution of this stock standard is 45.7 μ g/mL, which is equivalent to 0.95 mg/m³ based on a 48 L air volume.
- 3.3.2 Bracket sample concentrations with standard concentrations. If, upon analysis, sample concentrations fall outside the range of prepared standards, prepare and analyze additional standards to confirm instrument response, or dilute high samples with extraction solvent and reanalyze the diluted samples. For this evaluation,

standards in the range of 0.91 to 183 µg/mL were used. A check standard from a second source should be prepared to check the calibration.

3.4 Sample preparation

3.4.1 Remove the plastic end caps from the sample tubes and carefully transfer each adsorbent section to separate 2-mL vials. Discard the glass tube, urethane foam plug and glass wool plug.

3.4.2 Add 1.0 mL of extraction solvent to each vial using the same dispenser as used for preparation of standards.

3.4.3 Immediately seal the vials with poly(tetrafluoroethylene)-lined caps.

3.4.4 Agitate the vials on a shaker or rotator for 30 minutes.

3.5 Analysis

3.5.1 Gas chromatographic conditions

GC conditions

zone

temperatures: initial 50 °C, hold 1 min, ramp at 10 °C/min to 170°C, hold 7 min
250 °C (injector)
250 °C (detector)

run time: 20 min

column gas flow: 3.2 mL/min (hydrogen)

injection size: 1.0 µL (10:1 split)

column: 60-m × 0.32-mm i.d. capillary DB-1 (df = 1 µm)

retention times: 4.0 min (carbon disulfide); 7.0 min (DMF); 11.8 min (*p*-cymene);
15.2 min (DEGEAA)

FID conditions

hydrogen flow: 30 mL/min

air flow: 400 mL/min

makeup flow: 25 mL/min
(nitrogen)

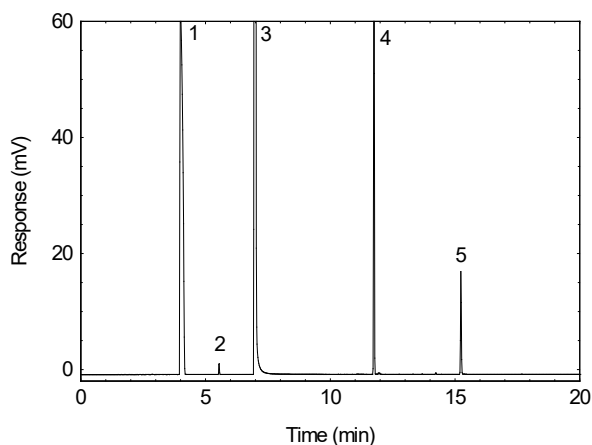


Figure 3.5.1 A chromatogram of 45.7 µg/mL DEGEAA in 99:1 CS₂:DMF with 0.25 µl/mL *p*-cymene internal standard. (Key: (1) CS₂; (2) benzene contaminant in the CS₂; (3) DMF; (4) *p*-cymene; (5) DEGEAA)

3.5.2 Peak areas are measured by an integrator or other suitable means.

3.5.3 An internal standard (ISTD) calibration method is used. A calibration curve can be constructed by plotting response of standard injections versus micrograms of analyte per sample. Bracket the samples with freshly prepared analytical standards over the range of concentrations.

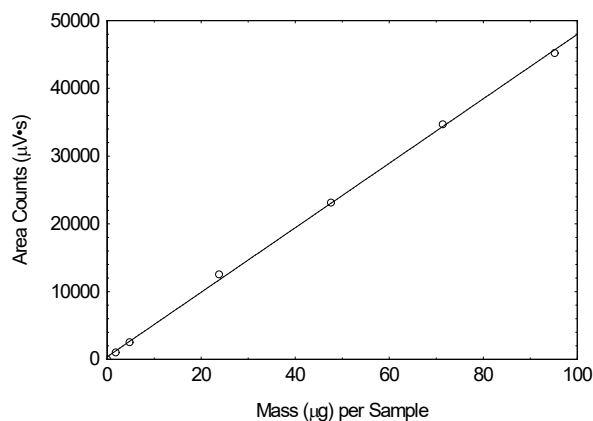


Figure 3.5.2 Calibration curve of DEGEEA. ($y = 476x + 388$)

3.6 Interferences (analytical)

3.6.1 Any compound that produces a GC response and has a similar retention time as the analyte is a potential interference. If any potential interferences were reported, they should be considered before samples are extracted. Generally, chromatographic conditions can be altered to separate an interference from the analyte.

3.6.2 When necessary, the identity or purity of an analyte peak may be confirmed by GC-mass spectrometry or by another analytical procedure. The mass spectrum in Figure 3.6.2 was from an analytical standard run on an Agilent 6890 GC with a 5973 Mass Selective Detector.

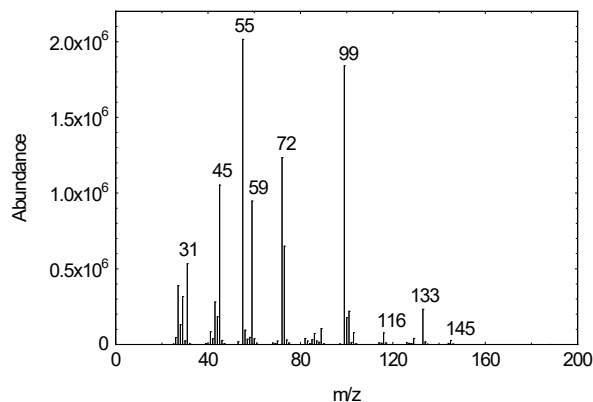


Figure 3.6.2 Mass spectrum of DEGEEA.

3.7 Calculations

The amount of analyte per sampler is obtained from the appropriate calibration curve in terms of micrograms per sample, uncorrected for extraction efficiency. This total amount is then corrected by subtracting the total amount (if any) found on the blank. The air concentration is calculated using the following formulas.

$$C_M = \frac{M}{VE_E}$$

where C_M is concentration by weight (mg/m³)
 M is micrograms per sample
 V is liters of air sampled
 E_E is extraction efficiency, in decimal form

4. Recommendations for Further Study

Collection, reproducibility, and other detection limit studies need to be performed to make this a fully validated method.