Investigation of SVOC in diesel fuel, engine lubricating oil and diesel engine emissions

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1. **INTRODUCTION**

- Uncertainties regarding the composition of vehicular particulate emissions

- Semi-volatile organic compounds (SVOC) emissions from diesel engines

- SVOC can partition between gas and particulate phase

- SVOC can contribute to the formation of secondary organic aerosol (SOA)

- Lack of substantial qualitative and quantitative data
1. Introduction

Objectives:

- Utilise TD-GC×GC-ToF-MS to quantify different classes of SVOC in diesel fuel, engine lubricating oil and diesel engine emissions
- Identify a wealth of homologous series from within the UCM of the chromatogram

TD: thermal desorption - GC: gas chromatography - ToF: time of flight
MS: mass spectrometry
2. Experimental Setup

- **Fuels:**
  - Ultra low sulphur diesel (ULSD), S<10 mg/kg
  - Low sulphur diesel (LSD), S<50 mg/kg

- **Engine Lubricating Oil:**
  - 5W-30 fully synthetic
  - 5W-30 part synthetic

- **Engine:**
  - 4 stroke, Light-duty
  - In-line CI, 4-cylinder

<table>
<thead>
<tr>
<th>Bore (mm)</th>
<th>86</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stroke (mm)</td>
<td>94.6</td>
</tr>
<tr>
<td>Capacity (cc)</td>
<td>2198</td>
</tr>
<tr>
<td>Compression Ratio</td>
<td>15.5:1</td>
</tr>
<tr>
<td>Injection System</td>
<td>DI Common Rail</td>
</tr>
<tr>
<td>Injectors</td>
<td>Solenoid, 7 Holes (0.15mm diameter)</td>
</tr>
</tbody>
</table>
2. Experimental Setup

Schematic of the engine test cell
2. Experimental Setup

- Exhaust Diluter:
  - Modified TSI model 3302A diluter
  - Dilution ratio: 1:30±5

- Gas Phase SVOC:
  - SS adsorption tubes (AT)

- Particle phase SVOC:
  - PTFE filter
  - Quartz filter
  - Nano-Micro Orifice Uniform Deposit Impactor (14 stages)
2. Experimental Setup

The modulator traps and releases sequential portions of the 1st column effluent and injects it into the 2nd column of different selectivity where it is separated and detected.
3. Results and Discussion

SVOC in:
- Diesel fuel
- Lubricating oil
- Diesel engine emissions

Diesel fuel
- $C_{20}$

Engine oil
- $C_{18} - C_{36}$

Diesel engine emissions
3. Results and Discussion

Diesel fuel

ULSD:
- n-Alkanes: C10-C24
- Alkyl-Cyclohexanes: C11-C23
- BTEX family

3-D plot

Contour plot
3. Results and Discussion

Diesel fuel

ULSD:

Total Mass of ULSD injected onto AT: ~ 8000 ng

Total Mass Identified: ~ 7800 ng

Total % of mass accounted for by compounds identified: > 97 %
3. Results and Discussion

Diesel fuel (Alkanes)

Compound classes can be further characterised into sub-groups and even isomers.

n-Alkanes (38.2% m/m)

branched-Alkanes (61.8% m/m)
3. Results and Discussion

Lubricating oil

Base Oil:
- n-Alkanes: C18 to C36
- Alkyl-Cyclohexanes: C18-C25
- BTEX family

3-D plot

Contour plot
3. Results and Discussion

Lubricating oil

>150 compounds identified

Alkanes (C25-C32) are present in abundance
3. Results and Discussion

Diesel engine emissions: (Gas phase)

- ULSD fuel
- Part synthetic 5W-30 engine oil
- Steady-state:
  - 5.9 bar BMEP
  - 1800 RPM
  - Before DOC

Straight & branched alkanes
(m/z = 41, 57, 71)

Naphthalenes
(m/z = 128, 142, 156, 170, 184)
3. Results and Discussion

Diesel engine emissions: (Particle phase)

- ULSD fuel
- Part synthetic 5W-30 engine oil
- Steady-state:
  - 5.9 bar BMEP
  - 1800 RPM
  - Before DOC
3. Results and Discussion

**n-Alkanes in gas phase**

- Active partitioning between the gas and particle phase
- Bimodal peak in gas phase
- LMW HC are more pronounced in gas phase
- HMW HC are more pronounced in the particle phase

**n-Alkanes in particle phase**

- Active partitioning between the gas and particle phase
- Bimodal peak in gas phase
- LMW HC are more pronounced in gas phase
- HMW HC are more pronounced in the particle phase
3. Results and Discussion

n-Alkyl-cyclohexanes in gas phase

n-Alkyl-Cyclohexanes:

- More HC in the gas phase
- LMW HC are more pronounced in gas phase
- HMW HC are more pronounced in the particle phase

n-Alkyl-cyclohexanes in particle phase
3. Results and Discussion

PAH:

- Naphthalene has the highest concentration in the PAH family
- Most of the LMW PAH were collected in the gas phase
4. Summary/Conclusions

- Requirement for characterisation of SVOC in diesel engine emissions
- Usefulness of a comprehensive gas chromatography technique
- Diesel fuel:
  - Alkanes (77.53% m/m) and Cyclo-alkanes (15.57% m/m) are the major components of ULSD.
- Engine lubricating oil:
  - Preliminary results indicate that HMW Alkanes (C25-C32) are abundant in oil.
- Diesel engine emissions:
  - They contain n- and branched Alkanes, alkyl-Cycloalkanes, alkyl-Benzenes, various aromatics and polycyclic aromatic hydrocarbons (PAH).
  - Gas phase SVOC are similar to compounds found in diesel fuel.
  - Particle phase SVOC are mainly similar to compounds found in lubricating oil while diesel fuel contribute to a less extent (under conditions studied).
5. On-going Research

- Tests with diesel oxidation catalyst (DOC)

Before DOC

After DOC

- Tests with DOC and diesel particulate filter (DPF)
- Modelling of SVOC dynamics in urban atmosphere
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Thank You!
Any Questions?
**Supporting Material**

- **Extraction:**
  - Filters and AT were spiked with deuterated internal standards
  - Dichloromethane (DCM) and n-Nonane were used as solvents for filters

**TD-GC×GC-ToF-MS**

- **TD:** AT desorbed using thermal desorption (Unity 2, Markes International)
- **GC×GC:** gas chromatograph (GC, 7890A, Agilent Technologies) equipped with a cryogenic modulator (Zoex ZX2)
  - First column: non-polar capillary column (30 m, 0.25 mm ID, 0.25 µm – 5% phenyl polysilphenylene-siloxane)
  - Second column: (4.0 m, 0.1 mm ID, 0.1 µm – 50% phenyl polysilphenylene-siloxane)
- **ToF-MS:** Bench-ToF-Select (ToF-MS, Markes International)
Gas/Particle Phase Distribution for n-alkane