



Diphenyl and Phenyl ether

Method number: PV2022

Target concentration: Diphenyl 0.2 ppm (1 mg/m³) OSHA TWA PEL
Phenyl ether 1 ppm (7 mg/m³) OSHA TWA PEL
Phenyl ether-Biphenyl mixture 1 ppm (7 mg/m³) OSHA TWA PEL

Procedure: Samples are collected by drawing a known volume of air through an XAD-7 tube. Samples are desorbed with carbon disulfide and analyzed by gas chromatography with a flame ionization detector (GC-FID).

Air volume and sampling rate studied: 100 minutes at 0.2 Lpm (20 L)

Status of method: Partially Validated method. This method has been only partially evaluated and is presented for information and trial use.

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Mary E. Eide

SOLVENTS BRANCH
OSHA Salt Lake Technical Center
Salt Lake City UT 84115-1802

1 General Discussion

1.1 Background

1.1.1 History of procedure

The OSHA Laboratory recently received air samples collected on XAD-7 sample tubes requesting analysis for diphenyl and phenyl ether. Desorption with carbon disulfide was tried and found to give desorption efficiencies of 99.7% for diphenyl and 98.6% for phenyl ether. Storage and retention efficiencies were similar.

1.1.2 Potential workplace exposure (Ref 5.1, 5.2, and 5.3)

Diphenyl-phenyl ether mixture is used as a heat transfer agent. Diphenyl is also used as a fungistat for citrus fruit on wrappers and cardboard boxes and in organic synthesis. Phenyl ether is used in perfumes, soaps, and organic synthesis.

1.1.3 Toxic Effects (This section is for information purposes and should not be taken as the basis for OSHA policy.) (Ref 5.1 and 5.3)

The mixture of diphenyl and phenyl ether is mildly irritating to skin, eyes, and mucous membranes, and can cause nausea. High exposures to diphenyl can cause convulsions, paralysis, and CNS depression.

1.1.4 Physical properties:

1.1.4.1 Diphenyl (Ref 5.1)

CAS:	92-52-4
IMIS:	1011
RTECS:	DU8050000
Synonyms:	biphenyl, xenene, bibenzene, lemonene, phenyl benzene
Molecular weight:	154.20
Melting point:	70 °C
Boiling point:	254 °C
Odor:	slightly sweet lemon
Color:	colorless leaflets
Molecular formula:	C ₁₂ H ₁₀

1.1.4.2 Phenyl ether (Ref 5.2)

CAS:	101-84-8
IMIS:	2047
RTECS:	KN8970000
Synonyms:	biphenyl oxide, diphenyl ether, diphenyl oxide, henoxybenzene, geranium crystals
Molecular weight:	170.20
Melting point:	28 °C
Boiling point:	259 °C
Flash point:	115 °C
Odor:	geranium
Color:	clear liquid
Molecular formula:	C ₁₂ H ₁₀ O

1.1.4.3 Diphenyl-Phenyl ether mixture

Synonym:	Dowtherm A
Content:	73.5% Phenyl ether 26.5% Diphenyl

1.2 Limit defining parameters

- 1.2.1 The detection limit of the analytical procedure is 1 ng/injection for each diphenyl or phenyl ether. This is the smallest amount that could be detected under normal operating procedures.
- 1.2.2 The overall detection limit for diphenyl based on a 20 liter air volume, 1 mL desorption volume, and a desorption efficiency of 99.7% is 0.008 ppm. The overall detection limit for diphenyl ether based on a 20 liter air volume, 1 mL desorption volume, and a desorption efficiency of 98.6% is 0.008 ppm. The ppm values reported throughout this study are based on a 20-liter air volume.

1.3 Advantages

- 1.3.1 The sampling procedure is convenient.
- 1.3.2 The analytical method is reproducible and sensitive.
- 1.3.3 Reanalysis of samples is possible.
- 1.3.4 It may be possible to analyze other compounds at the same time.
- 1.3.5 Interferences may be avoided by proper selection of analytical column and GC parameters.

1.4 Disadvantages

None known

2 Sampling procedure

2.1 Apparatus

- 2.1.1 A calibrated personal sampling pump, the flow of which can be determined within $\pm 5\%$ at the recommended flow.
- 2.1.2 Adsorbent tubes containing 15/50 mesh XAD-7 with a 100-mg adsorbing section with a 50-mg backup section separated by a 2-mm portion of urethane foam, with a silanized glass wool plug before the adsorbing section and a 3-mm plug of urethane foam at the back of the backup section. The ends are flame sealed and the glass tube containing the adsorbent is 7-cm x 6-mm o.d. and 4-mm i.d., SKC tubes or equivalent.

2.2 Sampling technique

- 2.2.1 The ends of the XAD-7 tube are opened immediately before sampling.
- 2.2.2 Connect the XAD-7 tube to the sampling pump with flexible tubing.
- 2.2.3 Tubes should be placed in a vertical position to minimize channeling, with the smaller section towards the pump.

- 2.2.4 Air being sampled should not pass through any hose or tubing before entering the XAD-7 tube.
- 2.2.5 Seal the XAD-7 tube with plastic caps immediately after sampling. Seal each sample lengthwise with Form OSHA-21 seal.
- 2.2.6 With each batch of samples, submit at least one blank tube from the same lot used for samples. This tube should be subjected to exactly the same handling as the samples (break ends, seal, & transport) except that no air is drawn through it.
- 2.2.7 Send the samples (and corresponding paperwork) to the lab for analysis.
- 2.2.8 Bulks submitted for analysis must be shipped in a separate container from the air samples.

2.3 Desorption efficiency

2.3.1 Diphenyl desorption efficiency was performed by liquid spiking six tubes at each loading of 2.45 ug (0.0194 ppm), 12.25 ug (0.0971 ppm), 24.5 ug (0.194 ppm), and 49 ug (0.388 ppm). They were allowed to equilibrate overnight at room temperature. They were then opened, each section placed into a separate 2-mL vial, desorbed with 1 mL of the desorbing solution for 30 minutes with occasional shaking, and analyzed by GC-FID. The overall average was 99.7%. (Table 1)

Table 1
Desorption Efficiency
(Diphenyl)

tube #	% desorption			
	0.1x PEL 2.45 µg	0.5x PEL 12.25 µg	1x PEL 24.5 µg	2x PEL 49 µg
1	98.9	99.2	101	97.1
2	99.8	99.3	100	100
3	102	101	101	99.0
4	97.8	96.4	100	99.8
5	97.9	97.6	102	100
6	lost	97.7	103	103
average	99.3	98.5	101	99.8

overall average = 99.7%
standard deviation = ±1.84

2.3.2 Phenyl ether desorption efficiency was performed by liquid spiking six tubes at each loading of 7.14 ug (0.0513 ppm), 14.28 ug (0.103 ppm), 71.4 ug (0.513 ppm), 142.8 ug (1.03 ppm) and 285.6 ug (2.05 ppm). They were allowed to equilibrate overnight at room temperature. They were then opened, each section placed into a separate 2-mL vial, desorbed with 1 mL of the desorbing solution, for 30 minutes with occasional shaking, and analyzed by GC-FID. The overall average was 98.6%. (Table 2)

Table 2
Desorption Efficiency
(Phenyl Ether)

tube #	% desorption				
	0.05x PEL 7.14 µg	0.1x PEL 14.28 µg	0.5x PEL 71.4 µg	1x PEL 142.8 µg	2x PEL 285.6 µg
1	98.7	97.4	97.2	96.7	98.4
2	105	102	97.4	96.6	99.2
3	103	96.4	97.6	96.7	98.7
4	103	97.1	94.2	97.3	99.6
5	99.9	lost	96.3	97.9	99.1
6	103	96.6	95.3	98.5	101
average	102	97.9	96.3	97.3	99.3

overall average = 98.6%
standard deviation = ±2.53

2.4 Retention efficiency

2.4.1 Diphenyl retention efficiency was performed by liquid spiking six tubes with 24.5 ug (0.194 ppm), allowed to equilibrate overnight, and had 20 liters humid air (93% RH) pulled through them. They were then opened, desorbed, and analyzed by GC-FID. There was no diphenyl found on the backup portions of the tubes. (Table 3) The retention efficiency averaged 98.1%.

Table 3
Retention Efficiency
(Diphenyl)

tube #	% recovered		total
	'A'	'B'	
1	101	0.0	101
2	97.4	0.0	97.4
3	96.5	0.0	96.5
4	97.3	0.0	97.3
5	98.3	0.0	98.3
6	98.3	0.0	98.3

average = 98.1%

2.4.1 Phenyl ether retention efficiency was performed by liquid spiking six tubes with 142.8 ug (1.026 ppm), allowed to equilibrate overnight, and had 20 liters humid air (93% RH) pulled through them. They were then opened, desorbed, and analyzed by GC-FID. There was no phenyl ether found on the backup portions of the tubes. (Table 4) The retention efficiency averaged 98.8%.

Table 4
Retention Efficiency
(Phenyl Ether)

tube #	% recovered		total
	'A'	'B'	
1	101	0.0	101
2	98.0	0.0	98.0
3	98.6	0.0	98.6
4	97.2	0.0	97.2
5	99.0	0.0	99.0
6	99.2	0.0	99.2

average = 98.8%

2.5 Storage

2.5.1 Diphenyl storage study was performed by spiking six XAD-7 tubes with 24.5 ug (0.194 ppm) and stored at room temperature until opened and analyzed. The recovery averaged 96.8% for the 11 days stored. (Table 5)

Table 5
Storage (Diphenyl)

days	% recovered
5	94.4
5	101
5	97.3
11	95.7
11	95.3
11	97.2
average	96.8

2.5.2 Phenyl ether storage study was performed by spiking six XAD-7 tubes with 142.8 ug (1.026 ppm) and stored at room temperature until opened and analyzed. The recovery averaged 96.5% for the 11 days stored. (Table 6)

Table 6
Storage (Phenyl Ether)

days	% recovered
5	94.5
5	99.3
5	95.0
11	96.3
11	95.9
11	98.0
average	96.5

2.6 Precision

2.6.1 Diphenyl precision was calculated using the area counts from six injections of each standard at concentrations of 2.45 ug/mL (0.0194 ppm), 12.25 ug/mL (0.0971 ppm), 24.5 ug/mL (0.194 ppm), and 49 ug/mL (0.388 ppm). (Table 7)

Table 7
Precision (Diphenyl)

injection number	0.1x PEL 2.45 µg/mL	0.5x PEL 12.25 µg/mL	1.0x PEL 24.5 µg/mL	2.0x PEL 49 µg/mL
1	15595	77862	153620	301240
2	15782	76074	151010	303400
3	16162	78347	156310	302800
4	16320	78708	155950	302310
5	16193	73582	153840	298250
6	15905	76457	150360	lost
average	15993	76838	153515	301600
standard deviation –	±277.9	±1905	±2453	±2033
CV -	0.01737	0.02479	0.01598	0.606741

pooled CV = 0.01776

2.6.2 Phenyl ether precision was calculated using the area counts from six injections of each standard at concentrations of 14.28 ug/mL (0.103 ppm), 71.4 ug/mL (0.513 ppm), 142.8 ug/mL (1.03 ppm), and 285.6 ug/mL (2.05 ppm) (Table 8).

Table 8
Precision (Phenyl Ether)

injection number	0.1x PEL 14.28 µg/mL	0.5x PEL 71.4 µg/mL	1.0x PEL 142.8 µg/mL	2.0x PEL 285.6 µg/mL
1	78598	384880	762450	1516500
2	77173	380770	744880	1483800
3	76326	386310	776930	1501340
4	78838	389970	773320	1496000
5	77326	378070	750070	1516800
6	78814	380180	lost	1478200
average	77846	383363	761530	1498773
standard deviation –	±1051	±4461	±12534	±16130
CV -	0.01350	0.01164	0.01646	0.01076

pooled CV = 0.01311

Where:

$$CV \text{ (Coefficient of Variation)} = \frac{\text{(standard deviation)}}{\text{(average)}}$$

$$\text{Pooled CV} = \sqrt{\frac{A1(CV1)^2 + A2(CV2)^2 + A3(CV3)^2 + A4(CV4)^2}{A1 + A2 + A3 + A4}}$$

A1, A2, A3, A4 = number of injections at each level
CV1, CV2, CV3, CV4 = Coefficients of variation at each level

2.7 Air volume and sampling rate studied

2.7.1 The air volume studied was 20 liters.

2.7.2 The sampling rate studied was 0.2 liters per minute.

2.8 Interferences

Suspected interferences should be listed on sample data sheets.

2.9 Safety precautions

2.9.1 Sampling equipment should be placed on an employee in a manner that does not interfere with work performance or safety.

2.9.2 Safety glasses should be worn at all times.

2.9.3 Follow all safety practices that apply to the workplace being sampled.

3 Analytical method

3.1 Apparatus

3.1.1 Gas chromatograph equipped with a flame ionization detector.

3.1.2 GC column capable of separating the analyte and an internal standard from any interference. The column used in this study was a 60-m (0.5 μm dr DB-Wax) capillary column.

3.1.3 An electronic integrator or another suitable method of measuring peak areas.

3.1.4 Two milliliter vials with PTFE-lined caps.

3.1.5 A 10- μL syringe or other convenient size for sample injection.

3.1.6 Pipets for dispensing the desorbing solution. The Glenco 1-mL dispenser was used in this method.

3.1.7 Volumetric flasks, 5-mL and other convenient sizes for preparing standards.

3.1.8 Analytical balance capable of weighing milligram amounts.

3.2 Reagents

3.2.1 Purified GC grade nitrogen, hydrogen, and air.

- 3.2.2 Diphenyl, Reagent grade
- 3.2.3 Phenyl ether, Reagent grade
- 3.2.4 Carbon disulfide, Reagent grade
- 3.2.5 p-Cymene, Reagent grade
- 3.2.6 The desorbing solution contains 1 uL/mL p-cymene as internal standard in carbon disulfide.

3.3 Sample preparation

- 3.3.1 Sample tubes are opened and the front and back section of each tube are placed in separate 2-mL vials.
- 3.3.2 Each section is desorbed with 1 mL of carbon disulfide with 1 uL/mL p-cymene internal standard.
- 3.3.3 The vials are sealed immediately and allowed to desorb for 30 minutes with occasional shaking.

3.4 Standard preparation

- 3.4.1 Stock standards are prepared by diluting a known quantity of diphenyl and phenyl ether with the desorbing solution.
- 3.4.2 At least two separate stock standards should be made.
- 3.4.3 Dilutions of the stock solutions are made to obtain working standards. A standard solution of diphenyl in the desorbing solution containing 24.5 ug/mL corresponds to 0.195 ppm based on a 20 liter air volume and a desorption efficiency of 99.7%. A standard solution of phenyl ether in the desorbing solution containing 142.8 ug/mL corresponds to 1.04 ppm based on a 20 liter air volume and a desorption efficiency of 98.6%.

3.5 Analysis

- 3.5.1 Gas chromatograph conditions.

<u>Flow rates</u>	<u>(mL/min)</u>	<u>Temperature</u>	<u>(°C)</u>
Nitrogen (makeup):	24	Injector:	180
Hydrogen (carrier):	1	Detector:	220
Air:	240	Column:	180
Hydrogen (detector):	1		
<u>Injection size:</u>	1 uL		
<u>Elution time:</u>	Diphenyl	12.67 min	
<u>Elution time:</u>	Phenyl ether	13.35 min	

Chromatogram: (See Figure 1)

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

3.6 Interferences (analytical)

- 3.6.1 Any compound having the general retention time of the analyte or the internal standard used is interference. Possible interferences should be listed on the sample data sheet. GC parameters should be adjusted if necessary so these compounds will pose no problems.
- 3.6.2 Retention time data on a single column is not considered proof of chemical identity. Samples over the target concentration should be confirmed by GC/Mass Spec or other suitable means.

3.7 Calculations

- 3.7.1 The integrator was calibrated on the working standards, and dilutions were analyzed to check the linearity of the detector.
- 3.7.2 To calculate the concentration of analyte in the air sample the following formulas are used:

$$\text{mass of analyte, } \mu\text{g} = \frac{(\mu\text{g} / \text{mL})(\text{desorption volume, mL})}{(\text{desorption efficiency, decimal})}$$

$$\text{moles of analyte} = \frac{(\text{mass of analyte, } \mu\text{g})(1 \text{ g})}{(\text{molecular weight})(10^6 \mu\text{g})}$$

$$\text{volume of analyte} = (\text{moles of analyte})(\text{molar volume})$$

$$\text{ppm} = \frac{(\text{volume of analyte})(10^6)^*}{(\text{air volume, L})}$$

* All units must cancel.

- 3.7.3 The above equations can be consolidated to form the following formula. To calculate the ppm of analyte in the sample based on a 20-liter air sample:

$$\text{ppm} = \frac{(\mu\text{g} / \text{mL})(\text{DV})(24.46)}{(20 \text{ L})(\text{DE})(\text{MW})}$$

Where:

$\mu\text{g/mL}$ = concentration of analyte in sample or standard
24.46 = Molar volume (liters/mole) at 25 °C and 760 mmHg.
MW = Molecular weight (g/mole)
DV = Desorption volume, mL
20 L = 20 liter air sample
DE = Desorption efficiency, decimal

- 3.7.4 This calculation is done for each section of the sampling tube and the results added together.

3.8 Safety precautions

- 3.8.1 All handling of solvents should be done in a hood.
- 3.8.2 Avoid skin contact with all solvents and wear safety glasses at all times.

4 Recommendations for further study

Collection studies need to be performed.

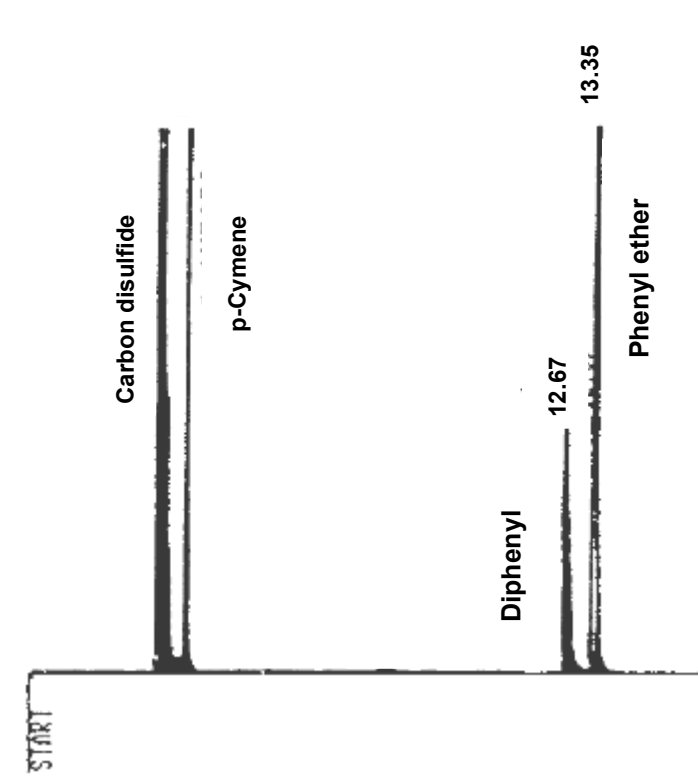


Figure 1 A standard containing 24.5 ug/mL (0.195 ppm) Diphenyl and 142.8 ug/mL (1.04 ppm) Phenyl Ether in Carbon disulfide with 1 uL/mL p-Cymene internal standard.

5 References

- 5.1 Windholz, M., "The Merck Index," Tenth Edition, Merck & Co., Rahway N.J., 1983, p. 485.
- 5.2 Windholz, M., "The Merck Index," Tenth Edition, Merck & Co., Rahway N.J., 1983, p. 1051.
- 5.3 "Documentation of the Threshold Limit Values and Biological Exposure Indices," Fifth Edition, American Conference of Governmental Industrial Hygienists Inc., Cincinnati, OH, 1986, p. 475.