**Atmospheric
Chemistry
and Physics**

Partially oxidised organic components in urban aerosol using GCXGC-TOF/MS

J. F. Hamilton[1], **P. J. Webb**[1], **A. C. Lewis**[1], **J. R. Hopkins**[1], **S. Smith**[2], **and P. Davy**[2]

[1]Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK
[2]Division of Life Sciences, Kings College London, London, SE1 9NN, UK

Abstract. Partially oxidised organic compounds associated with PM2.5 aerosol collected in London, England, have been analysed using direct thermal desorption coupled to comprehensive gas chromatography-time of flight mass spectrometry (GCXGC-TOF/MS). Over 10 000 individual organic components were isolated from around 10 μg of aerosol material in a single procedure and with no sample pre-treatment. Chemical functionalities observed using this analytical technique ranged from alkanes to poly-oxygenated species. The chemical band structures commonly used in GCXGC for group type identifications overlap for this sample type, and have required mass spectrometry as an additional level of instrument dimensionality. An investigation of oxygenated volatile organic compounds (o-VOC) contained within urban aerosol has been performed and in a typical sample around 130 o-VOCs were identified based on retention behaviour and spectral match. In excess of 100 other oxygenated species were also observed but lack of mass spectral library or pure components prevents positive identification. Many of the carbonyl species observed could be mechanistically linked to gas phase aromatic hydrocarbon oxidation and there is good agreement in terms of speciation between the urban samples analysed here and those degradation products observed in smog chamber experiments of aromatic oxidation. The presence of partially oxidised species such as linear chain aldehydes and ketones and cyclic products such as furanones suggests that species generated early in the oxidative process may undergo gas to particle partitioning despite their relatively high volatility.

1 Introduction

When volatile organic compounds (VOCs) are degraded in the atmosphere they produce, in addition to ozone, a by-product of peroxy radical – NO_x reactions, a series of stable oxygenated and nitrated compounds. These oxygenated compounds have the potential to degrade further via OH reaction and photolysis to produce smaller and increasingly oxidised components with generally decreasing vapour pressures. Significant amounts of organic carbon can be found in the particulate phase of the atmosphere, and may originate as either primary emissions or from secondary sources such as the condensation of gas phase oxidation products. Epidemiological studies have established that ambient particulate matter is associated with damaging effects on respiratory and cardiovascular systems of people with a history of heart and lung diseases, leading to health deterioration and even death (Dockery et al., 1993; Samet et al., 2000; Wichmann et al., 2000). Toxicological studies have shown that particulate matter (PM) induces oxidative stress and that oxygenated organic species such as quinones may be catalytically involved in the generation of reactive oxygen species (Tao et al., 2003; Ning et al., 2003). Epidemiological and toxicological studies have also shown links between ambient particulate matter and asthma (Peden, 2002; Hao et al., 2003; Utell and Frampton, 2000).

In addition to health effects small particles can grow in size via collisions or condensation from the vapour phase until they are large enough to scatter light, thus forming "haze" as a component in photochemical smog. Aerosols can also act as a medium for the condensation of water to form water droplets, affecting the optical properties and lifetime of clouds and contributing to the aerosol 'indirect effect' term in the earths radiative balance (Haywood and Boucher, 2000).

Sources of primary organic aerosol are both natural i.e. plant waxes, pollen, biogenic emissions, biomass burning and anthropogenic i.e. cooking, fossil fuel combustion and human induced biomass burning (Rogge et al., 1993). Common constituents include mono-carboxylic

Correspondence to: A. C. Lewis
(acl5@york.ac.uk)

acids, alkanes, terpenoids and poly aromatic hydrocarbons (PAH) (Fraser et al., 1999; Yu et al., 1999). Secondary organic aerosols generally contain more multi-functional oxygenated compounds, such as poly-carboxylic acids (Blando et al., 1998). The photo-oxidation of gas phase volatile organic compounds (VOCs), with hydroxyl radicals (OH) and/or ozone, leads to early generation partially oxygenated products, with lower volatility than the parent hydrocarbon (Asher et al., 2002). These relatively volatile products have been observed to partition into an organic aerosol phase at concentrations below their saturation concentrations (Pankow, 1994). Whilst for non-polar molecules the distribution between phases can be adequately parameterised in terms of compound vapour pressure, the mechanisms controlling distribution between phases is unclear for more polar molecules.

The reaction pathways of larger hydrocarbon compounds are complex and may have significant branching to numerous stable oxidation products. An example is the reaction of toluene with OH radicals in the presence of NO_x. Toluene can react with OH via several routes including H-abstraction and OH addition to the ring to produce, for example, peroxybicyclic, epoxy and cresol intermediates (Klotz et al., 1998). Although the toluene reaction has been studied extensively, the closure of the toluene-OH reaction carbon budget is far from complete (Smith et al., 1998). Toluene is one of several hundred monoaromatic compounds found in the gas phase of urban air (Lewis et al., 2000; Hamilton and Lewis, 2003), and their degradation mechanisms and fate of oxidised products is a key uncertainty in atmospheric chemistry. Whilst mechanistic studies have yet to complete closure of monoaromatic oxidation budgets, they have determined that a wide range of stable oxygenated species may potentially be formed from the array of aromatic compounds in urban air and that these species have chemical properties that suggest a potential to partition to the condensed phase. The speciated chemical composition of urban organic aerosol is far from complete however, with many studies concentrating on "group type" rather than structurally specific identifications. It has therefore been difficult, outside of the simulation chamber, to directly link oxidised organic compounds in aerosol with possible gas phase hydrocarbon precursors. Bulk aerosol characteristics have been measured using infrared spectroscopy, NMR, ion chromatography and aerosol mass spectrometry (Suzuki et al., 2001; Schmeling et al., 2000; Allen et al., 2003).

For speciated measurements of organics, aerosols are typically trapped onto quartz fibre filters and the organic material extracted using a solvent. The complexity of urban aerosol provides many analytical challenges and the resolution afforded by GC/MS (the most commonly used technique either directly or via derivatization) is insufficient to perform a complete speciation in a single step. Much of the offline sample preparation in currently applied methods is undertaken to reduce the complexity of sample introduced to the GC/MS and in most cases, sample preparation is the rate-determining step in the analysis. The choice of extraction solvent may have a very significant influence on the type of compounds that may be extracted, although a recent study by Alves et al. (2001) used a dichloromethane extraction to obtain the majority of the organic content from the aerosol samples collected. The total organic extract (TOE) was quantified after vacuum concentration and evaporation of the extract under a dry nitrogen atmosphere. Flash chromatography using various solvents allowed separation of the TOE into a series of fractions of increasing polarity. The alcohols and the fatty acids were then derivatised using N,O-bis-trimethylsilyl-trifluoroacetamide and a BF_3/methanol mixture (20%) respectively. The fractions were then separated and the components identified using GC/MS. This lengthy procedure provided one of the most comprehensive catalogues of organic matter in aerosol. However an essentially universal and potentially on-line method of analysis which retains speciated information is highly desirable, since at each step in the preparation process, analytes, and in particular volatile species, can be lost via inefficient extractions and evaporation.

The analysis of oxygenated compounds within aerosol is particularly difficult and has been performed using chemical derivatization before analysis most commonly by GC/MS. Whilst atmospheric degradation of hydrocarbons is an important source of such species there are also some direct emissions from both anthropogenic and biogenic sources (Kean et al., 2001). It is this oxygenated content in atmospheric aerosols where probably least data currently exists (Kiss et al., 1999), however, it is this class of compound which offers the greatest potential in elucidating the links between gas and condensed phases in the atmosphere. Furthermore, within this class, are compounds which act as ligands for transition elements such as iron. These entities may enhance the solubility of Fe^{3+} and provide active redox centres that have the potential to generate reactive oxygen species, which are considered important for the toxicity of PM (Okochi and Brimblecombe, 2002).

To attempt an analysis of organics within aerosol without any form of sample pre-treatment requires a separation and detection system with an exceedingly high specificity. Thermal desorption (TD) has been shown to be a sensitive and quantitative method for directly releasing semi-volatile compounds from heterogeneous matrices such as airborne particulate matter (Waterman et al., 2000) and eliminates much of the selectivity of solvent extraction. Importantly it also dramatically reduces the amount of material required for an analysis. For separation of complex mixtures orthogonal gas chromatography (GCXGC) showed far greater resolution of petrochemical and related mixtures than had previously obtained and the technique has been extended in the last 5 years to encompass atmospheric analysis. Its ability to separate complex mixtures of organics at low concentrations makes it an ideal technique to measure partially oxidised

species in hydrocarbon dominated urban air samples (Xu et al., 2003). Coupling of GCXGC to a fast acquisition mass spectrometer combines the improved analytical resolution of the GCXGC with mass spectral information obtained across the peak. Early attempts used a quadrupole mass spectrometer (Frysinger and Gaines, 1999) but the mass spectral acquisition rate was not ideal. Van Deursen et al. (2000), coupled a GCXGC system to a time of flight mass spectrometer capable of collecting spectra at up to 500 Hz and this technique has been used for the analysis of cigarette smoke, resolving over 7500 individual analytes (Dalluge et al., 2002).

The three independent analytical dimensions in TD-GCXGC-TOF/MS makes this technique potentially ideal for measuring the organic components within a complex matrix such as ambient particulate matter (Welthagen et al., 2003). The ability of GCXGC to separate oxygenated intermediates of aromatic oxidation in the gas phase has been shown previously (Hamilton et al., 2003) and in this paper we report the modification of the technique to analyse organic aerosol composition and in particular for oxygenated organics, without sample pre-treatment or fractionation.

2 Experimental

2.1 Sample collection

The samples were obtained using a Rupprecht and Patashnick Partisol-Plus 2025 dichotomous sampler at a roadside location at Acton Town Hall in the London Borough of Ealing. The sample type (EAL/Q 1947/a) is a PM2.5 deposit collected on a quartz 47 mm filter for 24 h (the chromatograms shown in this paper are from data collected on the 25 and 26 October 2002) at a sampling rate of $15 \, \text{L} \, \text{min}^{-1}$. Meteorological conditions over this 24 h period were; average temperature $10°C$, average wind speed $7.3 \, \text{m} \, \text{s}^{-1}$, relative humidity 59–83% and wind direction 160–180°. Prior to exposure the filter was baked at $600°C$ for at least one hour in a muffle furnace to remove possible organic contaminants. It can be assumed that the contribution of organic compounds absorbed onto the filter paper to the total organic carbon is not significant as a result of the long sampling time (Turpin et al., 1994). Additional samples were taken on the roof of the Chemistry department at the University of Leeds, close to the city centre, throughout November. Filters were stored in the freezer until analysis, usually between 2 weeks and 6 months after collection.

2.2 Direct thermal desorption

Approximately $10 \, \mu g$ of particulate collected on quartz microfibre filter was introduced into a cooled GC injection liner ($40°C$), which was subsequently heated at $20°C \, \text{min}^{-1}$ in a stream of helium to $300°C$, where it was held for 10 min. The organics released in this heating regime were collected in a silica capillary liquid nitrogen cold trap, inside the GC oven.

Following desorption from the PM matrix, the silica capillary trap was removed from the liquid nitrogen and rapidly heated to the ambient temperature. The slow thermal desorption step minimises any possible chemical reactions within the organic aerosol and reduces the possibility of artefacts during analysis. Compounds were then separated by the GCXGC system. The efficiency of vaporisation was tested using repeated desorptions on the same piece of filter paper. Second desorptions showed only trace quantities of the diesel range organics and oxygenated compounds. Further desorption yielded peaks just above the instrument noise. The direct thermal desorption technique was therefore found to efficiently remove at least 90% of the directly resolvable organics during the primary desorption step.

To ensure that the o-VOCs identified were associated with the PM and not with gas phase analytes absorbed onto the filter paper, blank edge and interstitial sections of filter paper were also analysed. Considerable amounts of aliphatic and aromatic matter were found to be absorbed onto the blank filter paper, however, concentrations of the majority of o-VOCs were found to be either zero or less than 10% of that found in the particulate phase. Notably the majority of cyclic o-VOCs were not found at all on the blank edge section of the filter paper and appeared to be associated only with the condensed phase.

2.3 GCXGC-TOF/MS

GCXGC-TOF/MS was carried out using a cryo-jet Pegasus 4D (Leco, St. Joseph, MI, USA) incorporating an Agilent 6890N Gas Chromatograph and a Pegasus III reflectron time-of-flight mass spectrometer. A liquid nitrogen cooled gas jet midpoint modulator, at approximately $-160°C$, was used to enable comprehensive two-dimensional separations. A secondary oven housed within the GC oven allowed independent column temperature controls.

The column set used in this experiment provides a primary volatility based separation followed by a secondary polarity based separation. The first dimension was a 5% phenyl-95% methyl-polysiloxane $10 \, \text{m} \times 180 \, \mu\text{m} \times 0.18 \, \mu\text{m}$ HP-5 (J&W Scientific, Wilmington, DE, USA). The second column was a 14% cyanopropylphenyl-polysiloxane $1.66 \, \text{m} \times 100 \, \mu\text{m} \times 0.1 \, \mu\text{m}$ DB17 (J&W Scientific, Wilmington, DE, USA). The GC was held at $40°C$ for five minutes and then raised at $3.5°C \, \text{min}^{-1}$ to $270°C$ and held at this temperature for a further ten minutes. The carrier gas was helium (99.9999%, BOC Gases, Guilford, UK) supplied at $1 \, \text{ml} \, \text{min}^{-1}$. The modulator and secondary oven were operated at $+30°C$ and $+15°C$ above GC oven temperature respectively.

m/z ratios between 20 and 350 amu were collected at 50 Hz over the entire course of the analysis. All analyte identifications presented have minimum similarity, reverse fit and statistical probabilities of 835/1000, 845/1000 and 7000/10 000 respectively.
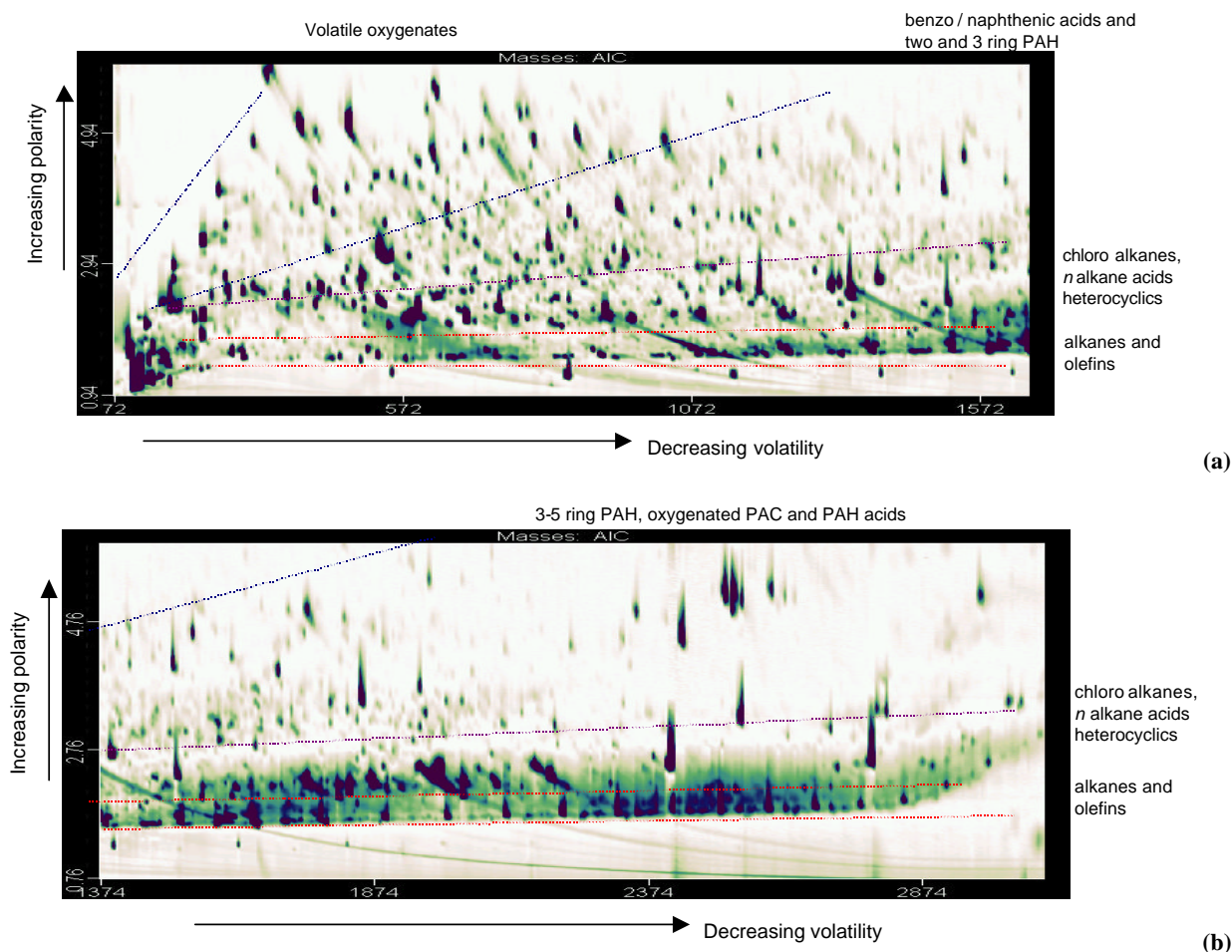
Fig. 1. (a) Two Dimensional Total Ion Chromatogram. First half of separation – volatiles. **(b)** Two Dimensional Total Ion Chromatogram. Second half of separation – semi volatiles.

3   Results

A total of 20 aerosol samples collected in London and Leeds during spring and winter months have been analysed using TD-GCXGC-TOF/MS and the sample collected in Ealing on the 25–26 October 2002 has been chosen as an example due to its highly oxygenated content. Figures 1a and b show an example of the separation and subsequent total ion current generated for a thermally volatilised PM2.5 urban aerosol sample. The analysis resolves species ranging in volatility from that equivalent to C_7 to C_{15} n-alkane in Fig. 1a and C_{16} to C_{30} in Fig. 1b. Each spot on the two images represents an individual compound for which a full mass spectrum was available. The thermal volatilisation and separation method resolved a polarity range from alkanes to mono substituted acids. Di-acids were seen to have relatively low recovery and poly-acids were not released. Group trend lines shown in Fig. 1 were determined using standard retention times and mass spectral data. Deconvolution software typically identified in excess of 10 000 analytically distinct compounds with

a S/N ratio greater than 50:1 in samples of this kind. As long as there is some degree of chromatographic separation, and at least 3 full mass scans, the software algorithm can deconvolute adjacent peaks and produce a true spectrum. The software defines a "unique" m/z ratio to each co-eluting peak and uses this to extract pure mass spectra of individual analytes across the unresolved area. This greatly aides the interpretation of co-eluting peaks and reduces data analysis times.

Previous comprehensive GC separations of gas phase organic content found between 600–1000 organic compounds in urban air (Lewis et al., 2000). The order of magnitude increase in number for particulate samples may be considered a natural consequence of the exponential relationship between isomeric forms and carbon number as we move to a sample containing generally larger, longer chain organic molecules.

The latter stages of the separation shown in Fig. 1b are dominated by higher boiling point species associated with unburnt fuel, partially burnt fuel and combustion products, such as polycyclic aromatic compounds, commonly observed in particle samples. These fractions are associated
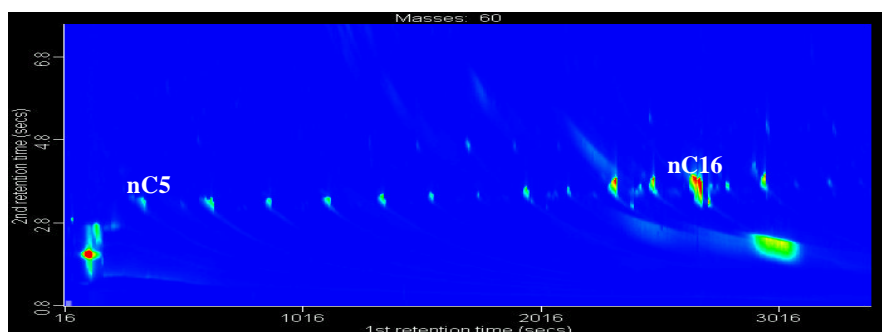
Fig. 2. Extraction of "group" of analytes (n-carboxylic acids). m/z 60 GCXGC contour plot.
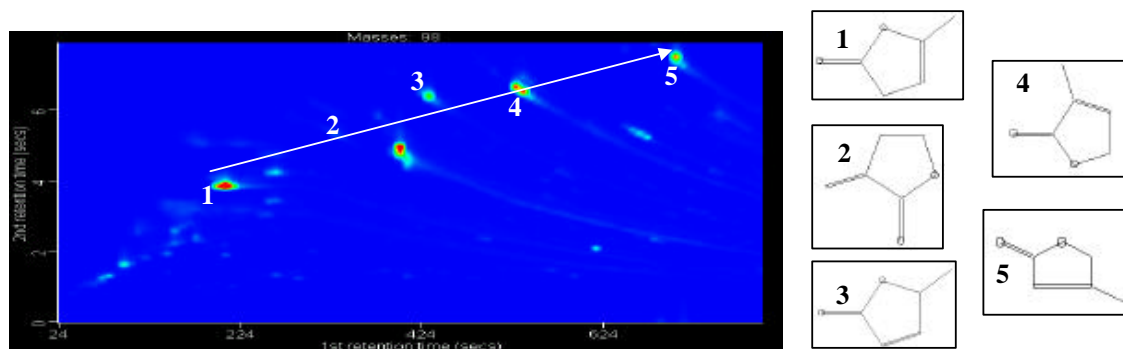

Fig. 3. Extraction of "isomers" (methyl-furanone). Left: m/z 98 GCXGC contour plot. Right: Structures of isomers.

with primary organic emissions, primarily from automotive exhaust. Of significance in this overview figure are the large numbers of analytes located at the top of Fig. 1a. These species are both volatile (from their early primary column retention times R_t) and moderately polar/oxygen containing (from their second column R_t). This region therefore contains those compounds that may be possible gas-phase oxidation products partitioning to the aerosol phase and a comprehensive compositional investigation of these components has been carried out. The chromatograms presented of urban aerosol have a similar pattern to those obtained by Welthagen et al. (2003) using TD-GCXGC-TOF. Welthagen et al. (2003) have a region in the upper right hand corner of the chromatogram which they have labelled "polar and volatile" but have not identified any of the peaks. Using a series of standard mixture we have identified these species and the results are shown below.

There are so many different group types present in this sample, that the conventional GCXGC ordering of the chromatogram presents no simple band structures, such as those seen in gasoline samples (Ledford et al., 1996). On the contrary, a number of bands overlap and even with the use of a complex set of standard mixtures, interpretation would be impossible based on retention times alone. Using GCXGC-TOF/MS it has been possible to plot GCXGC contour plots

for individual m/z ratios, allowing an additional level of instrument dimensionality over GCXGC-FID. Contour plots of appropriate mass fragments allow further resolution and it is possible to extract groups of analytes (i.e. carboxylic acids), isomers (i.e. methyl-furanones) or individual analytes (i.e. menadione) from the complex aromatic/aliphatic aerosol matrix, as shown in Figs. 2–4.

A typical inventory of o-VOCs found in PM2.5 London aerosol is presented in Tables 1–3. The o-VOCs have been split into three subsets: The linear group (including straight and branched chains), the substituted mono aromatics and the cyclic o-VOCs. Within each subset, a wide range of analyte types are present and analytes have been further categorised according to their oxygen functionality. Compounds which were also found in the blank filter paper chromatograms are shown in italics and may not be solely associated with the aerosol phase.

52 linear, 21 mono aromatic and 64 cyclic o-VOCs were identified giving a total speciation of 137 o-VOCs. There were at least 100 more o-VOCs present but at longer chain lengths and with increasing substitutions, there was insufficient data available in the mass spectral library since many of these species have never been produced synthetically. The lack of pure components and mass spectra is a severe limitation in identifying many of the oxygenated species present.
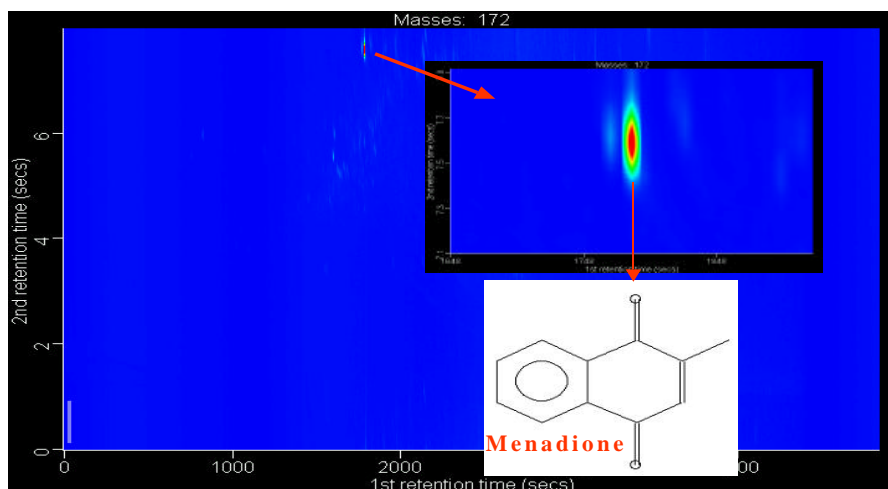
Fig. 4. Extraction of "single analyte" (menadione). m/z 172 GCXGC contour plot. Inset upper: Close up of peak. Inset lower: Structure of menadione.

Table 1. Linear o-VOC content of urban PM sample.

Aldehydes	Ketones	Carboxylic acids
nC5 to nC9 alkanals	nC8 to nC13 alkan-2-one	nC3 to nC8 mono acids
nC10 to nC12 alkanals	6-methyl-2-heptanone	nC9 to nC20 mono acids
2-hexenal	4-methyl-2-heptanone	2-ethyl-hexanoic acid
(E)-2-octenal	1-penten-3-one	
(E)-2-nonenal	4-methyl-penten-2-one	
(Z)-2-decenal	5-hexen-2-one	
	1-hepten-3-one	
	1-octen-3-one	
	5-methyl-4-hexen-3-one	

Alcohols	Others	
2-ethyl-1-pentanol	Butandial	
2-ethyl-1-hexanol	3-hexene-2,5-dione	
2-ethyl-4-methyl-1-pentanol	Paraformaldehyde	
3-nonen-2-ol		

Only in cases where there is a unique band pattern can species without unique spectra be identified with any degree of confidence; an example of which is given later for a dihydro-furanone series.

4   Discussion

In the absence of pure materials and with such a vastly complex mixture the production of a traditional set of calibrations is impossible. To give a guide to the abundance of individual species relative to a better characterised compound we have used an ion "abundance ratio". The ratio varies greatly between samples and the data has been presented as the range of ratios found in all the aerosol samples analysed to date.

This is presented in Tables 4 and 5, for a select number of o-VOCs and hydrocarbons, and is the ratio of total analyte ion counts relative to naphthalene ion counts. This is clearly very crude but at least offers a reasonable comparison between the abundance of individual species within a given class. Once again, compounds that were also found in the blank filter paper chromatograms are shown in italics. Preliminary quantification of the London 25/26 October aerosol sample gives a chrysene concentration of 0.45 ng m^{-3}.

The volatile and partially oxidised o-VOCs range widely in abundance but make up a very significant fraction of the total organics in the aerosol sample. Unsurprisingly one of the most abundant groups is the carboxylic acids, with *n*-hexadecanoic acid having an abundance ratio of between 10–33. Carboxylic acids can be emitted to the atmosphere

Table 2. Substituted mono aromatic o-VOC content of organic aerosol sample.

Carbonyl-	Hydroxy-	Others
benzaldehyde	phenol	hydroxybenzaldehyde
2-methyl-benzaldehyde	2xmethyl-phenol	2-methoxyphenol
3-methyl-benzaldehyde	dimethyl-phenol	benzoic acid
4-methyl-benzaldehyde	2-methyl-5-(1-methylethyl)-phenol	1-(2-hydroxyphenyl)-ethanone
benzene acetaldehyde	benzyl alcohol	
acetophenone	benzene-diol	
benzophenone		
1-(4-methylphenyl)-ethanone		
1-(2-methylphenyl)-ethanone		
E-cinnamaldehyde		

Table 3. Cyclic o-VOC content of organic aerosol sample.

Furanones	Cyclopentenones	Furans
butyrolactone	cyclopentanone	*furan*
2(3H)-furanone	2-cyclopenten-1-one	*2-methyl-furan*
2(5H)-furanone	2-methyl-2-cyclopenten-1-one	*furfural*
5-methyl-2(3H)-furanone	3-methyl-2-cyclopenten-1-one	*3-furaldehyde*
5-methyl-2(5H)-furanone	2,3-dimethyl-2-cyclopenten-1-one	*2-furan methanol*
3-methyl-2(5H)-furanone	2,4-dimethyl-cyclopenten-1-one	5-methyl-2-carboxaldehyde
4-methyl-2(5H)-furanone	3-ethyl-2-cyclopenten-1-one	
dihydro-3-methylene-2(3H)-furanone	2-cyclopentene-1,4-dione	
dihydro-5-methyl-2(3H)-furanone	3-methyl-1,2-cyclopentanedione	
dihydro-4-methyl-2(3H)-furanone	1H-indene-1,3(2H)-dione	
5-ethyl-2(5H)-furanone		
5,5-dimethyl-2(5H)-furanone		
2,5-dihydro-3,5-dimethyl-2-furanone		
5-ethyldihydro-2(3H)-furanone		
2,5-furandione (maleic anhydride)		
3-methyl-2,5-furandione (citraconic anhydride)		
3-methyl-dihydro-2,5-furandione		
dihydro-3-methylene-2,5-furandione		
3,4-dimethyl-2,5-furandione		
3-ethyl-4-methyl-2,5-furandione		
phthalic anhydride		
1(3H)-isobenzofuranone		
2,3-dimethyl-4-hydroxy-2-butenoic lactone		
5-acetyldihydro-2(3H)-furanone		
+nC3 to nC14 dihydro-2(3H)-furanones		

Cyclohexenones	Pyranones	Others
cyclohexanone	tetrahydro-2H-pyran-2-one	cis-3-cyclopentene-1,2-diol
cyclohexen-2-one	5,6-dihydro-2H-pyran-2-one	2-oxepanone
2-methyl-2-cyclohexen-1-one	2H-pyran-2-one	
3,5-dimethyl-2-cyclohexen-1-one		
2-methyl-5-(1-methylethylene)-2-cyclohexen-1-one [(s)-carvone)]		
1,4-cyclohexen-2-dione		
2-methyl-naphthoquinone		
7-methyl-naphthoquinone		

Table 4. Hydrocarbon, linear o-VOC and mono aromatic o-VOC ion abundance ratios.

Analyte	Abundance ratio (Ar)
HYDROCARBON	
naphthalene	1
n-dodecane	0.29–0.41
n-eicosane	0.82–1.41
toluene	2.31–17.29
ethyl benzene	0.97–1.27
n-butylbenzene	0.22–0.37
1-chloro-heptane	0.23–1.25
1-chloro-octane	0.41–1.41
eucalyptol	0.21–0.31
acenaphthlyene	0.02–0.17
chrysene	0.01–2.01
fluoranthene	0.06–1.2
LINEAR o-VOC	
heptanal	1.16–1.27
decanal	1.59–3.77
1-octen-3-one	0.17–0.21
heptanoic acid	0.07–1.08
hexadecanoic acid	10.18–33.23
MONO AROMATIC o-VOC	
benzaldehyde	0.47–3.53
3-methylbenzaldehyde	0.27–0.79
acetophenone	0.93–1.14
benzophenone	0.15–0.95
2-methylphenol	0.17–0.95
2-methoxy-phenol	0.30–0.45
hydroxybenzaldehyde	0.04–0.43

Table 5. Cyclic o-VOC abundance ratios

Analyte	Abundance ratio (Ar)
CYCLIC o-VOC	
2(3H)-furanone	0.26–1.42
2(5H)-furanone	2.05–16.33
5-methyl-2(3H)-furanone	2.54–2.80
5-methyl-2(5H)-furanone	1.60–3.40
3-methyl-2(5H)-furanone	1.64–4.77
4-methyl-2(5H)-furanone	0.33–2.49
5-ethyl-2(5H)-furanone	0.36–0.47
2,3-dimethyl-4-hydroxy-2-butenoic lactone	0.05–0.16
dihydro-5-methyl-2(3H)-furanone	0.61–0.74
dihydro-5-pentyl-2(3H)-furanone	0.2–0.46
2,5-dihydro-3,5-dimethyl-2-furanone	0.31–0.53
2,5-furandione	0–0.31
3-methyl-2,5-furandione	0–0.81
3-ethyl-4-methyl-2,5-furandione	0–0.22
2,5-furandione, dihydro-3-methylene-	0–0.17
3-methyl-dihydro-2,5-furandione	0–2.62
phthalic anhydride	0.09–11.13
1(3H)-isobenzofuranone	0.30–2.24
2-cyclo-pentene-1-one	1.39–6.22
3-methyl-2-cyclo-pentene-1-one	0.23–1.26
2-methyl-2-cyclo-pentene-1-one	0.35–0.6
3-methyl-cyclopentanedione	0.10–0.42
1H-indene-1,3(2H)-dione	0–0.03
cyclohexanone	0.56–1.36
3-methyl-2-cyclohexen-1-one	0.05–0.30
1-cyclohex-2-enedione	0.32–2.00
1,4-cyclohex-2-enedione	0.30–0.96
5,6-dihydro-2H-pyran-2-one	0–0.31
2H-pyran-2-one	0.09–0.14
furfural	0.68–12.96
5-me-2-furancarboxaldehyde	0.09–1.23
1-(2-furanyl)-ethanone	0.09–2.27
2-furanmethanol	0.16–15.96
benzofuran	0.07–0.38

from a number of sources, including primary biogenic emissions (soil and vegetation), direct anthropogenic emissions (e.g. food processing plants) and via photo-chemical oxidation (Chebbi and Carlier, 1996), with hexadecanoic acid being a significant portion of aerosol obtained from cooking and gasoline (Schauer et al., 1999; Chandramouli et al., 2003). Due to the lower vapour pressure of di- and poly-carboxylic acids, they are expected to be highly dominant in the aerosol phase. However, using thermal desorption, only a very limited amount of these compounds are found with respect to the mono-acids. Thermally assisted derivatisation or thermochemolysis is a possible means of releasing the more refactory dicarboxylic acids (Prati et al., 2003). Alternatively, a liquid extraction method could be used to analyse the di-functionality acids using a coupled GC method.

Aromatic compounds are particularly important precursors to atmospheric aerosol formation in urban areas where traffic emissions dominate. The total amount of secondary organic aerosol (SOA) produced from the oxidation of whole gasoline vapour can be represented as the sum of the contributions of the individual aromatic constituents of the fuel (Odum et al., 1997). Forstner et al. (1998) investigated the composition of SOA formed from the oxidation of mono aromatics in a series of smog chamber studies. Of the 79 semi-volatile oxygenates observed in the investigation of toluene and C$_2$-aromatic oxidation, we positively identify 29 of these to be present in ambient samples. In addition, a further 31 are strongly suspected to be present in the sample but their library match statistics are outside of our positive identification parameters. In addition to the alkyl-benzene oxidation products identified by Forstner et al. (1998), 2(3H)-furanone, 2(5H)-furanone and dihydro-2(3H)-furanone were identified within the urban aerosol with the 2(5H)-isomer almost 8–12 times more abundant than the 2(3H)-isomer. The saturated dihydro-2(3H)-furanone was also found in the aerosol phase and is 4 times more abundant than the (3H) isomer. A large number of the oxygenated compounds found in urban aerosol have also been identified in the gas phase of numerous smog chamber aromatic photo-oxidation experiments (Smith et al., 1999; Calvert et al., 2002).

Forstner et al. (1998) also found significant quantities of saturated anhydrides and suggested that they may result from photolytically induced hydrogenation of the furandiones in the particle phase as shown in Fig. 5. The saturated furandiones are not expected from the reaction mechanism, and have not been reported in previous gas phase studies. It was proposed that water, nitro-phenols and benzoic acid produce a slightly acidic environment in the particle, which allows relatively easy proton exchange to take place. In the GCXGC-TOF/MS analysis of the aerosol sample we have found considerable amounts of the saturated furanone in addition to the expected unsaturated furanones. If the primary source of these compounds is aromatic oxidation, their production pathway is not obvious from the reaction mechanism. Only the C_1 and C_2 substituted unsaturated furanones were found in the aerosol sample. In contrast, the nC_1 to nC_{14}-dihydro-2(3H)-furanones were identified and the extracted band structure is shown in Fig. 6. There were only mass spectra available in the library up to the nC_8-substituted dihydro-2(3H)-furanone. However, the unique band structure created by this group of compounds allows identification of the larger molecular weight compounds. Visual interpretation of the individual mass spectra confirms peak identifications.

A possible mechanism for the production of the dihydro-furanones is shown in Fig. 7. This mechanism is analogous to that for the anhydrides, with photolytic hydrogenation taking place in the particle phase, under acidic conditions. Dihydro-furanones have also been identified in secondary organic aerosol produced from the photo-oxidation of alkenes (Forstner et al., 1997). They identified the nC_5, nC_3 and nC_2-dihydro-2(3H)-furanones in secondary organic aerosol formed during the photo-oxidation of 1-decene. The lactones are readily formed from γ-hydroxycarboxylic acids, produced during alkene oxidation, in the presence of a small amount of acid (Streitwieser and Heathcock, 1976). At present there is no evidence to confirm which of the two proposed mechanisms is dominant. However, both the high molecular weight 1-alkenes (up to C_{23}) and n-alkyl-substituted alkyl-benzenes (up to C_{13}-substituted) were present in the aerosol particle and could contribute to the formation of the significant quantities of dihydro-2(3H)-furanones found in ambient aerosol. A number of furanones and the C_0-C_{14}-dihydro-2(3H)-furanones have been previously been identified in organic aerosol (Greaves et al., 1987; Alves et al., 2001).

In a similar smog chamber study of toluene oxidation, Jang and Kamens (2001) found the furanones in trace quantities in the gas phase only. The main ring-opened reaction products identified in the aerosol phase were primarily highly oxidised species such as oxocarboxylic acids and hydroxy-carbonyl products. They suggested that relatively high vapour pressure compounds in the aerosol could be explained through heterogeneous reactions in the aerosol phase. These reactions include aldol condensation, hydra-
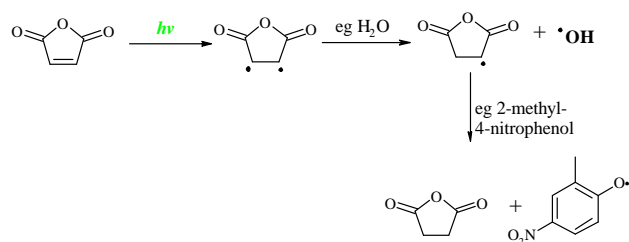

Fig. 5. Photolytically induced mechanism from 2,5-furandione to dihydro-2,5-furandione (taken from Forstner et al., 1997).

tion, polymerisation (Noziere and Riemer, 2003) in acidic solutions, similar to those found in atmospheric aerosol. The thermal desorption method of analysis would break apart these type of polymers during vaporisation. In addition, the very polar compounds would be subject to losses, similar to the di- and poly-carboxylic acids. Although we cannot make any quantitative comment about these proposed heterogeneous processes we would note that the temperature of thermal desorption from the PM has a significant impact on the abundance of small carbonyl type compounds. From relatively simple studies there appears to be a threshold temperature for the liberation of these species, at approximately 200°C. However there is no supporting information on the acidity of the aerosol samples presented in this paper.

Overall, we believe that the GCXGC-TOF/MS analysis show encouragingly good agreement with the Forstner et al. (1998) study, notably with speciation of furanone type products. We comment briefly that the gas phase composition in urban air has also been analysed using GCXGC-TOF/MS under a number of different meteorological conditions and to date the furanone-type compounds have not been found in detectable quantities.

5 Conclusions

A large number of volatile and semi-volatile oxygenated organic compounds have been observed in urban PM2.5 material analysed directly using on-line thermal desorption with GCXGC-TOF/MS. The non-selective nature of the extraction method resulted in a highly complex mixture with over 10 000 species of varying functional group types being resolved in a single separation. Of particular interest were the relatively low molecular weight and volatile oxygenated organic compounds found in the early stages of the separation. Many of the species could be mechanistically linked as products of gas phase hydrocarbon precursor oxidation with a large number being attributable to aromatic oxidation. The observations qualitatively indicate that species generated relatively early in the oxidative process may undergo gas to particle partitioning. It is worth noting that we have applied the same GCXGC-TOF/MS approach to the analysis of gas
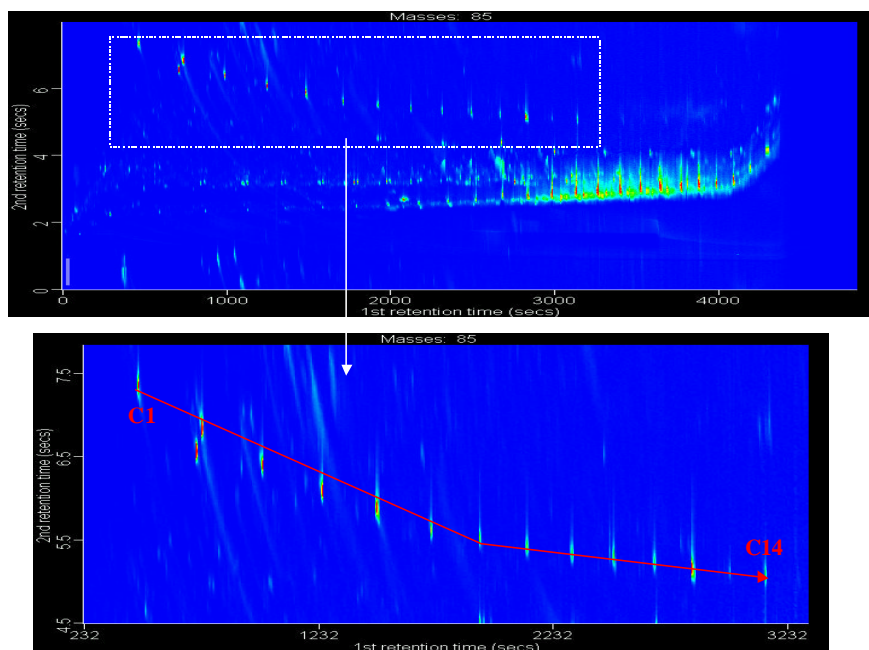
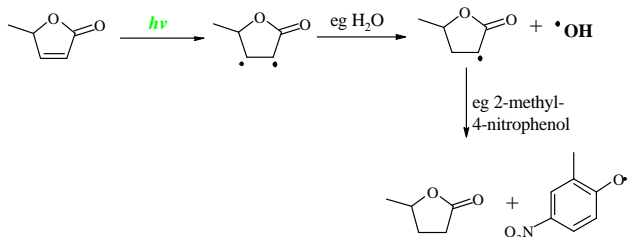**Fig. 6.** Dihydro-2(3H)-furanones extracted from aerosol matrix.

Fig. 7. Photolytically induced mechanism from 5-methyl-2(3H)-furanone to 5-methyl-dihydro-2(3H)-furanone.

phase organics and to date almost none of the aerosol bound cyclic o-VOC species have been observed in the gas phase. The mechanisms by which the species are able to exist in the condensed phase is the subject of much current discussion notably Jang and Kamens (2001) and Noziere and Riemer (2003). We are not able to provide evidence within this study to support or disprove any of the current theories, but comment that the GCXGC-TOF measurement approach appears extremely attractive in making direct measurements of key model compounds that are often used in gas particle partitioning models.

Edited by: U. Baltensperger

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