Gravimetric preparation strategies/methods of producing condensable multi-component primary reference gas mixtures (PRGMs)

Napo Ntsasa
Test & Measurement Conference
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Your measure of excellence
Objective

To develop gravimetric preparation of reference gas standards of volatile organic components (VOCs) traceable to the SI units

To obtain measurement international equivalence for VOCs

To develop measurement capability of VOCs at nmol.mol$^{-1}$

To disseminate reference gas standards of VOC to Southern Africa region
Introduction

BTEX are VOCs known to be responsible for the creation of tropospheric ozone.

BTEX compounds include:

- Benzene
- Toluene
- Ethyl benzene
- m,p,o-Xylene

<table>
<thead>
<tr>
<th></th>
<th>80°C</th>
<th>110°C</th>
<th>136°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bp</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P(vap kPa) at 20°C</td>
<td>9.95</td>
<td>29.1</td>
<td>1.33</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>143°C</th>
<th>138°C</th>
<th>138°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bp</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P(vap kPa) at 20°C</td>
<td>0.933</td>
<td>0.8</td>
<td>2.13</td>
</tr>
</tbody>
</table>

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Introduction

- Present in the atmosphere at amount fractions of nmol.mol\(^{-1}\) down to pmol.mol\(^{-1}\)
- Ambient air monitored to reduce the level of photochemically created ozone
- Concern in indoor air quality
- Benzene and chlorinated hydrocarbons are included in the EPA original list of hazardous air pollutants
- Benzene is also a known carcinogen
- Other VOCs are suspected of causing common health effects associated with photochemical smog
VOC sources

- Oil refineries
- Gas
- Vehicle emissions
- Burning Biomass
- Paint & Adhesives
Legislation

Local

• National environmental management: AIR QUALITY ACT 39 of 2004

Globally

• World Meteorological Organization (WMO) established Global Atmospheric Watch (GAW) in 1989

Atmospheric composition observations

• Given similar importance as for temperature, wind and precipitation

Global Atmospheric Watch (GAW)

• Several monitoring stations around the world
Mixture feasibility

- BTEX gas mixtures are complex
- Minimum of 6 components in a mixture
- Amount fraction in trace level (nmol.mol\(^{-1}\))
- Feasibility according to vapour pressure of liquids

Maximum filling pressure is given by:

\[ p_{\text{max}} = \frac{p^T_{\text{vap}}}{\chi} \ldots \text{equation 1}^a \]

Mole fraction: \( \chi_i = \frac{\left( \frac{m_i}{M_i} \right)}{\sum_{i=1}^{n} \left( \frac{m_i}{M_i} \right)} \ldots \text{equation 2}^b \]

Physical challenges

- Selection of apparatus
  - Cylinders type (aluminium vs. stainless steel)
- Molecules may adsorb onto the inner surfaces of transfer lines
- Dead volume
- Order of addition
- Loss of components
- Prevent condensation of some components
- Possible solutions
  - Properly passivated cylinders
  - Use of treated transfer lines
  - Gentle heating may be necessary
  - Design of special apparatus to minimise dead volume
Purity analysis

- Establishing traceability of chemical purity to International System of units (SI) of mass (kg) and amount of substance (mole)
- Contribution towards final measurement uncertainty
- Direct determination of the parent component
  - Qualitative analysis by GC-MS
  - Quantitative analysis by GC-FID
- Highest purity available for components of interest and diluent gas

<table>
<thead>
<tr>
<th>Parent component</th>
<th>Impurities (literature)a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>Cyclohexene, toluene, bicyclo[2,2,1]heptane</td>
</tr>
<tr>
<td>Toluene</td>
<td>bicyclo[2,2,1]heptane, ethylcyclohexane, cycloheptane</td>
</tr>
<tr>
<td>Ethyl benzene</td>
<td>ethylcyclohexane, cycloheptane, toluene</td>
</tr>
<tr>
<td>O-xylene</td>
<td>m-xylene, isopropylbenzene, p-xylene</td>
</tr>
<tr>
<td>M-xylene</td>
<td>p-xylene, o-xylene, ethylbenzene</td>
</tr>
<tr>
<td>P-xylene</td>
<td>m-xylene, o-xylene, ethylbenzene</td>
</tr>
</tbody>
</table>


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Purity analysis

GC parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carrier gas</td>
<td>Helium</td>
</tr>
<tr>
<td>Inlet temperature</td>
<td>250 °C</td>
</tr>
<tr>
<td>Split ratio</td>
<td>60:1</td>
</tr>
<tr>
<td>Column</td>
<td>DB-Wax (60m x 32mm i.d., df 0.5µm)</td>
</tr>
<tr>
<td>Oven temperature</td>
<td>45 °C(40min) ramp at 5 °C/min to 240 °C (hold 4min)</td>
</tr>
<tr>
<td>Detector</td>
<td>FID</td>
</tr>
</tbody>
</table>
Preparation methods

From ISO 6142

- Syringe method
- Glass tube method
- Vapour in a receptacle
- Minicylinder method
- U tube method

Analysis of prepared mixtures

- Analysis by GC-FID
- Pre-concentration (cryogenic)
  - Adsorbent tubes (carbotrap, carbosieve, tenax-TA)
  - Glass beads\(^a\)
  - Thermal desorption

- GC column of interest for analysis
  - 50m PLOT Al\(_2\)O\(_3\)/KCl
  - 60m DB1
  - 30m DB1
  - 30m CP-silica-PLOT

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Uncertainty of measurement

- purity of BTEX
- verification
- purity of nitrogen
- repeatability
- reproducibility
- recovery
- temperature
- balance resolution
- temperature
- buoyancy effect
- mass pieces
- weighing
- stability
- amount of component
Conclusion

Trace level to ultra-trace

Require traceable gas standards

Smaller uncertainty required

Our environment, our responsibility

Why VOC monitoring in South Africa is important
Acknowledgements

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Dr. P.B.C Forbes (UP)

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Mentor:  
Mr J Tshilongo

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"But what shall we do with the world once you've taken it over?"