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# Multidimensional Gas Chromatography – Time of Flight Mass Spectrometry of PAH in Smog Chamber Studies and in Smog Samples

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## 1. Introduction

Hans Falk (Falk et al., 1956; 1960) published the first papers demonstrating that polycyclic aromatic hydrocarbons underwent a transformation when exposed to ultraviolet light and oxidants. His experiments, in which concentrated spots of individual PAH were irradiated under UV light and exposed to ozone, suggested that PAH were oxidized to unknown products at a very slow rate of about 1 to 5% per hour. However, in 1977, it was shown (Lane & Katz, 1977) that PAH were, indeed, very sensitive to ozone by exposing monolayer distributions of PAH adsorbed on glass plates to ozone and irradiation which closely matched solar irradiation in the 2500Å to 5000Å region of the spectrum from a quartz lamp. Under lamp irradiation and 0.19 ppm O<sub>3</sub>, the half lives of Benzo[a]pyrene, Benzo[k]fluoranthene and Benzo[b]fluoranthene were 0.58 h, 3.9 h, and 4.2 h respectively (Lane, 1975). They also were the first to describe how multi-layering of PAH on particles could influence the apparent reaction rate of the PAH in Falk's experiment, and demonstrated that a rapid surface oxidation reaction formed a "crust" of oxidized products and was then followed by a slower penetration reaction involving the ozone accessing the subsurface material by penetrating the surface oxidized material - much like passing through a crust of bread. In the 1980s the group at the University of California, lead by Roger Atkinson began smog chamber studies to determine the rate of decomposition of a wide variety of PAH and PAH-related compounds when exposed to various oxidants. Their work clearly indicated that the OH radical was the dominant oxidant in the atmosphere (Atkinson et al., 1984; Atkinson, 1988). Most subsequent smog chamber studies to investigate the decomposition of PAH have utilized the OH radical as the oxidant of choice. The first report of a variety of oxidized products of the reaction of Naphthalene with the OH radical in a smog chamber was published in 1994 (Lane & Tang, 1994). Numerous publications have followed, describing the products of the OH radical reactions with naphthalene (Atkinson & Arey, 1994; Bunce et al., 1997; Sasaki et al., 1997; Mihele et al., 2002; Wang et al., 2007; Lee & Lane, 2009; Nishino & Arey, 2009); with acenaphene (Sauret-Szczepanski & Lane, 2004); with Alkylated naphthalenes (Banceu et al., 2001; Wang et al., 2007) and with phenanthrene (Helmig & Harger, 1994; Esteve et al., 2003; Lee & Lane, 2010).

Gas Chromatographic methods, because of their resolution and separation power over other analytical methods have been used to investigate the myriad of products found. With the advent of multidimensional gas chromatography, (GCxGC), the resolution and separation capabilities of gas chromatographic methods took a quantum leap forward. The combination of GCxGC with Time of Flight Mass Spectrometry, (GCxGC-TOFMS) has resulted in the most powerful instrument for the determination of oxidation products in chemical reactions. Numerous papers demonstrating the power of GCxGC-TOFMS for the determination of the products of the OH radical reactions with various PAH in smog chamber studies have been published. (Lee & Lane, 2009; 2010; Lane & Lee, 2010). Lee and Lane then searched for, and found, many of the oxidation products found the smog chamber studies in smog samples collected in Seoul, Republic of Korea (Lane & Lee, 2010).

An important aspect of looking for secondary organic compounds produced in smog chamber studies, is to determine how the products partition themselves between the gaseous and particulate phases. This has been facilitated by the development of Annular Diffusion Denuders for organic compounds. Johnson and co-workers (Johnson et al., 1985; Lane et al., 1988; 1992) utilized 8-channel, multi-annular denuders, coated with a combination of SE-54 silicone oil and crushed Tenax®. Although these denuders were primarily designed for the collection of ambient air samples for the analysis of chlorinated aromatics, they were also shown to be suitable for the determination of the gas/particle partitioning of PAH. In 1995 Gundel (Gundel et al., 1995) introduced a single-channel denuder coated with finely ground XAD-4 resin for the analysis of PAH in tobacco smoke. In 1993 a collaboration between Gundel and Lane resulted in the first Integrated Organic Gas And Particle Sampler (IOGAPS) (Gundel & Lane 1995) which was manufactured by URG in Chapel Hill NC. The denuder in this instrument was an 8-channel, 30cm long denuder operating at a flow rate of 16.7 L/min. For application to smog chamber studies, a smaller 5-channel 20-cm long denuder was utilized (Mihele et al., 2002). Coupled with a filter pack comprising a quartz or Teflon coated glass fiber filter backed up with 2 sorbent impregnated filters (SIFs) (Gundel & Herring, 1998; Galarneau et al., 2006), the denuder-filterpack proved extremely efficient for the determination of the gas particle partitioning of the products during the course of the smog chamber reaction studies.

In this chapter, the application of GCxGC-TOFMS to the determination of the phase-partitioned products of the OH radical reactions of PAH will be discussed. The utility of thermal desorption of samples directly into the GCxGC-TOFMS for the analysis of smog samples from the Republic of Korea will also be described.

## **2. Experimental**

### **2.1 Smog chamber**

The smog chamber in our laboratory is a 10 m<sup>3</sup> cylindrical chamber, essentially a cylindrical Teflon bag which is surrounded by a bank of fluorescent black lights. These may be turned on in 12 stages giving 12 levels of UV intensity. For the reactions described in this paper, full illumination was used. A fan, the blades of which were also coated with Teflon, inside the chamber caused efficient air mixing in the chamber. Air is supplied to the chamber by an AADCO model 737 pure air generator. The air in the chamber was monitored using a Columbia Science Chemiluminescence monitor for the appearance of ozone, and, when

ozone started to appear, it indicated that the NO, added to prevent the presence of ozone, had been used up. The reaction study was then terminated. NO was monitored by a Thermo Environmental Instruments INC. Model 42C NO-NO<sub>2</sub>-NO<sub>x</sub> instrument.

The OH radical was generated in the chamber by the photochemical reaction of isopropyl nitrite in the presence of NO (Mihele et al., 2002). When the fluorescent lamps were turned on, the OH radical was produced to a steady state in just a few milliseconds (Bunce et al, 1997). When the lamps were turned off, the OH radical disappeared almost as quickly, effectively stopping the reactions and freezing the product mix. Samples could then be withdrawn from the chamber for analysis of the products. After the samples had been collected, the lamps were turned back on for a specified period of time after which the lamps were turned off and another sample was collected. This process continued until the NO was used up and ozone began to appear.

## 2.2 Annular diffusion denuder sample collection and analysis

A 5-channel, 30 cm long annular diffusion denuder coated with finely ground (to an average particle diameter of 0.7 μm) XAD-4 resin and filterpack were used to collect samples from the smog chamber to evaluate the gas/particle partitioning of the products produced during the reactions. During collection of the air samples, the gas phase products were adsorbed on the denuder while the particle phase material passed through the denuder and were trapped on the filter in the filter pack. The filter pack consisted of a Teflon coated glass fiber filter and two XAD-4 sorbent impregnated filters (Gundel & Herring, 1998; Galerneau et al., 2006) to trap any products which might volatilize from the particles collected on the filter and pass through the filter. The denuder and the filters were solvent extracted with hexane (Lane & Gundel, 1996; Gundel & Lane, 1999). The solutions were reduced in volume, internal standards were added and the samples were injected into the GC × GC-TOFMS.

## 2.3 Multidimensional Gas Chromatography-Time of Flight Mass Spectrometry (GCxGC-TOFMS)

A Pegasus IV GCxGC-TOFMS (LECO Instruments Inc, Dearborne, MI) was used for the chemical separation and analysis of the products. The first dimension column (for separation based on vapor pressure), was a DB5-MS capillary column (30 m × 0.25 mm i.d. × 0.25 μm film thickness) and the second dimension column (for separation in the polar dimension) was a DB17-MS column (1.1 m × 0.18 mm i.d. × 0.18 μm film thickness). The secondary oven temperature was offset +10 °C relative to the main oven and the modulator temperature was offset +20 °C relative to the main oven. The temperature modulator was a liquid nitrogen cooled dual jet configuration with a cool time of 1.90 s between heating and cooling cycles. The main oven was commenced at 60 °C for 3.0 minutes then programmed at 3 °C /min to 300 °C and then held isothermally for 5 minutes. The interface between the Gas Chromatograph and the mass spectrometer was held at 320 °C and the ion source was maintained at 225 °C. Mass scans were taken from 35 to 600 daltons at 200 full scans.s<sup>-1</sup>. LECO's ChromaTOF software v 3.32 was used for the control of the system and for the collection of and processing of the data. National Institute of Standards and Technology (NIST), Willey and in-house PAH mass spectral libraries were used for the identification of the analytes. When the mass spectrum of a compound in the sample agreed with a library reference with a match of greater than 800 out of 1000, a positive identification was indicated.

## 2.4 Thermal desorption Multidimensional Gas Chromatography–Time of Flight Mass Spectrometry (TD-GC × GC-TOFMS)

Being provided with only a portion of a 47 mm diameter glass fiber filter that had collected particulate matter over a 24 hour period of time (less than 24 m<sup>3</sup> of sampled air) sensitivity concerns arose. It was realized that to extract and reduce the sample to one mL would result in injecting less than 0.1 percent of the total sample whereas, if two 4 mm punches of the filter were thermally desorbed, about 6.5% of the entire sample or 65 times more than a single liquid injection could be introduced into the GC column in a single injection. We coupled a Gerstel Thermal desorption (TDS-G) system to the front end of the Pegasus and thermally desorbed the filter punches. The TDS was interfaced directly to the GC of the Pegasus by a transfer line that was maintained at 320°C. To desorb the filter punches, the thermal desorption tube was ramped from 20°C to 300°C at 25°C/min and held for 3 min under a flow of He (BIP grade, Linde Gas, Canada). The extracted analytes were trapped at -60 °C using liquid N<sub>2</sub> as coolant in a programmable temperature vaporizing inlet system (PTV-CIS, Gerstel Inc., Baltimore, MD). The inlet was operated in the solvent venting mode. The thermal desorption system was then warmed to 20 °C. While the CIS was heated to 320 °C at 12 C<sup>o</sup> min<sup>-1</sup>, the analytes were transferred to the first dimension GC capillary column. During the transfer of analytes the TD transfer line was fixed at 320 °C.

## 3. Results

### 3.1 Chromatographic results

Analyses of the smog chamber samples of naphthalene, acenaphthene and phenanthrene revealed many oxidized products and included hydroxy, quinone and many ring opening

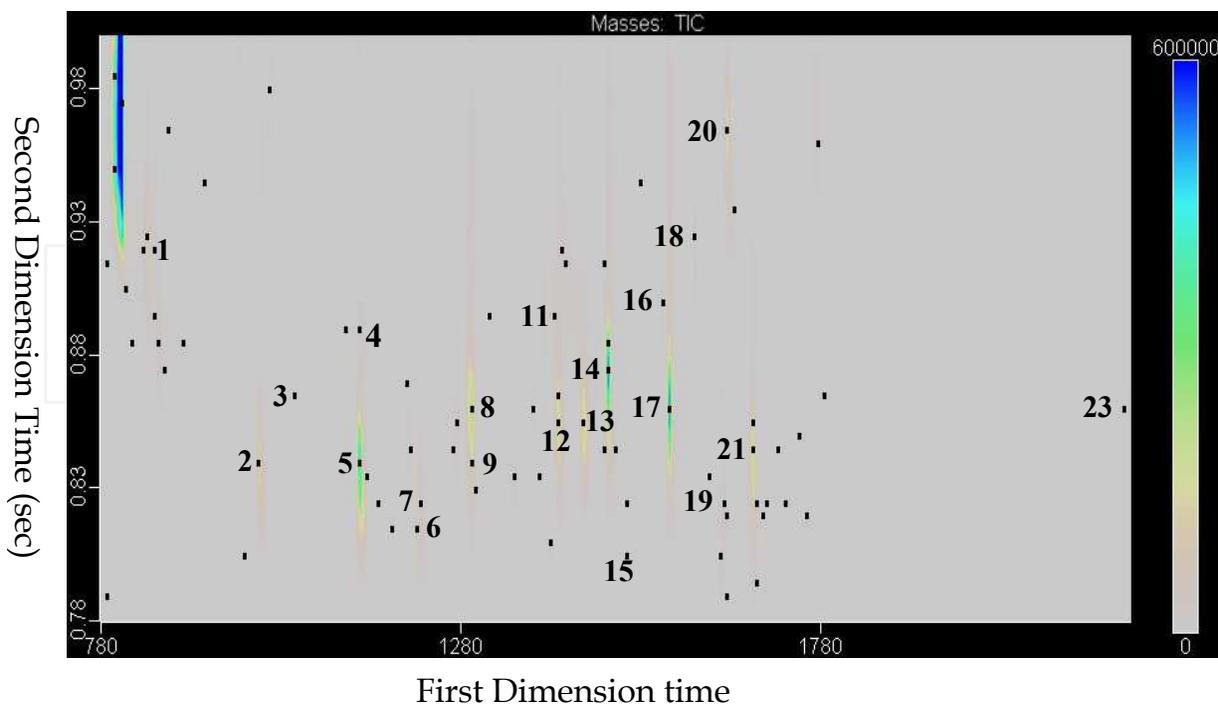


Fig. 1. Showing the 2 dimensional plot of the compounds found in the gas phase and collected by the annular diffusion denuder.

products (Sauret-Szczepanski & Lane, 2004; Lee & Lane, 2009; 2010). The results for the decomposition of naphthalene with the OH radical are shown in the contour chromatographic plots in Figures 1 and 2. In these figures, each black dot represents a distinctly separated and identified product. For some compounds in high concentration the colour surrounding the dot is an indication of intensity. Figure 1 shows the compounds that were trapped on the denuder and, therefore, were in the gas phase. Figure 2 shows the compounds that were extracted from the filter and SIFs. These were particle phase compounds. The numbers on the figures refer to the numbered compounds shown in Table 1 where the compound structure and the retention times on both columns are shown.

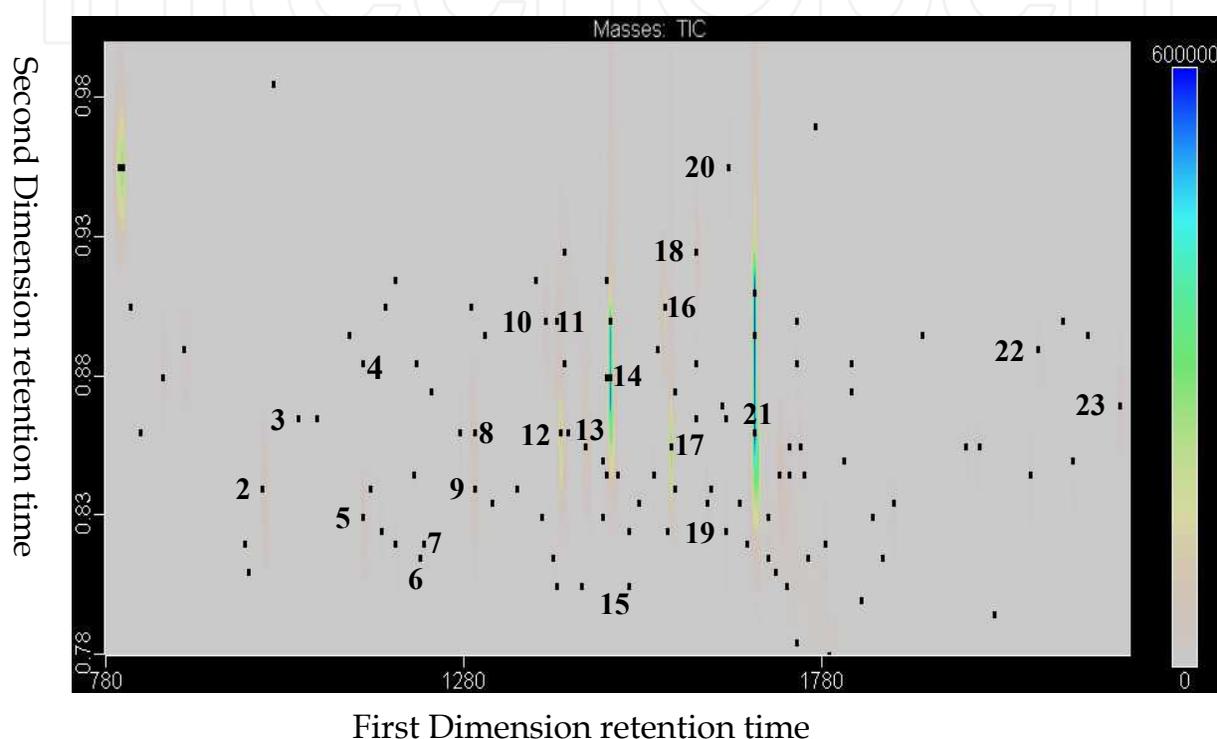
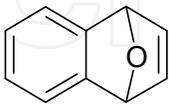
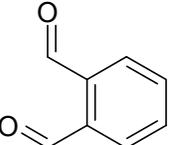
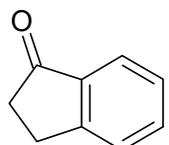
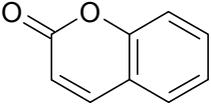
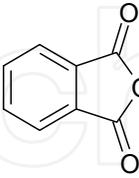
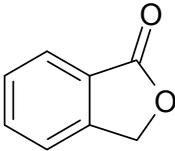
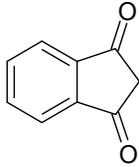
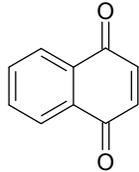
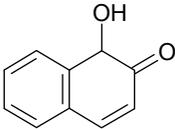
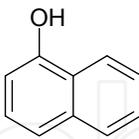
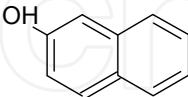
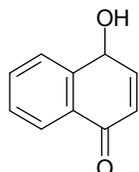
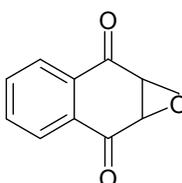


Fig. 2. Showing the contour plot for the particle phase compounds found on the filter and the SIFs.

# in Fig. 1	Products	Structure	Formula	M.W.	1 <sup>st</sup> R.T.*	2 <sup>nd</sup> R.T.*
1	1,4-dihydro-1,4-epoxy-Naphthalene					
2	Phthalaldehyde		C <sub>8</sub> H <sub>6</sub> O <sub>2</sub>	134	1000	0.85
3	Inden-1-one		C <sub>9</sub> H <sub>8</sub> O	132	1050	0.86

# in Fig. 1	Products	Structure	Formula	M.W.	1 <sup>st</sup> R.T.*	2 <sup>nd</sup> R.T.*
4	1,2-benzopyrone		C <sub>9</sub> H <sub>6</sub> O <sub>2</sub>	146	1140	0.895
5	Phthalic anhydride		C <sub>8</sub> H <sub>4</sub> O <sub>3</sub>	148	1140	0.845
6	Phthalide		C <sub>8</sub> H <sub>6</sub> O <sub>2</sub>	134	1220	0.815
7	1,3-indene-dione		C <sub>9</sub> H <sub>6</sub> O <sub>2</sub>	146	1225	0.82
8	1,4-naphthoquinone		C <sub>10</sub> H <sub>6</sub> O <sub>2</sub>	158	1295	0.865
9	1-hydroxy-naphthalen-2-one		C <sub>10</sub> H <sub>8</sub> O <sub>2</sub>	160	1295	0.845
10	1-naphthalenol		C <sub>10</sub> H <sub>8</sub> O	144	1205	0.87
11	2-naphthalenol		C <sub>10</sub> H <sub>8</sub> O	144	1410	0.9
12	1-hydroxy-naphthalen-4-one		C <sub>10</sub> H <sub>8</sub> O <sub>2</sub>	160	1415	0.86
13	2,3-epoxy-naphthoquinone		C <sub>10</sub> H <sub>6</sub> O <sub>3</sub>	174	1450	0.855

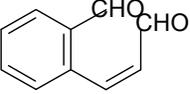
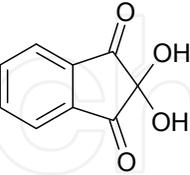
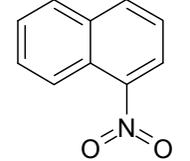
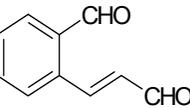
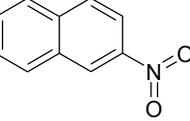
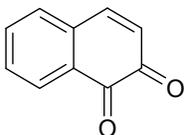
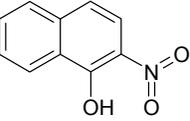
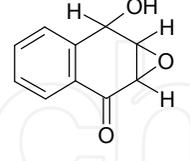
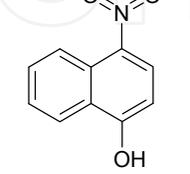
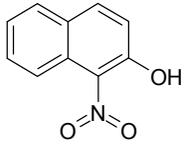
# in Fig. 1	Products	Structure	Formula	M.W.	1 <sup>st</sup> R.T.*	2 <sup>nd</sup> R.T*
14	(E)-2-formylcinnamaldehyde		C <sub>10</sub> H <sub>8</sub> O <sub>2</sub>	160	1485	0.89
15	2,2-dihydroxyindene-1,3-dione.		C <sub>9</sub> H <sub>6</sub> O <sub>4</sub>	178	1510	0.805
16	1-nitronaphthalene		C <sub>10</sub> H <sub>7</sub> NO <sub>2</sub>	173	1560	0.9
17	(Z)-2-formylcinnamaldehyde		C <sub>10</sub> H <sub>8</sub> O <sub>2</sub>	160	1570	0.87
18	2-nitronaphthalene		C <sub>10</sub> H <sub>7</sub> NO <sub>2</sub>	173	1605	0.92
19	1,2-naphthoquinone		C <sub>10</sub> H <sub>6</sub> O <sub>2</sub>	158	1645	0.82
20	2-nitro-1-naphthol		C <sub>10</sub> H <sub>7</sub> NO <sub>3</sub>	189	1650	0.965
21	2,3-epoxy-1-hydroxy-naphthalen-4-one		C <sub>11</sub> H <sub>12</sub> O <sub>2</sub>	176	1685	0.84
22	4-nitro-1-naphthalenol		C <sub>10</sub> H <sub>7</sub> NO <sub>3</sub>	189	2080	0.89
23	1-nitro-2-naphthalenol		C <sub>10</sub> H <sub>7</sub> NO <sub>3</sub>	189	2195	0.865

Table 1. The products of the OH radical reaction of Naphthalene with the OH radical are shown together with the retention times on each column.

The products determined for Acenaphthene and Phenanthrene may be found in other publications (Sauret-Szczepanski & Lane, 2004; Lee & Lane 2010).

### 3.2 Challenges in relating TOFMS data to the NIST and Wiley databases

We soon discovered that TOFMS mass spectral data differ significantly from those in the NIST or WILEY databases that were largely derived from quadrupole mass spectrometric data. This is because of the manner in which the mass scans are obtained. With quadrupole mass spectrometers, maximum practical scanning rates are about 300 daltons.sec<sup>-1</sup>, or about 1 to 1.5 full scans per second. This means that only about 3 scans can be taken across a single chromatographic peak. Because the mass of material being detected is constantly varying and because the scan takes about a second to be completed, the distribution of the peaks in a mass spectrum are biased high at the upper end of the spectrum as the peak is growing and are biased low at the upper end of the mass spectrum on the descending side of the peak. The reported mass spectra in the commercial databases are, of practical necessity, an average of the 3 or so peaks collected over one chromatographic peak. However, with TOFMS, full mass scans are taken at a rate of 200 per second. At such a rate, relative ion ratios are virtually constant at each point on a chromatographic peak. Approximately 600 spectra are taken over the width of a single chromatographic peak. It was for these reasons that chemical standards were obtained whenever possible and those standards used to generate an in-house library of TOFMS mass spectra. The agreement between samples and the in-house data were well above matches of 990 whereas the best matches with the NIST and WILEY libraries were on the order of 920-940. We had much greater confidence in the determinations of real world samples using our in-house library.

### 3.3 Retention times and mass spectral identification of products

Many of the products could be identified, although with lower match certainty than desired, through the use of the NIST and Wiley mass spectral databases, however, many more were not found in the databases and had to be determined by other means. For example, if standards or surrogate standards could be obtained mass spectra were obtained. It was also found useful to compare our spectra with mass spectral patterns published in the literature by other investigators. Their suggested identifications were of assistance in our own assignment of identities. Finally, when all else failed we identified the compounds through fundamental analysis of the mass spectra. To improve the match of environmental samples with the known products, we prepared an in-house database of the mass spectra of all reactants and for all products for which standards could be acquired. Thus matches between products in smog samples and database reference standards rose from about 650 to over 990 giving much greater confidence in the identity of the products.

### 3.4 Analysis of smog samples

A 3D image of the chromatograph of one of the Korean smog samples is shown below in Figure 3. From this sample, we successfully resolved almost 18,000 individual compounds. Many of the peaks could be identified by computer database searching. However, many were unidentified. This was partly due to the incompatibility of NIST and Wiley spectra with TOFMS data as outlined above and, more likely, because the compound in the air did not have a mass spectral signature in the databases.

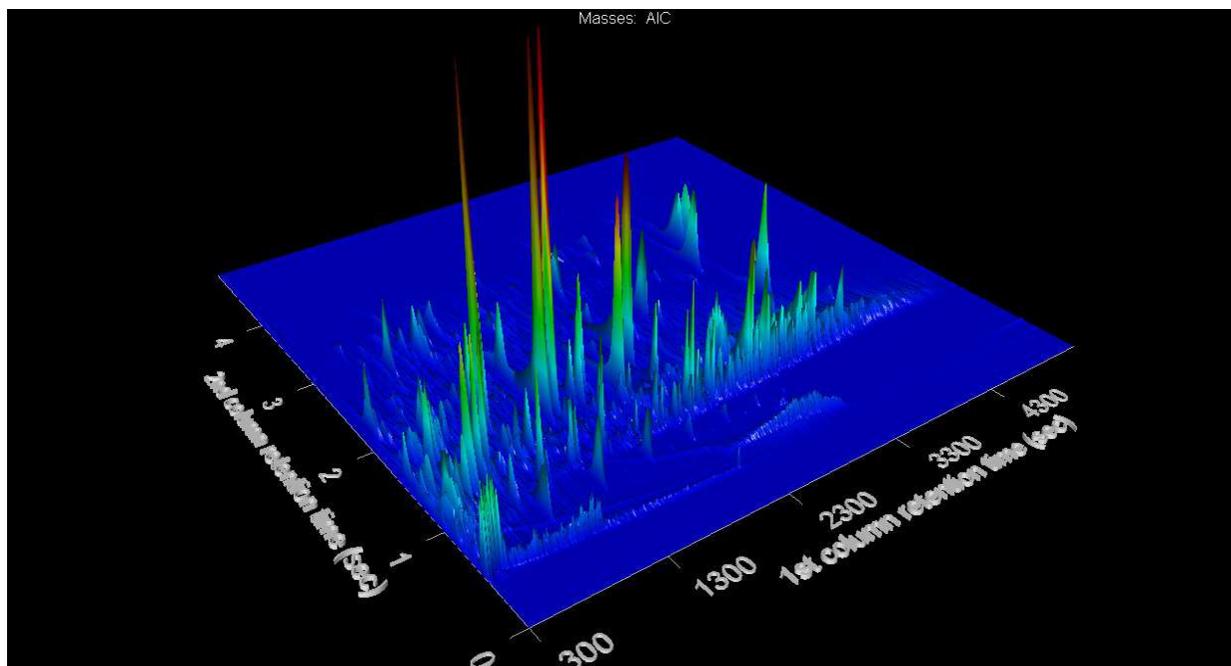
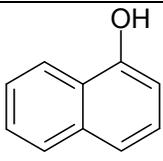
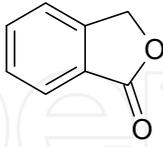
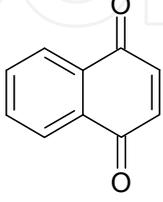
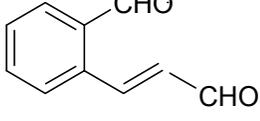
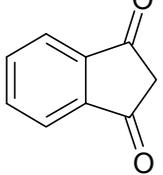
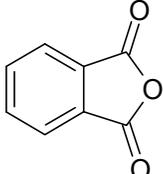
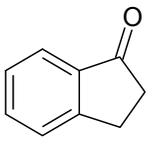
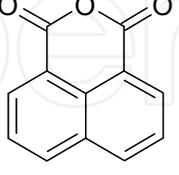
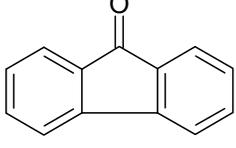
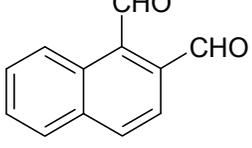


Fig. 3. The GCxGC trace of a Korean smog sample. The first column dimension is the vapor pressure dimension and is governed by chromatography on the DB-5MS column. The second dimension is the polar dimension and is governed by the polar DB-17MS column. The height of the peaks is proportional to the mass of the compound present.

However, for other unknowns or possibly improperly identified peaks, it was clearly a case of the compound not existing in the databases. We succeeded in finding 13 of the photochemical decomposition products from the chamber experiments in the Korean smog samples. The compounds from the decomposition of naphthalene, acenaphthene and phenanthrene that were found in the smog sample are shown in Table 2.

The above compounds were found in the particulate matter collected on the filter of a filter pack from Seoul, Republic of Korea. Since these compounds were found on the filter it is important to note that a) they were in the particle phase, 2) they may have suffered some volatilization or blow-off from the filter, but the degree to which that affected an estimation of the total compound in the atmosphere cannot be determined, and 3) many of the compounds detected such as the quinones, nitro derivatives and the hydroxynitro derivatives are known to be hazardous chemicals (Arey et al., 1989; Atkinson and Arey, 1994; Reisen and Arey, 2005 ). As many of these compounds, for example 1,2-naphthalenedicarboxaldehyde and (E)-2-formylcinnamaldehyde (Lane & Lee, 2010), are not known to originate in emissions, they must have been the result of atmospheric oxidation and this clearly indicates the formation of secondary aerosol material. It is important to note that there are no known anthropogenic sources of these two compounds. Recently Kroll and Seinfeld (Kroll and Seinfeld, 2008) have demonstrated the importance of atmospheric reaction products in the formation of secondary organic aerosol (SOA) and in the adverse effect of SOA to climate change and visibility in the atmosphere. A recent study (Robinson et al., 2007) has reported that research to estimate the organic aerosol budget, underestimates the production of SOA in the atmosphere when compared to actual field measurements. They suggested that the underestimate was due to the non-inclusion of the SOA produced from atmospheric semivolatile organic compounds.

Parent	Product	Structure
Naphthalene	1-naphthol	
	Phthalide	
	1,4-naphthalenedione	
	(E)-2-formylcinnamaldehyde	
	1,3-indandione	
	Phthalic anhydride	
	Indan-1-one	
Acenaphthene	1,8-naphthalicanhydride	
Phenanthrene	9-fluorenone	
	1,2-naphthalenedicarboxaldehyde	

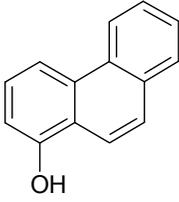
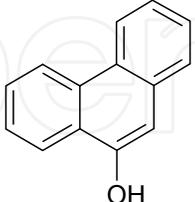
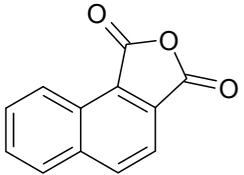
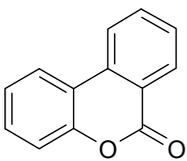
Parent	Product	Structure
	1-phenanthrol	
	9-phenanthrol	
	1,2-naphthalic anhydride	
	Dibenzopyranone	

Table 2. Above are presented the products found in the smog chamber during the studies of the reactions of naphthalene, acenaphthene and phenanthrene that were also found in the smog samples.

#### 4. Conclusions

In this chapter, we have demonstrated that GC×GC-TOFMS is an excellent technique to identify the oxidized products of the decomposition of PAH in reactions with the OH radical. When combined with thermal desorption, TD-GC×GC-TOFMS becomes a very powerful tool to examine air extracts for a very wide range of pollutant chemicals. This method provides greatly enhanced sensitivity to chemical components and permits the detection of many, otherwise impossible to detect, compounds. We have demonstrated unequivocally that PAH are oxidized in the atmosphere and form a plethora of oxidized, nitrated and ring-opened products. This lends strong support to the statements of Robinson et al. (Robinson et al., 2007) that the production of SOA is underrepresented in budgets of atmospheric aerosols. We have found known oxidation products, some known only as atmospheric oxidation products with no anthropogenic source, in smog samples. This alone has many implications for the effect of SOA on human health.

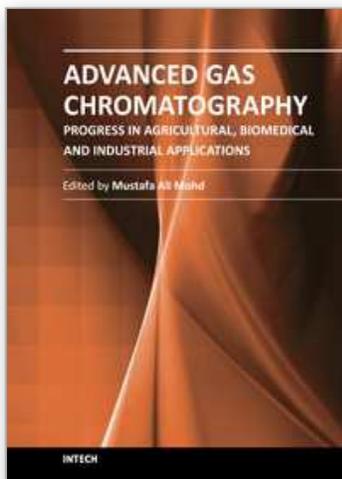
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Progress in agricultural, biomedical and industrial applications' is a compilation of recent advances and developments in gas chromatography and its applications. The chapters cover various aspects of applications ranging from basic biological, biomedical applications to industrial applications. Book chapters analyze new developments in chromatographic columns, microextraction techniques, derivatisation techniques and pyrolysis techniques. The book also includes several aspects of basic chromatography techniques and is suitable for both young and advanced chromatographers. It includes some new developments in chromatography such as multidimensional chromatography, inverse chromatography and some discussions on two-dimensional chromatography. The topics covered include analysis of volatiles, toxicants, indoor air, petroleum hydrocarbons, organometallic compounds and natural products. The chapters were written by experts from various fields and clearly assisted by simple diagrams and tables. This book is highly recommended for chemists as well as non-chemists working in gas chromatography.

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