

**CHLOROMETHYL METHYL ETHER (CMME)
AND BIS(CHLOROMETHYL) ETHER (BCME) IN AIR**

**Physical and Chemical Analysis Branch
Analytical Method**

Analyte:	CMME and BCME	Method No.:	P&CAM 220
Matrix:	Air	Range:	0.5—7.5 ppb (CCME or BCME)
Procedure:	Collection via impinger, GC- electron capture detector	Precision:	10% RSD
Date Issued:	6/27/75		
Date Revised:		Classification:	E (Proposed)

1. Principle of the Method

- 1.1 A known volume of air is drawn through glass impingers containing a methanolic solution of the sodium salt of 2,4,6-trichlorophenol.
- 1.2 CMME and BCME react with the derivatizing reagent to produce stable derivatives.
- 1.3 Sample is heated on a steam bath for 5 min, cooled, diluted with an equal volume of distilled water and 2 ml of hexane for extraction.
- 1.4 An aliquot of the hexane is analyzed by electron capture gas chromatography.
- 1.5 The peak heights of the CMME and BCME derivatives are measured and the concentration determined from standard curves.

2. Range and Sensitivity

- 2.1 A relative standard deviation of 10% can be expected within the concentration range of 0.02-0.3 ng/ μ l of both CMME and BCME.
- 2.2 The sensitivity of the method is 0.5 ppb (v/v) when a 10-liter air sample is used.

3. Interferences

- 3.1 The known components used in chloromethylation processes do not interfere with the determination of CMME or BCME.
- 3.2 Interferences can be expected from highly halogenated organic compounds or compounds that may produce same derivatives.
- 3.3 The quality of 2,4,6-trichlorophenol is important since impurities can be extracted with hexane and seriously interfere with the chromatographic analysis.

4. Precision and Accuracy

- 4.1 The precision of the sampling technique with an accurate, calibrated air sampling pump and analysis of the derivative samples is 10% relative standard deviation.

4.2 The accuracy of the method is typically affected by the efficiency in sampling, extraction, calibration and data handling.

5. Advantages and Disadvantages of the Method

- 5.1 The major advantage of this method is the sensitivity and the simultaneous analysis of both CMME and BCME.
- 5.2 The derivative stabilizes the CMME and BCME while significantly increasing the sensitivity.
- 5.3 Preparation of the derivatives eliminates further hazardous handling of both CMME and BCME during the analysis.
- 5.4 Disadvantages of the method are the handling of liquids, extractions and the dilution of the samples by the hexane extraction.

6. Apparatus

6.1 Sampling Equipment

The sampling unit for the impinger collection method consists of the following components:

- 6.1.1 Two standard air impinger assemblies, with fritted glass inlets.
- 6.1.2 Calibrated battery-powered pump, capable of drawing an accurate and reproducible volume of air through the impingers at a flow rate of 0.5 l/min is required.
- 6.1.3 Rotameter, calibrated for air. Parts should include only the sapphire ball and small Teflon tubing, inside at both ends.
- 6.1.4 Thermometer.
- 6.1.5 Stopwatch.
- 6.2 Steam bath. Any bath capable of maintaining a temperature of 65-90°C is adequate.
- 6.3 Gas chromatograph, equipped with a ⁶³Ni electron capture detector.
- 6.4 Gas chromatograph column. A 6-foot (1.83 m) × ¼-inch (6.35 mm) glass column is packed with 100/120 mesh textured glass beads (GLC-100) coated with a two component stationary phase consisting of 0.1% by weight QF-1 and 0.1% by weight OV-17. The column is equipped for on-column injection. The packed column is preconditioned at 160°C overnight with nitrogen carrier at a flow rate of 30-50 cm³/min.
- 6.5 Strip chart recorder, 1.0 mv full scale range.
- 6.6 Hamilton microsyringes.
- 6.7 Assorted laboratory glassware, pipettes, graduated cylinders, etc.

7. Reagents

All reagents are analytical reagent grade. An analytical grade of distilled water must be used.

- 7.1 Derivatizing reagent, prepared in the laboratory as described in the procedure.
- 7.2 Sodium methoxide, AR grade.
- 7.3 2,4,6-Trichlorophenol, M.P. 67-68°C.
- 7.4 Methanol and hexane, distilled in glass.
- 7.5 Chloromethyl methyl ether, B.P. 55-58°C.
- 7.6 Bis(chloromethyl) ether, B.P. 100-102°C.
- 7.7 Sodium hydroxide.

- 7.8 Preparation of derivatizing reagent. Twenty-five grams of sodium methoxide is weighed into a beaker and dissolved in one liter of methanol. Five grams of 2,4,6-trichlorophenol is weighed into the beaker and allowed to dissolve in the methanol-sodium methoxide solution. The reagent is stable for three or four weeks when stored in a dark brown bottle. The sodium methoxide should be added slowly to the methanol since the reaction is very exothermic.
- 7.9 The sensitivity of BCME can be increased 6-8 fold by using stoichiometric quantities of sodium methoxide and 2,4,6-trichlorophenol (16.0 g of 2,4,6-trichlorophenol and 4.4 g of sodium methoxide in one liter of methanol). When using this formulation, 2.0 N sodium hydroxide is used in place of distilled water prior to the hexane extraction of the derivative (see Section 8.3).

8. Procedure

8.1 **Cleaning of Equipment.** All glassware used for the analysis must be thoroughly washed, rinsed with distilled water and dried. The impinger assemblies can be rinsed with reagent grade methanol for repeated use.

8.2 Collection of Samples

- 8.2.1 CMME and BCME in air are sampled at a rate of 0.5 l/min (up to 2 hr, if necessary) through the two impinger assemblies each containing 10 ml of the derivatizing solution.
- 8.2.2 Teflon connections should be used for the attachment of the two impinger assemblies in series and the rotameter to the first impinger. Rubber tubing may be used for the connection of the second impinger to the intake of the pump.
- 8.2.3 A bypass flow of air can be established in case the pump does not operate at low flow rates. An appropriate syringe needle injected into the rubber tubing between the impinger and the intake of the pump should provide satisfactory flow rates. Also a needle valve connected through a T should produce adjustable flow rates.

8.3 Analysis of Samples

- 8.3.1 After sampling, the solutions are transferred to a vial that is capped loosely and placed on a steam bath for five minutes (any bath capable of maintaining a temperature of 65-90°C is suitable). The samples are allowed to cool and an equal amount of distilled water and 2 ml of hexane are pipetted into the vial. Then the sample is shaken for 5 min. The mixture is allowed to stand for a few minutes to allow the phases to separate.
- 8.3.2 **GC conditions.** The following are the recommended starting instrumental conditions. A gas chromatograph with a ⁶³Ni electron capture detector is equipped with a 6-foot long (1.83 m) by 1/4 inch (6.35 mm) glass column packed with 100-120 mesh textured glass beads (GLC-100) coated with a two component stationary phase consisting of 0.1% by weight QF-1 and 0.1% by weight OV-17. The column is equipped for on-column injection. The flow rate of the prepurified nitrogen carrier gas is set at 30 cm³/minute. The temperature of the sample injection zone is adjusted at 175°C and that of the detector at 250°C. The column oven is operated isothermally at 140°C. An oxygen filter is required on the carrier gas.
- 8.3.3 **Injection.** A 2-μl aliquot of the hexane extract is injected into the GC. A complete chromatogram should be obtained in about 6 min. Duplicate injections of each sample and a standard should be made.

9. Calibration and Standards

9.1 Preparation of Standard Curve

9.1.1 Two microliters of CMME and BCME are added to 50 ml of hexane. The weights of the components are obtained by using their respective specific gravities, 1.03 g/ml for CMME and 1.33 g/ml for BCME. This concentrated standard is then used for preparing a standard curve. Both of these compounds should be handled in a good hood only!!

9.1.2 Ten ml of the derivatizing reagent (Section 8.3) is pipetted into five 20-dram Kimble screw cap vials. Ten, five, two, one and zero microliters of the concentrated standard are added. These volumes are equivalent to 0.50, 0.25, 0.10, and 0.05 μg of bis-CME and 0.40, 0.20, 0.08 and 0.04 μg of CMME.

9.1.3 The vials are capped loosely and placed on a steam bath for 5 min. The standard is cooled and 10 ml of distilled water and 2 ml of hexane are pipetted into the vials. Then the standards are shaken for 5 min.

9.2 Standard curves are established by plotting the peak height of recorder response versus concentration in nanograms.

10. Calculations

10.1 Determine from the calibration curve the concentration of the desired component in nanograms.

$$\text{Component (ng)} = \frac{A \times B}{C}$$

where:

A = response for the component of interest in the sample

B = weight of CMME or BCME in the standard expressed in nanograms

C = response for the component of interest in the standard

10.2 The concentration of CMME and BCME in the sampled atmosphere can be calculated in ppb (v/v).

$$\text{ppb (v/v)} = \frac{D \times 24.45}{V_s \times \text{MW}}$$

where:

D = total ng concentration as determined in Section 10.1

24.45 = molar volume of an ideal gas at 25°C and 760 Torr

V_s = volume of air sampled in liters at 25°C and 760 Torr

MW = molecular weight of CMME and BCME, 80.5 and 115, respectively.

11. Reference

11.1 Solomon, R. A. and G. J. Kallos, Anal Chem 47:955, 1975.