

# A two-column method for long-term monitoring of non-methane hydrocarbons (NMHCs) and oxygenated volatile organic compounds (*o*-VOCs)

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A method has been developed for concurrent analysis of C<sub>2</sub>–C<sub>7</sub> hydrocarbons and C<sub>2</sub>–C<sub>5</sub> oxygenated volatile organic compounds (*o*-VOCs) including alcohols, aldehydes, ketones and ethers. A multi-bed, Peltier-cooled adsorbent trap, consisting of Carboxen 1000 and Carbopack B, was used to acquire one sample per hour. Upon injection the sample was split in an approximately 50:50 ratio between a 50 m aluminium oxide (Al<sub>2</sub>O<sub>3</sub>) porous layer open tubular (PLOT) column and a 10 m LOWOX column. Eluents from each column were then analysed using flame ionisation detection (FID). Regular calibration of the system was performed using a standard cylinder mixture at the parts per billion by volume (ppbV) level for non-methane hydrocarbons (NMHCs) and a permeation tube method for the oxygenated species. The system is fully automated with NMHC detection limits between 1 and 10 parts per trillion by volume (pptV) and *o*-VOC detection limits between 10 and 40 pptV.

## 1. Aim of investigation

Many oxygenated volatile organic compounds (*o*-VOCs), including aldehydes, are known to have direct detrimental effects on human health affecting the respiratory tract and irritating the eyes, in some cases they are mutagenic and/or carcinogenic (Nishikawa and Sakai,<sup>1</sup> Kean *et al.*,<sup>2</sup> Sin *et al.*<sup>3</sup>). As such, human exposure limits to this group of highly toxic compounds requires careful attention through their long-term monitoring in the urban environment. Source profiles for the *o*-VOCs are particularly complex due to their emission as primary pollutants from motor vehicle exhausts and industrial processes along with their *in-situ* production as photo-oxidation products of hydrocarbons. Seasonal profiles of *o*-VOCs are also complex and highly dependent on the local environment and meteorological conditions. Generally concentrations of *o*-VOCs are greater in winter compared with summer in urban environments (Sin *et al.*<sup>3</sup>), corresponding to periods of lower temperature and solar intensity, therefore reducing photo-chemistry. This highlights the importance of primary production and emissions to the atmospheric VOC burden in urban environments and also suggests the complexity of the atmospheric chemistry of the *o*-VOCs. Photo-oxidation of NMHCs leads to the formation of oxygenated species as secondary products. The concurrent increase in concentrations of OH, formed as intermediates in these reaction schemes and through increased photolysis of ozone during these periods of high solar intensity, may also react with and remove *o*-VOCs from the atmosphere and leads to complex competing reaction schemes.

Formaldehyde and acetaldehyde are the main oxygenated species found in urban environments, together contributing to more than half of the oxygenated species by mass (Kean *et al.*,<sup>2</sup> Sin *et al.*<sup>3</sup>) and have been shown to be highly correlated in winter, when photo-chemistry is at a minimum. The ratio of these two compounds has been used to provide information about the origins of air masses and in general the formaldehyde/acetaldehyde ratio is greater in summer than winter. During summer months, the greater degree of photo-chemistry

occurring in the atmosphere results in more conversion of alkenes to aldehydes, during this conversion formaldehyde is formed to a greater extent than acetaldehyde. Reaction rates of each of these species with OH are, however very similar ( $1 \times 10^{-11}$  and  $1.4 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for formaldehyde and acetaldehyde respectively) hence the ratio increases. In winter months the major sources for these compounds are from primary sources such as motor vehicles.

Acetone is a key atmospheric species, known to be involved in the chemistry of the upper troposphere where its photolysis leads to the production of peroxyacetyl nitrate (PAN), itself an important species, responsible for the long-range transport of nitrogen oxides to more remote regions of the globe. Sources of acetone are, however, as yet not well characterised.

Isoprene, emitted into the atmosphere from plants and trees, contributes greatly to the total emission of carbon into the atmosphere (Guenther *et al.*<sup>4</sup>). Oxidation of isoprene in the atmosphere by the OH radical and also through ozonolysis yields formaldehyde, methylvinylketone (MVK) and methacrolein (MACR). Ratios of these species, along with their parent molecule are also useful in determining the origins of sampled air masses, although caution should be exercised in the use of MACR due to the existence of a primary, motor vehicle exhaust, source for this compound (McClaren *et al.*<sup>5</sup>)

### 1.1. Existing methods

Current methods for the analysis of oxygenated hydrocarbons all too often rely on a chemical transformation of the target molecule into a derivatised relation containing an easily detectable functional group. For example 2,4-dinitrophenylhydrazine (2,4-DNPH) is regularly used in the detection of aldehydes (Helmig and Greenberg,<sup>6</sup> Kean *et al.*,<sup>2</sup> Sin *et al.*<sup>3</sup>) due to their reaction to form 2,4-dinitrophenylhydrazone, which can be easily analysed using chromatographic methods and are detected by a variety of techniques (including mass spectrometry and fluorescence). Derivatisation methods are not ideal for automated atmospheric chemistry applications, particularly for long-term studies. Routine manual operations are prone to

error, particularly in the field and so for atmospheric science equipment automation, with as little human interaction as possible, is a key consideration.

The importance of aldehydes to the chemistry of the atmosphere is clear from the particular attention aimed at this group of compounds. Nishikawa *et al.*<sup>7</sup> describe a system for the monitoring of formaldehyde at the sub-ppb level using derivatisation with *o*-pentafluorobenzoyloxime (PFBO) followed by gas chromatography coupled with electron capture detection (GC-ECD). The system requires a 5 l sample which can be collected in a period of only 5 min, however, the derivatisation stage of the process requires a period of 40 min before extraction with *n*-hexane can occur. This system was then adapted for the analysis of low molecular mass aliphatic aldehydes (Nishikawa *et al.*<sup>8</sup>). Due to the lower ambient concentrations of this group of compounds compared with that of formaldehyde, a greater sample volume (up to 30 l) was required for detection of 10–67 ppb of these compounds. The mixture was required to stand for 80 min for complete derivatisation to occur before extraction could be performed, coupled with the long sample acquisition time (1 h) this method of aldehydes analysis loses much of the fine detail and diurnal behaviour of this group of compounds. Nishikawa *et al.*<sup>9,10</sup> also describe similar methods for analysis of acrolein, an irritant to eyes, skin and the nasopharyngeal membrane (Nishikawa and Sakai<sup>1</sup>), and crotonaldehyde with detection limits ranging between 0.5 and 13 ppb. All of the methods described, however require derivatisation and report recovery/collection efficiencies between 80 and 98%. Mass spectrometry has also been used in the analysis and detection of aldehydes in the atmosphere (Wedel *et al.*<sup>11</sup>), again such a method suffers from the inefficiency of the derivatisation stage, requiring large sample volumes and therefore reducing the frequency of analysis.

Atmospheric monitoring of alcohols has received much less attention than other oxygenated species. Techniques used often give information of the combined total concentration of alcohols in each sample, due to difficulties encountered in their separation (Korenmann *et al.*<sup>12</sup>). Acetone, MVK and MACR are often determined in a similar way and thus it is rare that a full speciation is achieved.

State of the art methods for monitoring *o*-VOCs include proton transfer mass spectrometry (PTR-MS) and orthogonal two-dimensional gas chromatography (2D-GC). Whilst both methods are extremely useful for oxygenated measurements, isobaric interferences are a problem with higher molecular weight PTR-MS measurements whilst the data intensive nature of 2D-GC makes it useful for only short-term focussed measurement campaigns.

The work reported here indicates that an on-line carbon adsorbent-PLOT GC separation can be used with small sample volumes (1 l) and gives excellent sensitivity to on-line *o*-VOC analysis.

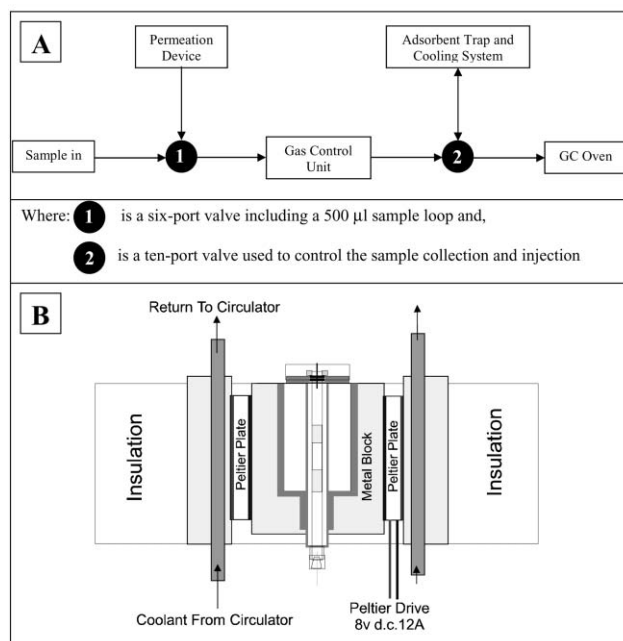
## 2. Experimental

Single column GC coupled with FID is a highly robust and sensitive method for atmospheric analysis and has been used for NMHC measurements for many years (Rudolph and Ehhalt,<sup>13</sup> Lewis *et al.*<sup>14</sup>). The nature of the instrumentation is such that continuous operation with minimum maintenance has been achieved on many occasions (Derwent *et al.*<sup>15</sup>). A barrier to automated underivatized GC measurements of light oxygenated volatile organic compounds (*o*-VOCs) has been the degree of selectivity that could be achieved in isolating these compounds from the dominant aliphatic/aromatic matrix. Using liquid film stationary phases the selective retention achieved resulted in co-elution problems. The addition of mass spectrometry helped little since electron ionisation (EI)

fragmentation of small organics yields often highly similar fragments.

The use of a new mixed phase porous layer open tubular column type, where a polar film is supported on a wall coated aluminium oxide (Al<sub>2</sub>O<sub>3</sub>) solid support, has been seen to lead to highly selective *o*-VOC retention, from experiments, the retention of acetaldehyde is seen to be greater than aliphatic C<sub>11</sub> compounds. Using this approach it is therefore possible to isolate *o*-VOCs chromatographically and detect them using a simple FID. Carbon adsorbents, similar to those used for NMHCs, may be used for quantitative pre-concentration and thermal desorption of *o*-VOCs. It is therefore possible that a single adsorbent unit is used to pre-concentrate both NMHCs and *o*-VOCs with the analytes split between two column and detector systems.

The experimental method was set-up for the concurrent analysis of NMHCs and *o*-VOCs (Fig. 1) and was based on an existing method for NMHC analysis (Lewis *et al.*<sup>16</sup>) due to its robust yet sensitive nature and its ease of automation. Samples must be dry for successful PLOT column analysis due to the dramatic change in retention times when water becomes adsorbed onto the column, which in turn prevents automated analysis of the chromatograms produced. A Nafion dryer was initially used but significant sample losses were observed using this method and so a condensation trap, immersed in a 50 : 50 water : ethylene glycol mix held at –30 °C, was incorporated for water removal. A multi-bed adsorbent trap, required due to the complexity of the air matrix and the wide range of volatilities of compounds required for analysis (Bishop and Valis<sup>17</sup>), was then used to pre-concentrate the analytes prior to injection into the GC system. The adsorbents used were packed in series (approximately 90 mg in total) in a single glass liner (Fig. 1B), separated by a small stainless steel frit, firstly Carboxen B (Supelco) was used for adsorption of all of the compounds of interest in the mixture. The lighter molecular weight and/or more volatile compounds (for example: ethene and acetylene), however, were found to break through this initial packing and so Carboxen 1000 (Supelco) was used to trap these species. Carboxen 1000 was found to be unsuitable



**Fig. 1** Schematic diagram of experimental set-up for A: the dual channel instrument, including the permeation device and B: the trap cooling system. The circulator operates at 12 °C, removing heat generated by the Peltier plates, the central block reaches a temperature of approximately –36 °C, and the trap itself is maintained at a steady –20 °C during sampling.

for all of the compounds in the mixture due to inefficiencies during desorption of higher molecular weight compounds, hence, the multi-bed system was used. Heavier weight hydrocarbons in the atmosphere are trapped efficiently by the adsorbents used here, but are ignored in the GC analysis due to the long time required for their elution. Instead, these compounds are sacrificed in order that more frequent data can be acquired. These heavier weight compounds slowly elute from the column at its maximum temperature, but seldom interfere with the compounds of interest. The trap was held at a constant temperature of  $-20\text{ }^{\circ}\text{C}$  during sample acquisition, this was achieved by a system of Peltier plates surrounding a metallic block into which the trap was placed (Fig. 1B), the heat generated by the peltier plates was removed from the system by circulation of ethylene glycol ( $12\text{ }^{\circ}\text{C}$ ) through the cooling cells on opposing sides of each of the plates. A sample gas flow rate of  $100\text{ ml min}^{-1}$ , maintained by mass flow controllers, was used and an overall sample volume of 1 l acquired, this provides a sample volume of 500  $\mu\text{l}$  to each of the columns within the oven. The trap was then flushed with helium for 2 min whilst cold, to allow for the removal of methane from the system which cannot be trapped quantitatively and inevitably disrupts the peak shape of the lighter molecular weight NMHCs, before being heated at  $16\text{ }^{\circ}\text{C s}^{-1}$  to  $400\text{ }^{\circ}\text{C}$  and all of the analytes desorbed into a constant flow of helium ( $40\text{ ml min}^{-1}$ ) and flushed into the GC system.

The sample was split in a 50:50 ratio between the two columns using a T-piece union in-line between the injector and the columns. A 50 m  $\text{Al}_2\text{O}_3$  PLOT column was used for analysis of NMHCs and a 10 m LOWOX column (both columns from Varian Inc.), with a  $50\text{ }\mu\text{m}$  restrictor to balance the flow through each channel, for analysis of *o*-VOCs. The GC oven was held at  $40\text{ }^{\circ}\text{C}$  for 3 min after the injection of the sample to allow for some focussing of the heavier molecular weight species, which are generally desorbed from the trap less rapidly than those of a more volatile nature. The oven programme was as follows:  $40\text{ }^{\circ}\text{C}$  for 3 min then heated at a rate of  $12\text{ }^{\circ}\text{C min}^{-1}$  to  $110\text{ }^{\circ}\text{C}$ , before being heated at  $7\text{ }^{\circ}\text{C min}^{-1}$  to  $200\text{ }^{\circ}\text{C}$ , where it remained for 20 min before cooling back to  $40\text{ }^{\circ}\text{C}$  ready for the next injection. The eluting analytes from each column were all analysed by FID.

### 2.1. Calibration of the system

Calibration was a major focus of much of the work in development of this system. The use of standard cylinders of known concentration of NMHCs is a regular feature of hydrocarbon analysis. The high reactivity and rapid deposition to surfaces of oxygenated species, however, makes such storage unreliable and an alternative method for calibration is required. The calibration system used is a permeation tube method using liquid samples contained in small sections of thin wall  $1/8\text{''}$  Teflon tubing capped at each end with standard Swagelok fittings. Each device is placed in a glass impinger housed in a solid block of aluminium held at constant known temperature, the impinger was continuously flushed with nitrogen at a flow rate of  $100\text{ ml min}^{-1}$ . Each device emitted a known quantity (calculated by mass loss of the device over a known period of time) into the flow of nitrogen thereby creating a known concentration of each *o*-VOC in nitrogen.

The concentration of each *o*-VOC generated is dependent on two factors, temperature and flow rate of nitrogen dilution gas. The standards generator was left to equilibrate for a period of several days to ensure that a stable temperature of each of the permeation devices was achieved. The flow rate of nitrogen over the permeation devices could be altered in order for a range of concentrations to be produced; a nitrogen flow of  $100\text{ ml min}^{-1}$  produces concentrations in the order of 100 ppb, to dilute to ambient concentrations (approximately 1 ppb) would require huge dilution and therefore large volumes of

**Table 1** Data obtained for calibration curves of DMS and acetone, showing good linearity over a wide range of concentrations

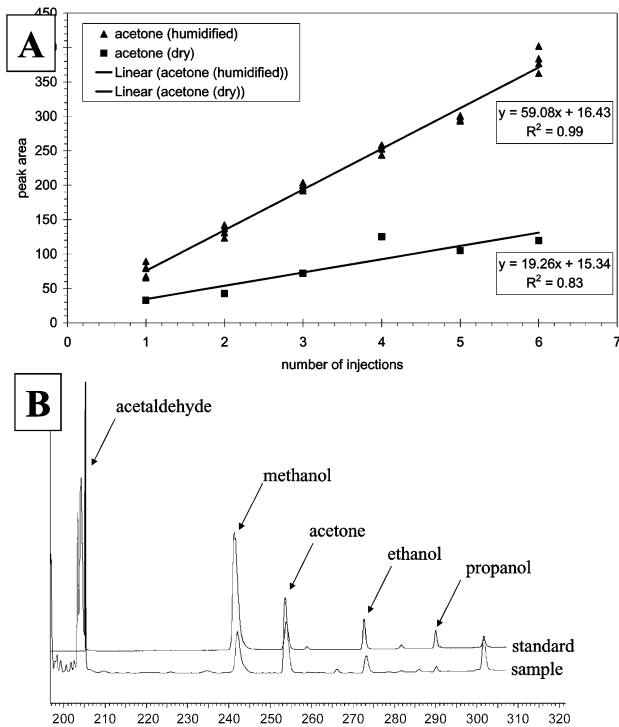
Number of injections	Peak area DMS/ $\mu\text{V s}^{-1}$ (LOWOX column)	Peak area DMS/ $\mu\text{V s}^{-1}$ (PLOT column)	Peak area acetone/ $\mu\text{V s}^{-1}$ (LOWOX column)
6	734.75	899.79	609.35
5	605.38	741.76	456.56
4	491.87	610.16	411.82
3	369.07	453.27	308.23
2	243.33	294.98	203.58
1	124.75	149.34	110.87
Gradient	121.68	149.99	95.86
$R^2$	1.00	1.00	0.99

nitrogen gas. Due to difficulties in attaining accurate and thorough mixing of the *o*-VOCs in nitrogen at high flow rates along with the long time periods required for stabilising the system, it was decided to use a low constant flow rate of nitrogen and hence deliver a fixed high concentration of each of the *o*-VOCs. The concentration delivered to the instrument was then altered *via* a sample loop injection system using a six-port valve. A loop of known volume ( $500\text{ }\mu\text{l}$ ) was continuously flushed with the high concentration *o*-VOC in nitrogen mix. During the sampling of nitrogen, the valve turns to deliver  $500\text{ }\mu\text{l}$  of the mixture into either zero nitrogen (for calibration) or sample (for spiking to gain an accurate retention time for each compound), the concentration could then be increased by increasing the number of injections over the sample period (see Table 1). Using this method it was possible to generate single figure parts per billion concentrations with low nitrogen usage and minimal dilution errors.

Difficulties were encountered, however, during the early stages of development of the calibration system in transfer of the generated standard from the permeation oven to the sampling system. Consecutive standard analyses were found to show good reproducibility, but over a period of days the response of the system was shown to vary greatly. It was found that the nitrogen gas used to clean the sample lines and acquire a blank for the instrument lead to the complete removal of water from all transfer lines in the system. When a standard mixture was then flowed through the lines, rapid deposition of *o*-VOCs to the internal surfaces of the tubing occurred. Using humidified nitrogen (the original nitrogen was bubbled through a vial of distilled water prior to flowing through the condensation trap and the sample lines in order to recreate conditions similar to those encountered in atmospheric sampling), the response of the instrument to a standard mixture was found to be reproducible (Fig. 2A) for consecutive analyses and over periods of many days. The addition of the humidifier also leads to more reproducible retention times for the *o*-VOCs as shown in Fig. 2B where an air sample and a standard are overlaid. The system has shown good linearity over a range of concentrations.

## 3. Results and discussion

A short monitoring campaign, sampling air from the window of a laboratory on the second floor of the Chemistry building at the University of Leeds, was set-up for a period of six days between November 2nd and November 8th 2001. From this few days of sampling, the instrument was assessed for automation and reliability for fieldwork use. The instrument ran continuously acquiring and analysing one sample approximately every hour and did not require any user interaction during the monitoring period. Fig. 3 shows examples of the chromatograms produced by the system and highlights a few peaks of interest, including the dual analyses for benzene.



**Fig. 2** A, the effect of moisture on the observed concentration of acetone generated using the permeation tube method for calibration. The response of the instrument is increased when the nitrogen is humidified and becomes increasingly reproducible. B, stability of retention times using humidified nitrogen for standard analyses, simplifying peak identification.

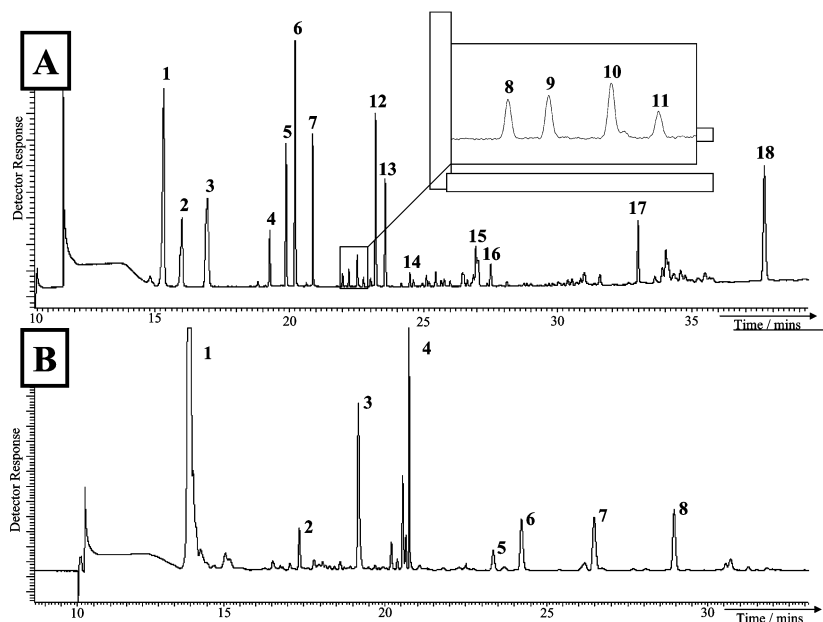
Using this system allows for detection of over twenty five NMHCs using the  $Al_2O_3$  PLOT column channel and up to fourteen oxygenated VOCs using the LOWOX column channel, these are listed in Table 2. Table 3 summarises the data collected for a few selected species along with their detection limits.

The urbanised environment surrounding the University of Leeds ensures that the majority of *o*-VOC species are produced

**Table 2** List of the compounds to be analysed by each column. There are 42 compounds in total, 6 of which (indicated by \*) can be analysed using both columns

$Al_2O_3$ PLOT column	LOWOX PLOT column
Ethane	Methanol
Ethene	Ethanol
Propane	Propanol
Propene	Butanol
iso-Butane	Acetaldehyde
n-Butane	Propanal
Acetylene	Butanal
<i>trans</i> -But-2-ene	Valeraldehyde
But-1-ene	Methyl vinyl ketone (MVK)
Iso-butene	Methacrolein (MACR)
<i>cis</i> -But-2-ene	Acetonitrile
iso-Pentane	Acetone
n-Pentane	Butanone
Buta-1,3-diene	Methyl tertiary butyl ether (MTBE)
<i>trans</i> -Pent-2-ene	Ethyl tertiary butyl ether (ETBE)
Cyclohexane	Benzene*
2-Methylpentane	Toluene*
3-Methylpentane	Ethylbenzene*
n-Hexane	<i>m+p</i> -Xylene*
Isoprene	<i>o</i> -Xylene*
n-Heptane	Dimethylsulfide (DMS)*
Dimethylsulfide (DMS)*	
Benzene*	
Toluene*	
Ethylbenzene*	
<i>m+p</i> -Xylene*	
<i>o</i> -Xylene*	

from primary sources, such as motor vehicle exhausts, which is reflected in the correlation of each of the compounds analysed. Time series plots for ethene and propanol are shown in Fig. 4 along with a plot of benzene *versus* buta-1,3-diene. These compounds are found to exhibit highly similar behaviour throughout the day and night. The sampling position, from the window of a second floor laboratory, was not ideally placed for urban background monitoring, high sided buildings surrounded the sampling point and the regular passing of vehicles beneath along with the close proximity of laboratories using large quantities of organic solvents resulted in large spikes in

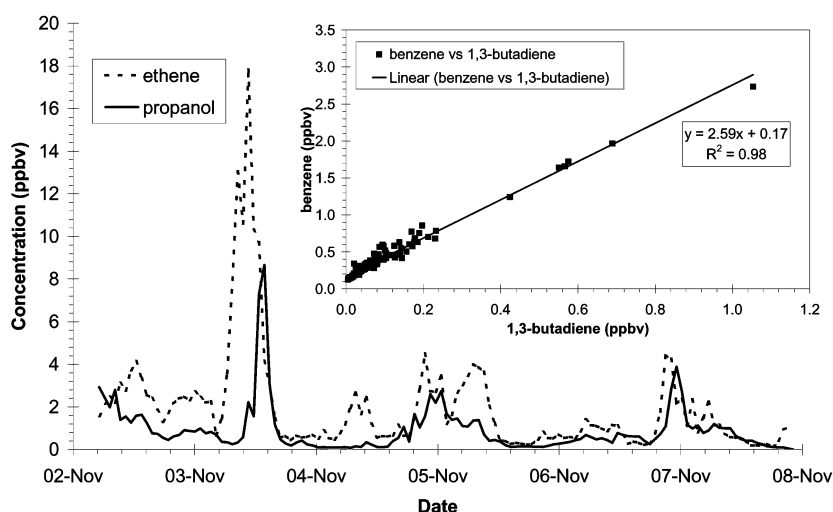


**Fig. 3** Sample chromatograms produced from A;  $Al_2O_3$  PLOT column where 1; ethane, 2; ethene, 3; propane, 4; propene, 5; iso-butane, 6; n-butane, 7; acetylene, 8; but-1-ene, 9; *trans*-but-2-ene, 10; iso-butene, 11; *cis*-but-2-ene, 12; iso-pentane, 13; n-pentane, 14; buta-1,3-diene, 15; 2+3-methylpentane, 16; n-hexane, 17; benzene, 18; toluene. And B; LOWOX column where 1; Aliphatic NMHCs, 2; benzene, 3; toluene, 4; acetaldehyde, 5; methanol, 6; acetone, 7; ethanol, 8; propanol.

**Table 3** Average concentrations for selected VOCs observed throughout the short monitoring campaign, the sample volume delivered to each channel was 500 ml. Where <sup>a</sup> refers to those compounds calibrated directly against a 30 component hydrocarbon mixture and <sup>b</sup> refers to those calibrated against a diluted permeation device

Selected VOC	Minimum value/ppbV	Maximum value/ppbV	Average value/ppbV	Detection limit/ppbV
Ethane <sup>a</sup>	2.06	22.87	4.89	9
Ethene <sup>a</sup>	0.12	17.82	1.97	7
Acetylene <sup>a</sup>	0.26	6.90	1.29	3
iso-But-2-ene <sup>a</sup>	0.01	0.81	0.18	2
Buta-1,3-diene <sup>a</sup>	> LOD	1.05	0.09	2
Benzene <sup>a</sup>	0.12	2.73	0.40	2
Toluene <sup>a</sup>	0.12	3.89	0.97	3
Acetaldehyde <sup>b</sup>	0.87	21.79	4.87	1 <sup>a</sup>
Acetone <sup>b</sup>	0.65	25.86	3.08	9
Methanol <sup>b</sup>	1.22	42.55	4.18	40
Ethanol <sup>b</sup>	0.53	16.34	2.82	15
Benzene <sup>a</sup>	0.08	2.44	0.34	2
Toluene <sup>a</sup>	0.10	4.92	1.18	2

<sup>a</sup>The acetaldehyde peak is particularly sharp with a peak width at base of just 6 s hence the low limit of detection for this compound.



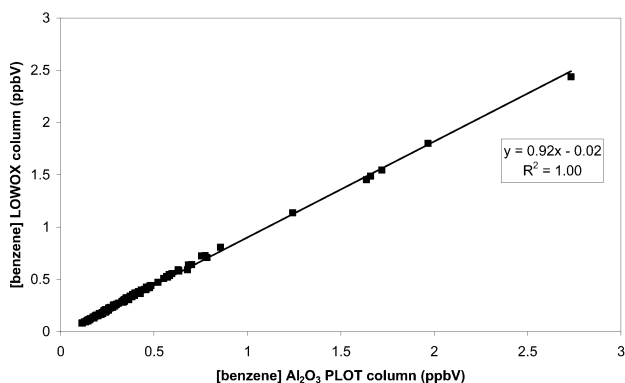
**Fig. 4** Time-series plot of ethene and propanol. These compounds follow the same general trend, highlighting their emission from common primary sources such as motor vehicle exhausts, and, in-set: Plot of benzene versus buta-1,3-diene showing good correlation for these two compounds.

the data. The aim of this monitoring period, however, was to assess the systems performance rather than acquire necessarily useful data.

Fig. 3 shows benzene eluting from both columns and being well separated from other peaks and Fig. 5 shows the excellent correlation revealed when these two peaks are quantified. The gradient of the straight line produced is slightly less than one, indicating that the sample split is not quite 50 : 50 and slightly more sample passes onto the Al<sub>2</sub>O<sub>3</sub> PLOT column. This slight

difference in sample volume, however, does not effect the quantitation of the instrument. The same set-up is used for analysing standard mixtures, therefore the same ratio of sample splitting is used for samples as it is for standards and hence are directly comparable, therefore quantitative analysis can still be performed.

The direct analysis of both NMHCs and *o*-VOCs in the atmosphere has been successfully performed with a dual channel GC-FID system. *In-situ* generation of *o*-VOC standards has been shown to be a valid calibration technique for such work, both for identification and quantification purposes. The instrument has been shown to run continuously without user intervention and thus is a valid technique for fieldwork use.



**Fig. 5** Excellent correlation between benzene concentrations measured on the PLOT column system with those measured on the LOWOX system.

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Query Reference	Query	Remarks
1	'Using' changed to 'The use of' at beginning of sentence ok?	
2	Is this iso-butene or but-2-ene?	