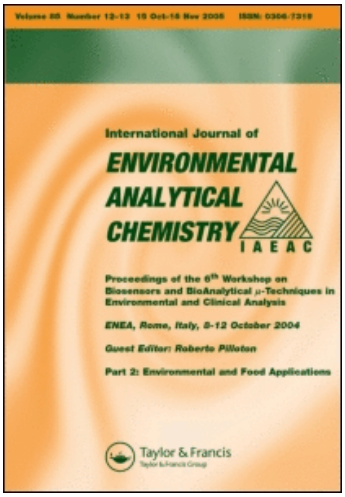

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F. C. G. M. Langelaan[a]; M. W. F. Nielen[a]
[a] Department of Analytical Chemistry, MT-TNO, Delft, The Netherlands

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DETERMINATION OF TRACE LEVELS OF CHLOROMETHYL-METHYLETHER AND BIS(CHLOROMETHYL)ETHER IN AIR

F. C. G. M. LANGELAAN and M. W. F. NIELEN*

MT-TNO, Department of Analytical Chemistry, P.O. Box 217, 2600 AE, Delft, The Netherlands

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A method has been developed for the trace level determination of the carcinogens chloromethyl-methylether (CMME) and bis(chloromethyl)ether (BCME) in air. The method consists of a preconcentration step on a Tenax adsorption tube followed by solvent desorption and derivatization with sodium pentafluorophenolate. The derivatives are analyzed by capillary gas chromatography with electron capture detection. Formation of the derivatives was demonstrated by comparison with a synthetic standard using mass spectrometry. The achievable detection limits were 15 ppt (v/v) CMME and 3 ppt (v/v) BCME, for a 30 liter sample.

KEY WORDS: Capillary gas chromatography, bis(chloromethyl)ether, preconcentration, derivatization, air sampling.

INTRODUCTION

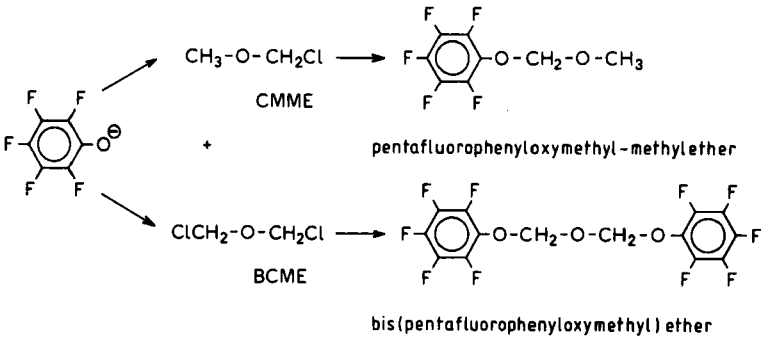
Bis(chloromethyl)ether (BCME) and—to a lesser extent—chloromethylmethylether (CMME) are highly carcinogenic substances.[1] Although the TLV for BCME is set at 1 ppb (v/v), even concentrations of 0.1 ppb (v/v) cannot be considered totally beyond suspicion of carcinogenity.

BCME and its intermediate CMME may be formed in several (industrial) processes in which ethers, aldehydes and chlorine atoms are involved.[1–3] It is obvious from its carcinogenity that the best analytical means are required in the control for the absence of these substances in workplace and outdoor atmospheres. NIOSH[4] has described an impinger method in which CMME and BCME are derivatized with sodium trichlorophenolate and analyzed by gas chromatography with electron capture detection (GC-ECD). However, the method suffers from artefact formation caused by the presence of sodium methoxide in the reagent and a relatively high detection limit (0.5 ppb (v/v)). Van der Ven and Venema[5] used a preconcentration method with subsequent solvent desorption, derivatization with *p*-phenylphenolate and flame ionisation detection (GC-FID), which resulted in 0.1 ppb (v/v) sensitivity, provided that 30 liters of air are sampled. Krost *et al.*[6] used a preconcentration method followed by on-line thermal desorption and gas chromatography with mass spectrometric detection (GC-MS). They reported breakthrough volumes on Tenax of several hundreds of liters. The attainable

detection limit was not determined but estimated to be 1 ppt(v/v) at the breakthrough volume (assuming 100% recovery and negligible blanks in the analytical procedure).

More recently, Widmer *et al.*[7] used a preconcentration step, on-line thermal desorption and multi-dimensional GC-FID in order to achieve low ppb(v/v) detection limits of BCME.

On-line thermal desorption methods, thereby using the entire sample, were not considered as a practical option because of the risk of losing the entire sample during the analysis (in which case new samples should have to be collected). We combined preconcentration on Tenax adsorption tubes with derivatization and GC-ECD for the determination of BCME and CMME in air at ppt(v/v) levels. Pentafluorophenolate was used as the derivatizing agent in order to obtain highly ECD-active products:



These derivatives possess high ECD sensitivity; besides stability has increased and toxicity decreased, which facilitates a lot of manipulations in the laboratory. In order to be able to study the derivatization yield of BCME and to identify the peak in the chromatogram, bis(pentafluorophenyloxymethyl)ether was synthesized in our laboratory.

EXPERIMENTAL

Apparatus

A Varian (Sunnyvale, CA, U.S.A.) model 3700 gas chromatograph was used and equipped with a falling needle injector (operated at 270°C), a ^{63}Ni electron capture detector (300°C), and a 25 m × 0.32 mm I.D. (d_f 1.2 μm) CP-Sl 5 CB capillary column (Chrompack, Middelburg, the Netherlands). The GC-oven temperature was programmed from 100 to 250°C at 3°C/min. Carrier gas: helium (2 ml/min); make-up gas: nitrogen (30 ml/min). The injection volume was 3 μl.

The formation of derivatives was checked with the aid of a Hewlett Packard (Sunnyvale, CA, U.S.A.) model 5880A gas chromatograph equipped with a Hewlett Packard model 5970A Mass Selective Detector (GC-MSD). The GC-MSD was

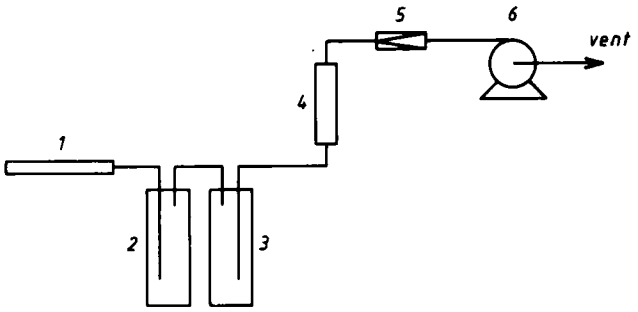


Figure 1 Air sampling of CMME and BCME: 1 = Tenax tube; 2 = impinger with alcoholic sodium hydroxide; 3 = impinger (empty); 4 = flow meter; 5 = critical orifice; 6 = vacuum pump.

operated in the scan mode (40–450 a.m.u.) or the selected ion mode (44, 45, 105, 167, 197, 198, 227 and 228 a.m.u.)

Materials

Home-made glass tubes (8 cm × 7 mm I.D.) equipped with 1/4 inch brass Swagelok caps and PTFE-ferrules were packed with 300 mg of Tenax GC (Chrompack). The packing was retained by plugs of quartz wool. The adsorption tubes thus obtained were conditioned by purging with 20 ml/min of purified helium in an oven at 250°C during 16 hours.

Nanograde-hexane was obtained from Promochem Mallinckrodt; analytical-grade sodium hydroxide was obtained from J. T. Baker; analytical-grade dimethylformamide (DMF) was obtained from Fluka and dried on molecular sieve 5 A. Bis(chloromethyl)ether was obtained from Ultra Scientific RCC. Chloromethylmethylether was received as a gift from AKZO Chemicals (The Netherlands). Sodium pentafluorophenolate and bis(pentafluorophenyloxymethyl)ether were synthesized and purified by our Department of Organic Chemistry.

Procedures

Stock solutions of CMME (1 mg/ml) and BCME (3.5 mg/ml) were prepared in *n*-hexane and diluted with DMF to the required concentrations. The derivatization proceeded as follows: 10 mg of sodium pentafluorophenolate were dissolved in 50 ml of DMF. To 1.0 ml reagent, 5.0 ml of a diluted standard solution of CMME (2 ng/ml) and BCME (7 ng/ml) were added. The mixture was placed in a waterbath at 35°C during 2.5 h after which 10 ml of 2 M sodium hydroxide were added in order to hydrolize unreacted CMME and BCME. Next the mixture was shaken for 30 min after the addition of 1.0 ml *n*-hexane. The excess of reagent remains in the aqueous layer, the derivative in the organic layer; 3 μl of the organic layer are injected in the GC-ECD.

Air sampling was performed using the equipment shown in Fig. 1. The preconcentrated volume was typically 30 liters. The Tenax tubes were eluted in the

laboratory (as soon as possible) with DMF and the eluate was derivatized as described above.

RESULTS AND DISCUSSION

Derivatization

Initially derivatization was carried out at room temperature in the dark, which resulted in a derivatization yield for BCME of 15–20%. Increasing the temperature to 35°C was very beneficial: The yield increased to $47.5 \pm 5\%$ ($n=3$) and became more reproducible. Possibly a further increase of temperature would have resulted in higher yields. However, one should realize that the applicable temperature is restricted by the relatively high vapour pressure of, especially, CMME. Therefore we used 35°C in all further experiments. The derivatives, on the other hand, possess a low vapour pressure thereby allowing injection of 3 μl in the GC-ECD via the falling needle injection technique.

A standard solution of CMME (2 mg/ml) and BCME (7 mg/ml) was derivatized and analyzed by GC-ECD. The pentafluorophenolates of CMME and BCME were identified using the retention times, relative peak heights and the retention time of the synthetic bis(pentafluorophenyloxymethyl)ether. The same sample was also analyzed by GC-MSD. Parts of the corresponding mass spectra are given in Fig. 2. The proposed fragmentation patterns are given in Fig. 3. The peaks in the ECD chromatogram were found to correspond indeed to the pentafluorophenyloxy derivatives of CMME and BCME.

Characteristics of the Preconcentration Tube

In order to avoid the preparation of a carcinogenic test atmosphere, adsorption data were taken from ref. 5. These authors found a breakthrough volume for BCME of at least 80 l/g Tenax which was, in addition, independent of the relative humidity of the sample. The desorption efficiency of BCME was studied by spiking four Tenax tubes with 70 ng of BCME, followed by flushing with 10 liters of dry and purified nitrogen (1 l/min). Next the tubes were desorbed with 5.0 ml of DMF and the eluates were derivatized and analyzed by GC-ECD. Using the derivatization yield of 47.5% (cf. above), the desorption efficiency of BCME was calculated to be $97 \pm 8\%$ ($n=4$).

Calibration and Quantitation Data

A calibration plot for the GC-ECD analysis was made using dilutions of bis(pentafluorophenyloxymethyl)ether in *n*-hexane, with concentrations in the range of 0–200 ng/ml ($n=7$). The calibration plot was found to be linear ($r=0.9999$). Contrary to BCME, no synthetic derivative of CMME was available.

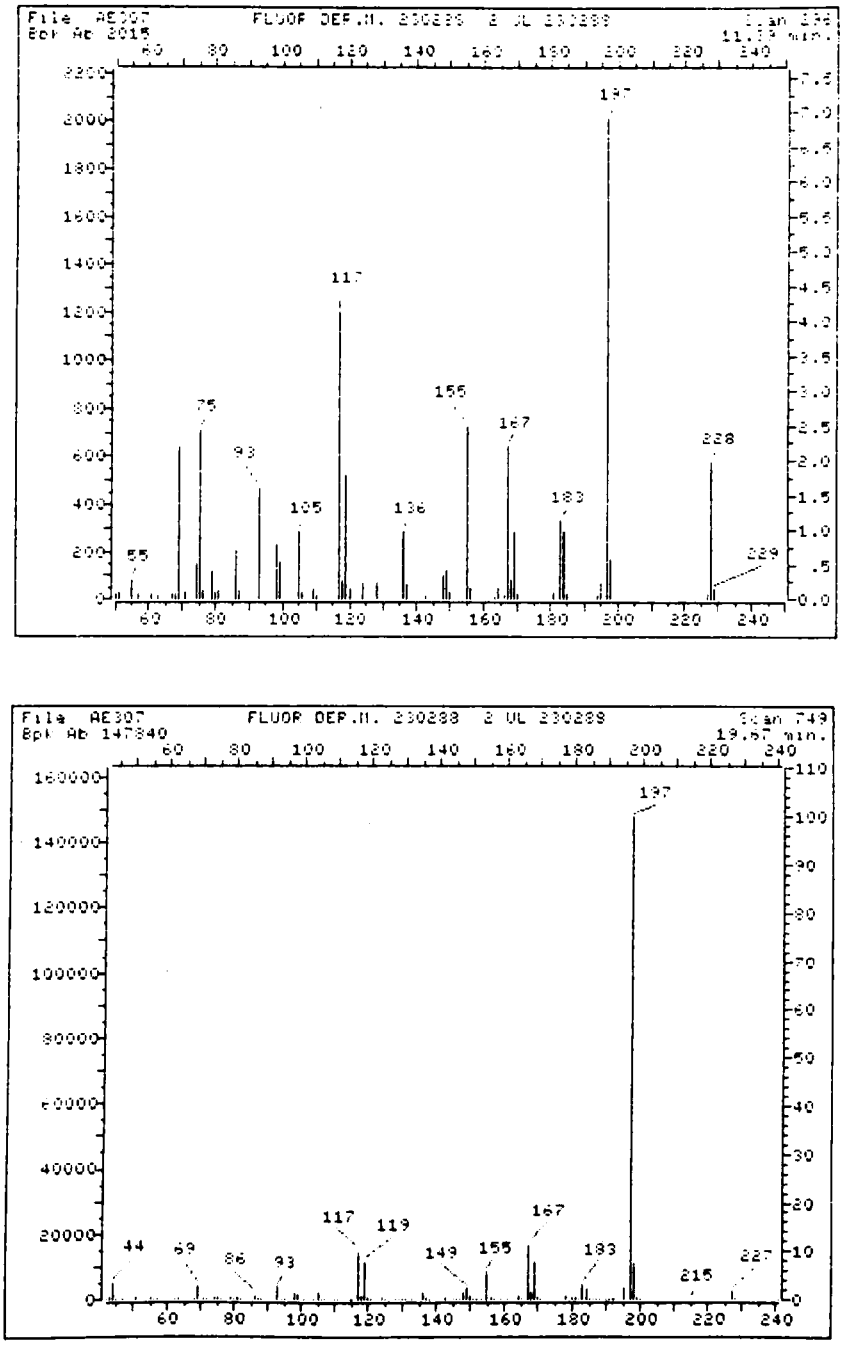


Figure 2 Mass spectra of (a) pentafluorophenyloxymethyl-methylether and (b) bis(pentafluorophenyloxymethyl)ether.

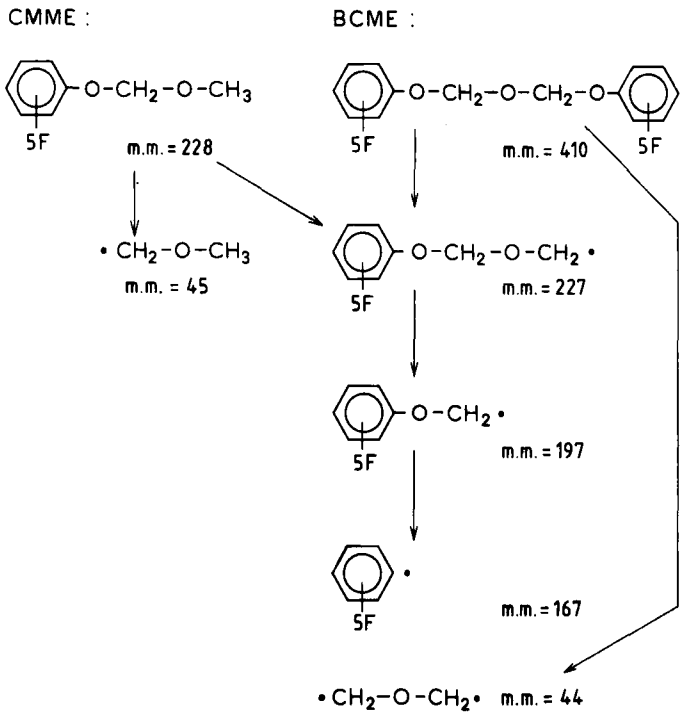


Figure 3 Proposed fragmentation patterns of the derivatives of CMME and BCME.

Therefore the amount of CMME was calculated using a mean response factor which was obtained via spiking of Tenax tubes with known amounts of CMME, elution, derivatization, GC-ECD analysis and, finally, plotting of the obtained peak areas versus the loaded amounts of CMME. The response factor thus obtained includes also relevant aspects such as derivatization yield and desorption efficiency.

The repeatability of the method was determined by spiking five Tenax tubes with CMME (7 ng) and BCME (35 ng). The tubes were flushed with 10 liters (1 l/min) of dry nitrogen with, next, elution, derivatization and GC-ECD analysis. The detection limit was calculated with the aid of the obtained chromatogram, using a signal-to-noise ratio of 3:1. The results and the achievable detection limits are given in Table 1.

Table 1 Analytical data for the analysis of Tenax tubes spiked with CMME and BCME. Conditions, see text

Compound	*Spike/tube (ng)*	*Repeatability (%RSD; n = 5)*	*Detection limit (sample 30 l)*	
			ng	*ppt (v/v)*
CMME	7	8.7	1.6	15
BCME	35	7.6	0.5	3

The results compare favourably with those in ref. 5, in which a repeatability of 20% was reported for 30 ng BCME, and a detection limit of 100 ppt (v/v).

Stability and Selectivity

Because of the hydrolysis of BCME in the presence of water, as a rule sampled adsorption tubes have to be analyzed within a few hours. In fact, there is a strong correlation between the stability and the relative humidity of the sampled air.[5] We spiked two Tenax tubes with 350 μg of BCME. Then 30 liters of indoor air having a relative humidity of approx. 35% were sucked through the spiked tubes. One tube was stored in the dark at room temperature and analyzed after 48 h. Due to the relatively low water content, the recovery was found to be still 100% as compared to the other tube which was analyzed immediately. Obviously for indoor air measurements, analyzing within a few hours is not really necessary.

The selectivity of the method towards hydrolyzed CMME and BCME was demonstrated as follows: 1.0 ml of 2 M sodium hydroxide was added to a concentrated standard solution of CMME (7 mg) and BCME (35 mg) in order to convert CMME and BCME into their corresponding α-hydroxyethers. Next, derivatization with sodium pentafluorophenolate was performed followed by GC-ECD. The recoveries were less than 0.07%, thereby showing the excellent selectivity of the derivatization towards CMME and BCME in the presence of their hydrolysis products.

Application to Air Samples

30 liters of outdoor air were sampled on three different days in the neighbourhood of a potential CMME and BCME emission source. The adsorption tubes were eluted with DMF, the eluate was derivatized and analyzed by GC-ECD. A typical chromatogram is shown in Fig. 4. From the chromatogram, the selectivity towards outdoor air is obvious; no traces of CMME and BCME were present in these samples.

CONCLUSIONS

For the determination of CMME and BCME in indoor and outdoor air at ppt (v/v) levels preconcentration on Tenax and subsequent derivatization with sodium pentafluorophenolate offers the required sensitivity and selectivity. The method described has good linearity and repeatability. The disadvantage is the relatively long reaction time (2.5 h). Further optimization of the reaction conditions will be of interest in order to obtain a further improvement of the derivatization yield at a reduced reaction time.

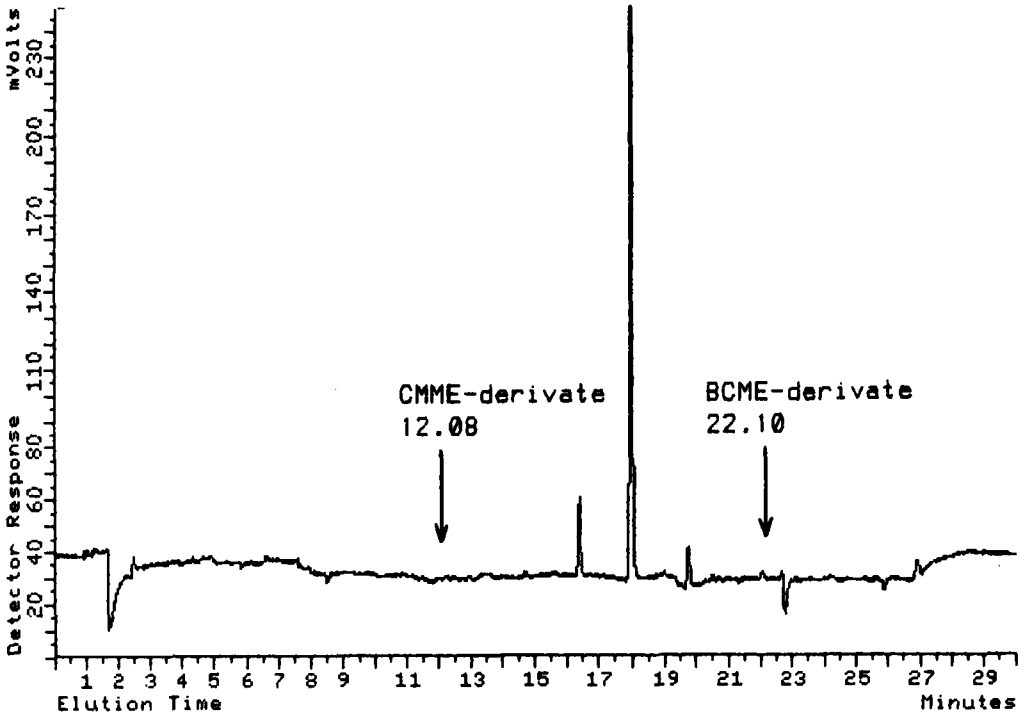


Figure 4 ECD chromatogram of an outdoor air sample (30 l) after preconcentration on Tenax, elution with DMF and derivatization with sodium pentafluorophenolate.

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References

1. S. Z. M. Travenius, *Scand. J. Work, Environ. Health* **8** (suppl. 3), p. 86 (1982).
2. F. Caesar, *Fres. Z. Anal. Chem.* **329,** 875 (1988).
3. G. J. Kallos and J. C. Tou, *Env. Sci. Technol.* **11,** 1101 (1977).
4. NIOSH Manual of Analytical Methods, 2nd ed. (part 1), 213 and 220 (1977).
5. L. G. J. van der Ven and A. Venema, *Anal. Chem.* **51,** 1016 (1979).
6. K. J. Krost, E. D. Pellizzari, S. G. Walburn and S. A. Hubbard, *Anal. Chem.* **54,** 810 (1982).
7. H. M. Widmer, J.-F. Erard and G. Grass, *Intern. J. Environ. Anal. Chem.* **18,** 1 (1984).