METHOD FOR THE QUANTITATIVE DETERMINATION OF POLYCHLOROBIPHENYL IN WORKPLACE AIR

SCOPE

This method determines the concentration of polychlorobiphenyl (PCBs) in air from 0.1 to 1.0 mg/m^3). The standard (Threshold Limit Value) of PCB is 0.5 mg/m^3. The procedure can determine average worker exposure over an eight-hour day or for short sampling periods.

PRINCIPLE

This method is based on the collection of PCB in an adsorption tube containing Tenax GC. In the laboratory, the samples are solvent desorbed with hexane and analyzed by electron capture gas chromatography. The procedure is only valid if the chromatogram of the sample matches the chromatogram of a PCB standard mixture because of the wide range of LC response of different PCB isomers.

PROCEDURE

1. Preparation and Conditioning of Collection Column

   Collection columns containing about 0.16 g of Tenax GC are prepared and conditioned by the procedure in Spectroscopy Special Study S-76-SS-14. Shortly before sampling, recondition the collection columns in a GC at 250°C for 15-20 minutes. Carrier flow of the GC should be ca 30 ml/min. Check collection columns periodically for changes in flow rate due to extended use (see S-76-SS-14).

2. Sampling Pumps

   a. Choosing Pump Flow Rate

      Breakthrough volume is the amount of air that can pass through a collection column before the component being collected begins eluting from the column. This limits possible sample size. With this size Porapak N collection column at 80°F, the breakthrough volume of PCB is greater than 30 liters. A typical sample is 10 liters. Increasing sampling temperature will decrease the breakthrough volume.

      Depending on the pump available one may need a sample splitter. The purpose of a splitter is to reduce the flow rate through the column. This permits sampling below the breakthrough volume. For PCB, a flow rate ca. 20 ml/min is required if an 8-hour sampling is desired (see 2b). We have found the personnel pump SKC-222-451 model with a splitter very satisfactory for collecting samples at this rate. A very slow flow rate pump such as the SKC-222-3-12 model without a splitter also works well. See Spectroscopy Special Study S-76-SS-10 for a description of sample splitters and their use.

   b. Determining Breakthrough Volumes

      The most convenient way we find to measure breakthrough volumes is described below:

(1) Attach a freshly conditioned collection column inside the GC to the injection port.

(2) Connect the other end of the column to a piece of tubing, preferably glass, that will connect to the detector.

(3) Adjust the flow rate to the flow you will be using when you sample.

(4) Inject 1 µl of PCB into the GC and allow it to run at room temperature. You will probably get a very broad peak. The point at which the base line begins to rise is the breakthrough point.

(5) Determine the time from injection to the breakthrough point and calculate as below:

$$\underset{\text{(liters)}}{\text{Breakthrough}} = \underset{\text{(ml/min)}}{\text{flow through column}} \times \underset{\text{(min)}}{\text{time at breakthrough point}} \times \underset{\text{(liters/ml)}}{10^{-3}}$$

c. Calibration of Sampling Pump

(1) Take a 2-ft piece of tubing and attach it to the dimpled end of a collection tube.

(2) Attach the other end of the tubing to a personnel monitoring pump.

(3) Be sure the tubing fits tightly over all connections.

(4) Adjust the flow rate of the pump so breakthrough does not occur in the desired sampling time (see below).

The flow rate can be measured with a soap bubble meter of the type used in calibrating flow rates for GC carrier gases. It is essential when checking flow rates to have the collection column (or columns if two in series are to be used) in the system. If you wish to sample for 8 hours, the pump flow should not exceed 20 ml/min. This is calculated below:

$$8 \text{ hrs} \times \frac{60 \text{ min}}{\text{hr}} = 480 \text{ min}$$

$$10 \text{ liter} \times \frac{1000 \text{ ml}}{1 \text{ L}} = 10{,}000 \text{ ml}$$

$$\text{pump flow} = \frac{10{,}000 \text{ ml}}{480 \text{ min}} \simeq 20 \text{ ml/min}$$

d. Column Capacity

The capacity of these collection tubes for PCB is at least 0.01 mg. We have not investigated higher concentrations. The presence of high (mg) levels of other organic chemicals will probably effect the column capacity for PCB. If over 0.02 mg of organic material will likely be collected, sampling should be carried out with two columns in series. Both columns are then analyzed to insure capacity has not been exceeded.

3. Sample Collection

Replace the tube used for calibration with a freshly conditioned collection column. If personnel monitoring is planned, the pump can be attached to the worker's belt or put in a pocket. The collection tube should be positioned in the breathing zone. Either wrap the tubing around the back of the neck and let the tube hang on the shoulder or clip it to the collar. Start the pump. Record the time. After the end of the sampling period, turn the pump off and record the final time. Disconnect the collection tube and wrap each end with teflon tape. DO NOT USE any other type of tape because of possible contamination.

If you anticipate the data will be presented to OSHA or other regulatory agencies, use of a back-up sampling column is recommended. Do this by connecting two columns in series with a small piece of tubing (not rubber). It may be convenient to clip the first tube to the clothing and let the second hang over the shoulder (see attached figure). By analyzing both tubes, you can show no sample was lost. NIOSH charcoal tube methods include the guideline that if the back-up tube content exceeds 25% of that found on the front column, the possibility of sample loss exists. We recommend sampling be repeated if such is the case.

The conditions for collecting PCB are:

Maximum Sample Size: 30 liters air

Pump Flow: Adjust for desired sampling period (20 ml/min for 8-hour sampling)

4. Analysis

a) 1. Attach the undimpled end of the collection tube to system similar to figure 3.

2. Place 10 ml of hexane in funnel and force through the sample tube with N_2.

3. Record the volume of extract

4. Repeat

5. Analyze by EC/GC as described below.

b) Prepare standards by weighing ca 0.17 g PCB into a 100 ml volumetric flask. Dilute to mark with nanograde hexane. Three µl of this solution injected into a GC is equivalent to 0.5 µg/l PCB in a 10 liter air sample (the TLV). Calculate the PCB concentration in mg/ml. Inject the standard into the EC/GC. EC/GC parameters for PCB are:

Electron Capture Gas Chromatographic Procedure

Instruments - A gas chromatograph equipped with isothermal oven temperature control.

Detector - High-temperature Ni Electron Capture Cell.

Column - A 6-mm by 6 ft. (1.8-m) glass column, 4% XE-60 on 80/100 mesh Chromosorb W, high-performance.

Column Temperature - 190°C isothermal.

Detector Temperature - The detector temperature shall be 250 to 300°C.

Injection Port Temperature - The injection port temperature shall be 220°C.

Pulse - The pulse rate shall be 50 µs.

Flow Rates - The flow rates shall be as follows:

Helium Carrier - 60 ml/min
90% Argon-10% Methane Purge - 20 ml/min.

Using EC/GC as the determinative step, inject in duplicate 2 to 8 µl of each sample solution into the chromatograph. By comparison with standard solutions injected, under the same operating conditions, determine the amount and type of Aroclor using the total area method.

Quantitative Determination

Quantitative determinations employing the electron capture detector are non-stoichiometric measurements made by comparing the total areas for known concentrations with those for unknown concentrations. Four variations of the area quantification procedure have been employed as follows:

Case I - EC gas chromatogram of PCB unknown unchanged with respect to standard PCB with no evidence of interferences.

Case II - EC gas chromatogram of PCB unknown altered with respect to standard PCB with no evidence of interference.

Case III - EC gas chromatogram of PCB unknown unchanged with respect to standard PCB with evidence of interference.

Case IV - EC gas chromatogram of PCB unknown altered with respect to standard PCB with evidence of interference.

Determine the PCB level in Case I and II samples by comparison of the total area of the peaks in the unknown with a calibration curve prepared by plotting the total area of the peaks in the electron capture chromatogram of the corresponding standard versus the number of nanograms of the standard injected. Initially subject Case III and IV samples to the chemical cleanup procedure and follow by chromatography on alumina. If the interferences are removed by this treatment, calculate the PCB levels for Cases III and IV in the same manner as Cases I and II. If dominant interference(s) is(are) still present, estimate the maximum PCB level in accordance with Cases I and II after correcting the total area for that of the interfering peak(s). In all cases, the response of the electron capture must be linear for quantitative analysis.

Calculations

Assuming that the calibration curve is prepared by plotting the electron capture response (total peak area) versus nanograms of the PCB standard injected, calculate the PCB level present in the air, water, or sediment-soil sample as follows:

Air Samples:

$$F = \frac{[(A/B)(D \times 10^3\ \mu l)/ml\ (10^{-6}\ mg/ng)]}{G(28.32\ liter/ft^3)(m^3/10^3 liter)(P_o - P_1/P_o)(T_o/273 + T_1)}$$

where:

A = PCB in unknown from calibration curve, ng,

B = final concentrate injected into the instrument µl,

D = volume of final concentrate, m.,

E = sample, weight, kg,

F = concentration of PCBs in air sample, mg/m^3, at one atmosphere and 25°C.

G = air sampled from meter, ft^3 ,

P_o- differential pressure of gas stream, mm Hg,

P_1= standard pressure, 760 mm Hg,

T_o= standard temperature 298 K, and

T_1= temperature of sampled gas, °C,

The corrections for the pressure drop through the scrubbers and for the gas temperature are necessary to get an accurate measurement of gas volume sampled.

DISCUSSION

We validated this method by injecting the standard directly on the absorption column and solvent desorbed the material with nanograde hexane. Comparison with EC/GC standards gave us this result -

VALIDATION CONCENTRATION	% RECOVERY PCB		PCB INJECTED ON TUVE (µg)	EQUIVALENT CONCENTRATION IN 1 LITER AIR (µg/l)
0.2 Standard	109 120	114	1	0.1
Standard	95 87	91	5	0.5
2.0 Standard	91 99	95	10	1.0

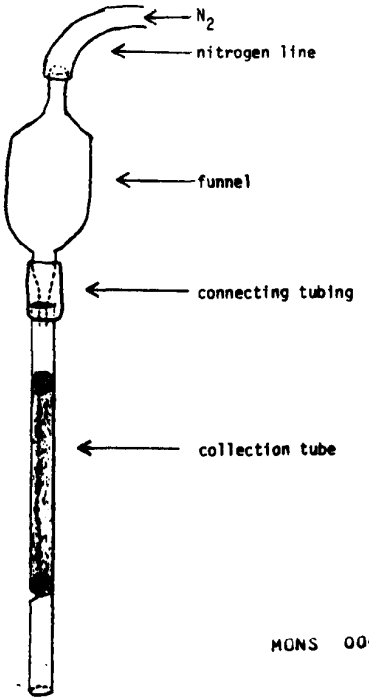
References: Spectroscopy Special Studies S-76-SS-10, S-76-SS-11, S-76-SS-14, S-76-SS-15; GC File #76-234

omc
Attachment
Monsanto Industrial Chemicals Co., Applied Sciences, St. Louis, Mo.
12/76 - L. M. Chapman, C. E. Hoffmann, M. W. Dietrich


tubing
back-up column
connecting tubing
collection column


connecting tubing
collection column
back-up column
tubing

MONS 004034


N_2
nitrogen line
funnel
connecting tubing
collection tube

MONS 004035