ELSEVIER

Journal of Chromatography A, 690 (1995) 187–195

JOURNAL OF CHROMATOGRAPHY A

Gas chromatographic determination of volatile alkenes with on-column bromination and electron-capture detection

Xu-Liang Cao, C. Nicholas Hewitt*

Institute of Environmental and Biological Sciences, Lancaster University, Lancaster LA1 4YQ, UK

First received 16 June 1994; revised manuscript received 30 August 1994

Abstract

A method is described for the gas chromatographic–electron-capture detection determination of alkenes via on-column bromination reactions. Pyridinium bromide perbromide (PBPB) was used as the Br_2 source, and a cholesterol–glass beads mixture, treated with methanol, was used to remove excess Br_2. The optimum ratio of cholesterol to glass beads was found to be 1:10, at which 93% of the bromine released from PBPB can be removed, without removal of the derivitized analytes. The conversion efficiency of alkene to the brominated derivative is extremely low (less than 2%) for ethene, whereas for propene and 1-butene it is 41 and 79%, respectively. For C_3–C_5 alkenes, this method is 200–300 times more sensitive than analysis of the underivitized analytes by using conventional flame ionization detection.

1. Introduction

Few hydrocarbons (or volatile organic compounds, VOCs) are toxic in their own right at the concentrations found in the ambient atmosphere, and their main contribution to air pollution stems from their role in the atmospheric formation of ozone, peroxyacetyl nitrate (PAN), hydrogen peroxide and other secondary air pollutants [1]. Because of their extremely low ambient concentrations [volume mixing ratios of $<10^{-12}$ ppt (v/v) to 10^{-9} ppb (v/v)], detection of hydrocarbons in the atmosphere requires sensitive analytical methods. As the more reactive hydrocarbons (e.g., alkenes) have a greater reactivity towards OH radicals (and thus have higher potential for ozone formation) than the non-reactive hydrocarbons (e.g., alkanes), the priority in atmospheric monitoring programmes which focus on photochemical ozone production is the determination of the reactive VOCs, rather than of the non-reactive species. Under some circumstances it may therefore be advantageous to utilize a detection system that has enhanced sensitivity towards alkenes but is relatively insensitive to alkanes and other less reactive VOC species.

Attempts have been made to develop analytical methodologies that have enhanced sensitivity towards alkenes relative to the behaviour of conventional flame ionization detection (FID). For example, recently, reduction gas detection (RGD), originally developed for detecting the reducing gases CO and H_2 [2], has been used for the detection of acetaldehyde and acetone [3] and isoprene [4]. The response of RGD to a variety of reactive hydrocarbons has been investigated using gas chromatography

* Corresponding author.

0021-9673/95/$09.50 © 1995 Elsevier Science B.V. All rights reserved
SSDI 0021-9673(94)00855-8

(GC) with packed columns [5]. It was shown that it is considerably more sensitive to alkenes than is FID, and has much greater sensitivity to alkenes than alkanes. RGD has also been developed successfully for the capillary GC determination of hydrocarbons up to C_6 with high resolution [6,7].

In this work, electron-capture detection (ECD) was applied to the detection of alkenes following a derivitization step. ECD is a very sensitive and selective GC detection method for organic compounds containing highly electronegative elements such as Cl, Br and N. Its sensitivity towards organic molecules that do not contain O, N or halogen atoms is very low. However, if an element of high electronegativity could be added to the alkene via an on-column reaction, then it might be expected that alkenes could be detected by ECD with much higher sensitivity than by FID.

The GC–ECD detection of alkene compounds via bromination reactions was investigated. This required the attachment of bromine atoms to the alkenes, to render them amenable to ECD, and removal of excess bromine prior to detection.

2. Experimental

2.1. Principle

To use bromination reactions successfully for the ECD of alkenes requires that the derivitization reactions be very rapid and proceed to completion within a few seconds, otherwise the eluting peaks will be small and broad in the chromatogram, and the sensitivity will be reduced. The principle of this work is based on the reactions of bromine with alkenes to form the *o*-dibromoalkane derivatives:

$$RCH{=}CHR' + Br_2 \rightarrow RCHBrCHBrR' \qquad (1)$$

This reaction is an electrophilic addition reaction, and can be affected significantly by the presence of polar substances. In most cases it can proceed very quickly and quantitatively at room temperature in the polar liquid phase, without light or catalysis.

Although the possible role of bromine compounds in the chemistry of the atmosphere has promoted the study of the kinetics of the reactions of bromine atoms with hydrocarbons [8–10], little information is available on the addition reactions of bromine molecules with alkenes in the gas or vapour phase. However, it is expected that, so long as polar conditions can be realized, these reactions may also proceed very quickly in the gas phase and thus may be used for this purpose.

Although the hydrogen atoms in alkanes can be easily displaced by bromine atoms under conditions of light, heat or catalysis, alkanes do not react with bromine in darkness and at room temperature. It should therefore be possible to control the conditions of bromination to prevent the bromination of alkanes while still derivatizing the more reactive alkenes.

2.2. GC system

GC measurements were made using a Hewlett-Packard 5890 Series II gas chromatograph fitted with an electron-capture detector. The carrier and the auxiliary gas was helium. The configuration of the whole GC–ECD–bromination system is shown in Fig. 1. The GC column used was an HP-1 (10 m × 0.53 mm I.D., film thickness 2.65 μm). Tubes 1 and 2 are glass tubes (10 cm × 3 mm I.D.). Tube 1 was packed with either glass beads (80–100 mesh, 0.254–0.284 cm) or the brominating reagent, and tube 2 was packed with either glass beads or the substance for removing the excess bromine, depending on the purpose of the experiment.

2.3. Materials

Pyridinium bromide perbromide (PBPB) and cholesterol were obtained from Aldrich. A 15 ppm (v/v) standard vapour mixture of C_2–C_6 1-alkenes (Scotty) was used. This contains equal concentrations of ethene, propene, 1-butene, 1-pentene and 1-hexene. Their reaction products with bromine will thus be 1,2-dibromoethane, 1,2-dibromopropane, 1,2-dibromobutane, 1,2-dibromopentane and 1,2-dibromohexane, respectively. 1,2-Dibromoethane, 1,2-dibromo-

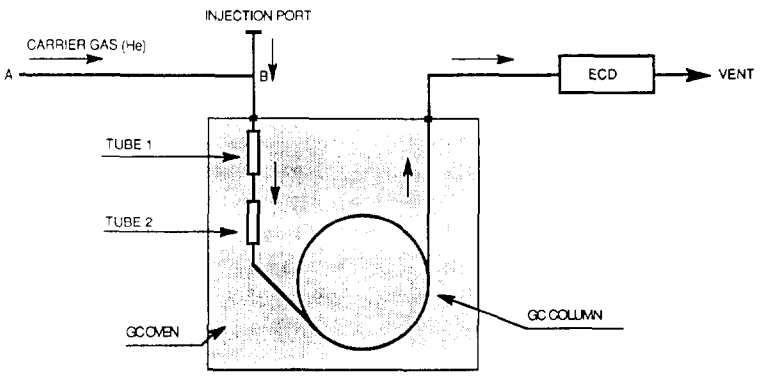

Fig. 1. Schematic diagram for the GC–bromination–ECD system.

propane and 1,2-dibromobutane were obtained from Aldrich for peak identification by comparison of retention times. Their standard vapour mixtures were prepared by the static dilution bottle methods [11,12]. Known amounts of liquid dibromoalkanes were injected into a 1-l glass flask which had been purged with nitrogen for 3 min. Further serial dilutions were made by withdrawing known amounts of vapour from the flask and injecting them into other similar flasks. Flasks and gas-tight syringes were kept at 55 ± 5°C in order to prevent vapour condensation of adsorption.

3. Results and discussion

3.1. Release of Br_2 from pyridinium bromide perbromide (PBPB)

PBPB is a red, crystalline salt ($C_5H_5NHBr \cdot Br_2$, M_r 319.84, m.p. 135–136°C). From its structural formula it is expected that it can release free bromine molecules, so when substituted for bromine in any standard bromination procedure the reaction should proceed in the normal manner. Because this reagent can be handled and stored more easily than liquid bromine, it has been used as a brominating reagent since the 1940s [13–15]. However, all such applications of PBPB have been in the liquid phase in which the free bromine was released from solutions of PBPB in glacial acetic acid or methanol. Its use as a source of vapour-phase Br_2 molecules for the on-line derivitization of alkenes was first proposed by Simmonds [16].

In order to check if the perbromide can release bromine vapour from its solid phase or not, tube 1 in Fig. 1 was packed with 0.27 g of PBPB and tube 2 with 0.72 g of glass beads (80–100 mesh). It was observed that the rate of release of Br_2 by the PBPB, as detected by ECD, increased with increasing carrier gas flow-rate passing through it, and especially with increasing GC oven temperature. The ECD signals responding to the bromine released from the PBPB varied from a few thousand mV to the maximum (i.e., saturation of the ECD). Even at a constant carrier gas flow-rate (e.g., 20 ml/min) and GC oven temperature (e.g., 30°C), the ECD signal due to the bromine released from the PBPB still varied significantly, from 2000 to 5000 mV.

3.2. Bromine filter

Following derivatization of the alkenes in an air sample, excess bromine from the PBPB will still be present in the gas flow and must be removed prior to entry into the detector. This is necessary for at least three reasons: (1) to allow detection of trace amounts of the brominated analytes the concentration of free Br_2 must be reduced to an absolute minimum; (2) the ECD sensitivity will be progressively reduced by formation of $NiBr_2$ when it is continuously exposed

to bromine vapour; (3) to avoid damage of the GC capillary column by bromine due to its highly oxidizing properties. The bromine filter should ideally be in the solid phase under normal conditions, and it should be able to remove bromine (by adsorption or absorption) efficiently, but it should not have any effect on the brominated products.

Silver powder was investigated for this purpose, and it was found that it can remove bromine efficiently at room temperature by forming AgBr via the following reaction:

$$2Ag + Br_2 \rightarrow 2AgBr \downarrow \quad (2)$$

However, the brominated alkenes were also removed very efficiently by reaction with silver via the following reaction (taking 1,2-dibromoethane as an example):

$$BrCH_2CH_2Br + 2Ag \rightarrow CH_2{=}CH_2 + 2AgBr \downarrow \quad (3)$$

Hence silver and other similar metals cannot be used for this purpose.

Large organic molecules with double bonds may also be able to remove bromine via bromine addition reactions, but may have no effect on the brominated alkenes. Cholesterol ($C_{27}H_{46}O$, M_r 386.67, m.p. 146–149°C) is a white, crystalline solid with a double bond and its use for this purpose was suggested by Breuer [17]. Its molecular structure is shown in Fig. 2.

In order to check if cholesterol can remove bromine or not, tube 1 in Fig. 1 was packed with

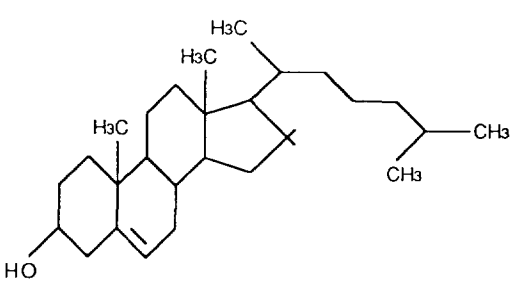

Fig. 2. Molecular structure of cholesterol.

0.27 g of PBPB and tube 2 with 0.20 g of cholesterol. A carrier gas flow-rate of 20 ml/min, optimized on the basis of peak width and Br_2 production rate, and an oven temperature of 30°C, kept as low as possible to minimize the release rate of Br_2 from the PBPB and to minimize the volatilization of cholesterol, which contains an OH group to which the ECD is sensitive, were used. Under these conditions, it was observed that the ECD signal from the PBPB was not reduced by the cholesterol. This suggests that cholesterol itself does not react sufficiently rapidly with bromine. This may be due to the lack of polar conditions, since the addition reactions of bromine with alkenes are electrophilic.

In order to create the optimum polar conditions for the cholesterol–bromine addition reactions, a series of different mass ratios of cholesterol–glass bead mixtures, treated with methanol, were prepared: 1:1, 1:2, 1:4, 1:5, 1:7, 1:9, 1:10, 1:11, 1:12 and 1:15. These mixtures were prepared by dissolving known amounts of cholesterol in methanol (20 ml) with gentle heating. Known amounts of glass beads were added to the solution and the methanol was removed by evaporation to dryness. At ratios of 1:1 and 1:2, no reduction in the ECD signal due to the PBPB was observed. At ratios of 1:4 and 1:5, the ECD signal was reduced to 700–800 mV for about 10 min, and then increased rapidly to above 1000 mV again. At a ratio of 1:7, the ECD signal from the PBPB was reduced to and stabilized at about 600 mV, and at ratios of 1:9, 1:10, 1:11 and 1:12 the signal stabilized at about 300 mV. Considering the average ECD signal due to PBPB alone (3000 mV), the ECD baseline signal (about 30 mV) and the ECD signal from cholesterol alone (about 50 mV) under the conditions used, the bromine removal efficiency of the cholesterol–glass bead mixture at ratios of 1:9, 1:10, 1:11 and 1:12 is about 93%. At a ratio of 1:15, the ECD signal from the PBPB was reduced to about 400 mV, but increased rapidly again to above 1000 mV, suggesting that insufficient cholesterol was available for complete continuous reaction with the bromine.

3.3. Effect of different cholesterol–glass beads ratios on the bromination of alkenes

It is expected that the methanol-treated cholesterol–glass bead mixture can provide suitable polar conditions, not only for bromine removal by cholesterol, but also for bromine addition reactions with the alkenes. As in the case of bromine removal by cholesterol, the mass ratios of the cholesterol–glass bead mixture may also be important for the bromine addition reactions with alkenes. In order to investigate this effect, the same amounts of C_2–C_6 1-alkenes were injected into the system at cholesterol-to-glass bead ratios of 1:7, 1:9, 1:10, 1:11 and 1:12. A typical chromatogram is shown in Fig. 3. On the basis of retention times relative to those of the standard dibromoalkanes, it is concluded that the alkenes were successfully derivitized under the conditions used and that sufficient excess Br_2 has been removed by the bromine filter to allow their detection by ECD.

The response factors for the brominated compounds (assuming complete derivitization of the alkenes) were calculated at different cholesterol-to-glass bead ratios and the results are shown in Fig. 4. Because the elution time of 1,2-dibromohexene is very long (70 min, see Fig. 3),

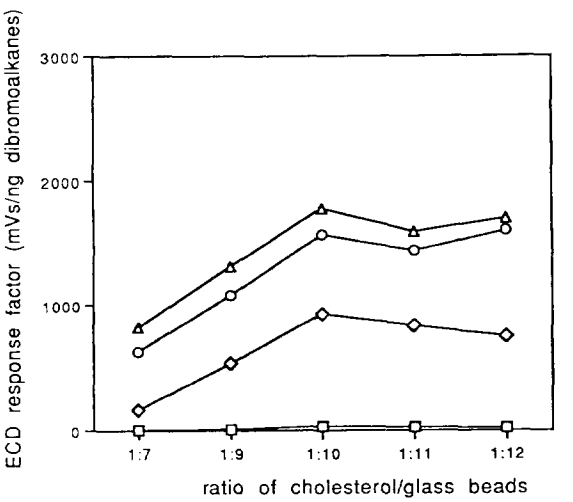

Fig. 4. Variation of ECD response factors for brominated compounds with mass ratio of cholesterol to glass beads. □ = 1,2-Dibromoethane; ◇ = 1,2-dibromopropane; □ = 1,2-dibromobutane; △ = 1,2-dibromopentane.

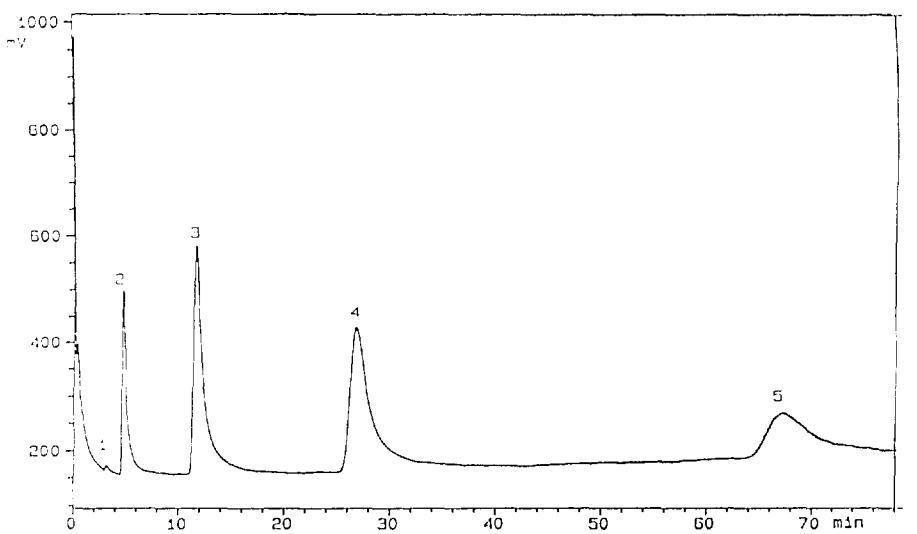

Fig. 3. Chromatograms of brominated compounds: 0.2 ml 15 ppm alkenes (C_2–C_6). GC oven temperature, 30°C; carrier gas flow-rate, 20 ml/min; column, 10 × 0.53 μm HP-1; tube 1, PBPB; tube 2, cholesterol–GB (1:10). Peaks: 1 = 1,2-dibromoethane; 2 = 1,2-dibromopropane; 3 = 1,2-dibromobutane; 4 = 1,2-dibromopentane; 5 = 1,2-dibromohexane.

only the brominated products of C_2–C_5 alkenes were investigated further.

It can be seen from Fig. 4 that for each alkene, the response factor of its corresponding brominated compound increased when the cholesterol-to-glass bead ratio increased from 1:7, to a maximum at 1:10, and then dropped slightly as the ratio increased to 1:12. The optimum mass ratio of the cholesterol–glass bead mixture is therefore in the range 1:10–1:12.

The conversion efficiencies of C_2–C_4 alkenes to the brominated compounds were calculated at each mass ratio of cholesterol to glass beads by comparing the response factors of the brominated derivitives with those of the standard brominated compounds. The results are shown in Table 1. It can be seen that at a constant ratio, the conversion efficiency increases with increasing carbon number. The conversion efficiency for ethene was found to be extremely low, but is adequately high for propene and 1-butene, increasing to 74% for the latter compound at a mass ratio of 1:12.

3.4. Effect of PBPB and cholesterol–glass beads on the brominated compounds

There may be two reasons for the extremely low derivitization efficiency of ethene: (1) its reaction with bromine molecules is very slow under the conditions employed or (2) the recovery of its brominated product, 1,2-dibromoethane, may be much lower than that of the other brominated products owing to the adsorption effects of PBPB and the cholesterol–glass bead mixture. In order to investigate the effect of PBPB and the methanol-treated cholesterol–glass bead mixture on the brominated compounds, known amount (about 1.5 ng) of standard vapour mixtures of 1,2-dibromoethane, 1,2-dibromopropane and 1,2-dibromobutane were injected on to the GC column with tube 1 packed with PBPB and tube 2 with cholesterol–glass beads (1:10). Their recoveries from the PBPB and the cholesterol–glass bead mixture were calculated by comparing these results with the corresponding signal obtained by injecting the same amount of the standard brominated compound mixture on to the GC column with tubes 1 and 2 both packed with glass beads. The recoveries with a GC oven temperature of 30°C and a carrier gas flow-rate of 20 ml/min were $72.31 \pm 2.11\%$ for 1,2-dibromoethane, $84.80 \pm 4.01\%$ for 1,2-dibromopropane and $92.30 \pm 2.23\%$ for 1,2-dibromobutane. Hence the recovery of the brominated compounds from the PBPB and cholesterol–glass bead mixture increased with increasing carbon number, with the recovery of 1,2-dibromoethane being the lowest. This may be due to removal on the polar surface of the methanol-treated cholesterol–glass bead mixture and the fact that the polarity of these brominated compounds decreases as the carbon number increases.

This adsorption effect due to the presence of polar surfaces on the cholesterol–glass bead mixture can also be seen from the chromatograms of these brominated compounds, shown in Fig. 5. Their chromatographic peaks are much broader than after passage over glass beads

Table 1
Conversion efficiencies (%) of alkenes to the brominated compounds at different ratios of cholesterol to glass beads

Alkene	Mass ratios of cholesterol to glass beads				
	1:7	1:9	1:10	1:11	1:12
Ethene	0	0.3 (0.4)	1.1 (1.5)	0.8 (1.2)	0.7 (0.9)
Propene	6.1 (7.2)	19.8 (23.4)	34.4 (40.5)	30.9 (36.5)	27.8 (32.7)
1-Butene	28.9 (31.3)	49.9 (54.1)	72.5 (78.6)	66.5 (72.0)	74.1 (80.3)

The values in parentheses were calculated by considering the adsorption effect of PBPB and cholesterol–glass beads.

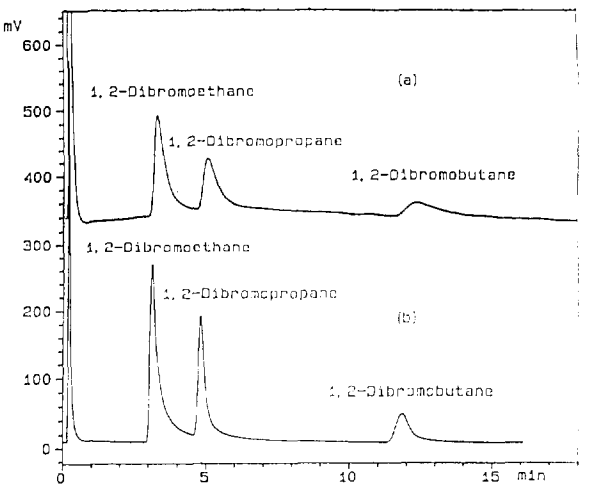

Fig. 5. Chromatograms of dibromoalkanes. GC oven temperature, 30°C; carrier gas flow-rate, 20 ml/min. (a) Tube 1, PBPB; tube 2, cholesterol–glass beads. (b) Tubes 1 and 2, glass beads.

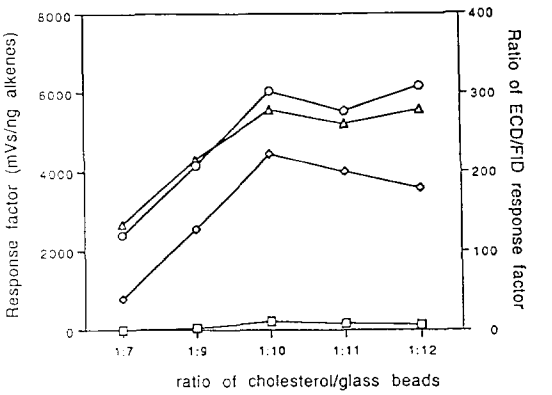

Fig. 6. Variation of the ECD response factors and the mass ratios of ECD and FID response factors for alkenes with the mass ratio of cholesterol to glass beads. □ = Ethene; ◇ = propene; ○ = 1-butene; △ = 1-pentene.

alone. However, even by considering the adsorption effect of the PBPB and the cholesterol–glass bead mixture (see the results in parentheses in Table 1), the conversion efficiency of ethene is still extremely low (less than 2%). This suggests that the bromine addition reaction with ethene is so inefficient that the method may not be suitable for the determination of ethene.

3.5. Comparison of the sensitivity of FID with the bromination–ECD method for alkenes

Fig. 6 shows the ECD response factors for the derivitized alkenes as a function of the mass of alkene introduced, and relative to the response factors of FID to the alkenes (about 20 mV s/ng), at different ratios. It can be seen that with cholesterol–glass bead mixtures of 1:10–1:12, ECD is about 200–300 times more sensitive to the C_3–C_5 alkenes via the bromination reactions than is FID to the underivitized alkenes. Little increase in sensitivity is achieved by bromination–ECD relative to FID for ethene.

The minimum detectable amounts of alkenes using the present GC–bromination–ECD system, based on a signal-to-noise ratio of 2, were 0.08 ng for propene, 0.11 for 1-butene and 0.14 ng for 1-pentene. Although they are higher than the typical detection limits currently obtainable with high-resolution capillary GC–FID (about 0.01 ng), it will be possible to lower them substantially by improving the chromatography and hence the peak shapes of the derivitized compounds.

3.6. System linearity

In order to check if the bromination–ECD system is linear with respect to the amount of alkene injected, different amounts of alkenes were injected on to the GC column, with tube 1 packed with PBPB and tube 2 packed with a 1:10 cholesterol–glass bead mixture. The results are shown in Fig. 7. It can be seen that the method is linear up to masses of ca. 2, 3 and 8 ng for propene, 1-butene and 1-pentene, respectively. That is, the range of linearity becomes broader with increasing carbon number. This is consistent with the fact that the conversion efficiency of the alkenes to the brominated derivatives increases with increasing carbon number. Hence, the range of linearity depends on the conversion efficiency of the bromination reactions. As the conversion efficiency for ethene is extremely low, its range of linearity is not relevant in this context.

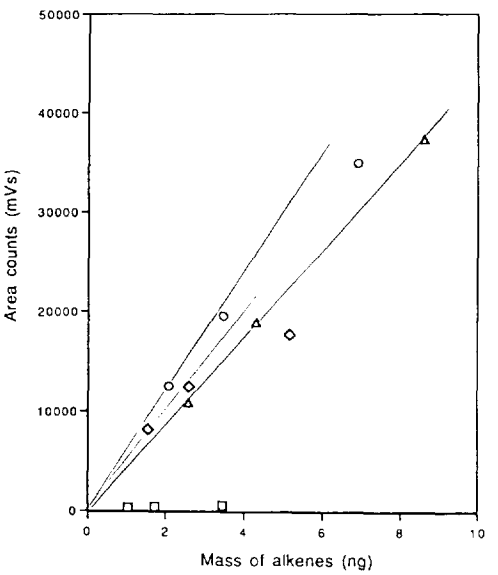

Fig. 7. Linearity of the ECD responses to the brominated alkenes. □ = Ethene; ◇ = propene; ○ = 1-butene; △ = 1-pentene.

3.7. Further discussion on the bromination of alkenes

The above results suggest that the rates of the addition reactions of bromine with alkenes are much lower for the lighter molecules, especially for ethene. This may be due to the low temperature (30°C) at which the alkene bromination reactions were carried out throughout this work. The reaction rates may be improved by using higher reaction temperatures, but this would be inappropriate in this application as the bromine-releasing rate of PBPB is extremely sensitive to temperature change, as is the volatilization rate of cholesterol. Experiments were carried out at 40°C, but the brominated products were not observable against an enhanced background ECD signal of ca. 1000 mV.

An attempt was made to use a higher GC oven temperature without enhancing the Br_2 production rate by removing the tube containing the PBPB (tube 1) from the oven and placing it between points A and B in the carrier gas line shown in Fig. 1. With this configuration, the same amounts of C_2–C_6 alkenes as those used above were injected on to the GC column but, surprisingly, no brominated products appeared. This suggests that the alkene vapour must pass through the PBPB tube to allow sufficient reaction with bromine molecules. It therefore appears that the bromination reactions have to be carried out isothermally at or around 30°C.

Without further development the method may not be suitable for the determination of heavier alkene molecules ($\geq C_6$). In addition, the insertion of the two packed tubes, negates some of the chromatographic advantages given by capillary columns and no additional benefit will result from using very high-resolution columns.

4. Conclusions

ECD has been successfully used for the GC determination of alkenes via on-column bromination reactions. The most important aspects of the method can be summarized as follows:

(i) PBPB can release bromine vapour at room temperature, and its bromine-releasing rate increases with increasing carrier gas flow-rate and, especially, with increasing temperature.

(ii) A methanol-treated cholesterol–glass bead mixture may be used to remove the excess bromine produced by the PBPB. The electrophilic nature of the addition reactions of Br_2 with alkenes requires the use of a polar medium: reaction with cholesterol alone is extremely slow. At the optimum ratio of the cholesterol–glass bead mixture of 1:10, 93% of the bromine released from PBPB can be removed.

(iii) The conversion efficiencies of the individual alkenes to their brominated products is very low for ethene (less than 2%), but increases with carbon number, reaching 74% for 1-butene.

(iv) The sensitivity of ECD to brominated C_3–C_5 alkenes is about 200–300 times higher than that of conventional FID without derivitization. Current detection limits with the GC–bromination–ECD system are higher than those with high-resolution GC–FID. It is expected that by using a two-oven system, that is, the reaction oven (for tubes 1 and 2) and the oven for the separation (for the capillary column), significant improvements in the chromatography, and hence

the detection limits, of the derivitized compounds will be obtained since the temperatures of the two ovens can be controlled separately.

(v) The amount of brominated compound produced from the alkene derivitization procedure increases linearly with increasing mass of analyte, but the range of linearity depends on the conversion efficiency of the bromination reactions.

The method described here allows the extremely sensitive detection of C_3–C_5 alkenes. Further development work (using a two-oven system) will be carried out in the future to allow application of the method to the detection of heavier alkenes ($\geq C_6$) at low concentrations in ambient air; the work to date provides a framework for this purpose.

Acknowledgements

This work arose from initial discussions with Dr. P.G. Simmonds and we gratefully acknowledge his assistance. We thank Dr. S. Breuer for suggesting the use of cholesterol as a bromine filter and for stimulating discussions. We thank the Government of the People's Republic of China, the British Council and the Natural Environment Research Council for funding.

References

[1] R.G. Derwent and M.E. Jenkin, *Hydrocarbon Involvement in Photochemical Ozone Formation in Europe*, AERE-R 13736, HMSO, London, 1990.
[2] W.M. Doizaki and M.D. Levitt, *J. Chromatogr.*, 285 (1984) 210–213.
[3] D. O'Hara and H.B. Singh, *Atmos. Environ.*, 22 (1988) 1623–1625.
[4] R. Fall and P. Zimmerman, personal communication.
[5] X.-L. Cao, C.N. Hewitt and K.S. Waterhouse, *Anal. Chim. Acta*, in press.
[6] X.-L. Cao, C.N. Hewitt and K.S. Waterhouse, *J. Chromatogr.*, 679 (1994) 115–121. Chrom. 26229
[7] X.-L. Cao and C.N. Hewitt, *J. Chromatogr.*, 648 (1993) 191–197.
[8] I. Barnes, V. Bastian, K.H. Becker, R. Overath and Z. Tong, *Int. J. Chem. Kinet.*, 21 (1989) 499–517.
[9] T.J. Wallington, L.M. Skewes, W.O. Siegl and S.M. Japar, *Int. J. Chem. Kinet.*, 21 (1989) 1069–1076.
[10] G. Yarwood, N. Peng and H. Niki, *Int. J. Chem. Kinet.*, 24 (1992) 369–383.
[11] C.M. Morris, R. Berkley and J. Bumgarner, *Anal. Lett.*, 16 (1983) 1585–1593.
[12] C.M. Morris, J.V. Dangtridge and J. Bumgarner, *Standard Operating Procedure for the Preparation and Use of Standard Organic Mixtures in a Static Dilution Bottle*, AREAL/RTP-SOP-MRDD-036, US Environmental Protection Agency, Research Triangle Park, NC, 1990.
[13] J.A. Vona and P.C. Merker, *J. Org. Chem.*, 14 (1949) 1048–1050.
[14] T. Williams, J. Krudener and J. McFarland, *Anal. Chim. Acta*, 30 (1964) 155–162.
[15] T.R. Williams and S. Wakeham, *Anal. Chim. Acta*, 52 (1970) 152–154.
[16] P.G. Simmonds, personal communication.
[17] S. Breuer, personal communication.