A field-portable thermal desorption time-of-flight mass spectrometer

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Overview

• TOF-MS for field applications
• Kore Technology MS200
  – direct vapour sampling dual membrane inlet TOF
  – performance
• Modifications for rapid detection of semi-VOCs
  – Trap-Evacuate-Desorb (TED)
  – novel thin membrane
  – high temperature valve
• Prototype system
  – performance
• Summary
TOF-MS for field applications

**Advantages**
- all masses sampled in parallel
- high duty cycle
  - sensitive
- capable of high resolution
- unlimited mass range
- simple
  - rugged

**Disadvantages**
- high vacuum required
  - more power required
- ionisation mechanisms restricted
  - less adaptable
- not capable of MS/MS
  - less selective
Kore MS200

- Field-portable membrane inlet TOF-MS
  - sealed system
  - ion/ getter pumps
  - no consumables
  - battery powered
  - weight ~ 20 kg
  - library matching of unknowns
  - low ppb sensitivity
  - relatively low cost ~ £30K
  - VOC detection

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Converging annular reflectron TOF

• Annular 70 eV EI filament source
  – more ions created than in point source
  – retains focussing benefits of point source

• $10^{-7}$ mbar operating pressure
  – $10^{-9}$ mbar base pressure
  – ion pump only requires low power

• Complete spectrum generated each analysis cycle
  – 50000 cycles per second

• High efficiency of analyser results in very high sensitivity
Membrane inlet

- Rate of permeation depends on:
  - membrane material
  - chemical and physical properties of analyte
  - temperature
  - partial pressure of the analyte on the two sides of the membrane

Membrane selectivity causes more of the analyte (red) to pass than the background (green).

The concentration of analyte compared to the background is increased, although total pressure is much lower.

- Results in much improved sensitivity
MS200 standard inlet

- **Peristaltic pump**
- **Inlet temperature ~ 50°C**
- **Polymer tipped inlet valve**
- **Interchangeable outer membrane (50um)**
- **Inner membrane (125um)**
- **Atmospheric pressure**
- **High vacuum**
- **TOF chamber**
- **Room temp**

Room temp
MS200 standard inlet

- Sample in
- Sample out
- Atmospheric pressure
- Inlet temperature ~ 50°C
- Peristaltic pump
- Intermediate vacuum
- Polymer tipped inlet valve
- Outer membrane (50um)
- Inner membrane (125um)
- High vacuum
- TOF chamber
- Room temperature
MS200 standard inlet

Sample in

Atmospheric pressure

Inlet temperature ~ 50°C

Peristaltic pump

Intermediate vacuum

Polymer tipped inlet valve

Sample out

Outer membrane (50um)

High vacuum

TOF chamber

Room temp

Inner membrane (125um)
MS200 standard inlet

- Sample in
- Atmospheric pressure
- Inlet temperature ~ 50°C
- Peristaltic pump
- Intermediate vacuum
- Polymer tipped inlet valve
- Sample out
- Outer membrane (50μm)
- High vacuum
- TOF chamber
- Room temp
- Inner membrane (125μm)
### Sampling location

<table>
<thead>
<tr>
<th>Description</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
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<tbody>
<tr>
<td>Upwind (control)</td>
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<td>Active dumping</td>
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<tr>
<td>50m downwind of 5</td>
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</table>

### Compound Measured concentration (ppb)

<table>
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<th>Compound</th>
<th>Measured concentration (ppb)</th>
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<tbody>
<tr>
<td>dichloromethane</td>
<td>BQL 893 6022 145711 1899 273</td>
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<tr>
<td>benzene</td>
<td>BQL 227 1112 5684 BQL 218</td>
</tr>
<tr>
<td>naphthalene</td>
<td>BQL 132 4037 22144 1321 449</td>
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<tr>
<td>tetrachloroethylene</td>
<td>BQL BQL 113 3988 89 22</td>
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<tr>
<td>toluene</td>
<td>BQL 182 165 9458 3784 398</td>
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<tr>
<td>trichloroethane</td>
<td>BQL 423 6451 58322 3231 553</td>
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<tr>
<td>xylene</td>
<td>BQL 153 512 12080 3098 336</td>
</tr>
</tbody>
</table>

**File # 1 : DOWNWIND104#1**

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Requirements for semi-VOC analysis

- Pre-concentrate sample
- Higher temperature operation
  - inlet valve critical
- Increase speed of analysis cycle
  - thinner membrane
  - faster pump-down
Pre-concentration & sampling

• Utilise Tenax tube (2 L/min sampling)
  – Tenax causes significant background
    • reduces selectivity and sensitivity
    • long sample release time
• Alternative pre-concentrator materials tested
  – polymer coated nickel foams
    • similar background problems
    • uncoated foams better (but lower capture efficiencies)
• Background subtraction important
Hand-held sampling unit
Single membrane with tenax trap

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Desorb heater unit

- Ceramic Body
- O-Ring sealed End Cap
- Heater Wire
- Trap
- Thermocouple

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Retro-fit MS200 unit

- Bolt on desorber
  - incorporates Tenax tube holder
- Additional heater controller
# Thinner membrane

- Must be robust to withstand pressure differential
- Use mechanical support
- Maintain conductance and concentrating power
- Reduce equilibration time

<table>
<thead>
<tr>
<th>thickness</th>
<th>$\phi$</th>
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<tr>
<td>125</td>
<td>2mm</td>
<td>4</td>
</tr>
<tr>
<td>50</td>
<td>800µm</td>
<td>10</td>
</tr>
<tr>
<td>25</td>
<td>400µm</td>
<td>20</td>
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<tr>
<td>2.5</td>
<td>40µm</td>
<td>200</td>
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</table>
Response time – DMNB (ICAO taggant)

DMNB single membrane

Time/s

15 µm 35 µm 125 µm
Response time – DMMP (CW simulant)

DMMP saturated vapour (~1350ppm)

Time (s)
Analysis time

- Analysis time significantly reduced
  - incorporated new miniature scroll pump (Air Squared)
  - pump down to < 0.1 mbar in < 5 sec (previously 1 min)
High temperature inlet valve

• To enable higher temperature operation
  – original valve has polymer tip (limited to 75 °C)
    • acts as sponge for analytes
    • deforms if baked under load
• Approach #1: Novel sapphire on copper sealed valve
  – lacked robustness
• Approach #2: Stainless steel on copper sealed valve
  – leak and robustness tested
  – retro-fitted to instrument
Prototype unit
Desorber
Detection Limit Improvement

- Butane
- Pentane
- Hexane, 2-methyl
- Hexane, 3-methyl
- Octane, 4-methyl
- Decane, 5-methyl
- Tridecane, 3-methyl
- Tridecane, 7-methyl

Detection Limit Improvement

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Summary

• MS200 is a robust field-portable dual membrane inlet TOF-MS
  – VOC detection and identification

• Significant instrument improvements
  – Trap-Evacuate-Desorb (TED) unit
  – thin membrane for fast response time
  – high temperature valve for heated inlet region
  – scroll pump for rapid sample pump-down
  – 2 orders of magnitude sensitivity improvement (sub-ppb)

• Increased range of detectable compounds
  – semi-VOC detection and identification

• Selectivity limits instrument capability for more complex mixtures
  – signal processing and rapid separation techniques under development

• Field trials underway
Acknowledgements

- Dstl
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- Kore Technology
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  - Dr Frank Nuber
  - Dr Fraser Reich
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Questions