Unravelling the complexity of the atmosphere using high-resolution separations

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Wolfson Atmospheric Chemistry Laboratories

- A new research facility for the study of urban and global air pollution, stratospheric ozone depletion and climate change
- 5 academics and 30 research staff and students
- Multidisciplinary – from fundamental lab kinetics to field measurements through to global modelling
Air pollution and atmospheric aerosol

- **Urban population**
  - 3% in 1800’s to 47% by the end of the 21st century

- **As such urban air pollution has become a significant factor in global health**
  - Costs UK society up to £20 billion per year
  - Exposure to particulate matter alone estimated to reduce life expectancy ~ 7-8 months

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Pollution link to irregular heartbeat and lung clotting
By Helen Briggs
BBC News, Health, Science, Environment

Air pollution kills millions each year, says study
By Mark Kinver
Environment reporter, BBC News

- Outdoor air pollution is estimated to contribute to more than two-and-a-half million deaths each year, a study has suggested.
- It calculated that, each year, 470,000 people died as a result of ozone and 2.1 million deaths were linked to fine particulate matter.
- Air pollution increased respiratory and heart disease risks, with the young, elderly and infirm most vulnerable.
- The findings appear in the Environmental Research Letters journal.

- Epidemiological studies have shown that ozone and PM2.5 (particulates with a diameter of less than 2.5 microns - about 30 times thinner than the width of a human hair) have significant influences on human health, including premature mortality,” an international team of scientists wrote.

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Pollution link to premature mortality, BBC News
Volatile Organic Compounds and Air Quality

Volatile organic compounds (VOC) + Oxidants (OH, O₃, NO₃)

Anthropogenic and biogenic gaseous emissions

Less volatile organics

Condensation/coagulation

Gas phase oxidation

Particulate Matter

Gas phase oxidation (NOx)

Ozone

Volatile organic compounds (VOC) + Oxidants (OH⁻, O₃, NO₃⁻)
Why is measuring VOCs difficult?

- Low concentrations
- Complex matrix
- Huge range of polarities

- For $C_{10}$ – more than a million organic compounds possible
- Many of which are likely in the atmosphere

Number of possible isomers of alkanes and alcohols

Goldstein and Gallbaly, ES&T, 2007
Analytical methodology for VOC analysis

Sample collection
- Offline – Canisters, bags, absorbent tubes
- Online – thermal desorption

Separation
- Gas Chromatography

Detection
- Flame Ionisation Detector
- Mass Spectrometry
Comprehensive two-dimensional gas chromatography (GC × GC)

- 2 GC columns used with different separation mechanisms
- Connected via a modulator
  - cryogenic, thermal, valve

Allows much better speciation of complex mixtures

Viewed as a contour plot
GC × GC – TOFMS for VOC analysis

- GC × GC-TOFMS – Agilent 6890 GC with a Leco Pegasus 4D with cryogenic jet modulator
  - **Column 1** - BPX-5 (50 m x 0.32mm x 1.0 μm d.f) (SGE)
  - **Column 2** - Rtx50 (4.5 m x 0.18mm x 0.2 μm d.f) (Thames Restek)
  - **Modulation time** = 2 seconds
  - 40 °C (4 min) $\rightarrow$ 3 °C min$^{-1}$ to 160 °C $\rightarrow$ 50 °C min$^{-1}$ to 200 °C (1.2 min)

- **Thermal Desorption** – Markes Unity 2 with CIA8 Airserver
  - VOCs collected onto sorbent bed (10 °C) at 100 ml min$^{-1}$ for 10 minutes
  - Water removed using cold finger in ethylene glycol (- 30 °C)
Measuring transport of pollutants

- **Whole air sampling (WAS)**
  - Stainless steel canisters – 3L (filled to 3 atm)
  - UK NERC Facility for Airborne Atmospheric Measurements aircraft (BAe-146)

- **RONOCO campaign (Role of Night-time chemistry in controlling the oxidising capacity of the atmosphere)**
  - Involved flights from East Midlands airport during winter and summer 2010
  - Involved Universities of Cambridge, York, Leeds, Leicester, UEA
Testing the system using a gas standard

- Method development and calibration is done using gas standards
  - VOCs at ppbV mixing ratios (Apel-Reimer/NPL) in N₂ or air
  - During analysis, standards run every 8-16 GC × GC samples

TD-GC × GC – TOFMS of a 74 component gas standard

Linear response (10 ppt-250 ppt)

Excellent sensitivity

Limit of detection < 0.1 ppt
RONOCO VOC profile - polluted outflow from London

- In total 191 samples were collected and analysed over two 6 week periods
- The atmosphere is much more complex than the
Comparison to GC-FID measurements

- WAS bottles also analysed using a conventional GC-FID system
- Excellent agreement was obtained for species measured on both instruments

Octane

Benzene
Advantages of TOFMS detector

- By plotting extracted ion chromatograms, the complex air matrix can be removed.
- Can observed many more low concentration species.

Halogenated organics

\[ m/z \, 63+83+86+93+112+117+166+170+172+174 \]
Overview of TD-GC × GC – TOFMS

• Allowed unprecedented VOC speciation and excellent sensitivity
• First use of GC × GC for VOCs measured from aircraft
• Provided insights into the sources and transport of VOCs from the UK

But ...........
  o Samples had to be driven back to the lab in York every 2 days
  o Needs liquid nitrogen
  o TOFMS not very portable

Lidster et al., Atmos. Chem. Phys
Valve modulators are cryogen free but do suffer poorer sensitivity than cryogenic modulators.

Flow restriction leads to slowing down of carrier gas flow.

Needs an entirely different column combination.

Valve modulator schematic

Here we use a diaphragm valve.

*Lidster et al., J. Sep. Sci., 2011, 7, 8*
Total Transfer Valve Modulated GC × GC-FID

- Column 1
  - BPX-5 (25 m x 0.15 mm, 0.4 µm df) at 50 psi.
- Column 2
  - BP-20 (5 m x 0.25 mm, 0.25 µm df) at 23 psi.

- 5 second modulation time

- Controlled using *in-house* software

- Data processed using Zoex GC Image software
Air sampling using the GC × GC-FID

- For a field deployable instrument we use a Markes TT24-7 dual trap thermal desorption system.

- Issues with injection onto column

Liquid Injection Gasoline

74 component gas standard
Automated Refocussing

- Introduced a refocussing step at head of column 1
- Cyroblast refocussing

Impact of 60 s CO$_2$ pulse on peak shape
Field Portable GC × GC-FID

- Sampler, water trap and GC × GC-FID were built into a single rack
- Deployed to London during the Clean Air for London Project
VOCs in London
Simplifying the complexity

- GC Image software allows peaks to be grouped for integration.
- Even though species not identified they can be quantified using closest n-alkane calibration.

<table>
<thead>
<tr>
<th>Groups</th>
<th>Isomers</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆ Aliphatics</td>
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<tr>
<td>C₇ Aliphatics</td>
<td>10</td>
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<tr>
<td>C₄ substituted monoaromatics</td>
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</tr>
<tr>
<td>Monoterpenes</td>
<td>25</td>
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</tbody>
</table>
Daily trends of VOCs in London

- **NO\textsubscript{x}**, 24 hour daily cycle
- **Isoprene**, 24 hour daily cycle
- **Toluene**, 24 hour daily cycle
- **C\textsubscript{13}** grouped aliphatics, 24 hour daily cycle


Openair software for R
The future – more compounds please!

- The valve based GC × GC-FID can only measure the lower volatility VOCs (i.e. above pentane)
- Isoprene response is not very reliable but it has the highest global emissions (biogenic sources)
- Need to increase the range of VOCs that can be trapped
- Introduce an additional heart cut PLOT column (50 m Al₂O₃)
  - GC-GC × GC-FID
GC-GC × GC setup

Volatile Stage-
- $C_3-C_7$
  - Isoprene
  - Benzene

Heart-cut down Plot column (first 5 mins)
VOCs in the tropics

Instrument deployed to Bachok in Malaysia in Jan

Isoprene
Conclusions

- VOCs play a key role in formation of the most harmful pollutants ozone and particulate matter
- GC × GC allows significant improvements in the degree of speciation of VOCs in atmospheric samples
- Allows us to investigate the sources of VOCs and study their oxidation chemistry

- Miniaturization and cryogen free modulators offer the potential of truly portable instrumentation

Miniature restively heated column ovens

*Edwards et al., Analytical Methods, 2013, 5, 141-150*
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