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

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Abstract

A method is described for the GC–electron-capture detection determination of ultra trace quantities of alkenes via on-column bromination reactions. Copper bromide coated onto a non-polar solid support, Gas Chrom Q (100–120 mesh) acted as the bromine source. At a temperature of 90–110°C, steel wool may be used to remove selectively up to 90% of the bromine bleed from the reactor. The conversion efficiency of an alkene to the dibrominated derivative is extremely high, up to 90% for ethene, propene, butene and pentene. The bromination of acetylene is also possible, but is not as efficient.

1. Introduction

Alkenes are a series of hydrocarbons that are of both natural and anthropogenic origin distributed throughout the global environment. They are comparatively unstable compounds in the atmosphere due to their high photochemical reactivity. The low-molecular-mass alkenes are believed to be precursors for peroxyacylnitrates (PANs) [1]. Alkenes are also an urban health hazard owing to their metabolic conversion to genotoxic epoxides [2,3].

The approximate atmospheric concentrations and lifetimes of the more important alkenes are shown in Table 1.

The bulk of the alkenes enter the environment through their widespread industrial use and from the incomplete combustion of fossil fuels.

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Ethene is the most abundant naturally produced alkene, a product of the ripening of fruit, hence the atmospheric concentration from this source is seasonal.

The accurate determination of alkenes in the atmosphere is hindered by both their extremely low concentrations (< 1 ppb) and the detection limit of the current analytical instruments, which are based on gas chromatographic separation coupled to flame ionization detection (FID).

The limit of sensitivity of FID is approximately 50 pg per component, and increases in proportion to the number of hydrogen and carbon atoms present in the analyte. This sensitivity is insufficient to determine the concentrations of alkenes present in ambient air without the use of extensive preconcentration systems.

Electron-capture detection (ECD) is particularly responsive towards electrophores and hence has a high sensitivity towards halogen containing

Table 1
Approximate atmospheric concentration and lifetimes of alkenes

Alkene	Approximate atmospheric concentration (ppt)	Approximate lifetime
Ethene	150–1000	36 h
Propene	150–1000	10 h
Acetylene	150–1000	Days
1-Butene	50–150	10 h
Isobutene	50–150	5 h
Isopropene	50–150	3 h
1-Pentene	1–50	9 h
cis-2-Butene	1–50	5 h
trans-2-Butene	1–50	4 h
Propadiene	1–50	20 h
1,3-Butadiene	1–50	4 h

compounds, in the order of 0.05 to 1 pg, with a linear range from 10 ppt to 1 ppb. The device has been used extensively for the monitoring of halogen-containing compounds, e.g. chlorofluorocarbons in the ambient environment [4,5].

However, the ECD response towards the low-molecular-mass alkenes is poor because of the lack of an electrophoric group. If alkenes could be derivatised, through the addition of an electronegative atom (bromine), by an in situ procedure immediately prior to the chromatographic column, this may then permit the near real-time detection of atmospheric alkenes.

2. Experimental

2.1. Principle

The successful use of on-column bromination reactions for the ECD of alkenes requires the derivatization to be very rapid and proceed to completion within a few seconds, otherwise the eluting peaks will be broad and diffuse, so reducing resolution and detection limit. The principle of the present work is based on the reactions of bromine with alkenes to form the dibromoalkane derivatives.

$$R-CH = CH-R' + Br_2 \rightarrow R-CHBr-CHBr-R'$$
$$(1)$$

This is an electrophilic addition reaction.

In most cases it can proceed rapidly and quantitatively at room temperature in a polar liquid phase, without light or catalysis, but this is not compatible with a routine method of gas chromatographic analysis.

For the vapour phase bromination of volatile alkenes, the gas is passed through a heated tube containing a metal halide catalyst coated on an inert support, such as $Cu(II)Br_2$ on activated alumina [6].

$$R-CH = CH-R'$$
$$+ 2CuBr_2 \rightarrow R-CHBr-CHBr-R'$$
$$+ 2CuBr \qquad (2)$$

The temperature required for reaction 2 is dependent on the ease with which the respective olefins can be polarised. Hence, hexene undergoes bromine addition at lower temperatures than ethene. Acetylene is particularly difficult to brominate completely due to the extremely high bond energy of the σ and two π bonds. The bromo derivative of acetylene most readily formed, is 1,2-dibromoethene.

The possible role of bromine compounds in the chemistry of the atmosphere has promoted study of the kinetics of the reaction of bromine molecules with hydrocarbons [7]. Work has been carried out on the halogenation of olefins in the liquid phase [8,9], but little information is available on the bromination of very volatile alkenes in the gas or vapour phase [10–12].

Conditions were sought that would maximize the bromine addition reaction with alkenes while minimizing substitution (3) reactions with alkanes naturally present in the complex matrix of an ambient atmospheric air sample.

$$R-CH_2-CH_2-CH_3 + Br_2 \rightarrow R-CH_2-CH_2-$$
$$CH_2Br + HBr \qquad (3)$$

2.2. Instrumentation

System 1

A Pye 104 fitted with an FID system allowed both the efficiency of the bromination phase and

identification of the derivative peaks to be determined. Replacing FID with ECD allowed determination of the detection limit.

Two packed, wide-bore glass columns were used (2 m × 7 mm I.D.), containing a non-polar separation phase [5% (w/w) silicone gum OV-101–Gas Chrom Q (100–120 mesh)]. One column contained 400 mg of the bromination phase packed into the inlet, the second column containing separation phase only, to be used as a reference.

System 2

To enhance the detection limit of each of the brominated alkenes, the GC configuration was altered to incorporate a capillary system. The equipment involved the use of two Pye 104 gas chromatographs coupled via a heated fused-silica capillary tube acting as a gas transfer line. One oven housed a column containing the brominating phase (38 cm × 0.762 mm I.D.), preceding the separation column (25 m × 0.5 mm I.D. support-coated open tubular OV-101), in the second oven. The object of this was to allow separate temperature control of both the brominating reaction phase and chromatographic separation column. The detector used was a ^{63}Ni ECD system.

2.3. Reagents and materials

For preparation of the brominating phase, iron(III) bromide, chromium(III) bromide and pyridine hydrobromide perbromide polymer bound, were purchased from Aldrich (Gillingham, UK). Copper(II) bromide only and copper(II) bromide coated onto alumina 30% (w/w), were obtained from Fluka (Gillingham, UK). Inert chromatographic support phases used were silica, 80–120 mesh, obtained from BDH (Poole, UK) and Gas Chrom Q and Chromosorb W, 100–120 mesh, from Alltech (Deerfield, IL, USA). Aluminium oxide to be used as a support phase for copper(II) bromide was also purchased from BDH.

Materials used for the removal of bromine bleed were steel wool (fine grade), from a commercial source and iron powder (pure) from

BAS (Middlesborough, UK). Copper turnings and silver wool were purchased from Alltech. Squalene, copper(II) nitrate and thallium(I) nitrate were obtained from BDH.

2.4. Preparation of alkene standards

For the preparation of low concentration gaseous mixtures, a 1000 ppm (v/v) alkenes standard (Scotty, Alltech) was used. The mixture contained equal concentrations of ethene, propene, but-1-ene, pent-1-ene and hex-1-ene. For the preparation of 10 and 1 ppm (v/v) standards, two 40-ml glass bottles were filled with nitrogen while submerged in water and stoppered with gas-tight seals. Using a gas syringe, 400- and 40-μl samples of the Scotty standard were injected into the bottles, preparing 10 and 1 ppm (v/v) standards, respectively.

Standard solutions (1 ppm and 1 ppb) of the respective dibromoalkane derivatives were prepared by serial dilution, employing doubly distilled hexane from an all-glass system.

2.5. Preparation of bromination phases

Thermogravimetric analysis (TGA) of the metal bromides, iron(III) bromide, chromium(III) bromide and copper(II) bromide, was carried out using a Stanton Thermobalance TR-1, capable of reaching 900°C. The results indicated the copper halide to be most suitable for the purpose of a brominating phase. Copper(II) bromide is a black crystalline salt but reduction at 150°C to copper(I) bromide is accompanied by a colour change from black to cream.

A series of brominating phases were prepared by coating copper(II) bromide onto: 100–120 mesh Chromosorb W (50:50, w/w); 100–120 mesh Gas Chrom Q (50:50, w/w); aluminium oxide (50:50, w/w); 80–120 mesh silica (20:80, w/w).

The same method of preparation was used for each phase.

Copper(II) bromide was dissolved in hot methanol and added to the support phase, preheated to 100°C. Most of the excess methanol boiled off immediately, while the remainder was

removed under vacuum. The phase was then conditioned under nitrogen for 24 h at 60°C.

Pyridine hydrobromide perbromide polymer bound, and copper(II) bromide coated on alumina (30:70, w/w), were purchased in a state ready for direct use as brominating phases.

2.6. Preparation of a phase to remove bromine bleed

Three metals, copper turnings, silver wool, iron powder and iron wool, were examined as scrubbing phases to adsorb the bromine bleed from the brominating phase. Other possible scrubbing phases were also investigated but required preparation using simple manipulative procedures.

(i) Copper coated onto Chromosorb W (25:75, w/w).

(ii) Copper coated onto Gas Chrom Q (25:75, w/w).

(iii) Thallium(I) nitrate coated onto Chromosorb W (25:75, w/w).

(iv) Thallium(I) nitrate coated onto Gas Chrom Q (25:75, w/w).

(v) Silver coated onto Chromosorb W (25:75, w/w).

(vi) Silver coated onto Gas Chrom Q (25:75, w/w).

(vii) Copper(I) bromide coated onto Gas Chrom Q (50:50, w/w).

(viii) Squalene coated onto Gas Chrom Q (20:80, w/w).

Preparation of phases i and ii

Copper(II) nitrate was dissolved in water and a slurry prepared with the support phase. The slurry was placed in a muffle oven at 450°C to decompose the copper(II) salt and form the oxide. This phase was then cooled and packed into a glass column which was placed in a GC oven at 150°C, with hydrogen passing through it. Coupling the column to a FID system and introducing air at the detector allowed the hydrogen to be burnt as the copper oxide was reduced.

Preparation of phases iii and iv

Thallium(I) nitrate was dissolved in water and a slurry prepared with the support phase. This mixture was then dried in an oven at 110°C.

Preparation of phases v and vi

These phases were prepared using silver(I) nitrate, preparing a slurry with the support phase and heating it to 450°C, producing the desired silver phase.

Preparation of phase vii

The phase was prepared by heating the phase copper(II) bromide/Gas Chrom Q, at 150°C for approximately 24 h until the colour change of the phase from black to cream indicated the formation of copper(I) bromide.

Preparation of phase viii

Squalene was dissolved in acetone and a slurry prepared with the support phase. The solvent was removed under a vacuum while heated at 60°C. Further conditioning was carried out at 85°C for 4 h.

3. Results and discussion

3.1. The bromination phases; general observations

The thermal gravimetric analyses of the bromination phases mentioned indicated the temperatures at which these metal bromides were reduced. This provided an estimate of the decomposition temperature and the quantity of bromine bleed caused by an increase in temperature. Such information provided an assessment of the suitability of each metal halide for the purpose of on-column bromination. The results are summarized in Fig. 1.

Chromium(III) bromide undergoes steady reduction at temperatures beginning below 100°C up to 310°C and was thus expected to cause problems with continuous bromine bleed.

Iron(III) bromide appears to be reduced at 250°C, while below this temperature little bromine appeared to be released. The metal
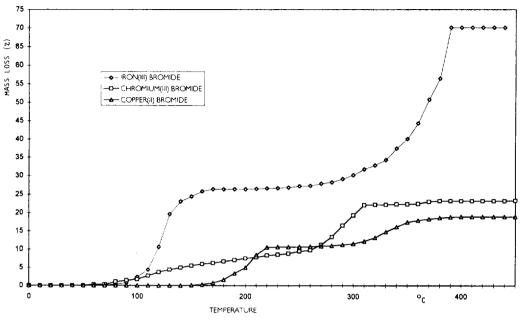
Fig. 1. TGA of (□) chromium(III) bromide, (◇) iron(III) bromide and (△) copper(II) bromide. Graph of temperature against % mass loss of metal halides.

halide, when supported on Gas Chrom Q or Chromosorb W, 100–120 mesh (50:50, w/w), did not afford bromine addition of the alkenes. It was apparent that a series of substitution reactions were occurring as shown by the elution of compounds with very long retention times, when compared to those of the dibrominated haloalkane standards used for peak identification purposes.

Copper(II) bromide decomposes and is reduced at 150°C with some bromine bleed below this temperature. The metal halide, when supported on Chromosorb W, was seen to bring about bromine addition. The efficiency of bromination can be increased by using a less polar support phase, Gas Chrom Q 100–120 mesh. However, when aluminium oxide was used as a support phase for the metal bromide, no evidence of bromination was observed. Although the dibromo derivative was probably formed on passing through the reactor, dehydrobromination also occurred, resulting in reformation of bromine and the respective alkene [13]. This was confirmed by passing a dibromoethane vapour sample through the brominating phase, which resulted in two peaks with the retention times of bromine and ethene.

Silica, 40–100 mesh, coated with the copper(II) bromide (80:20, w/w), was an effective bromination reagent. However, considerable adsorption of the brominated derivatives was evident due to a substantial increase in their peak widths, thought to be caused by the incomplete coating of silica.

Pyridine hydrobromide perbromide, polymer bound, was also tested as a bromination reagent [14,15], but resulted in continuous bromine bleed at temperatures above ambient. Derivatization of the alkenes using system 1 proved possible at 30°C, although such a low temperature resulted in generally poor chromatography, with inadequate detection limits. Increasing the temperature of this phase above 35°C improved the yield of the dibromoalkanes, but resulted in a dramatic rise in the level of bromine bleed. The bleed made the use of this particular brominating material difficult when using system 1 fitted with ECD. None of the scrubbing phases tested had adequate capacity to remove selectively the level of excess bromine, and yet at the

same time not adversely effect the elution of the dibromoalkane derivatives.

From observations made using the various bromination phases, copper(II) bromide coated onto Gas Chrom Q 100–120 mesh appeared to be the most promising phase for vapour phase bromination.

3.2. Using copper(II) bromide coated onto Gas Chrom Q (50:50, w/w) as the brominating phase

In order to check that bromine was being released from the copper(II) bromide phase, 100 mg were packed into a stainless-steel column, 51 cm × 0.762 mm I.D., and placed in the first GC oven (system 2) prior to the separation phase in the second oven. The temperature of the GC oven housing the bromination phase was increased incrementally from 55 to 96°C. The ECD standing current decreased linearly as the temperature of the copper(II) bromide phase was increased, indicating that the release of bromine was temperature dependent.

When using 100 mg or less of the copper(II) bromide phase, 80% of the ECD standing current (1.00 nA) was maintained at temperatures up to 96°C. Thus, if bromination of the alkene vapours was possible at or below this temperature, the problem of excess bromine bleed would be ameliorated. When using amounts of bromination phase in excess of 150 mg, a scrubbing phase is essential to remove the bromine bleed, and thus facilitate a good ECD standing current.

The release of bromine bleed was generally independent of the nitrogen carrier gas flow-rate. A decrease in the ECD standing current was observed during the initial moments when increasing the flow-rate, however the original value was soon restored.

3.3. Identification of the haloalkane derivatives

Using FID (system 1) allowed the identification of the derivatives to be made without regard to the bromine bleed. Nitrogen carrier gas flow-rates were adjusted to give identical retention times for the elution of a reference gas,

methane, through each column. The alkenes were injected onto the column containing the bromination phase, also a standard solution of the respective haloalkanes (1 ppm) was injected onto the reference column for identification purposes.

3.4. Determination of the efficiency of bromine addition

Again using FID (system 1), integrated peak areas of both the unreacted alkene and brominated derivative allowed an indication of the efficiency of the brominating phase to be determined at different temperatures. Due to the lack of sensitivity of FID, the procedure meant that relatively high concentrations of alkene vapours had to be used to enable detection. Hence, a true measure of the efficiency of a very small amount of the brominating phase could not easily be determined using this instrumental system.

The brominating efficiency of the copper(II) bromide/Gas Chrom Q was found to be dependent upon two parameters: (i) temperature of the copper(II) bromide phase and (ii) contact time between the olefin and the brominating phase.

(i) There appears to be a minimal temperature, above which bromine addition to an individual olefin would occur, and a maximum temperature that the brominating phase may be employed before bromine substitution also occurred. From the preliminary investigations with the system 1 configuration, using 400 mg of bromination phase, temperatures in excess of 50°C but below 125°C were suitable for conversion of the C_2–C_5 olefins to dibromoalkanes. However, a more detailed investigation was performed using a system 2 experimental arrangement, employing 70 mg of bromination phase with no scrubbing phase present. The results (Fig. 2) show maximum bromination of propene requires temperatures in excess of 85°C. The optimum temperature for the bromination of butene appears to be in the region of 80°C, with any increase resulting in bromine substitu-
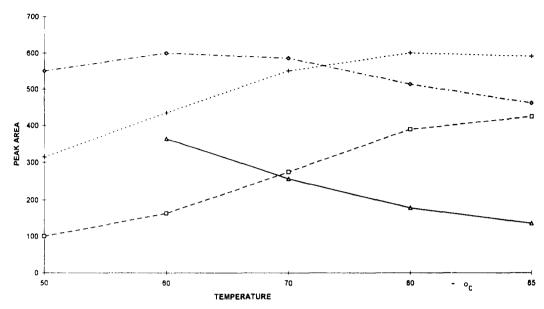
Fig. 2. Using system 2. Graph showing the effect of the temperature of copper(II) bromide phase on the addition of bromine to olefins. From this, the optimum temperature of the phase for bromine addition is indicated. □ = Dibromopropane; + = dibromobutane; ◇ = dibromopentane; △ = dibromohexane.

tion reactions, causing a loss in peak area of the dibromo derivative. However, for pentene a significantly lower temperature, around 60°C, allowed maximum conversion to dibromopentane with substitution occurring above 70°C. With hexene, temperatures below 60°C could not be employed since this did not allow ready elution (< 1 h), of the corresponding brominated compound from either the bromination phase or the capillary column. Clearly substitution reactions became significant for hexene derivatization, shown by the successive decrease in peak area with an increase in temperature of the bromination phase.

(ii) Increasing the contact time between the bromination phase and the olefin also improved the reaction efficiency. As with the temperature of the bromination phase, an optimum contact time was sought that allowed maximum bromine addition to the lowest-molecular-mass olefins without interference of substitution reactions for the heavier ones.

Using system 1 with 400 mg of the bromination phase at 90°C, the percentage bromination

of ethene as a function of carrier gas flow-rate was examined.

The percentage of ethene dibrominated decreased linearly as the carrier gas flow-rate was increased. The optimum flow-rate for 80% bromination of ethene was 6.5 ml/min, equivalent to a contact time between the ethene and bromination phase of 15 s.

Using system 2 the maximum amount of copper(II) bromide phase used to maintain a good ECD standing current, without the need of a bromine scrubbing phase, was 100 mg. Incremental changes in the carrier gas flow-rate (2.5–14.0 ml/min) allowed the effect on the bromination of olefins to be studied. Fig. 3 portrays these results. The conversion of ethene to 1,2-dibromoethane was too low to be successfully measured, particularly at the higher flow-rates, thus only data for propene and higher olefins is given. For propene the flow-rate must be 2.5 ml/min or less to allow maximum conversion, this being equivalent to a contact time between the propene and bromination phase of 5.6 s. At shorter contact times, i.e. higher flow-
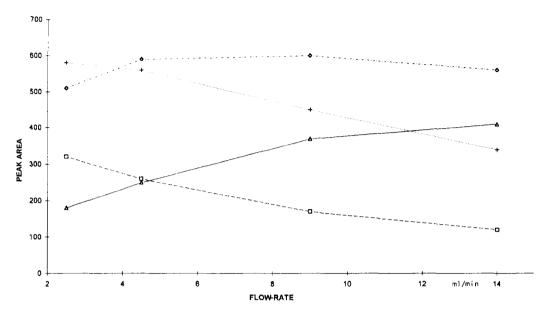
Fig. 3. Using system 2. Graph showing the effect of the carrier gas flow-rate, i.e. contact time between olefins and bromination phase, on the efficiency of bromine addition to olefins. From this the optimum carrier flow-rate is indicated. Symbols as in Fig. 2.

rates, the conversion of propene was less efficient. A similar result is seen for the conversion of butene. However, there is little change in the conversion of pentene which is essentially complete with a contact time of 3.2 s. Longer contact times for hexene allow substitution reactions to occur, thus causing a decrease in the amount converted to dibromohexane, producing a fall in the area of the sought for peak. Thus as contact time is reduced, opportunities for substitution reactions to occur are minimized.

Therefore, temperatures in excess of 70°C, with a contact time of approximately 5 s, provides a reasonable compromise for optimum conversion of all the olefins. While these conditions will not allow complete bromination of ethene, they are optimum for the conversion of propene and olefins of higher molecular mass, allowing minimal substitution. Such a performance is satisfactory for clean ambient air samples since, the level of ethene is very much higher than the levels of the higher-molecular-mass olefins, which are principally derived from vehicular emissions. Where urban air samples are to be investigated, the lowering of the bromination

phase temperature together with an increase in carrier gas flow-rate, could be beneficial.

3.5. Determination of the detection limit of olefins

For the determination of detection limits of brominated alkenes, system 1 was used, but fitted with ECD in place of FID. Detection of the derivatives was restricted due to the reduced ECD standing current caused by the continuous bromine bleed from the brominating phase. This problem was alleviated by the use of phases prepared to remove the bromine selectively. The bromine scrubbing phase was packed in the glass column after the brominating phase, but prior to the separation phase and the detector.

Due to the relatively low flow-rate of carrier gas required and the presence of the scrubbing phase, the chromatography because of band spreading, did not allow good detection limits to be achieved. The values are ethene $2\ \mu l \times 10$ ppm (v/v) (25 pg), propene $1\ \mu l \times 10$ ppm (v/v) (19 pg), butene $1\ \mu l \times 10$ ppm (v/v) (25 pg).

Using system 2 with 70–100 mg of the cop-

per(II) bromide phase at temperatures between 55 and 85°C, allowed detection of very low concentrations of C_2–C_5 olefin vapours.

Thus with 70 mg of copper(II) bromide phase packed into a 38 cm × 0.762 mm I.D. stainless-steel tube, heated to 68°C and a nitrogen carrier gas flow of 2.5 ml/min (contact time 4.2 s) the detection limits for olefin vapour samples derivatized were (see Fig. 4): ethene 1 μl × 1 ppm (v/v) (1.3 pg), propene 1 μl × 1 ppm (v/v) (1.9 pg), butene 1 μl × 1 ppm (v/v) (2.5 pg), pentene 1 μl × 1 ppm (v/v) (3.1 pg). The detection limit of acetylene was approximately < 5 μl × 10 ppm (v/v) (60 pg).
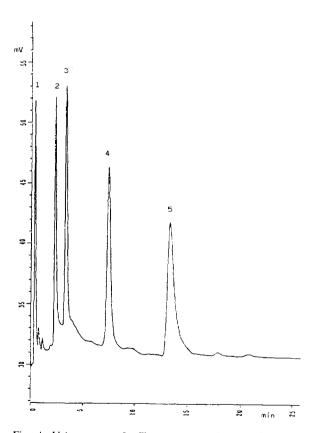

Fig. 4. Using system 2. Chromatogram showing the separation of the brominated olefins from an injection of 5 μl × 1 ppm (v/v) Scotty mix (ethene, propene, butene and pentene). Bromination phase, 70 mg copper(II) bromide phase heated at 68°C and the separation column oven at 100°C. Peaks: 1 = oxygen; 2 = dibromoethane; 3 = dibromopropane; 4 = dibromobutane; 5 = dibromopentane.

Efficiency of the bromination of ethene is limited by the percentage derivatization.

Using 100 mg of copper(II) bromide phase packed into a 51 cm × 0.762 mm I.D. stainless-steel tube, heated to 75°C and a nitrogen carrier gas flow of 5 ml/min, it was evident that the percentage of ethene derivatised increased. An injection of 5 μl × 1 ppm (v/v) of ethene and propene in nitrogen gave two well separated peaks of approximately equal area, indicating efficient bromination of ethene. However, under these conditions, an injection of 5 μl × 1 ppm (v/v) of the Scotty olefin mixture resulted in the elution of only two derivatives, dibromoethane and dibromopropane, the remaining olefins undergoing extensive bromine substitution.

3.6. Reproducibility of detection limits

The relative standard deviation values calculated from the derivatization of 10 μl × 1 ppm alkene standards were: ethene 0.61%, butene 0.71%, propene 0.69%, pentene 0.72%.

3.7. Bromine bleed scrubbing phase

All of the scrubbing phases listed in the Experimental section were found to adsorb the bromine bleed with varying degrees of efficiency. Many of them were also found to adsorb both the olefin derivatives or standard mixtures of the respective halocarbons. Only steel wool, iron powder and squalene were found to discriminate between the bromine bleed and the derivatives produced.

Steel wool was found to selectively remove the bromine bleed, but allowed the elution of the dibromoalkane derivatives at temperatures between 90 and 110°C without causing significant degradation or loss in signal compared to dibromoalkane standards. Injection of dilute dibromoalkane standard solutions allowed the detection of 2 pg of dibromoethane and dibromopropane. The use of this scrubbing phase had the disadvantage of increasing peak widths of the eluting compounds, which in turn reduced detection limits.

The use of pure iron powder as a scrubbing

phase proved possible, but the work was not easily reproduced. The reason for this was thought to be due to the changing degree of oxidation the iron powder underwent while in use or storage. When the iron powder was used initially, it proved too efficient, in that both the bromine bleed and the haloalkane derivatives were adsorbed. After 1 h of operation, only bromine vapour was removed, with good recoveries of the dibromocompounds. After approximately 12 h the bromine vapour broke through as seen by a reduction of the ECD standing current, with consequent loss in detector performance. Repetition of this process using a fresh portion of the iron powder was possible but as the iron powder in the bottle aged (> 1 month), rapid breakthrough of the bromine vapour became evident when it was used. Thus, as the degree of oxidation of the iron powder is critical, no further investigation was carried out.

Squalene coated onto Gas Chrom Q 100–120 mesh (20:80, w/w) was able to remove the bromine bleed, while allowing the elution of the derivatives. The main disadvantage was the resulting increase in peak width of the derivatives. The squalene was obviously acting as a further stationary phase towards the dibromoalkanes, both retaining and diffusing the peaks. Increasing the temperature of this phase above 100°C caused severe bleeding of the squalene, hence limiting its use.

4. Conclusions

The use of a copper(II) bromide reagent for the addition of bromine to alkenes in the vapour phase has been demonstrated. The process is efficient with conversion rates normally greater than 80% for the C_2–C_5 olefins. Coupling this bromination reagent with an electron-capture detector permits the direct determination of atmospheric olefins at the 2 pg level.

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