# Alkene determination by bromination and gas chromatography with element-selective atomic plasma spectroscopic detection

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## Abstract

A gas chromatography (GC) method for the determination of alkenes in complex hydrocarbon mixtures containing aromatic and saturated hydrocarbons is presented. The method enables selective and quantitative bromination of alkenes without affecting aromatic and saturated compounds. The dibromoalkanes formed are detected with minimal interference from coeluting hydrocarbons by bromine-selective atomic emission detection, with sub-nanogram bromine sensitivity. The method is applied to alkenes in gasolines, wherein those having lower octane number contain higher amounts of alkenes and those with higher octane number contain relatively lower levels. This method has potential for further refinement for alkene analysis in different types of hydrocarbon samples. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Gasoline; Detection, GC; Derivatization, GC; Alkenes; Organobromine compounds

## 1. Introduction

Microwave-induced helium plasma atomic emission detection (MIP–AED) for gas chromatography (GC) provides specific elemental information on the composition of chromatographic eluates. Element- and functionality-selective GC detectors, such as the electron-capture, alkali flame thermionic, flame photometric and the Hall detectors, are useful for limited elements. However, the atomic emission detector can detect any element, with the potential for simultaneous multielement detection along with a wide dynamic measurement range, good sensitivities and selectivity over background elements [1]. One can also monitor a particular molecular functionality by means of specific reactions with derivatives containing elemental 'tags'.

GC–AED has made analysis of complex samples, such as petroleum products, more convenient and can give important compositional information [2]. The AED elemental response approaches structural independence under controlled conditions and, therefore, a single standard can be used for the quantitative determination of targeted hetero-atom molecular species [1–4]. The determination of sulfur- and oxygen-containing species in gasoline samples was facilitated by this approach [3,5]; various aliphatic aromatic sulfur compounds gave the same sulfur elemental response; thus, a single standard for sulfur could be used for quantitative analysis. The total amount of sulfur in a gasoline sample was obtained by adding the peak areas and using the sulfur element calibration curve [3]. Gasoline samples have similar sulfur chromatographic profiles, although the

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individual sulfur species vary in absolute and relative amounts. During the analysis of shale oil, it was observed that complete resolution of sulfur compounds from hydrocarbons was not necessary for sulfur analysis [6]. Multielement simulated distillation profiles for hydrogen, carbon and sulfur, obtained by GC–AED, gave good approximations for composite CHS elemental formulae at different stages of carbon evolution [7]. Recent improvements in GC–AED optimization for sulfur and nitrogen compounds in gasoline through to diesel range samples have allowed elemental quantitation to better than a percent precision and accuracy at low ppm levels [8].

Hydroboration–oxidation has been used to determine alkenes in petroleum samples [9]. This method is based on selective and quantitative conversion of olefins to alcohols, which are recovered from the hydrocarbon fraction by elution on an alumina column, followed by GC–MS determination. Saturated, aromatic and alkene compounds in gasoline can be determined by a variety of methods, including multidimensional gas chromatography (MD-GC) [10–12], which gives class and carbon number information but involves multiple columns, traps and valves. Single capillary column GC–MS involving a sulfonation precolumn trap was used to sulfonate and trap alkenes and aromatics, with samples being compared with and without trapping [13].

The complete selective determination of alkenes in complex hydrocarbon mixtures by GC–flame ionization detection (FID) is difficult, even with very high column resolution. GC of alkenes in the presence of alkanes has been achieved by brominating alkenes to the corresponding dibromoalkanes [14]. One such method, selective olefin stripping (SOS), which is used to distinguish between alkanes and alkenes in very dilute samples, involves bromination of alkenes by saturated aqueous bromine, adsorption of the resulting products on a silica gel column, followed by gas chromatography of the eluent alkanes. The procedure is also effective in removing aromatic hydrocarbons. Determination of alkenes in a light hydrocarbon oil was achieved by first obtaining chromatograms of the whole sample and comparing the resulting chromatograms after removal of olefins by the SOS method [14].

The bromine adduct of pyridinium bromide $[C_5H_5NH]Br_3$ was also used to brominate alkenes [15], with millimolar $C_6–C_8$ alkenes being determined in the corresponding alkanes by GC–FID. Larsen et al. [16] quantitatively determined alkenes at a level of <0.5% (w/w) in a light hydrocarbon mixture by bromination.

Volatile alkenes in air were determined by gas chromatography using on-column bromination and electron-capture detection [17,18]. The degree of bromination of alkenes was subject to the temperature, contact time and carrier gas flow through the bromination tube placed before the capillary GC column; a scrubber was needed to remove most of the elemental bromine bleed from the bromination reagent. Even so, high detector background compromised detection limits of dibromoalkanes and the precolumn bromination tube and scrubber tube cause peak-broadening, thereby decreasing peak resolution.

The present study describes the determination of alkenes in the presence of saturates and aromatic compounds by a single capillary column bromine-specific GC–AED method in which alkenes are derivatized by selective and quantitative bromination without affecting aromatic and saturated compounds. The methodology is applied to the analysis of alkenes in commercial gasolines, to investigate the potential for developing an alkene analysis method.

## 2. Experimental

### 2.1. Instrumentation

GC–AED was performed with a model 5890 II Hewlett-Packard (HP) gas chromatograph equipped with a model 5921A atomic emission detector, an HP 35920A automatic sampler, and was controlled by HP 35920A GC–AED software resident in a HP 300 computer (Hewlett-Packard, Little Falls, DE, USA). A VOCOL column (Supelco), 60 m×0.25 mm I.D. and with a film thickness of 1.5 μm, was used for most work. Some of the preliminary studies were on a Rtx-5 column (Restek, State College, PA, USA) of 30 m×0.25 mm I.D., 0.25 μm film thickness. Injections were made with a 10:1 inlet split. Helium was used as a carrier gas in a constant pressure mode. The injection port and column transfer line were maintained at 230°C when the VOCOL column

was used and at 280°C when the Rtx-5 column was used. The flow-rate was 0.6 ml/min for the VOCOL column and 1 ml/min for the Rtx-5 column.

GC–MS was performed with a model 5890 Hewlett-Packard gas chromatograph equipped with a HP 5970B mass-selective detector and a HP 59970 MS ChemStation, which was loaded with HP 59970C ChemStation software. The MSD system had a 70-eV electron impact ionization source, quadrupole mass analyzer and electron multiplier tube ion detector. The VOCOL column was used and total ion chromatograms recorded. Injections were made with a 10:1 inlet split. Helium was used as the carrier gas in a constant pressure mode. The injector and detector were maintained at 230°C.

## 2.2. Materials

1-Bromononane, cyclohexene, cyclooctene, 2,3-dimethyl-1,3-butadiene, ethylbenzene, 1,5-hexadiene, mesitylene, α-methylstyrene, methyl *tert.*-butyl ether, naphthalene, *n*-octane, 1-octene, 1-pentadecene, toluene and 4-vinyl-1-cyclohexane (Aldrich, Milwaukee, WI, USA) were at least 98% pure and were redistilled as required. Isooctane and *p*-xylene were obtained from Eastman Kodak (New York, NY, USA). Benzene, toluene, carbon tetrachloride (certified ACS, spectranalyzed), liquid bromine (reagent ACS grade) and anhydrous magnesium sulfate were obtained from Fisher Scientific (Fairlawn, NJ, USA). Reagent-grade sodium hydrogensulfite was obtained from Mallinckrodt (St. Louis, MO, USA). Three gasolines, gasoline A (octane number 87), gasoline B (octane number 89) and gasoline C (octane number 94), were obtained from local sources.

## 2.3. Bromination reaction

Optimization of the alkene bromination reaction was carried out using a 17-component hydrocarbon mixture containing 0.25% (v/v) of each hydrocarbon in carbon tetrachloride, i.e. 4.5% (v/v) of total hydrocarbons. Hydrocarbon solution was reacted with 1% (v/v) bromine in $CCl_4$. Typically, 10 ml of hydrocarbon solution in $CCl_4$ and 38 ml of 1% (v/v) bromine in $CCl_4$ were mixed, at a bromine-to-hydrocarbon mole ratio of 2:1. Each hydrocarbon, including the saturated hydrocarbons, was treated as having

a double bond and, hence, excess bromine was added to ensure complete bromination of alkene. Both reactants were separately cooled in an ice bath and bromine solution was added to the hydrocarbon solution in a single step. The reaction was carried out in the ice bath with constant stirring and the reaction vessel was covered with aluminum foil to exclude ambient light. After 2 min, unreacted bromine was quickly removed by shaking the reaction mixture thrice with an excess of ice-cold saturated aqueous $NaHSO_3$ solution in a solvent extraction flask. The colorless hydrocarbon solution was separated and dried by adding solid anhydrous $MgSO_4$, the solution was filtered and 1 µl samples chromatographed. The chromatograms before and after bromination of hydrocarbon solution were compared to ensure olefins were selectively and quantitatively brominated.

For the gasoline bromination, a 1.0-ml sample was used, containing 0.90 ml of gasoline and 0.10 ml of 1-pentadecene, which was diluted to 10.00 ml with $CCl_4$; the excess 1-pentadecene was added as a marker to verify quantitative bromination; this was indicated by the complete disappearance of the pentadecene chromatographic peak upon bromination. A 0.90-ml volume of gasoline was taken to be equivalent to 0.90 ml of 1-octene and the appropriate amount of bromine was taken. Three commercial gasolines were analyzed for olefin content, with three replicate samples of each gasoline type being brominated. (1) Gasoline A, octane 87, (2) gasoline B, octane 89 and (3) gasoline C, octane 94.

For quantitative analysis, 1-bromononane standards were made in $CCl_4$. Ten standards were made by diluting from 0.10 to 15.00 µl of 1-bromononane to 10.00 ml with $CCl_4$. Each standard and each brominated gasoline sample was analyzed three times by GC–AED and the average result was calculated.

## 3. Results and discussion

The experimental factors that selectively and quantitatively affect bromination of alkenes in the presence of aromatic and saturated hydrocarbons were optimized, i.e., reactant concentration, temperature, time and the nature of the solvent being studied.

Preliminary experiments indicated that bromine attacks some aromatic as well as olefinic compounds. The aromatic compounds benzene, toluene, ethylbenzene and xylenes (BTEX) are important constituents of gasolines, hence the need to optimize the bromination method such that aromatic compounds remain unaffected. It was observed that mesitylene is more reactive than toluene, ethylbenzene and xylene, even under mild conditions, but benzene and naphthalene were found to be unreactive towards bromine under similar conditions. Mesitylene was thus used as an 'extreme case' test example for optimization of reaction conditions. Ensuring that it reacted minimally under the chosen reaction conditions in turn guaranteed that other aromatic components reacted minimally. Hexane was initially chosen as the solvent for the bromination of mesitylene, although $CCl_4$ was eventually substituted as an inert, nonpolar solvent, since hexane may be susceptible to photobromination [16]. Mesitylene in hexane gave several partially brominated products; reduction of the bromine concentration diminished the bromination of mesitylene, giving only one brominated product. Bromination at room temperature and subzero temperature did not show significant differences

in product patterns, hence, it was concluded that the bromine concentration effect is more critical than the temperature factor. Nevertheless, lower temperatures produced lower amounts of by-products, giving less complicated chromatograms.

It was thought that, in $CCl_4$ solution, mesitylene might not react, so a mole ratio of hydrocarbon–bromine of 1:2 mol) was used in subsequent experiments. This mole ratio should brominate alkenes completely if the reaction time is optimized. Bromination products were observed after a 5-min reaction time, with 1-pentadecene being fully brominated and mesitylene partially so. A 1-min reaction showed only partial 1-pentadecene bromination and an optimum reaction time of 2 min gave approximately 92% bromination of the 1-pentadecene. In a hydrocarbon mixture containing aromatic, alkenes and saturated hydrocarbons, excess bromine will be present since saturated hydrocarbons were also considered as alkenes and a corresponding amount of bromine was taken. A 2-min reaction time was thus considered to be adequate; the reaction being conducted in the dark to prevent possible photobromination of saturates and alkyl substituents on the aromatic rings [16].

Table 1
Hydrocarbon mixture in carbon tetrachloride (17 components)

| No. | Hydrocarbon | Hydrocarbon class |
|---|---|---|
| 1 | *n*-Octane | Saturated hydrocarbons |
| 2 | Isooctane | |
| 3 | Cyclohexane | |
| 4 | 1-Octene | Monoalkenes |
| 5 | 1-Pentadecene | |
| 6 | α-Methylstyrene | |
| 7 | Cyclooctene | |
| 8 | 4-Vinyl-1-cyclohexane | Dialkenes |
| 9 | 2,3-Dimethyl-1,3-butadiene | |
| 10 | 1,5-Hexadiene | |
| 11 | Benzene | Aromatic hydrocarbons |
| 12 | Naphthalene | |
| 13 | Toluene | |
| 14 | Ethylbenzene | |
| 15 | *p*-Xylene | |
| 16 | Mesitylene | |
| 17 | Methyl *tert*.-butyl ether (MTBE) | Oxygenated hydrocarbon |

A mixture representative of a complex sample such as gasoline (Table 1) [19], containing 17 compounds including alkenes, aromatics and saturated compounds, was brominated with a 1% (v/v) solution of bromine in CCl$_4$ at a mole ratio of hydrocarbon to bromine of 2:1; the reaction was carried out for 2 min in the dark and in an ice bath. Methyl *tert.*-butyl ether (MTBE) was included as representing oxygenates in commercial gasolines. The composition of this sample remained constant for more than 45 days, with no increase or decrease

in the number of peaks, as determined by GC. Naphthalene was used as a reference compound as it was unreactive towards bromination (Fig. 1). Upon bromination of the hydrocarbon mixture, aromatic and saturated compounds were unbrominated but the alkenes were quantitatively brominated (Figs. 2–4). Comparison of chromatograms of the non-brominated and brominated hydrocarbons shows that the alkene peaks have been completely removed. Also, the GC–AED chromatograms (bromine and carbon) show that there are no significant peak(s) in the
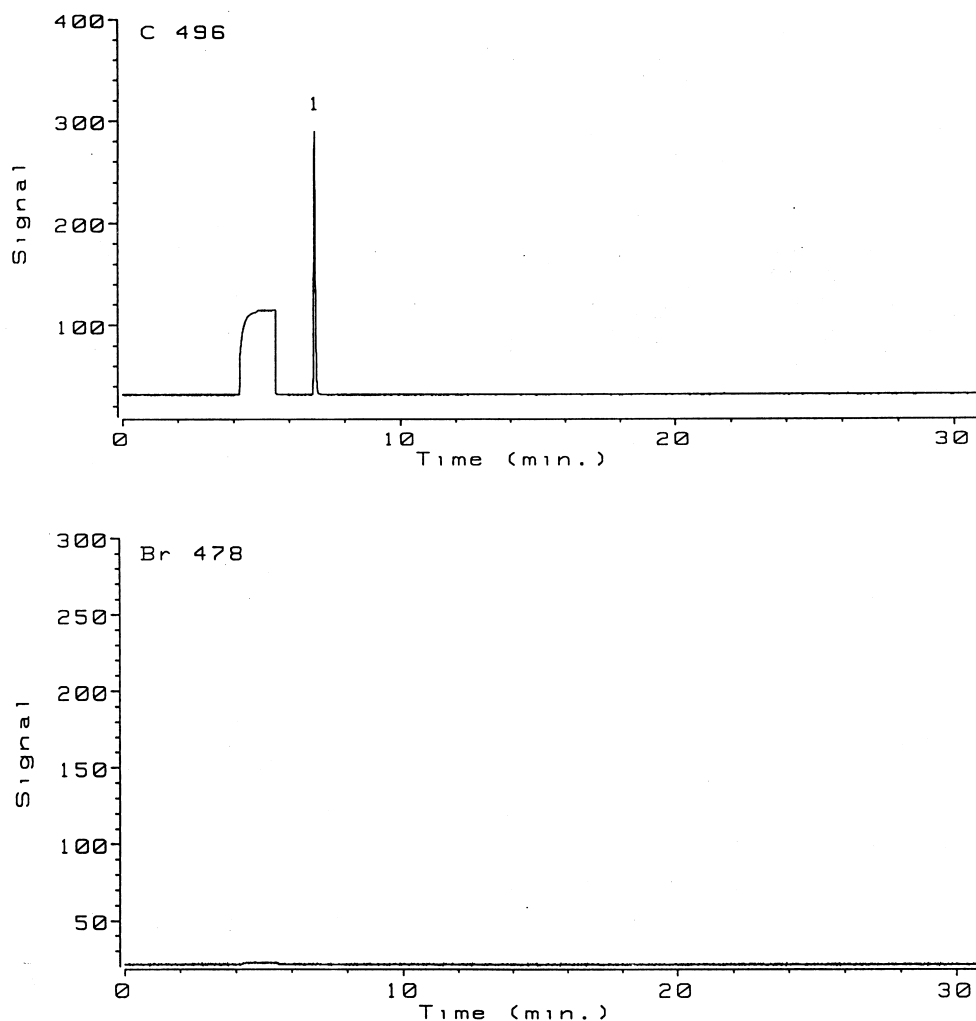


Fig. 1. GC–AED chromatogram of naphthalene bromination products. Peak 1=naphthalene. Reaction conditions: 1% (w/v) naphthalene in carbon tetrachloride reacted with 1% (v/v) bromine in carbon tetrachloride; reaction time, 2 min; reaction was carried out in the dark and in an ice bath, at a 1:10 mole ratio of naphthalene–bromine. GC conditions: SE-30 column, 150°C isothermal for 1 min then programmed at 10°C/min to 250°C, then isothermal for 20 min. Injection split ratio, 1:9.
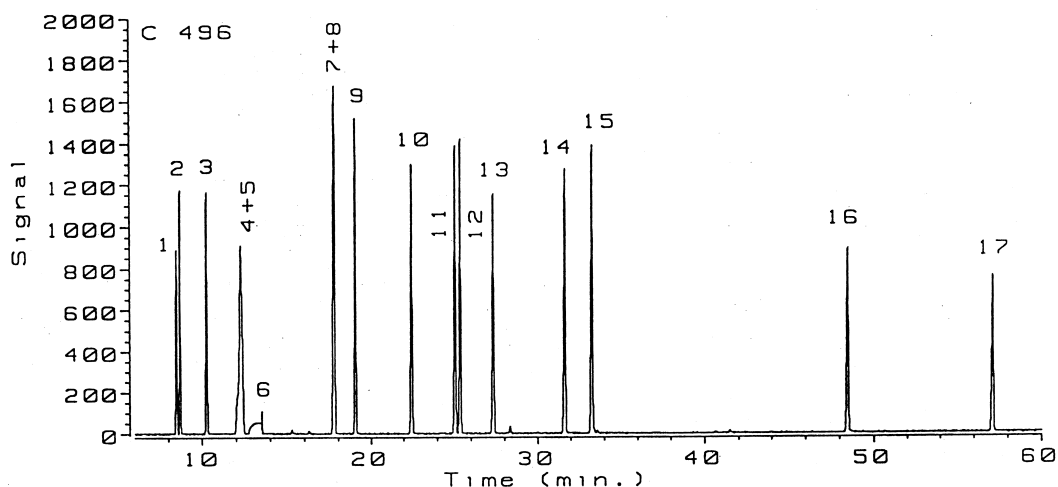
Fig. 2. GC–AED chromatogram of a 17-component hydrocarbon mixture in carbon tetrachloride [4.5% (v/v) hydrocarbons]. GC oven conditions: VOCOL column, 60°C isothermal for 1 min then programmed at 3°C/min to 220°C, then isothermal for 25 min. Injection split ratio, 1:13. Peaks: 1=MTBE, 2=1,5-hexadiene, 3=2,3-dimethyl-1,3-butadiene, 4+5=isooctane+cyclohexane, 6=benzene, 7+8=1-octene+*n*-octane, 9=toluene, 10=4-vinyl-1-cyclohexene, 11=ethylbenzene, 12=*p*-xylene, 13=cyclooctene, 14=mesitylene, 15=α-methylstyrene, 16=naphthalene and 17=1-pentadecene.

region of 50.66 min retention time, which is that of brominated mesitylene. To test whether saturated and aromatic compounds remained unaffected, naphthalene was used as an internal standard, with peak area ratios of naphthalene to hydrocarbon(s) being com-

pared for two chromatograms, i.e., for non-brominated and brominated hydrocarbons. The peak area ratios obtained from both chromatograms were found to be in the same range (Table 2).

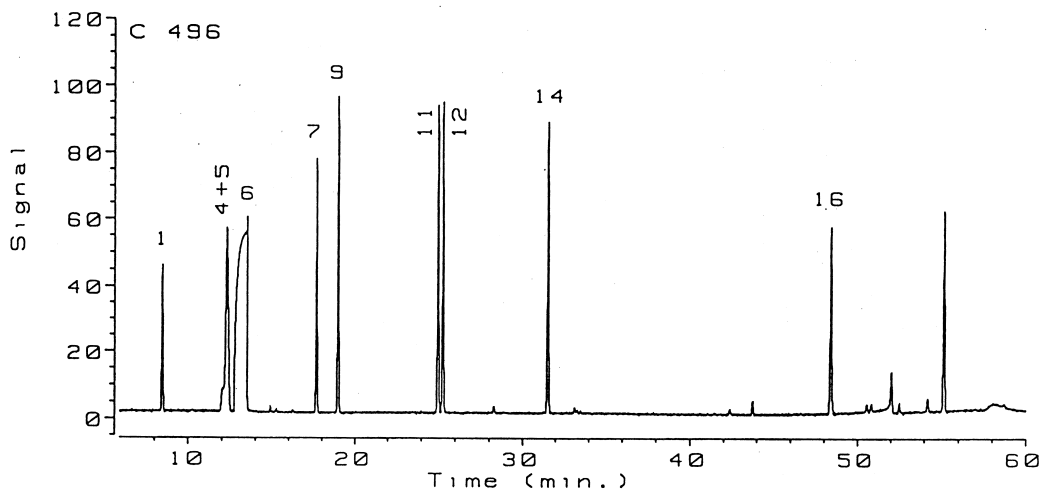Before applying the bromination reaction proce-



Fig. 3. GC–AED chromatogram of a hydrocarbon mixture after the bromination reaction [4.5% (v/v) hydrocarbons]. GC oven conditions: VOCOL column, 50°C isothermal for 1 min then programmed at 3°C/min to 220°C, then isothermal for 160 min. Injection split ratio, 1:13. Peaks: 1=MTBE, 4+5=isooctane+cyclohexane, 6=benzene, 7=*n*-octane, 9=toluene, 11=ethylbenzene, 12=*p*-xylene, 14=mesitylene, 16=naphthalene.
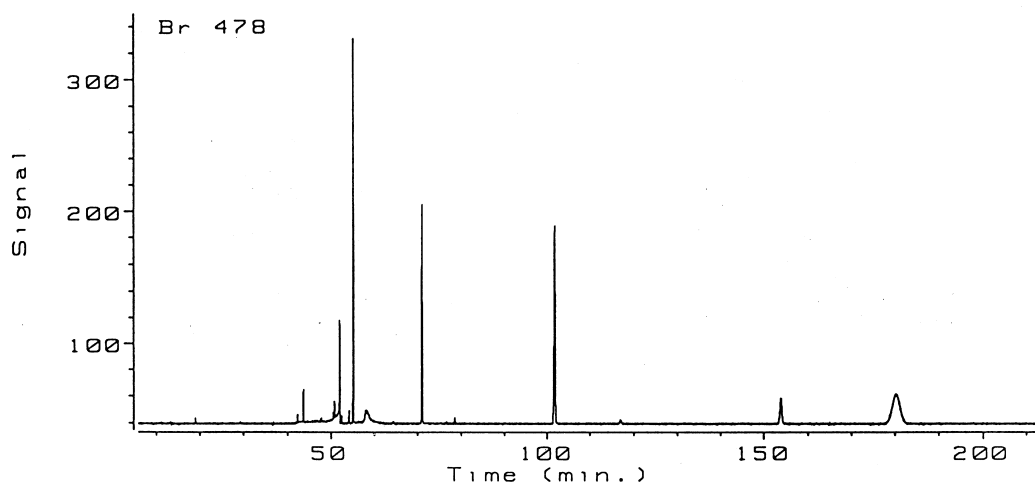
Fig. 4. GC–AED chromatogram of a hydrocarbon mixture after the bromination reaction [4.5% (v/v) hydrocarbons]. GC oven conditions: VOCOL column, 60°C isothermal for 1 min then programmed at 3°C/min to 220°C, then isothermal for 160 min. Injection split ratio, 1:13.

dure to gasoline samples, further tests were conducted on individual aromatic compounds. It was demonstrated that bromination of toluene, ethyl benzene and p-xylene occurred to an extent of less than 1%, even when bromine is reacted in large amounts. Hence, BTEX present in gasoline in significant amounts should not be affected. Fig. 5 shows that mesitylene brominates at a level up to 10% when excess bromine is used, but, upon gasoline bromination, there was no significant peak present at the brominated mesitylene retention time. Gasoline solution in $CCl_4$ did not show the presence of

bromine components in the GC–AED bromine chromatogram.

The bromine calibration curve had a correlation coefficient of 0.9932. It should be noted that the curve is for bromine element and not for bromoalkanes or alkenes. The elemental response of the AED system is largely compound-independent, hence, it does not matter where the elemental bromine is derived. Any bromoalkane can be used as a standard to obtain the 'universal' bromine calibration curve and, thus, the amount of bromine in the plasma. Also, the detection limits for carbon will be

Table 2
Peak area ratios obtained from the GC–AED chromatograms (Figs. 3 and 4)[a]

| Peak ratio type | Ratios before bromination | Ratios after bromination | % Ratios=(peak area ratio, brominated)/(peak area ratio, nonbrominated) |
|---|---|---|---|
| MTBE/naphthalene | 0.68 | 0.63 | 92.7 |
| (Isooctane+cyclo-hexane)/naphthalene | 1.96 | 2.00 | 102.0 |
| Benzene/naphthalene | [b] | [b] | [b] |
| Toluene/naphthalene | 1.33 | 1.37 | 103.0 |
| Ethylbenzene/naphthalene | 1.36 | 1.41 | 103.7 |
| p-Xylene/naphthalene | 1.34 | 1.39 | 103.7 |
| Mesitylene/naphthalene | 1.39 | 1.39 | 100.0 |

[a] The reactant hydrocarbon mixture contained 4.5% (v/v) total hydrocarbons, i.e., 0.25% (v/v) of each hydrocarbon in carbon tetrachloride.

[b] Benzene coeluted with carbon tetrachloride, hence, peak area measurements could not be done.
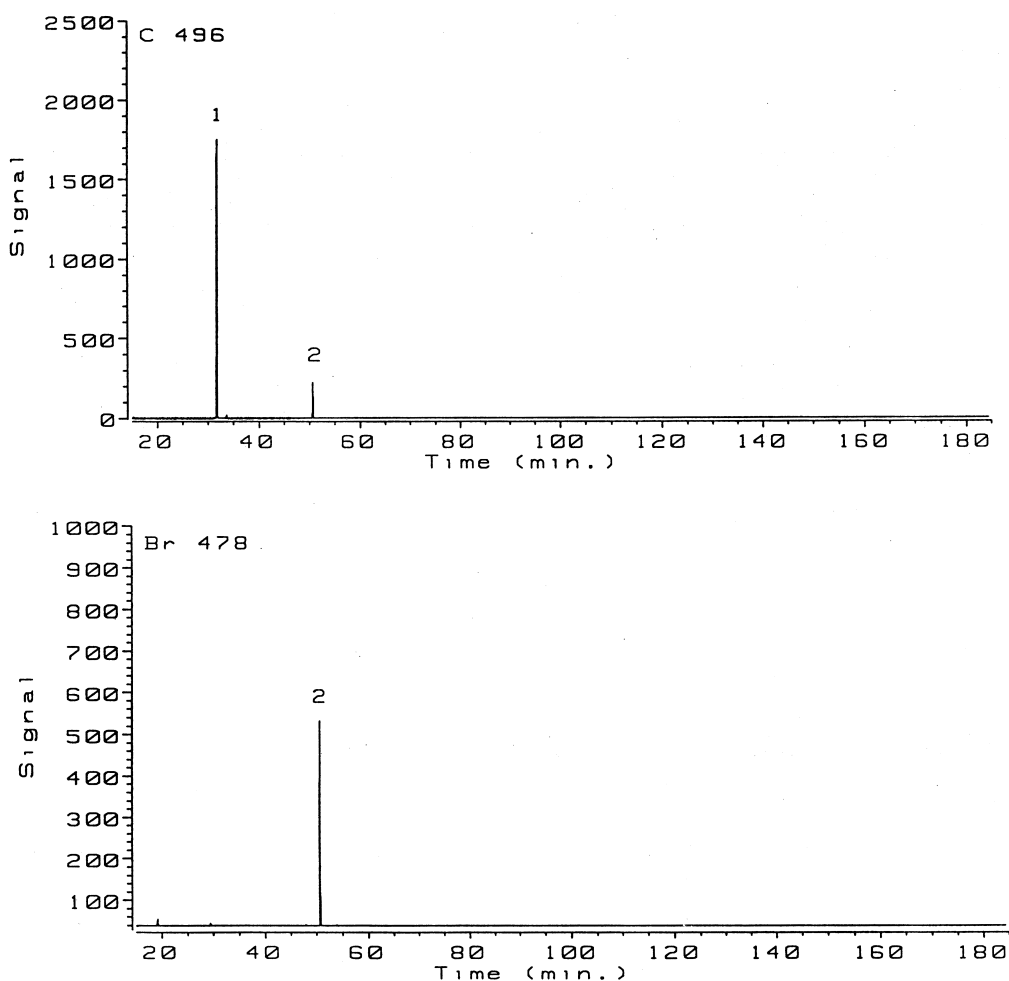
Fig. 5. GC–AED chromatogram of mesitylene bromination products. Peaks: 1=mesitylene, 2=brominated mesitylene. Reaction conditions: 1% (v/v) mesitylene in carbon tetrachloride reacted with 1% (v/v) bromine in carbon tetrachloride; reaction time, 2 min; reaction was carried out in the dark and in an ice bath; mole ratio of mesitylene–bromine, 1:6. GC conditions: VOCOL column, 60°C isothermal for 1 min then programmed at 3°C/min to 220°C, then isothermal for 130 min. Injection split ratio, 1:13.

the same irrespective of the type of bromoalkane. Using stoichiometry, one can back-calculate the moles of bromoalkanes and/or alkenes that were present in the analyte. One mole of alkene with one double bond will give one mole of corresponding dibromoalkane.

The detection limit for bromine was ca. 300 pg (bromine on the column) at a signal-to-noise ratio ($S/N$) of four. The detection limit for carbon was ca. 400 pg (carbon on the column) at a $S/N$ of four. An injection split ratio of 1:13 was used. It was observed from the bromine-selective chromatograms of the

brominated gasolines that the profiles are similar for all gasoline types, except for the presence of a large peak at about 16 min (Fig. 6). This peak may be due to a bromination product of butene, a light olefin present in some gasoline. Although the bromine chromatogram profile is similar for all of the gasolines, the peak areas of individual peaks varies, indicating that the individual dibromoalkanes are present in various amounts. The bromine amounts in all three types of gasolines can be correlated to the octane number. The lower the octane number, the higher is the amount of bromine consumed, i.e.
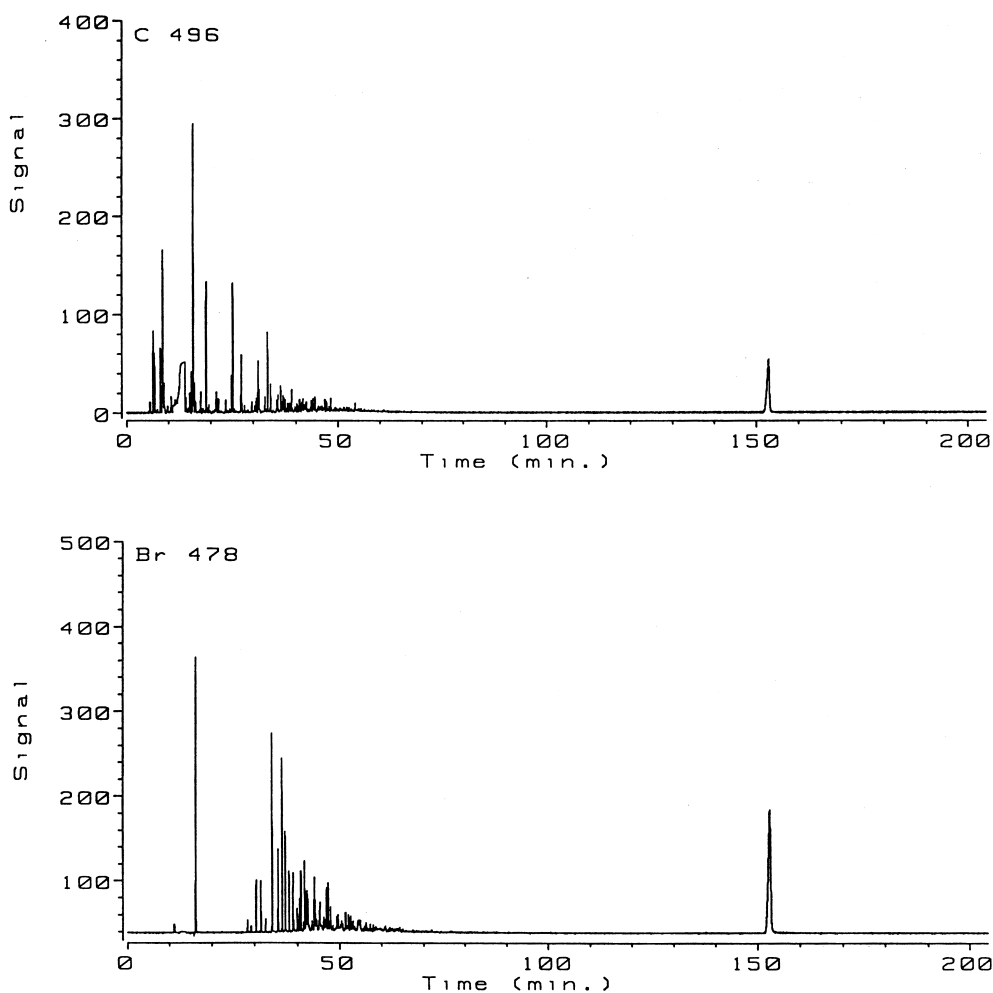
Fig. 6. GC–AED chromatogram of gasoline A bromination products. Reaction conditions: 9% (v/v) gasoline and 1% (v/v) 1-pentadecene in carbon tetrachloride reacted with 1% (v/v) bromine in carbon tetrachloride; reaction time, 2 min; reaction was performed in the dark and in an ice bath. GC conditions: VOCOL column, 60°C isothermal for 1 min then programmed at 3°C/min to 220°C, then isothermal for 150 min. Injection split ratio, 1:13.

olefin content is higher for low octane gasoline. Thus, gasoline C with octane number 94 has the lowest olefin content and gasoline A with octane number 87 has the highest olefin content. The ratio of bromine content for gasoline A to gasoline C was observed to be $1.55\pm0.13$ whereas for gasoline A to gasoline B, it was seen to be $1.39\pm0.15$.

A series of standard solutions of a selected bromoalkane should give a bromine calibration curve if the bromine elemental emission signal is monitored, the curve being in the form of bromine peak area (arbitrary units) as a function of moles of bromine (or moles of bromoalkane) on the chromatographic column. Analysis of an unknown will give the number of moles of bromine or bromoalkanes present, whence one can back-calculate the amount of alkene that was present originally. One mole of an alkene with one double bond will give one mole of corresponding dibromoalkene. For mixtures of alkenes, retention times of corresponding dibromoalkanes must be known. In a 'bromine' chromatogram, each dibromoalkane will have a unique retention time and so each bromine peak will give moles of bromine and, hence, moles of dibromoalkane or

alkene. Atomic emission detection provides a reasonably compound-independent bromine elemental response for brominated alkanes. Although the identities of bromoalkanes cannot be determined using GC–AED alone, moles of double bonds can be calculated. As one bromine molecule is consumed per double bond, one can get the number of moles of double bonds from the number of moles of bromine. Further investigation is needed on the correlation of 'bromine number' with the quantitative yield of bromoalkenes.

## 4. Conclusions

The selective determination of alkenes in complex hydrocarbon mixtures was performed using selective elemental tagging of alkenes and GC–AED. The optimized bromination method makes it feasible to brominate alkenes selectively and quantitatively in the presence of aromatic and saturated hydrocarbons. This optimized alkene derivatization method, coupled with the use of element-specific detection, helps one to acquire a qualitative and quantitative picture of alkenes in complex hydrocarbon mixture such as gasoline by a single capillary gas chromatography procedure without interference from aromatic and saturated hydrocarbons. Determination of alkenes in commercial gasolines shows a correlation between the quantitative alkene content and the octane number. Lower octane number gasoline contains higher amounts of olefins and vice versa, as would be expected. Work is underway to further develop the bromination method by utilizing a suitable bromination reagent, such as pyridinium bromide, in a suitable solvent, such as hexane. The determination of alkenes in higher boiling petroleum fractions may also be possible using such a bromination method and GC–AED.

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