Method number:	PV2002
Target concentration:	100 ppm (1170 mg/m^3)
Procedure:	Samples are collected by drawing a known volume of air through glass sampling tubes containing Chromosorb 106. Samples are extracted with carbon disulfide and analyzed by GC using a flame ionization detector.
Recommended sampling time and sampling rate:	100 min at 0.1 L/min (10 L)
Reliable quantitation limit:	11.3 ppb
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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1. General Discussion

1.1 Background

1.1.1 History

Air samples were received at SLTC collected on Chromosorb 106 tubes requesting analysis for 2,2,4-trimethyl-1,3-pentanediol diisobutyrate. Analysis by gas chromatography with a flame ionization detector was chosen, because this compound is a liquid at room temperature. Carbon disulfide was selected for the extraction solvent and was found to give an extraction efficiency of 100.1%. The analyte was found to be well retained on the Chromosorb 106 tubes, with a retention efficiency recovery of 100.4% and the storage stability recovery of 99.5% on Day 14 of ambient storage. Along with these studies, charcoal tubes were also explored. The extraction efficiency on charcoal tubes using carbon disulfide as a solvent showed non-linear extraction, with an extraction efficiency of 98.1% for a loading of 23.34 mg to 88.6% for a loading of 1.167mg. The extraction efficiency with 99:1 carbon disulfide:dimethyl formamide averaged 100.8% over the range of 1.167 to 23.34 mg. The retention efficiency averaged 99.8%. The storage at ambient temperature was 98.2% on Day 14, indicating that charcoal tubes are a good alternative to the Chromosorb 106 tubes..

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

2,2,4-Trimethyl-1,3-pentandiol diisobutyrate is a contact irritant affecting the skin and mucous membrane.

1.1.3 Workplace exposure[2,3]

2,2,4-Trimethyl-1,3-pentanediol diisobutyrate is used as an intermediate in the manufacture of plasticizers, surfactants, pesticides, and resins. It is used as a viscosity control agent in plastisol, rotomolding, and rotocasting operations. It is used in the production of vinyl flooring as a hardening agent. Production exceeds one million pounds annually.

1.1.4 Physical properties and other descriptive information[4]

CAS number:	6846-50-0		
RTECS number:	SA1420000	molecular weight:	286.41
melting point:	-70 °C	boiling point:	280 °C
appearance:	clear liquid	molecular formula:	$C_{16}H_{30}O_4$
odor:	musty	flash point:	109 °C (230 °F)(cc)
autoignition temperature:	423 °C	density:	0.941
synonyms:	Isobutyric acid, 1-isopropyl-2,2-dimethyltrimethyl ester; Kodaflex TXIB; 2,2,4-trimethylpentanediol-1,3-diisobutyrate; TXIB		
solubility:	acetone, alcohol, benzene, and carbon tetrachloride		

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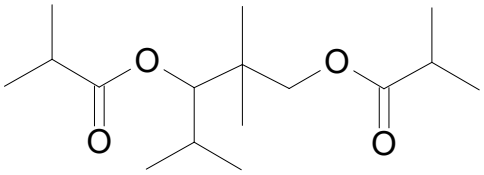
[1] Lewis, R., *Sax's Dangerous Properties of Industrial Materials,* Van Nostrand Reinhold: New York, 1992, p 3415.

[2] Howe-Grant, M., Kroschwitz, J., Ed, *Encyclopedia of Chemical Technology,* John Wiley & Sons: New York, 1992, vol 4 p 741.

[3] Environmental Defense Fund. http: www.scorecard.org/chemical-profiles/summary.tcl?edf_substance_id=6846-50-0 (accessed 11/16/99).

[4] Material Safety Data Sheet: 2,2,4-trimethyl-1,3-pentandiol diisobutyrate, Aldrich Chemical Co., Milwaukee, WI, Oct. 1999.

IMIS:[5] T350
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 concentrations, based on the recommended sampling parameters. Ten samplers were spiked with equal descending increments of analyte, such that the highest sampler loading was 10.35 µg of 2,2,4-trimethyl-1,3-pentanediol diisobutyrate. This is the amount spiked on a sampler that would produce a peak approximately 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 770.3 and the SEE was 101.8. 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 0.397µg and 1.32 µg respectively.

Table 1.2
Detection Limit of the Overall Procedure
for 2,2,4-Trimethyl-1,3-pentanediol diisobutyrate

mass per sample (µg)	area counts (µV-s)
0.00	0
1.04	638
2.07	1368
3.11	2265
4.14	3170
5.18	3966
6.21	4640
7.25	5620
8.28	6409
9.32	7029
10.35	7767

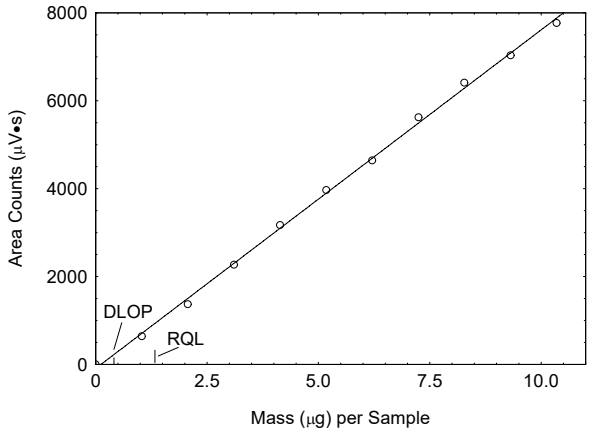


Figure 1.2.1. Plot of data to determine the DLOP/RQL for 2,2,4-trimethyl-1,3-pentandiol diisobutyrate. (Y = 770X - 90.8)

Below are chromatograms of the RQL level.

[5] OSHA Chemical sampling Information. Http://www.osha-slc.gov/ChemSamp_data/CH_273990.html (accessed 11/17/99).

[6] Burright, 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.

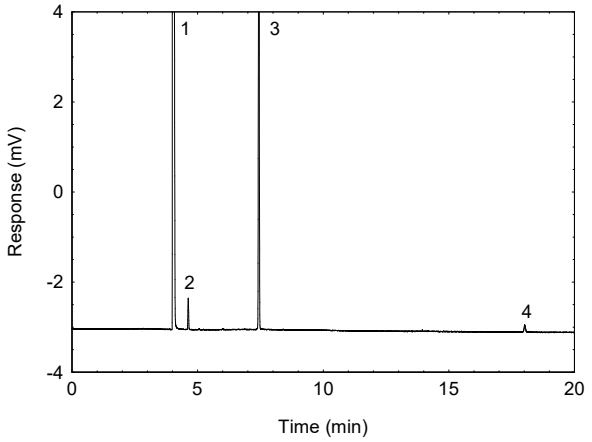


Figure 1.2.2. Chromatogram of the RQL of 2,2,4-trimethyl-1,3-pentanediol diisobutyrate. (1 = carbon disulfide; 2 = benzene (contaminant in the carbon disulfide); 3 = *p*-cymene; and 4 = 2,2,4-trimethyl-1,3-pentanediol diisobutyrate)

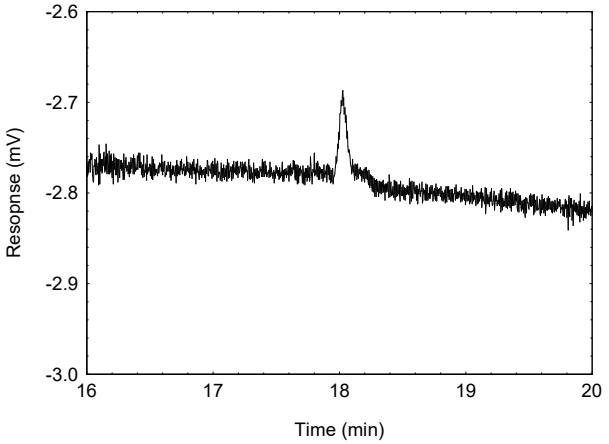


Figure 1.2.3 Chromatogram of the 2,2,4-trimethyl-1,3-pentandiol diisobutyrate peak in the standard near the RQL.

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 ±5% of the recommended flow rate.

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

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 ends. 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 sampler 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 (mL/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 liquid-spiking Chromosorb 106 with 2,2,4-trimethyl-1,3-pentandiol diisobutyrate at 0.1 to 2 times the target concentration. These samples were stored overnight at ambient temperature and then extracted for 30 minutes with occasional shaking, and analyzed. The mean extraction efficiency over the studied range was 100.1%. The wet extraction efficiency was determined at 1 times the target concentration by liquid spiking the analyte onto Chromsorb 106 tubes which had 10-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 99.8%.

Table 2.4
Extraction Efficiency (%) of 2,2,4-Trimethyl-1,3-pentandiol diisobutyrate

level		sample number						
× target concn	mg per sample	1	2	3	4	5	6	mean
0.1	1.17	97.4	100.0	101.6	99.6	100.6	99.6	99.8
0.25	2.92	99.9	100.4	100.8	99.7	100.4	100.3	100.3
0.5	5.83	99.3	99.2	99.7	100.5	100.0	101.4	100.0
1.0	11.7	100.9	101.2	102.0	101.8	98.9	99.1	100.7
1.5	17.5	100.1	100.4	99.5	99.3	99.9	100.1	99.9
2.0	23.3	99.2	100.3	98.7	100.2	100.1	99.9	99.7
1.0 (wet)	11.7	99.8	100.1	99.1	100.4	99.5	99.9	99.8

2.5 Retention efficiency

Six Chromosorb 106 tubes were spiked with 23.34 mg (199.2 ppm) of 2,2,4-trimethyl-1,3-pentanediol diisobutyrate and allowed to equilibrate for 6 h. The tubes had 10 L humid air (absolute humidity of 15.9 mg/L of water, about 80% relative humidity at 22.2 °C) pulled through them at 0.1 L/min. The samples were extracted and analyzed. The mean recovery was 100.4%. There was no analyte found on the backup section of any of the tubes.

Table 2.5
Retention Efficiency (%) of 2,2,4-Trimethyl-1,3-pentandiol diisobutyrate

	sample number						
section	1	2	3	4	5	6	mean
front	100.8	100.4	99.1	102.1	100.5	99.5	100.4
rear	0.0	0.0	0.0	0.0	0.0	0.0	0.0
total	100.8	100.4	99.1	102.1	100.5	99.5	100.4

2.6 Sample storage

Nine Chromosorb 106 tubes were each spiked with 11.67 mg (99.62 ppm) of 2,2,4-trimethyl-1,3-pentanediol diisobutyrate. They were allowed to equilibrate for 6 h, then 10 L of air, with an absolute

humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2 °C), was drawn through them. Three samples were analyzed immediately, and the rest were sealed and stored at room temperature. Three more were analyzed after 7 days of storage and the remaining three after 14 days of storage. The amounts recovered, which are corrected for extraction efficiency, indicate good storage stability for the time period studied.

Table 2.6
Storage Test for 2,2,4-Trimethyl-1,3-pentanediol diisobutyrate
(% Recovery)

	sample number			
time (days)	1	2	3	mean
0	100.9	101.2	101.2	100.3
7	98.0	99.1	99.1	98.6
14	99.6	99.6	99.6	99.5

2.7 Recommended air volume and sampling rate.

Based on the data collected in this evaluation, 10-L air samples should be collected at a sampling rate of 0.1 L/min for 100 minutes.

2.8 Interferences (sampling)

2.8.1 There are no known compounds which will severely interfere with the collection of 2,2,4-trimethyl-1,3-pentanediol diisobutyrate.

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. For this evaluation, a Hewlett-Packard 5890A Series II Gas Chromatograph equipped with a 7673A Automatic Sampler was used.

3.1.2 A GC column capable of separating 2,2,4-trimethyl-1,3-pentanediol diisobutyrate from the desorption solvent, internal standard and any potential interferences. A 60-m × 0.32-mm i.d. capillary DB-WAX with a 0.5-µm df (J&W Scientific, Folsom, CA) was used in the evaluation.

3.1.3 An electronic integrator or some other suitable means of measuring peak areas. A Waters Millennium[32] Data System was 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 desorbing solvent to prepare standards and samples. If a dispenser is not available, a 1.0-mL volumetric pipet may be used.

3.1.7 Volumetric flasks - 10-mL and other convenient sizes for preparing standards.

3.1.8 Calibrated 10-µL syringe for preparing standards.

3.2 Reagents

3.2.1 2,2,4-Trimethyl-1,3-pentandiol diisobutyrate, Reagent grade. Aldrich 99% (lot 08515DS) was used in this evaluation.

3.2.2 Carbon disulfide, Reagent grade. Omni-Solv 99.99% (lot 34279) was used for this evaluation.

3.2.3 *p*-Cymene, Reagent grade. Aldrich 99% (lot 11703TR) was used in this evaluation.

3.2.4 The extraction solvent was 0.25 µL/mL *p*-cymene in carbon disulfide.

3.2.5 GC grade nitrogen, air, and hydrogen.

3.3 Standard preparation

3.3.1 Prepare working analytical standards by injecting microliter amounts of 2,2,4-trimethyl-1,3-pentanediol diisobutyrate into volumetric flasks containing the extraction solvent. An analytical standard at a concentration of 11.67 mg/mL (12.4 µL/mL) is equivalent to 99.61 ppm based on a 10-liter air volume.

3.3.2 Bracket sample concentrations with working standard concentrations. If sample concentrations are higher than the concentration range of prepared standards, either analyze higher standards, or dilute the sample. The higher standards should be at least as high in concentration as the highest sample. Diluted samples should be prepared with extracting solvent to obtain a concentration within the existing standard range. The range of standards used in this study was from 0.001 to 28.23 mg/mL.

3.4 Sample preparation

3.4.1 Remove the plastic end caps from the sample tubes and carefully transfer the adsorbent sections 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 Shake the vials vigorously by hand several times during the next 30 minutes.

3.5 Analysis

3.5.1 Gas chromatograph conditions.

<u>GC conditions</u>	
zone temperatures:	100°C (column), hold 2 min, ramp at 10°C/min to 180°C, hold 10 min 250°C (injector) 250°C (detector)
run time:	20 min
column gas flow:	2.9 mL/min (hydrogen)
septum purge:	1.9 mL/min (hydrogen)
injection size:	1.0 µL (19:1 split)
column:	60-m × 0.32-mm i.d. capillary DB-WAX (0.5-µm df)
retention times:	3.98 min (carbon disulfide); 4.61 min (benzene contaminate in the carbon disulfide); 7.41 min (*p*-cymene); 18.01 min (2,2,4-trimethyl-1,3-pentanediol diisobutyrate)
<u>FID conditions</u>	
hydrogen flow:	38 mL/min
air flow:	450 mL/min
makeup flow:	30 mL/min (nitrogen)

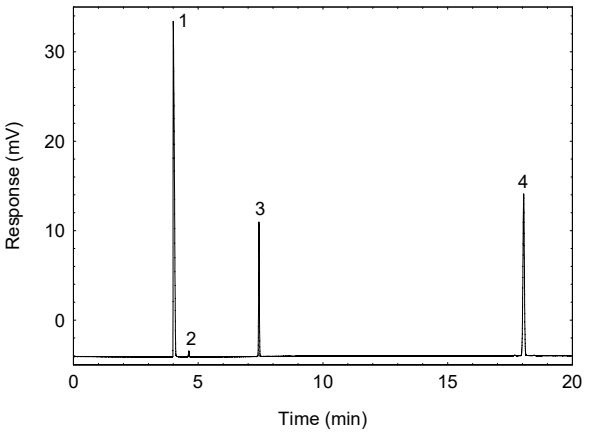


Figure 3.5.1. A chromatogram of 941 µg/mL 2,2,4-trimethyl-1,3-pentanediol diisobutyrate in carbon disulfide with 0.25 µL/mL *p*-cymene internal standard. Key: (1) carbon disulfide; (2) benzene contaminant in the carbon disulfide; (3) *p*-cymene; (4) 2,2,4-trimethyl-1,3-pentanediol diisobutyrate.

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 ISTD-corrected response of standard injections versus milligrams of analyte per sample. Bracket the samples with freshly prepared analytical standards over a range of concentrations.

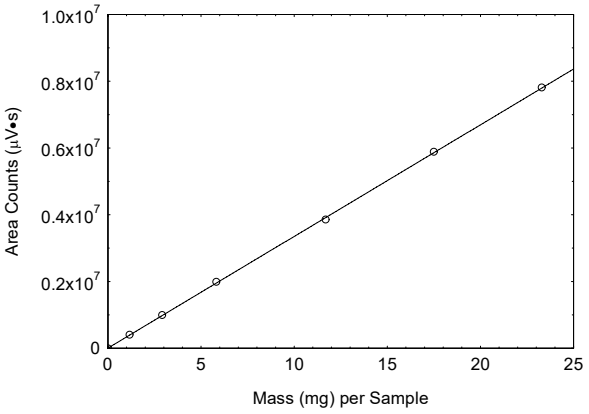


Figure 3.5.3. Calibration curve of 2,2,4-trimethyl-1,3-pentanediol diisobutyrate. (Y = 3.34E5x + 5808).

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 mass spectrometry or by another analytical procedure. The mass spectrum in Figure 3.6.2 was from the NIST spectral library.

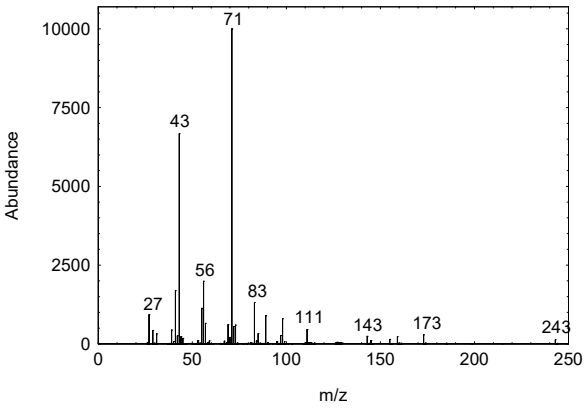


Figure 3.6.2. The mass spectrum of 2,2,4-trimethyl-1,3-pentanediol diisobutyrate.

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/m^3)
M is micrograms per sample
V is liters of air sampled
E_E is extraction efficiency, in decimal form

$$C_V = \frac{V_M C_M}{M_r}$$

where C_V is concentration by volume (ppm)
V_M is molar volume at 25 °C and 1 atm = 24.46
C_M is concentration by weight
M_r is molecular weight = 286.41

4. Recommendations for Further Study

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