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Note

Direct capillary trapping and gas chromatographic analysis of bromomethane and other highly volatile air pollutants

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Bromomethane is still commonly used as a soil fumigant in green-houses and on strawberry cultivations, and as a methylating agent in warehouses and quarantine facilities. The analysis of the carry over residues of the fumigant in foodstuffs as well as the traces in ambient air have at least local interest[1].

Studies on *Klebsiella pneumoniae*[1], *Salmonella typhimurium*[1,2] and *Escherichia coli*[2] indicate a relatively low mutagenic efficiency of bromomethane. Tests on animals have suggested that bromomethane may cause disorders in the central nervous system. The LC-50 value (95% confidence) was 302 ppm in rats[3] and the oral LD-50 value was 214 mg/kg body weight when the subchronic oral toxicity in rats was investigated[4]. Danse *et al.*[4] also showed that a 3-month oral test caused carcinomas in the forestomach of a rat. Furthermore, it was found that bromomethane is a genotoxically active compound in the somatic cells of *Drosophila* larvae[5].

Trichloronitromethane (chloropicrin) is used as a lachrymatory factor in the bromomethane fumigants. Chloropicrin was found to be mutagenic to *E. coli* and *S. typhimurium*[2].

Krost *et al.*[6] developed a useful method for the analysis of bromomethane in air with capillary columns and electron-capture detection (ECD). The sample was collected in Tenax traps, desorbed thermally, cryofocused in a nickel capillary tubing and analysed after a second heat desorption step. The detection limit was found to be about 500 pg in 1 l of air. Attention had to be paid, however, especially to the breakthrough and recovery measurements. An obvious problem with a 0.5 mm I.D. capillary was the plugging of the tube with water. Some previously used air sampling methods like that of Noack *et al.*[7] and Brown and Purnell[8] are less sensitive, or less useful, in bromomethane analysis.

The aim of the present study was to develop a method to analyze highly volatile air pollutants like bromomethane with direct capillary trapping and fused-silica capillary columns.

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EXPERIMENTAL

Air pollutant trapping

Ambient air was sucked through a 35 cm × 0.32 mm (or 0.53 mm) deactivated fused-silica capillary tube with a pump. The centre part of the tubing (15 cm) was placed in a cold trap filled with solid carbon dioxide acetone (−78°C) or liquid nitrogen (−196°C) during trapping. The volume of air passed through the capillary varied from 20 to 2000 ml.

In order to check for possible breakthrough of the volatiles, the following experiment was conducted. A 100-cm fused-silica capillary tube (0.53 mm I.D.) was coiled into two loops. The bottom halves of the loops (15 cm) were placed in the cold trap and the upper halves were kept at ambient temperature. One end of the tube was connected to a pump. The reference gas samples (*ca.* 1000 pg bromomethane and *ca.* 100 pg chloropicrin) were injected directly into the column chilled in solid carbon dioxide–acetone bath by using a 10-μl gas-tight syringe equipped with a 0.25 mm O.D. fused-silica capillary needle. An 100-ml volume of air was pumped in about 14 min by sucking through the sampling tube, then the tube was removed from the pump and cut into two pieces (each 50 cm). All the ends were sealed with SE-30 liquid phase material. The traps were kept chilled until analysis by gas chromatography (GC).

GC analysis of trapped samples

For the GC analysis an Hewlett-Packard 5890 chromatograph equipped with nickel-63 ECD was interfaced to an HP 3390A integrator. The outlet end of the sampling trap was connected to the on-column injector (J&W Scientific, Forsom, CA, U.S.A.) and the other end to the analytical column with a zero-dead-volume union. The trap was kept chilled all the time. A 60 m × 0.25 mm I.D. (film thickness 0.25 μm) bonded phase DB-1 or a 30 m × 0.32 mm I.D. (0.25 μm) bonded phase DB-1301 fused-silica capillary column (J&W Scientific) was used for GC analysis. When the connections were completed, the carrier gas (helium) was switched on for 1 min to purge oxygen from the column and the chilling trap was removed. The oven door was closed and the program was started.

Identification of the peaks on the gas chromatogram was performed by a co-injection method. The authentic reference gases were injected on-column before the cold trap was removed. The reference compounds were retained in the tubing with the trapped substances.

Threshold and linearity of detection

The linearity and detection threshold values of the ECD for bromomethane and chloropicrin were tested. Standard solutions of the analytes were made in hexane, and 1,2-dichloroethane (10^5 ng/ml) was added as an internal standard. Liquid samples, 0.3 μl, were introduced in the DB-1 column with on-column injection without cryofocusing. The contents of the analytes in hexane varied from 10 to 10^5 ng/ml and the amounts injected between 3 and $3 \cdot 10^4$ pg.

RESULTS

The cryosucking method was tested by collecting the impurities from laborato-

ry and ambient air and by analysing the electronegative volatiles (mainly halogenated compounds) by ECD. Fig. 1a shows a chromatogram of the laboratory air analysed with DB-1 liquid phase and Fig. 1b with DB-1301 liquid phase. The volume of the air samples trapped with liquid nitrogen in the deactivated capillary tube (0.32 mm I.D.) was in both cases 50 ml. Fluorotrichloromethane (Freon-11), di-, tri- and tetrachloromethanes and trichloroethylene were identified on the basis of co-injections with the reference compounds used in routine work in the laboratory. The relative and absolute amounts of the solvent traces varied all the time in the air, but the main peaks in the chromatograms were always present. Fig. 1a and b are not comparable to each other by quantitative means because the analyses were not carried out on the same day.

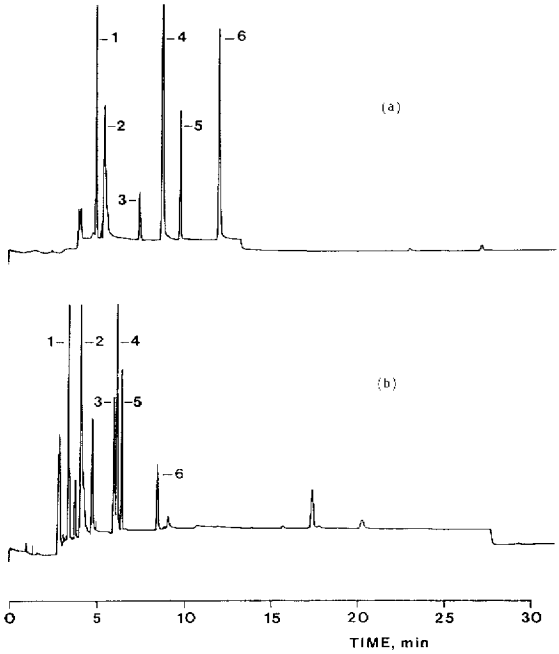

Fig. 1. Separation of some impurities in 50 ml of laboratory air collected by cryosucking in a capillary tube chilled in liquid nitrogen: 1 = fluorotrichloromethane (Freon 11); 2 = dichloromethane; 3 = trichloromethane; 4 = unknown; 5 = tetrachloromethane; 6 = trichloroethane. (a) 60 m × 0.25 mm DB-1 column, helium flow-rate 25 cm/s, isothermal 25°C. (b) 30 m × 0.32 mm DB-1301 column, helium flow-rate 21 cm/s, isothermal at 28°C. Detector temperature: 300°C.

An example of the breakthrough analysis of the volatiles is shown in Fig. 2a and b. No removal of water with a precondenser was done, which guaranteed a 100% introduction of all the volatiles in the air into the capillary tube. The compounds including bromomethane and chloropicrin were adsorbed in the first trapping loop (Fig. 2a). This was verified by GC analysis of the components in the second loop (breakthrough trap) shown in Fig. 2b.

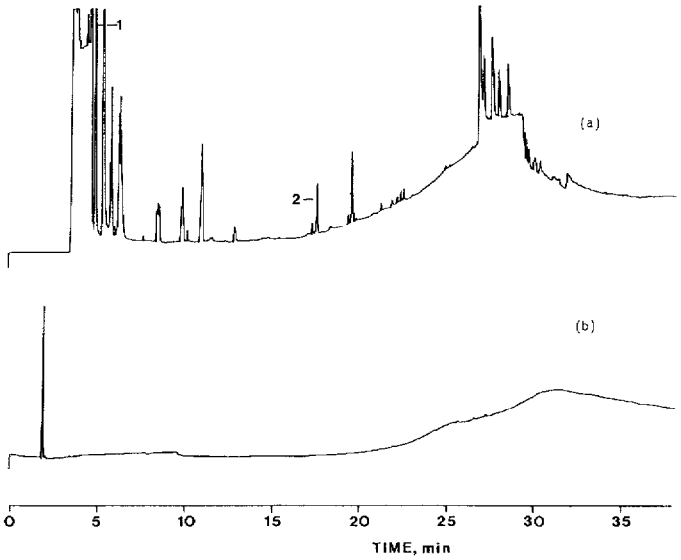

Fig. 2. Breakthrough test of the ambient air (100 ml) volatiles collected by cryosucking in capillary tube chilled in solid carbon dioxide–acetone. Bromomethane (1) and chloropicrin (2) co-injected in the tube at the beginning of the collection. (a) First trapping loop; (b) second trapping loop. Column: 60 m × 0.25 mm DB-1; isothermal at 29°C for 11 min, then programmed at 5°C/min to 100°C, finally held for 30 min. Detector temperature: 300°C.

The response curves for bromomethane and chloropicrin in hexane were determined by using 1,2-dichloroethane as an internal standard. Because of the varying ratio of the standard compound to the analyte in different samples, the correction factor was not constant. The lower the amount of the analyte, the higher was the correction factor. The relative responses of the compounds are presented in Fig. 3. Bromomethane had a far lower response than did chloropicrin; one bromine atom

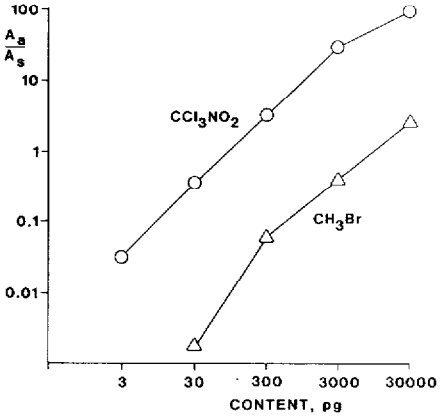

Fig. 3. Standard curves of bromomethane and chloropicrin analysed by a 60 m × 0.25 mm DB-1 column, isothermal at 60°C for 15 min, then programmed at 5°C/min to 100°C, finally held for 10 min. Internal standard: 1,2-dichloroethane, constant content $3 \cdot 10^4$ pg per injection. A_a = Area of the analyte peak; A_s = area of the internal standard peak.

against three chlorine atoms and one nitro group. The lowest point of the curve of bromomethane in Fig. 3 represents 30 pg of the compound and is close to the detection threshold value. The accurate value could not be determined due to some impurities in the redistilled hexane which were eluted at the same retention time as that of bromomethane, which was taken into account by subtracting the background. The threshold for chloropicrin was 3 pg.

DISCUSSION

The cryosucking of volatile samples in a capillary column or tubing for direct GC analysis is a very effective tool with many advantages and some limitations. The method developed may be compared with that of Kolb *et al.*[9], called "capillary head trapping", the principal differences being in the sample introduction.

Once the gaseous sample has been introduced into the capillary tube placed in the cold trap, no desorption steps using solvents or heat are needed. These operations might easily cause changes in the composition of the samples. Artifact formation is thus minimized with the capillary method proposed. Also the loss of volatiles is not a problem as long as the breakthrough during the sampling is verified to be zero (Fig. 2b). The collection should not be performed by compressing the air through a pump into a trap; only sucking is recommended. In this way the possibility of the collection of artifacts originating from the equipment can be minimized.

A piece of a capillary column or a whole column might be used as traps instead of the deactivated tubings. The use of liquid phase allows higher temperatures in the cold traps, also when volatiles with very low capacity factors are collected. When using the whole column as a trap, one connection in the column line can be avoided, which makes the procedure easier to operate. An obvious limitation is, however, the possible deterioration of the liquid phase due to sucking large amounts of air through the column. The polar phases, in particular, will be oxidized very rapidly, changing the selectivity and lowering the column efficiency.

When the sampling procedure is completed, the trap has to be inserted deeper into the coolant, to ensure that all the compounds retained are well chilled until analyzed. This is especially important with deactivated tubes without a liquid phase. The ends of the traps might be sealed with, for example, some viscous GC liquid phase like SE-30 or OV-1, which prevents the gas flow in the column during storage.

The connected capillary trap in the gas chromatograph has to be removed from the bath very slowly, starting from the injector side which was the outlet end of the tube when the sample was collected. In this way the most volatile compounds, like bromomethane, can be focused to a very short starting band. The problem of double peaks can easily be avoided and maximum column efficiency may be achieved even with thin film columns. Sampling traps should not be any longer than necessary to eliminate breakthrough of the compounds being analyzed.

The moisture content in the air might be a problem, when analyzing the very minor impurities, which exist at the level of ng/m^3 (ref. 10). During our ambient air experiments (temperature 32°C and relative humidity 48%), 1 l of air contained 16.2 mg of water. This amount blocked the megabore trapping capillary after about 0.5 l air was pumped through. With special movement of the trap in the coolant, maximum volume of air was aboyut 2 l. This indicates that, without removal of the water,

chloropicrin at concentrations of a few nanograms in 1 m^3 of air can be analyzed. In the case of bromomethane, the threshold level is about ten-fold when compared to chloropicrin.

In the case of the most volatile compounds, the main problem is not how to perform the collection nor how to remove the water. The problem appears usually when trace amounts of compounds with very low retentions have to be analyzed together with some major overlapping compounds. This is not, however, caused by the collection method, but a question of the efficiency and selectivity of the liquid phase.

The method as a whole is useful, because the only factor limiting the resolution is the column efficiency[11]. Therefore, the sensitivity in the case of bromomethane is about ten-fold that of the method of Krost *et al.*[6]. The cryosucking method may be used not only for air pollutant research, but also for food volatile analysis, both in the static and dynamic headspace procedures. In the case of foodstuffs with high water vapour pressure, such as sugar syrups, the maximum water loading capacity may be exceeded with as little as 20–30 ml volumes. Therefore, with liquid foodstuffs, a more accurate headspace introduction may often be possible with on-column injection by using a gas-tight syringe[12].

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