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Application of 2D-GCMS Reveals Many Industrial Chemicals in Airborne Particulate Matter

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1 **ABSTRACT**

2 Samples of airborne particulate matter (PM$_{2.5}$) have been collected in Birmingham, UK and

3 extracted with dichloromethane prior to analysis by two-dimensional GC separation and TOFMS

4 analysis. Identification of compounds using the NIST spectral library has revealed a remarkable

5 diversity of compounds, some of which have not been previously reported in airborne analyses.

6 Groups of compounds identified in this study include a large number of oxygenated VOC including

7 linear and branched compounds, substituted aromatic compounds and alicyclic compounds,

8 oxygenated polycyclic aromatic and alicyclic compounds, organic nitrogen compounds, branched

9 chain VOC and substituted aromatic VOC, phthalates, organo-phosphates and organo-sulphate

10 compounds. Many of the compounds identified are mass production chemicals, which due to their

11 semi-volatility enter the atmosphere and subsequently partition onto pre-existing aerosol. Their

12 contribution to the toxicity of airborne particulate matter is currently unknown but might be

13 significant. The diverse industrial uses and potential sources of the identified compounds are

14 reported.

15

16 Keywords: 2D GCMS, airborne chemicals, industrial chemicals, plasticisers, fire retardants

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INTRODUCTION

Atmospheric aerosol particles are complex mixtures of nonvolatile and semi-volatile inorganic and organic compounds, directly released from a variety of sources, including vehicle emissions, combustion and vegetation, and may also be formed as products of gas to particle conversion through atmospheric reactions. These atmospheric aerosols affect the global radiation balance both directly and indirectly, by absorbing and scattering solar radiation, and by acting as cloud condensation nuclei, respectively. The determination of aerosol particle composition is therefore of significant interest owing to the potential impacts upon climate and human health (Zhang et al., 2012; Harrison and Yin, 2000).

Since a substantial fraction of atmospheric aerosol consists of thousands of organic compounds with a broad range of solubilities, reactivities and physical properties, identification of these species remains a challenge, with many compounds remaining unidentified (Goldstein et al., 2007). Added complexities to the analyses of these aerosols are the trace-level concentrations of organics and difficulties in sampling. The majority of studies have collected aerosol samples onto filters, where the compounds of interest are removed by solvent extraction or thermal desorption, followed by analysis with gas chromatography coupled to mass spectrometry (GC-MS) (Tomashuk et al., 2012; Yin et al., 2010; Harrison and Yin, 2010). However, owing to the large variety of compounds present in samples, conventional GC often proves inadequate for the separation of components, thus leading to severe peak co-elutions and poor chromatography resulting from insufficient resolving power.

Some studies have made extensive use of one-dimensional GC-MS together with selective extractions and derivatisation procedures to identify large numbers of compounds in airborne particulate matter. These include Pio et al. (2001) who identified around 400 individual organic compounds in particulate matter from a Portuguese rural area. By specifically targeting

homologous series and functional groups, they were able to identify aliphatics, polycyclic aromatic

hydrocarbons (PAHs), oxy-PAH, ketones, aldehydes, alcohols, n-alkanoic acids, n-alkenoic acids,

aliphatic dicarboxyclic acids, terpenic constituents and some VOC oxidation products. In a study of

particulate matter sampled in Kuala Lumpur, Malaysia, Omar et al. (2007) reported concentrations

of PAH (14 compounds), petroleum molecular markers (4), n-alkanols (7), triterpenols (6), n-

alkanoic acids (7), soil and biomass burning carbohydrates (1), sterols (5), products of plastics

combustion (3), n-alkanoic acids (4) and mono and diacylglycerols (3). In all, within samples from

the urban area, the specific compounds analysed accounted for 5.3 µg m^{-3} out of a total solvent

extractable organic matter concentration of 18.1 µg m^{-3}.

Recent advances in comprehensive two-dimensional gas chromatography (GC×GC) have led to its

successful application in measuring a wide range of volatile and semi-volatile organic compounds

in air (Adahchour et al., 2008; Laitinen et al., 2010; Arsene et al., 2011). For example, the

unresolved complex mixture (UCM) clear from the white line in Figure 1(A) in a traditional 1D

GCMS separation typically makes up about 95% of the area of the chromatogram and is usually

unresolved by analysis. 2D GCMS techniques provide an enormous advance in terms of resolving

individual peaks but have yet to be exploited very fully in atmospheric analysis. Arsene et al.

(2011) have recently reviewed the application of GC×GC-MS hyphenated techniques for the

analysis of volatile and semi-volatile compounds in air. They report only 12 published studies of

atmospheric measurements, which are focussed largely on lower molecular mass species (less than

C_{12}), oxygenates, or forest atmospheres. The studies demonstrate applicability to alkanes up to C_{30}

(Laitinen et al., 2010) and roadside nanoparticles (Ochiai et al., 2007).

GC×GC was first exploited in atmospheric analysis by Lewis et al. (2000), who isolated and

classified more than 500 VOCs in urban air. This powerful technique has since been combined with

flame ionisation detection (FID) and with time of flight mass spectrometry (TOFMS) in several

studies (Pratt et al., 2012). For example, Xu and co workers (Xu et al., 2003a,b) utilised GC×GC–TOFMS to measure C_7–C_{11} aromatic and *n*-alkane hydrocarbons in air, isolating approximately 650 individual peaks of which 235 were identified using published retention indices. Lee et al. (2006) exploited the use of GC×GC–FID to study VOC ratios of high molecular mass aromatics which could not be speciated using conventional GC–MS. Welthagen et al. (2003) and Hamilton et al. (2004) used direct thermal desorption GC×GC–TOFMS for the characterisation of semi-volatile organic compounds in $PM_{2.5}$ detecting (but not identifying) 15,000 and 10,000 peaks, respectively. Of these 10,000 peaks, Hamilton et al. (2004) report the positive identification of 130 OVOCs, where a further 100 oxygenated species were observed but not positively identified owing to the lack of mass spectral library or pure components. Williams et al. (2010) reported the first hourly in-situ measurements of speciated organic aerosol composition in an urban environment, where approximately 300 nonvolatile and semivolatile organic compounds were identified using thermal desorption. More recently, this technique was further improved by coupling GC×GC to thermal desorption aerosol gas chromatography and has been deployed in both chamber studies investigating the photo-oxidation of diesel exhaust (Isaacman et al., 2011) and field studies (Worton et al., 2012), allowing real time measurements of a diverse range of compound classes.

2D GC-MS has extended knowledge of organic compounds present in the atmosphere particularly in the directions of organo-nitrogen compounds and oxidised compounds. However, the knowledge that thousands of VOC and SVOC compounds exist in samples that are collected from various studies and are yet to be identified and routinely measured, provides motivation for this study. GC×GC-TOFMS was applied to identify organic compounds in atmospheric aerosol collected in Birmingham, UK. In this study, we have not reported groups of compounds such as n-alkanes and PAH which have been widely reported before, but have focussed particularly on compound types which have rarely, if ever, been previously reported in the atmosphere by selecting peaks for

1 characterisation which were not part of the main homologous series identifiable from the

2 chromatograms.

3

4 **EXPERIMENTAL**

5 **Site Location**

6 Samples of airborne fine particulate matter ($PM_{2.5}$) were collected at the Elms Road Observatory

7 Site (EROS, 1.93ºW; 52.45ºN). EROS is an urban background site within the University of

8 Birmingham campus. The site is approximately 3.5 km southwest of Birmingham city centre and is

9 subject to anthropogenic emissions from a nearby railway, some moderately busy roads and

10 surrounding activities from local residents.

11

12 **Sampling**

13 Daily $PM_{2.5}$ samples were collected for 5 days (9-14 February 2011) using a high volume air

14 sampler TE-6070 (Tisch Environmental, Inc). The high volume sampler involves drawing large

15 volumes of air (800-1000 m^3) through a 20×25 cm quartz fibre filter (QMA) substrate. Filters were

16 pre-heated at 550ºC for 12 hours and stored in a freezer prior to sampling. After exposure the filters

17 were enclosed with clean pre-heated foil and stored in an air tight metal box under conditions of

18 approximately -18ºC prior to analysis. No attempt was made to evaluate or correct for sampling

19 artefacts, which can be both positive (adsorption of vapour to the filter or collected particles) or

20 negative (loss by volatilisation).

21

22 **Extraction and Analysis**

23 Whole quartz fibre filters were extracted with two 30 ml aliquots of DCM (HPLC grade) and

24 methanol (HPLC grade) sequentially. The extracts were combined, filtered and concentrated using a

25 turbo evaporator and then blown down under a gentle nitrogen flow to a final volume of 250 μL.

26 Comprehensive two-dimensional gas chromatography/time of flight mass spectrometry (GC×GC-

TOFMS) was utilised to analyse the sample extracts with conditions similar to that reported by Rowland et al. (2012). Briefly, analyses were conducted using an Agilent 7890A gas chromatograph (Agilent Technologies, Wilmington, DE, USA) equipped with a Zoex ZX2GC×GC cryogenic modulator (Houston, TX, USA) interfaced with a Almsco BenchToFdx™ time of flight mass spectrometer (Almsco International, Lantrisant, UK) operated in positive ion electron ionisation mode and calibrated with perfluorotributylamine. The scan speed was 50 Hz. The first-dimension column was 50 m × 0.25 mm × 0.40 µm VF1-MS (Varian, Palo Alto, CA, USA). The second-dimension column was 2.5 m × 0.15 mm × 0.15 µm VF-17MS (Varian). 1 µL of sample was injected in a splitless mode at 280°C. The initial temperature of the oven (60°C) was held for 1 minute and then increased at 5°C min^{-1} to 325°C and held for 10 minutes. The modulation period was 4 seconds. The transfer line temperature was 280°C and the ion source temperature was 300°C. Helium was used as the carrier gas at a constant flow rate of 0.8 mL min^{-1}. Subsequent data processing was conducted using GC Image™ v2.1 (Zoex).

RESULTS AND DISCUSSION

Five high volume urban aerosol samples collected in Birmingham, on 9–14 February 2011 were analysed utilising GC×GC-TOFMS, to identify compounds within the collected samples. A typical two-dimensional separation and subsequent total ion count is presented in Figure 1(B), where each coloured spot represents an individual compound with a corresponding full mass spectrum. The intense yellow spots are major peaks, while the magenta and dark blue spots are medium and small peaks, respectively. Compounds were separated on a volatility basis in the first dimension (X-axis) and polarity in the second (Y-axis). Approximately 1,500 peaks were found in the two-dimensional chromatogram, using the blob detection routine performed by GC Image v2.1b3 (Zoex Corporation, Houston, US) software.

1 Peak identification was based on mass spectral data from the NIST library, where two match factors

2 were used to assess the similarity between the library and measured mass spectra. These similarity

3 factors were: (*i*) match factor (MF) – described how well the library equivalent matched the entire

4 mass spectra of the selected chromatography peak, and (*ii*) reverse match factor (RMF) – described

5 how well the explicit masses present in the library equivalent matched the masses measured for the

6 selected peak. Positive identification was based on MF and RMF of above 750 and 800,

7 respectively, consistent with previous studies (Dalluge et al., 2002; Ozel et al., 2009).

8

9 Although a large number of peaks were unidentifiable owing to insufficient data available in the

10 mass spectral library, various compound groups including alkanes, alkenes, cycloalkanes,

11 aldehydes, ketones, carboxylic acids and esters, PAHs, oxygenated-PAHs and substituted aromatics

12 were positively identified. The ordered appearance of chemically related compounds in the

13 GC×GC chromatogram enables further identification of species owing to the physicochemical

14 similarities within compound classes and their steady changes with increasing chain length and/or

15 molecular sizes. This allows the identification of unknown species without unique mass spectra, as

16 demonstrated for the dihydro-furanone series by Hamilton et al. (2004) and amides by Ozel et al.

17 (2009).

18

19 Further information regarding the identification of compound classes can be achieved by producing

20 GC×GC contour plots for selected mass fragments. An example of a selected ion chromatogram is

21 shown in Figure 1(C), for *m*/*z* 85 (a branched alkane fragment), demonstrating the increased

22 resolution and ordered appearance of chemically related compounds. Mass pattern selection rules

23 were developed by Welthagen et al. (2003) in order to group peaks into distinct chemical classes,

24 facilitating interpretation of the peaks detected in $PM_{2.5}$ samples. These selection rules provided an

25 estimate for the identification of specific compound classes that have been extensively reported in

1 earlier studies (see Welthagen et al., (2003) for ion abundance rules). Their retention time selection

2 rules, however, were not absolute and therefore were not taken into consideration in this study.

3

4 Figures 2, 3 and 4 illustrate the positive identification of a range of compounds from both natural

5 and industrial sources, based on the NIST spectral library match. The measured mass spectra

6 demonstrate the excellent agreement between our spectra and the reference spectra contained within

7 the NIST library. Example spectra for some naturally occurring compounds are illustrated in Figure

8 2; these include three methyl esters emitted from pine resin and plants (Figure 2, A-F) and cis-

9 pinonic acid (Figure 2, G-H), an atmospheric organic compound produced by the oxidation of

10 terpenes (Li et al. 2010).   The spectra contained within Figure 3, demonstrate the positive

11 identification of industrial chemicals used in PVC (Figure 3, A-B), other plastics (Figure 3, C-F)

12 and nylon (Figure 3, G-H). Caprolactam (shown in Figure 3, G-H) was present in four out of five

13 samples. Other industrial compounds identified are shown in Figure 4, which include chemicals

14 used in paper production (Figure 4, A-B), as non ionic surfactants (Figure 4, C-D), as pesticides

15 (Figure 4, E-F) and as flame retardants (Figure 4, G-H). All positively identified compounds were

16 further confirmed by assessing the consistency between the two retention times measured within the

17 five different samples.

18

19 In the ambient $PM_{2.5}$ samples collected at Birmingham, UK, 100 out of the 1,500 peaks detected

20 were qualitatively identified, exclusive of *n*-alkanes ($C_{10} – C_{31}$), *n*-alkanals ($C_{18} – C_{29}$), *n*-alkanoic

21 acids ($C_5 – C_{25}$), furanones and polycyclic aromatic hydrocarbons (PAHs), all of which have been

22 extensively reported in earlier studies. The compounds reported in this study were present in at least

23 three of the five samples collected and have been split into five groups: (*i*) Oxygenated volatile

24 organic compounds (OVOC), Table 1; (*ii*) Organic nitrogen compounds (ON), Table 2; (*iii*)

25 Oxygenated polycyclic aromatic and alicyclic hydrocarbons, Table 3; (*iv*) other semi-volatile

26 organic compounds (VOC), Table 4; and (*v*) Phthalates, organic phosphates and organic sulphates,

Table 5. All compounds are reported with their corresponding retention times, MF, RMF and industrial use. The postulated industrial uses of the compounds listed in Tables 1-5 are not exclusive primary sources for each compound, as many of these compounds may also be products of secondary reactions in the atmosphere. For example 9,10-anthracenedione may be a primary component of vehicle emissions (Jakober et al., 2007) and is utilised in the production of dyes, paper and pesticides; but is also a product from the oxidation reaction of its parent PAH compound, anthracene, in the atmosphere. The industrial uses and potential sources of the identified compounds were gathered using internet search engines, emission databases and Wikipedia. Compounds for which little information was available in the literature were traced back to manufacturers to deduce a potential industrial uses / sources.

As explained for 9,10-anthracenedione, a component of organic aerosol (OA) can have a direct source of emission and is then termed as primary organic aerosol (POA), or be formed via partitioning of oxidised gas phase species, when it is known as secondary organic aerosol (SOA). OA compounds therefore have a wide range of organic functionalities and volatilities, making it extremely difficult to distinguish between primary and secondary sources in PM samples, without the aid of source apportionment techniques such as chemical mass balance (Yin et al., 2010), principal component analysis (Mari et al., 2010) and/or positive matrix factorisation (Williams et al., 2010). Hamilton et al. (2004) identified 130 OVOC in urban aerosol using direct thermal desorption (DTD) coupled to GC×GC-TOFMS, based on retention behaviour and spectral matches. They collected their samples at both roadside locations in London and on a rooftop close to Leeds city centre. Many of the carbonyl species observed in their study could be mechanistically linked to gas phase aromatic hydrocarbon oxidation, and hence could be secondary in nature. Many of the compounds detected by Hamilton et al. (2004) were not identified in the aerosol samples collected in this study, which may be due to differing sampling locations and local atmospheric composition. Roadside sampling sites include fresh gasoline and diesel vehicle emissions of VOCs, many of

1 which may be oxidised rapidly, dependent upon gas-phase and heterogeneous reaction rates with

2 respect to atmospheric oxidants (George et al., 2010). The majority of OVOCs observed in this

3 study are widely used in industry (see Table 1), but may also be secondary in origin owing to long

4 range transport and atmospheric processing. Of increasing interest is 7,9-di-tert-butyl-1-

5 oxaspiro(4,5)deca-6,9-diene-2,8-dione (see Figure 3, E-F), a degradation product of antioxidants

6 used as additives for plastic materials and engine oils, which has recently been identified as a water

7 contaminant due to leaching from water pipes. To date, however, its toxicity has not been assessed

8 and may be of significance.

9

10 Twelve of the 16 priority PAHs, defined by the United States Environment Protection Agency

11 (EPA), were observed in more than three of the samples. Four PAHs that were not identified in any

12 of the samples were anthracene, indeno(1,2,3-cd)pyrene, dibenz(a,h)anthracene and coronene.

13 Although the absence of these PAHs may be due to them having lower emission rates relative to

14 other PAHs, their fast conversion to PAH derivatives by atmospheric oxidants cannot be ruled out.

15 The gas phase reaction of anthracene + OH is reported as approximately $1\times 10^{-10}\,cm^3\,molecules^{-1}\,s^{-1}$

16 (Goulay et al., 2005), which is found to be an order of magnitude slower than the more abundant

17 PAH, phenanthrene. This relatively fast conversion of anthracene to its corresponding quinone

18 compound may therefore partially explain the absence of anthracene and explain the presence of

19 9,10-anthracenedione in all samples, as well as primary emissions from vehicles and the production

20 of dyes, paper and pesticides in the area. Recently, indeno(1,2,3-cd)pyrene, which is known as a

21 relatively stable PAH, has been shown to undergo considerable degradation when exposed to

22 atmospheric oxidants and was also not observed in any of the samples collected in this study

23 (Ringuet et al., 2012). The compounds, [1R-(1α,4aβ,10aα)]-1,2,3,4,4a,9,10,10a-octahydro-1,4a-

24 dimethyl-7-(1-methylethyl)-1-phenanthrenecarboxylic acid, methyl ester (see Figure 2, A-B); 7-

25 oxodehydroabietic acid (dehydroabietic acid), methyl ester (see Figure 2, C-D) and 16ßH-kauran-

26 16-ol, however, are found naturally in the environment (see Table 2).

1   While there have been extensive studies of oxygenated organics in the atmosphere, relatively little

2   attention has been given to organic nitrates, despite their environmental importance. A number of

3   ON species have been listed by the EPA as hazardous air pollutants (*e.g.* nitro-PAHs), yet the lack

4   of satisfactory methods for analysing ON compounds means that there is limited information in the

5   literature. Although no nitro-PAHs were identified in this study, possibly owing to their low

6   concentration in the samples, only a few ON compounds were identified in three or more samples

7   (Table 3). Hexadecanamide was present in all samples, in agreement with the results of Ozel et al.

8   (2009), who utilised direct thermal desorption (DTD) in combination with GC×GC-TOFMS to

9   analyse ON compounds in urban aerosol samples from the same site. DTD permits the analysis of

10 samples without any prior solvent extraction or sample preparation, where the samples are placed

11 directly onto a desorption tube and subjected to controlled heating. The desorbed volatiles are then

12 injected directly into the column. The authors reported between 17 and 57 ON compounds in any

13 one sample, with the lowest being recorded during February. The modest number of ON

14 compounds reported in Table 3 suggests that the chemical composition of the samples collected

15 here varies from day to day, owing to changing meteorology and complexity of emission sources,

16 consistent with Ozel et al. (2009). A further reason for the discrepancy between the number of ON

17 compounds reported by Ozel et al. (2009) and those reported in this study may be due to the

18 differing analytical procedures employed.

19

20 Table 4 reports the detection of a number of hydrocarbons, not commonly reported as present in the

21 atmosphere. For example, 2,6,10,14-tetramethyl-hexadecane, (or phytane) has been used as a

22 biomarker in petroleum geochemistry, where ratios of pristane and phytane have been exploited as

23 indicators of maturity and extent of biodegradation (Hunt et al., 2002), but to our knowledge has not

24 been routinely measured in atmospheric / environmental studies. Hexatriacontane occurs in

25 lubricating oils manufactured within the petroleum industry; thus the presence of hexatriacontane in

1 all five aerosol samples indicates that routine measurements may benefit future studies, serving as

2 an oil tracer determining the unburned oil contribution to PM (Zielinska et al., 2008).

3

4 Table 5 shows some of the many compounds which are used in industry, as plasticizers, flame

5 retardants and paint solvents. These compounds have received less attention in airborne analyses.

6 Phthalates and organophosphates are ubiquitous chemicals in the environment and are used

7 commercially as plasticizers and flame retardants, but are not usually measured in the atmosphere.

8 The majority of these compounds were detected in all the samples, with abundances considerably

9 larger than that found in the filter blank (compounds found in the filter blank are shown with an

10 asterisk in Table 5). Some studies have evaluated the concentration of phthalates and

11 organophosphates in indoor air (Bergh et al., 2011), but relatively few studies have focused on

12 levels in outdoor environments owing to suspected levels being an order of magnitude lower (Rudel

13 et al., 2009). Although volatilisation from environmental surfaces such as soil may not be a

14 significant source to the atmosphere (Harrad et al., 2006), the adsorption of these compounds by

15 dust particles may be responsible for the widespread distribution of these chemicals. Furthermore,

16 dependant upon volatility, phthalates, organophosphates and organosulphates may be adsorbed to

17 airborne particulate matter and may be subject to degradation by atmospheric oxidants, such as O_3,

18 OH and NO_3. The rate of degradation of these compounds, both in the vapour and condensed

19 phases, by atmospheric oxidants has not been experimentally measured. However, half lives of 1-

20 100 days have been estimated by using structure activity relationship methods for phthalates in the

21 vapour phase with respect to OH (Atkinson et al., 1987; Meylan et al., 1992). These predicted half

22 lives suggest that oxidation by OH radicals could be the major degradation pathway, transforming

23 these plasticizers released into the atmosphere and could subsequently form further products of

24 varying toxicity.

25

26

CONCLUSIONS

Earlier GC-MS studies of semi-volatile compounds in atmosphere aerosol have focused on specific groups of compounds and have therefore not captured the remarkable range of compounds present. This study has deliberately taken the opposite line of ignoring those groups of compounds for which there are a number of reports in the literature, but focussing on unrelated compounds in order to get a measure of the diversity of those present. As a consequence, it has revealed a quite exceptionally diverse range of compounds, many of which are in use by industry and incorporated into consumer products, for example, as plasticisers or fire retardants. Given the vapour pressures of such substances, it is not surprising that small amounts enter the atmosphere and future research on airborne particulate matter and health needs to take account of their presence. While individually they are unlikely to represent a toxic hazard, collectively, they may contribute significantly to the toxicity of airborne particulate matter. It seems far more likely that the phthalate plasticisers, for which there is evidence of endocrine disruptive potential (Sharpe and Irvine, 2004), or organo-phosphate fire retardants, present a significantly greater contribution to toxicity than the alkanes which are more commonly measured. While the polycyclic aromatic hydrocarbons probably contribute the majority of the carcinogenicity of urban particulate matter, contributions from some of the other compounds present cannot be ruled out.

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3   environment, and human health. Atmospheric and Oceanic Science Letters, 5, 156-161.
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1 **TABLE LEGENDS**

2

3 **Table 1.** Oxygenated volatile organic compounds detected in samples collected in Birmingham,
4 UK, between 9 Feb – 14 Feb 2011
5 RMF – reverse match factor; MF – match factor; tR1 – retention time 1 (minutes); tR2 – retention
6 time 2 (minutes)

7

8 **Table 2.** Oxygenated polycyclic aromatic and alicyclic compounds detected in samples collected in
9 Birmingham, UK, between 9 Feb – 14 Feb 2011
10 RMF – reverse match factor; MF – match factor; tR1 – retention time 1 (minutes); tR2 – retention
11 time 2 (minutes)

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13 **Table 3.** Organic nitrogen compounds detected in samples collected in Birmingham, UK, between
14 9 Feb – 14 Feb 2011
15 RMF – reverse match factor; MF – match factor; tR1 – retention time 1 (minutes); tR2 – retention
16 time 2 (minutes)

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18 **Table 4.** Other semi-volatile organic compounds detected in samples collected in Birmingham,
19 UK, between 9 Feb – 14 Feb 2011
20 RMF – reverse match factor; MF – match factor; tR1 – retention time 1 (minutes); tR2 – retention
21 time 2 (minutes)

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23 **Table 5.** Phthalates, organophosphates and organosulphate compounds detected in samples
24 collected in Birmingham, UK, between 9 Feb – 14 Feb 2011
25 RMF – reverse match factor; MF – match factor; tR1 – retention time 1 (minutes); tR2 – retention
26 time 2 (minutes)
27 * Compounds with an asterisk were also found in the filter blank at a lower concentration

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Table 1.

Compound	CAS No	Molecular Formula	MF	RMF	tR1	tR2	Industrial Use/Source
Linear and branched OVOCs							
Propanedioic acid, propyl-	616-62-6	$C_6H_{10}O_4$	885	903	18.734	0.629	
Hexanoic acid, 2-ethyl-	149-57-5	$C_8H_{16}O_2$	906	906	23.334	0.704	Stabiliser for PVC industry / preparation of metal derivatives
Ethanol, 2-(2-butoxyethoxy)-	112-34-5	$C_8H_{18}O_3$	920	923	26.000	1.081	Paints, cleaning, automotive products
Dipropylene glycol monomethyl ether	34590-94-8	$C_7H_{16}O_3$	813	829	29.134	1.081	Paint solvents
Ethanol, 2-(2-butoxyethoxy)-, acetate	124-17-4	$C_{10}H_{20}O_4$	885	886	30.000	1.333	Buildings / furnishings / paint solvents
Vanillin	121-33-5	$C_8H_8O_3$	839	885	31.600	2.639	Food industry
2,4,7,9-Tetramethyl-5-decyn-4,7-diol	126-86-3	$C_{14}H_{26}O_2$	892	894	31.934	0.955	Non-ionic surfactant
2,2,4-Trimethyl-1,3-pentanediol diisobutyrate	6846-50-0	$C_{16}H_{30}O_4$	816	824	36.600	0.327	Food Packaging
Propanoic acid, 2-methyl-, 1-(1,1-dimethylethyl)-2-methyl-1,3-propanediyl ester	74381-40-1	$C_{16}H_{30}O_4$	840	892	36.734	1.081	Plasticizer, PVC
Octane, 1,1'-oxybis-	629-82-3	$C_{16}H_{34}O$	904	906	37.867	0.88	Irradiated oil emissions
Isopropyl Myristate	110-27-0	$C_{17}H_{34}O_2$	903	903	41.000	1.131	Cosmetic and topical medicinal preps.
2-Pentadecanone, 6,10,14-trimethyl-	502-69-2	$C_{18}H_{36}O$	912	915	41.534	1.181	Component of essential oil of plants
Bis(2-ethylhexyl) maleate	142-16-5	$C_{20}H_{36}O_4$	786	828	46.934	1.911	Paints
Hexadecanoic acid, butyl ester	111-06-8	$C_{20}H_{40}O_2$	881	881	47.534	1.634	Soaps / cosmetics / food industry / plants
2-Propenoic acid, tridecyl ester	3076-04-8	$C_{16}H_{30}\,O_2$	857	869	49.334	1.684	Adhesives / inks
Octadecanoic acid, 2-methylpropyl ester	646-13-9	$C_{22}H_{44}O_2$	841	859	50.800	1.684	Cosmetic products
Hexanedioic acid, bis(2-ethylhexyl) ester	103-23-1	$C_{22}H_{42}O_4$	893	895	50.934	1.91	Plasticizer
Tetracosanoic acid, methyl ester	2442-49-1	$C_{25}H_{50}O_2$	874	877	55.600	2.187	Food / beverage additives
Glycerol tricaprylate	538-23-8	$C_{27}H_{50}O_6$	789	834	58.667	3.066	Pharmaceutical
Substituted aromatic OVOCs							
Ethanone, 2-(formyloxy)-1-phenyl-	55153-12-3	$C_9H_8O_3$	845	960	28.334	1.935	
Terpin Hydrate	2451-01-6	$C_{10}H_{22}O_3$	912	914	29.400	1.534	Oil of turpentine
Ethanone, 1,1'-(1,4-phenylene)bis-	1009-61-6	$C_{10}H_{10}O_2$	873	897	32.267	2.614	
cis-Pinonic acid	473-72-3	$C_{10}H_{16}O_3$	884	907	32.334	1.885	Oxidation product of terpenes
Ethanone, 1-[4-(1-hydroxy-1-methylethyl)phenyl]-	54549-72-3	$C_{11}H_{14}\,O_2$	847	855	33.400	2.362	
α,α,α',α'-Tetramethyl-1,4-benzenedimethanol	2948-46-1	$C_{12}H_{18}O_2$	864	888	34.134	2.136	Rubber and Plastics
2,6-Dimethoxybenzoquinone	530-55-2	$C_8H_8O_4$	805	826	34.934	0.101	Plants / anti-cancer
Cyclopentaneacetic acid, 3-oxo-2-pentyl-, methyl ester	24851-98-7	$C_{13}H_{22}O_3$	837	855	37.400	1.96	Plants / fragrance
3,5-di-tert-Butyl-4-hydroxybenzaldehyde	1620-98-0	$C_{15}H_{22}O_2$	848	894	40.334	2.086	Food additive
2-Propenoic acid, 3-(4-methoxyphenyl)-, 2-ethylhexyl ester	5466-77-3	$C_{18}H_{26}O_3$	867	892	47.334	2.815	Cosmetics
Phenol, 4,4'-(1-methylethylidene)bis-	80-05-7	$C_{15}H_{16}O_2$	771	846	48.334	0.528	Plastics
Cyclic-OVOCs							
Succinic anhydride	108-30-5	$C_4H_4O_3$	880	900	18.467	3.244	Paper production
4,8,12,16-Tetramethylheptadecan-4-olide	96168-15-9	$C_{21}H_{40}O_2$	853	871	50.467	2.238	Water repellent
7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione	82304-66-3	$C_{17}H_{24}O_3$	917	943	43.134	2.312	Plastic materials
1H-Naphtho[2,1-b]pyran, 3-ethenyldodecahydro-3,4a,7,7,10a-pentamethyl-, [3R-(3α,4aβ,6aα,10aβ,10bα)]-	596-84-9	$C_{20}H_{34}O$	915	918	45.800	1.985	

Table 2.

Compound	CAS No.	Molecular Formula	MF	RMF	tR1	tR2	Industrial Use/Source
OPAHs & Alicyclic Compounds							
1H-Phenalen-1-one	548-39-0	$C_{13}H_8O$	899	899	43.800	0.603	
9,10-Anthracenedione	84-65-1	$C_{14}H_8O_2$	898	900	45.067	0.277	Dyes, paper making, pesticides
1,8-Naphthalic anhydride	81-84-5	$C_{12}H_6O_3$	857	860	46.134	1.232	Dyes, pigments
9,10-Anthracenedione, methyl-	84-54-8	$C_{15}H_{10}O_2$	863	877	47.467	0.327	
Naphthalene, 1-(phenylmethoxy)-	607-58-9	$C_{17}H_{14}O$	931	934	48.000	0.025	Heat sensitive paper
2H-Phenanthro[9,10-b]pyran		$C_{17}H_{12}O$	758	848	50.200	3.946	
8H-Naphtho[1,2-b]pyran-8-one, 3-ethyldodecahydro-3,4a,7,7,10a-pentamethyl-, [3R-(3α,4aβ,6aα,10aβ,10bα)]-	55836-76-5	$C_{20}H_{34}O_2$	754	807	50.467	3.091	
2-Ethyl-trans-4a,cis-4b,trans-8a,cis-10a-perhydro-trans-2,4a,8a-trimethylphenanthrene		$C_{19}H_{32}O$	780	814	50.667	3.795	
1-Phenanthrenecarboxylic acid, 1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-, methyl ester, [1R-(1α,4aβ,10aα)]-	1740-19-8	$C_{20}H_{28}O_2$	891	896	50.934	3.218	Pine resin
7-Oxodehydroabietic acid, methyl ester	17751-36-9	$C_{21}H_{28}O_3$	835	847	54.534	0.327	Terpenic resin
16ßH-Kauran-16-ol	5354-44-9	$C_{20}H_{34}O$	803	813	49.934	2.791	Plants

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Table 3.

Compound	CAS No.	Molecular Formula	MF	RMF	tR1	tR2	Industrial Use/Source
Linear and branched ONs							
Urea, triethyl-	19006-59-8	$C_7H_{16}N_2O$	764	812	25.867	1.634	
Hexadecanamide	629-54-9	$C_{16}H_{33}NO$	845	845	47.400	2.438	
Substituted aromatic ONs							
Penoxaline	40487-42-1	$C_{13}H_{19}N_3O_4$	881	885	45.867	2.966	Pesticide
Cyclic-ONs							
2,5-Pyrrolidinedione	123-56-8	$C_4H_5NO_2$	864	869	22.534	2.741	Silver plating / antibacterial agent
Caprolactam	105-60-2	$C_6H_{11}NO$	913	913	27.267	2.967	Nylon
1,3-Diethyl-2,4,5-trioxoimidazolidine		$C_7H_{10}N_2O_3$	881	884	28.267	2.263	Plant Metabolism
1-Ethyl-4,4-dimethyl-2,5-dioxoimidazolidine		$C_7H_{12}N_2O_2$	808	811	28.400	2.439	
Quinoline, 2-methyl-	91-63-4	$C_{10}H_9N$	798	852	29.600	2.137	Dyes, Solvent for resins and terpenes

Table 4.

Compound	CAS No.	Molecular Formula	MF	RMF	tR1	tR2	Industrial Use/Source
Linear and branched VOCs							
Nonadecane, 2-methyl-	1560-86-7	$C_{20}H_{42}$	820	824	40.000	0.729	
Hexadecane, 2,6,10,14-tetramethyl-	638-36-8	$C_{20}H_{42}$	892	895	41.000	0.805	Petroleum
Hexatriacontane (C_{36})	630-06-8	$C_{36}H_{74}$	800	802	61.134	2.538	Lubricating oils
Substituted aromatic VOCs							
1,1':3',1"-Terphenyl, 5'-phenyl-	612-71-5	$C_{24}H_{18}$	887	919	60.267	3.493	
Polycyclic aromatic VOCs							
Stigmastane	601-58-1	$C_{29}H_{52}$	791	801	62.734	0.327	

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3 **Table 5.**
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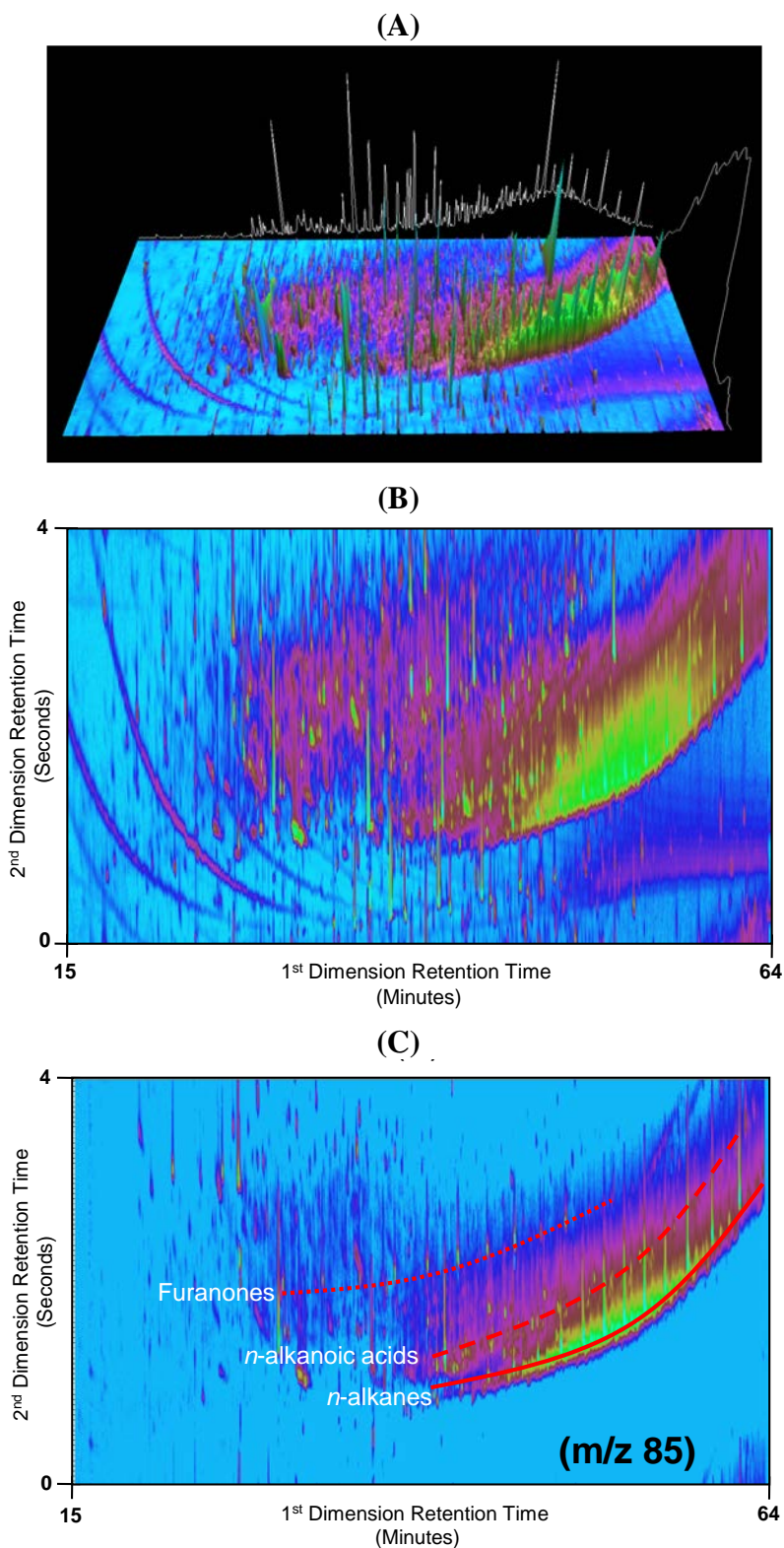| Compound	CAS No.	Molecular Formula	MF	RMF	tR1	tR2	Industrial Use/Source
Phthalates							
Phthalic anhydride *	85-44-9	$C_8H_4O_3$	947	948	29.134	2.967	Plasticizer
Diethyl Phthalate	84-66-2	$C_{12}H_{14}O_4$	885	905	36.000	2.414	Plasticizer, detergent bases and aerosol sprays
Phthalic acid, isobutyl octyl ester *		$C_{20}H_{30}O_4$	879	880	41.800	2.312	
1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester *	84-69-5	$C_{16}H_{22}O_4$	859	859	41.867	2.287	
Phthalic acid, butyl hexyl ester *		$C_{18}H_{26}O_4$	917	917	43.600	2.564	
Dibutyl phthalate *	84-74-2	$C_{16}H_{22}O_4$	882	886	43.667	2.538	
Benzyl butyl phthalate	85-68-7	$C_{19}H_{20}O_4$	903	916	50.467	0.025	Plasticizer
1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester *	4376-20-9	$C_{16}H_{22}O_4$	896	898	53.200	2.69	
1,2-Benzenedicarboxylic acid, dinonyl ester	84-76-4	$C_{26}H_{42}O_4$	783	800	56.734	3.317	Plasticizer
Terephthalic acid, di(2-ethylhexyl) ester	6422-86-2	$C_{24}H_{38}O_4$	771	839	56.134	2.69	Plasticizer
Organophosphates							
Tributyl phosphate *	126-73-8	$C_{12}H_{27}O_4P$	759	801	33.867	1.282	Plasticizer
2-Methyl-2-propyl methylphosphonofluoridate *		$C_5H_{12}FO_2P$	773	905	33.934	1.257	Plasticizer
Tri(2-chloroethyl) phosphate	115-96-8	$C_6H_{12}Cl_3O_4P$	900	903	39.400	2.464	Flame retardant
2-Propanol, 1-chloro-, phosphate (3:1) *	13674-84-5	$C_9H_{18}Cl_3O_4P$	897	902	40.467	2.413	Flame retardant
Octicizer (Diphenyl-2-ethylhexyl phosphate)	1241-94-7	$C_{20}H_{27}O_4P$	855	862	51.600	3.544	Plasticizer
Organosulphates							
Benzenesulfonamide, N-butyl-	3622-84-2	$C_{10}H_{15}SO_2N$	855	886	40.400	3.368	Plasticizer
1-Propanesulfonic acid, ethyl ester	91284-43-4	$C_5H_{12}O_3S$	817	817	51.534	1.206	

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FIGURE LEGENDS

Figure 1. (A) Total ion current chromatogram of an urban aerosol sample (Birmingham, UK) examined by GC×GC-TOFMS illustrating improved chromatographic resolution by GC×GC compared with GC/MS (white line on background). (B) Contour plot of total ion current chromatogram of an urban aerosol sample examined by GC×GC-TOFMS. Colours indicate the intensities of the response (green>yellow>pink). (C) Example selected ion chromatogram (*m/z* 85, *n*-alkane fragment). Red lines signify the ordered appearance of compounds with similar physicochemical properties. Solid line – *n*-alkanes, dashed line – *n*-alkanoic acids, dotted line – furanones with varying alkyl chain length. Sample taken 09-02-11.

Figure 2. Example mass spectra of naturally occuring compounds positively identified in urban aerosol samples (Birmingham, UK). Compounds (A) and (B) are compound and reference mass spectra for 1-phenanthrenecarboxylic acid, 1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-, methyl ester, [1R-(1α,4aβ,10aα)]; (C) and (D) are compound and reference mass spectra for 7-oxodehydroabietic acid, methyl ester; (E) and (F) are compound and reference mass spectra for cyclopentaneacetic acid, 3-oxo-2-pentyl-, methyl ester; and (G) and (H) are compound and reference mass spectra for cis-pinonic acid. (Reference spectra reproduced with permission from the National Institute of Standards & Technology spectral database ver. 2.0f Oct8 2008).
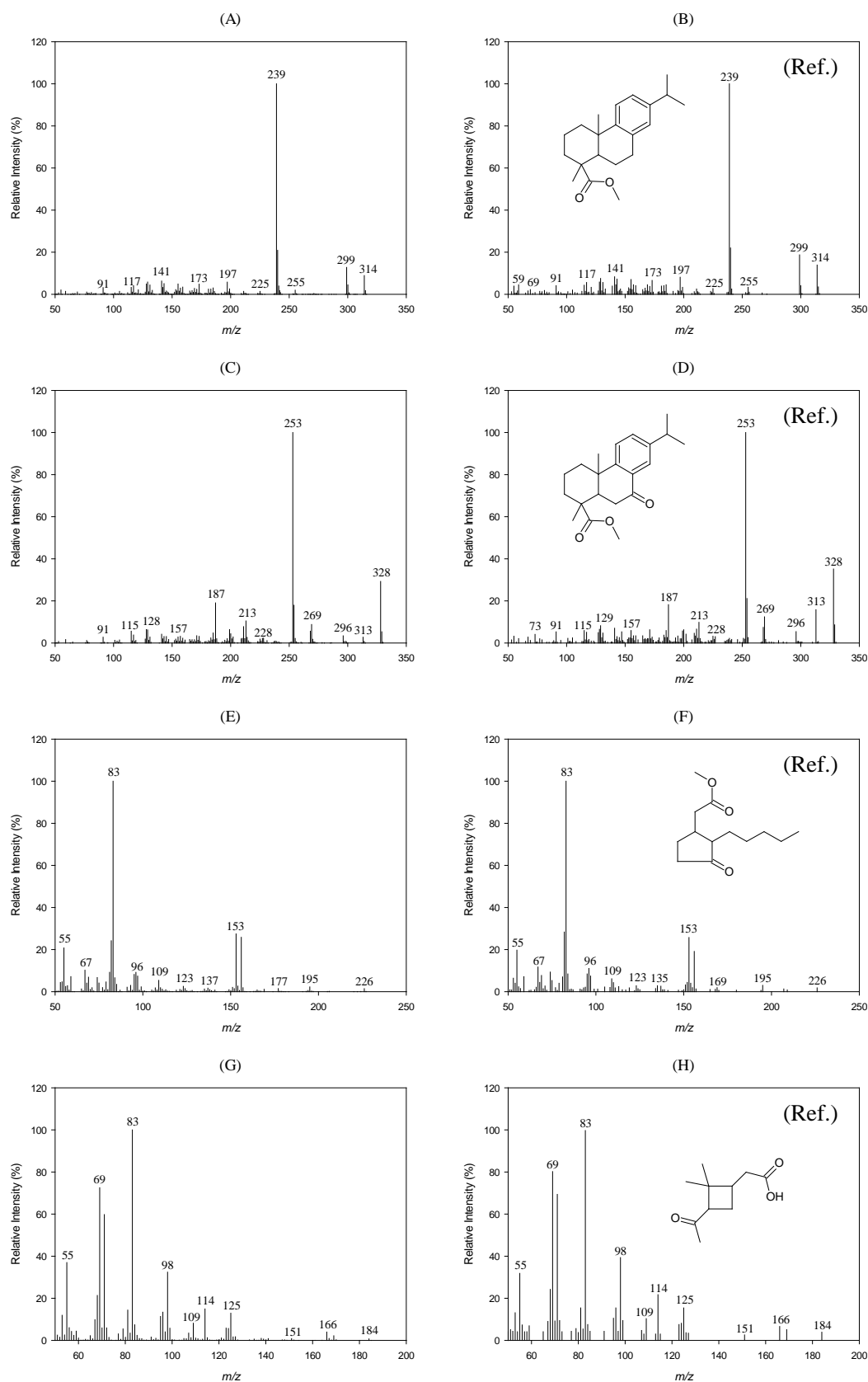
Figure 3. Example mass spectra of industrial compounds emitted from plastics, rubber and PVC, positively identified in urban aerosol samples (Birmingham, UK). Compounds (A) and (B) are compound and reference mass spectra for hexanoic acid, 2-ethyl-; (C) and (D) are compound and reference mass spectra for α,α,α',α'-tetramethyl-1,4-benzenedimethanol; (E) and (F) are compound and reference mass spectra for 7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione; and (G) and (H) are compound and reference mass spectra for caprolactam. (Reference spectra reproduced with permission from the National Institute of Standards & Technology spectral database ver. 2.0f Oct8 2008).

Figure 4. Example mass spectra of pesticides, flame retardants and compounds used in paper production indutries, positively identified in urban aerosol samples (Birmingham, UK). Compounds (A) and (B) are compound and reference mass spectra for naphthalene, 1-(phenylmethoxy)-; (C) and (D) are compound and reference mass spectra for 2,4,7,9-Tetramethyl-5-decyn-4,7-diol; (E) and (F) are compound and reference mass spectra for penoxilane; and (G) and (H) are compound and reference mass spectra for tri(2-chloroethyl) phosphate. (Reference spectra reproduced with permission from the National Institute of Standards & Technology spectral database ver. 2.0f Oct8 2008).
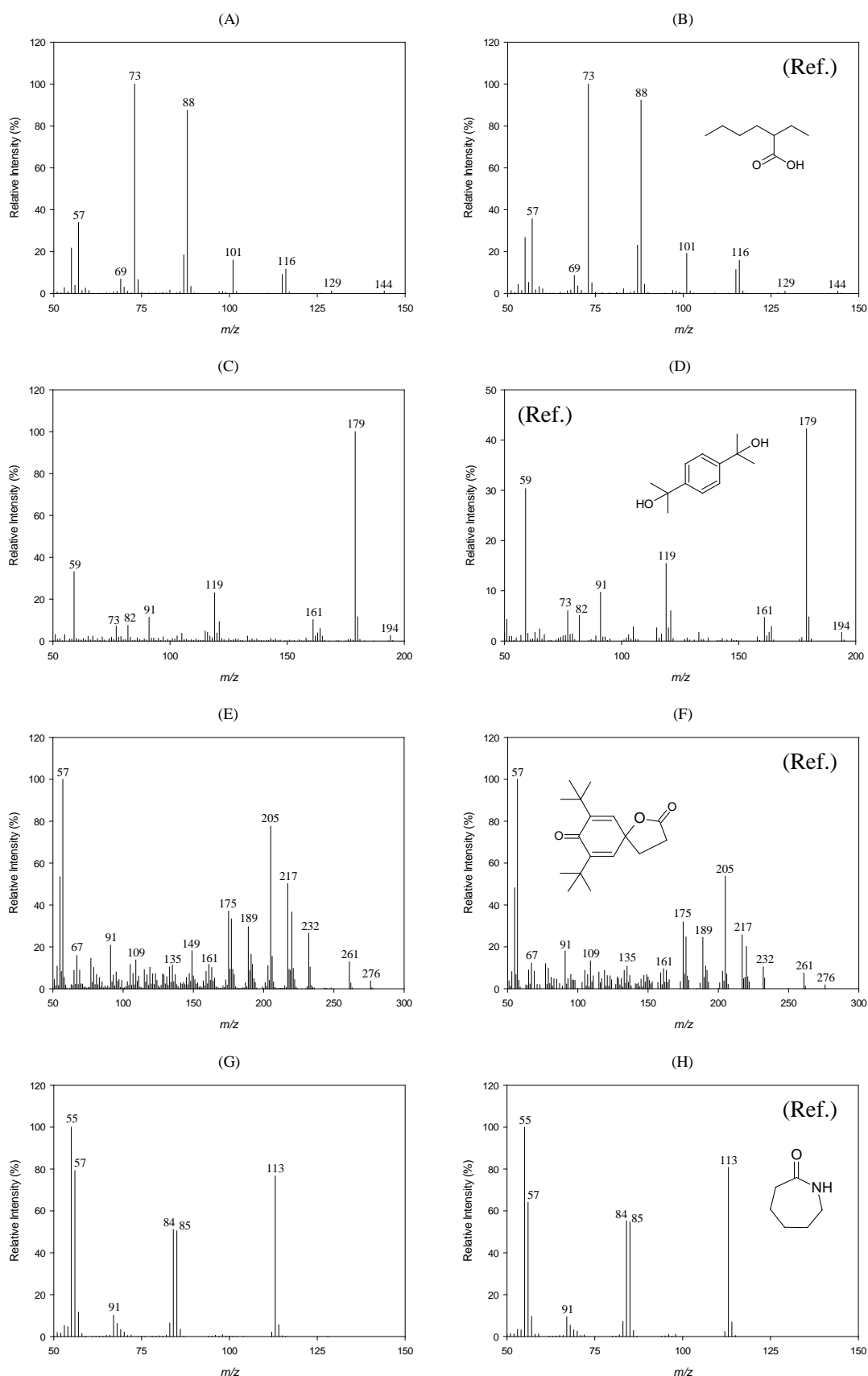
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(A)

(B)

(C)

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3 **Figure 1.** (A) Total ion current chromatogram of an urban aerosol sample (Birmingham, UK) examined by
4 GC×GC-TOFMS illustrating improved chromatographic resolution by GC×GC compared with GC/MS
5 (white line on background). (B) Contour plot of total ion current chromatogram of an urban aerosol sample
6 examined by GC×GC-TOFMS. Colours indicate the intensities of the response (green>yellow>pink). (C)
7 Example selected ion chromatogram (*m/z* 85, *n*-alkane fragment). Red lines signify the ordered appearance
8 of compounds with similar physicochemical properties. Solid line – *n*-alkanes, dashed line – *n*-alkanoic
9 acids, dotted line – furanones with varying alkyl chain length. Sample taken 09-02-11.
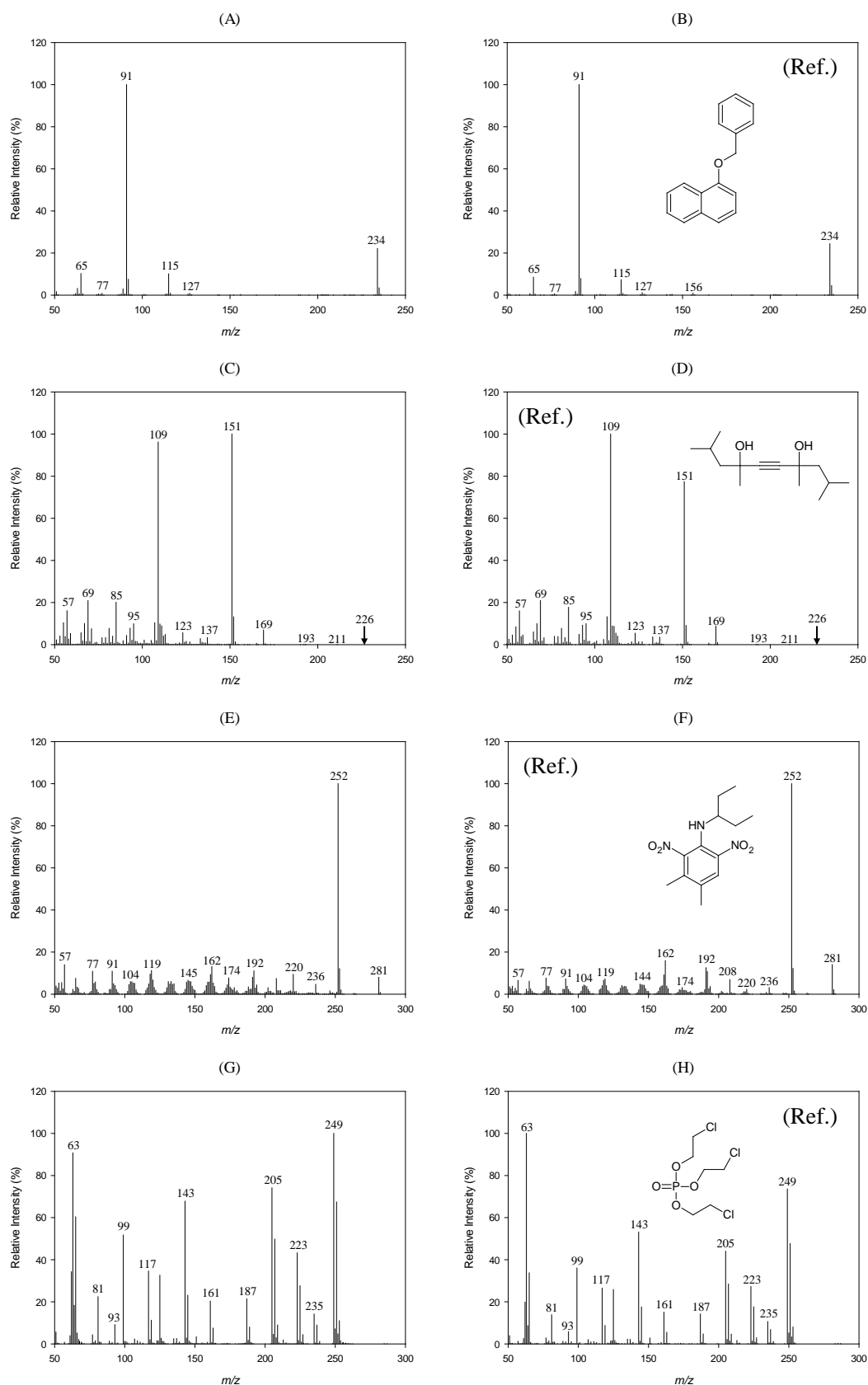10

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2   **Figure 2.** Example mass spectra of naturally occuring compounds positively identified in urban aerosol
3   samples (Birmingham, UK). Compounds (A) and (B) are compound and reference mass spectra for 1-
4   phenanthrenecarboxylic acid, 1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-, methyl ester,
5   [1R-(1α,4aβ,10aα)]; (C) and (D) are compound and reference mass spectra for 7-oxodehydroabietic acid,
6   methyl ester; (E) and (F) are compound and reference mass spectra for cyclopentaneacetic acid, 3-oxo-2-
7   pentyl-, methyl ester; and (G) and (H) are compound and reference mass spectra for cis-pinonic acid.
8   (Reference spectra reproduced with permission from the National Institute of Standards & Technology
9   spectral database ver. 2.0f Oct8 2008).

1
2 **Figure 3.** Example mass spectra of industrial compounds emitted from plastics, rubber and PVC, positively
3 identified in urban aerosol samples (Birmingham, UK). Compounds (A) and (B) are compound and reference
4 mass spectra for hexanoic acid, 2-ethyl-; (C) and (D) are compound and reference mass spectra for α,α,α',α'-
5 tetramethyl-1,4-benzenedimethanol; (E) and (F) are compound and reference mass spectra for 7,9-di-tert-
6 butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione; and (G) and (H) are compound and reference mass spectra
7 for caprolactam. (Reference spectra reproduced with permission from the National Institute of Standards &
8 Technology spectral database ver. 2.0f Oct8 2008).

Figure 4. Example mass spectra of pesticides, flame retardants and compounds used in paper production indutries, positively identified in urban aerosol samples (Birmingham, UK). Compounds (A) and (B) are compound and reference mass spectra for naphthalene, 1-(phenylmethoxy)-; (C) and (D) are compound and reference mass spectra for 2,4,7,9-Tetramethyl-5-decyn-4,7-diol; (E) and (F) are compound and reference mass spectra for penoxilane; and (G) and (H) are compound and reference mass spectra for tri(2-chloroethyl) phosphate. (Reference spectra reproduced with permission from the National Institute of Standards & Technology spectral database ver. 2.0f Oct8 2008).