Chlorodiphenyl (54% Chlorine)

Method Number:	PV2088
Target Concentration:	0.5 mg/m^3 (Skin) is the OSHA PEL.
Procedure:	Samples are collected by drawing known volumes of air through OSHA versatile sampler (OVS-2) tubes, containing a glass fiber filter and two sections of XAD-2 adsorbent. Samples are extracted with toluene and analyzed by gas chromatography (GC) using an electron capture detector (ECD).
Recommended air volume and sampling rate:	60 minutes at 1.0 L/min (60 L)
Detection limit of the overall procedure	17 µg/m^3 (based on the recommended air volume and the analytical detection limit):
Status of method:	Partially validated method. This method has been partially evaluated and is presented for information and trial use only.

December 1988

George F. Lewis

Carcinogen and Pesticide Branch
OSHA Analytical Laboratory
Salt Lake City UT-84115

1 General Discussion

1.1 Background

1.1.1 History of procedure

The OSHA Lab has received numerous requests for a collection procedure for chlorodiphenyls, also known as polychlorobiphenyls (PCBs). Since there are many different varieties, the acronym PCBs will be used to represent all chlorodiphenyls. This paper was written specifically for chlorodiphenyl (54%). The collection devices sent out by the lab were OVS-F (Florisil) and OVS-2 tubes. Originally, the Florisil was used in place of XAD-2 adsorbent. Brownlow and Que Hee showed Chromosorb 102 and Florisil have the same percent recovery for chlorodiphenyl (54%) (Ref. 5.1). Chromosorb 102 and XAD-2 adsorbent are made from styrene-divinylbenzene adsorbent with only small differences in surface area and pore size. Thus, it was felt that XAD-2 adsorbent would be a good substitute for Florisil since this laboratory was already using OVS-2 samplers for other compounds.

This evaluation was undertaken to determine the effectiveness of the OVS-2 tube as a sampling device for chlorodiphenyl (54%). It follows the procedure developed for several organophosphorus pesticides (Ref. 5.2).

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

It has been recognized for a long time that PCBs in humans cause yellow atrophy of the liver, dermatitis, and fatty degeneration of the liver in chronic exposure. PCBs are poorly metabolized and accumulate in living tissues and organs rich in lipids. The penta- and more highly chlorinated biphenyls appear to accumulate in greater amounts since the tetra and less chlorinated biphenyls are hydroxylated and excreted. PCB toxicities vary greatly from species to species due to differences in metabolic rates and physiology (Ref. 5.3). Signs and symptoms include eye and skin irritation along with acneform dermatitis (Ref. 5.4).

1.1.3 Potential workplace exposure

PCBs are synthetic chlorinated diphenyls which have a wide variety of application due to their general stability, inertness, and dielectric properties. This makes them suitable for the electrical industry and in coolant systems. PCBs are used as sealants for wood and cement surfaces. Other uses are in hydraulic fluids, cutting oils and vapor suppressant for insecticide preparations.

PCBs have been prepared industrially since 1929. Monsanto is the major producer in the USA and Great Britain.

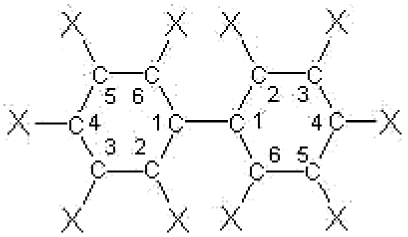
Exposure is due to inhalation and skin absorption. PCBs may enter the air during the destructive burning or gradual wear and weathering of manufactured articles containing chlorodiphenyls. An estimated 0.4 million Kg of PCBs were released into the atmosphere by waste-disposal burners in the U.S. in 1970 (Ref. 5.5) and 1-2 million Kg of PCBs entered the air from the vaporization of plasticizers (Ref. 5.6).

It appears that PCBs can be found everywhere; not only in the air and rain but also in the soil and surface water as well as in animals and plants. (Ref. 5.6)

1.1.4 Physical properties (Ref. 5.3, 5.7)

CAS #:	11097-69-1
Average Molecular weight:	327
Empirical formula:	$C_{12}H_5Cl_5$ (Chlorine 54.30%)
Specific gravity:	1.495 - 1.505 (65/15.5 °C)
Vaporization rate:	0.00053 g/cm^2/hr at 100 °C
Appearance:	light-yellow viscous liquid
Solubility:	Insoluble in water, very soluble in most of the common organic solvents: hexane, toluene, benzene, xylene; soluble in amyl alcohol, n-butyl alcohol, carbon disulfide, and nitrobenzene
Synonyms:	(general) Chlorinated biphenyl, chlorinated diphenyl, chlorinated diphenylene, chlorobiphenyl, chloro-1,1-biphenyl, polychlorinated polyphenyls, polychlorobiphenyl
Trade names:	(general) Aroclor, Clophen, Chlophen, Chloextol, Dykanol, Funicular, Inerteen, Kanechlor, Mentor, Norflamol, Phenochlor, Funicular, Pyralene, Pyranol, Santotherm FR, Sovol, Therminol, Therminol, Therminol FR-1

Structure:



X represents either chlorine or hydrogen

1.2 Limit defining parameters

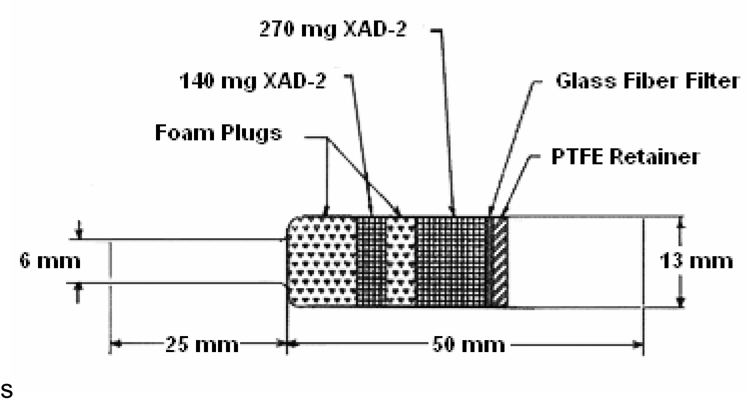
The detection limit of the analytical procedure is 0.0064 ng per injection which takes a split ratio of 32:1 into account. This is the amount of analyte which will give a unique pattern distinguishable from other PCB patterns.

2 Sampling procedure

2.1 Apparatus

2.1.1 A personal sampling pump that can be calibrated to within ±5% of the recommended flow rate with the sampling device in line.

2.1.2 OVS-2 tubes, which are specially made 13-mm o.d. glass tubes that are tapered to 6-mm o.d. These tubes are packed with a 140-mg backup section and a 270-mg sampling section of cleaned XAD-2 adsorbent. The backup section is retained by two foam plugs and the sampling section is between one foam plug and a 13-mm diameter glass fiber filter. The glass fiber filter is held next to the sampling section by a polytetrafluoroethylene (PTFE) retainer.



2.2 Reagents

No sampling reagents are required.

2.3 Sampling technique

2.3.1 Attach the small end of the OVS-2 sampling tube to the sampling pump with flexible, plastic tubing such that the large, front section of the sampling tube is exposed directly to the atmosphere. Do not place any tubing in front of the sampler. Attach the tube vertically (large end down) in the worker's breathing zone in a manner, that does not impede work performance.

2.3.2 After sampling for the recommended time, remove the sampling device and seal the tube with plastic end caps.

2.3.3 Wrap each sample end-to-end with a Form OSHA-21 seal.

2.3.4 Submit at least one blank with each set of samples. Handle the blank the same as the other samples except no air is drawn through it.

2.3.5 Submit bulk samples for analysis in a separate container. Do not ship them with the air samples.

2.4 Extraction efficiency

A 13-mm glass fiber filter and an amount of XAD-2 adsorbent equal to the sampling section (270 mg) of an OVS-2 tube were placed in each of six 20 mL scintillation vials which were then capped with PTFE-lined septa after liquid spiking.

These glass fiber filters were each liquid spiked using a 1.584 mg/mL solution of chlorodiphenyl (54%). The first two filters were each spiked with 9 µL of solution. The second two filters were each spiked with 19 µL and the last two filters were each spiked with 38 µL of solution. These vials were allowed to sit overnight at ambient temperature, then extracted with 5.0 mL of toluene containing mirex as an internal standard, and analyzed according to Sections 3.4 and 3.5.

Table 2.4
OVS-2 Extraction Study

tube #	0.5 PEL	1.0 PEL	2.0 PEL
1	0.986	0.961	0.941
2	0.960	0.966	0.937
average	0.973	0.964	0.939

2.5 Retention efficiency

Four OVS-2 tubes were each liquid spiked with 38 µL of a 1.584 mg/mL solution of chlorodiphenyl (54%) in toluene by placing it on the glass fiber filter. Sixty liters of humid air were drawn through three tubes and 125 liters of humid air were drawn through the fourth tube. They were stored overnight in a drawer at ambient temperature then extracted and analyzed as in Sections 3.4 and 3.5. The results of the fourth tube showed no breakthrough and a recovery of 0.947.

Table 2.5
Retention Efficiency Study

tube #	PEL
1	0.957
2	0.979
3	0.918
average	0.951

2.6 Sample storage

Sixteen OVS-2 tubes were each liquid spiked with 20 µL (1 PEL) of a 1.584 mg/mL solution of chlorodiphenyl (54%). The next day, 60 liters of humidified air were drawn through each tube. Half of the tubes were stored in a drawer at ambient temperature, and the other half were stored in a freezer (-5 ºC). They were stored according to Table 2.6, extracted, and analyzed as in Sections 3.4 and 3.5.

Table 2.6
Storage Study

days	ambient	averages	freezer	averages
0	0.909		0.921	
	0.908	0.908	0.950	0.936
7	0.949		0.910	
	0.917	0.933	0.912	0.911
12	0.948		0.949	
	0.948	0.948	0.939	0.943
16	0.885		0.964	
	0.984	0.935	0.931	0.948

average recovery (ambient) = 0.931
average recovery (freezer) = 0.934

2.7 Recommended air volume and sampling rate

2.7.1 The recommended air volume is 60 L.

2.7.2 The recommended flow rate is 1.0 L/min.

2.8 Interferences (sampling)

There are no known compounds which will interfere with the collection of chlorodiphenyl (54%). Suspected interferences should be reported to the laboratory with submitted samples.

2.9 Safety precautions (sampling)

2.9.1 Attach the sampling equipment in such a manner that it will not interfere with employee's work performance or safety.

2.9.2 Follow all safety practices that apply to the work area being sampled.

3 Analytical procedure

3.1 Apparatus

3.1.1 A GC with an ECD. A Hewlett-Packard 5890A GC equipped with both an ECD and a Hewlett-Packard 7671A automatic sampler was used in this evaluation.

3.1.2 A GC column capable of resolving PCB components into a distinguishable pattern. A 60-m × 0.32-mm i.d. (0.25-μm d_f SE-30) capillary GC column was used in this evaluation.

3.1.3 An electronic integrator or other suitable means of measuring peak areas. A Hewlett-Packard 3357 data system was used in this evaluation.

3.1.4 Vials, 2-mL and 20-mL glass, capped with PTFE-lined septa.

3.1.5 Volumetric flasks, pipettes, and syringes.

3.2 Reagents

3.2.1 Hydrogen, air, oxygen, and nitrogen, GC grade.

3.2.2 Toluene, Pesticide grade.

3.2.3 Chlorodiphenyl (54%). A 100% pure standard from EPA was used.

3.2.4 Desorbing solution. If an internal standard method is used, the desorbing solution is prepared by adding the internal standard to the toluene. A 0.5 μg/mL solution of mirex, 95.5% pure from EPA, was used as the internal standard in this evaluation. Otherwise, toluene is used to desorb the samples.

3.3 Standard preparation

Prepare standard stock solutions by adding toluene or desorbing solution (if an internal standard is used) to preweighed amounts of chlorodiphenyl (54%). Prepare working standards from stock standards by diluting with toluene or desorbing solution. Store stock and dilute standards in a freezer. Upon completing analysis, dispose of standards and samples according to EPA and DOT regulations.

3.4 Sample preparation

3.4.1 Transfer the 13-mm glass fiber filter and the 270-mg section of the sampling tube to a 20-mL scintillation vial. Place the first foam plug and the 140-mg section in a separate 20-mL vial. A small glass funnel can be used to facilitate the transfer of the adsorbent. Discard the rear foam plug. Do not discard the glass sampling tube; it can be reused.

3.4.2 Add 5.0 mL of toluene or desorbing solution to each vial.

3.4.3 Seal the vials with PTFE-lined septa and desorb them for 1/2 hour on a mechanical shaker.

3.5 Analysis

3.5.1 GC conditions

GC column: 60-m × 0.32-mm i.d., (0.25-μm d_f SE-30) capillary column

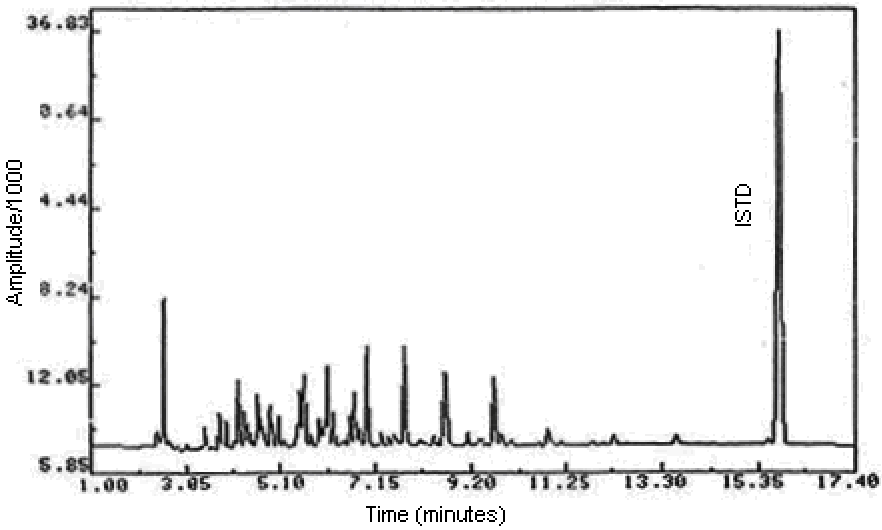
Injector temperature: 250 °C
Column temperature: 220 °C (isothermal)
Carrier gas: hydrogen
Flow rate: 1.97 L/min
Column head pressure: 15 psi

ECD conditions

Makeup gas: nitrogen
Flow rate: 20 mL/min
Detector temperature: 300 °C

Injection volume: I μL
Split ratio: 32:1

3.5.2 Chromatogram



3.6 Interferences (analytical)

3.6.1 Any compound appearing in the same retention time window desorbing as chlorodiphenyl (54%) and capable of causing an ECD response is a potential interference. Generally, chromatographic conditions can be altered to separate interference from an individual component peak.

3.6.2 The retention time pattern on a single column is not proof of chemical identity. Analysis using an alternate GC column or by mass spectrometry are additional means of confirmation.

3.7 Calculations

3.7.1 If necessary, delete the areas of interfering peaks from the sum total peak area using the appropriate computer commands and programs.

3.7.2 Construct a calibration curve by plotting the sum total area of the chlordiphenyl (54%) peaks versus its standard concentration.

3.7.3 Determine the concentration of chlorodiphenyl (54%) in a sample from the calibration curve. If chlorodiphenyl (54%) is found on the backup section, make blank corrections for each section separately before adding the results together.

3.7.4 Determine the air concentration by the following formula.

$$mg/m^3 = \frac{(\mu g/mL,\ \text{blank corrected})(\text{desorption volume, } mL)}{(\text{air volume, } L)(\text{desorption efficiency, decimal})}$$

3.8 Safety precautions (analytical)

3.8.1 Avoid exposure to all standards.

3.8.2 Avoid exposure to all solvents.

3.8.3 Wear safety glasses at all times.

4 Recommendations for further study

4.1 This method should be fully validated.

4.2 A better internal standard might be found.

4.3 The XAD-2 adsorbent could be replaced in the OVS-2 sampler with Florisil, 30-60 mesh. Preliminary data indicates this may be a good alternate solid adsorbent.

5 References

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5.4 Proctor, Nick H.; Hughes, James P., "Chemical Hazards of the Workplace," J.B. Lippincott Co., 1978; pp 166-167.

5.5 Nisbet, I.C.T.; Sarofim, A.F., "Rates and Routes of Transport of PCB'S in the Environment," Environm. Hlth. Perspect., 1, 1972; 21-38.

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