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Test & Measurement conference
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Introduction

- Photochemical formation of ozone reveals a link to global climate changes
- High levels of ozone contributes towards human impact
- The studies in ozone formation indicate (VOCs) as precursors
- Production of photo-oxidants and secondary pollutants
- Ozone key air pollutants- Air quality act 2004 (Act No.39 of 2004)
VOCs such as NMHCs are major precursors to ozone formation

NMHCs has implications to human and ecosystem health

Air Quality Management in South Africa

Studied for their role towards climate change

In South Africa studies of these compounds have not yet been done.

Research proposal to study and develop the primary reference material VOCs (NMHCs) in South Africa
Sources of VOCs

- NMHCs released into the atmosphere by a variety of natural and anthropogenic sources.
VOCs gas mixtures

Why VOCs gas mixtures?

- Traceable standards are required for reliable VOCs measurements
- Accurate prediction of the influence of climate change
- Identification of emission ranges from different anthropogenic sources
- Accurately determine the impact VOCs on human and other living organisms
- Provide measurement traceability to South African industry and SADC region
Project plan

| Gravimetric preparation-International Organization for Standardization (ISO 6142) |
| Internal consistency among the mixtures |
| Analysis of standards- gas chromatograph with flame ionisation detector (GC-FID) |
Preparation process

Preparation of ethane, propane, iso-pentane, n-pentane and hexane in nitrogen gas mixtures

Most of the NMHCs are in liquid phase

Ethane and propane- starting material gas phase

iso-pentane, n- pentane and hexane- starting material liquid phase

Syringe preparation technique will be described
Preparation overview

Accurate mixing (Gravimetric)
Verification by comparison
Short-term stability
Long-term stability
Preparation of gas mixtures

- Production diagrams of C\textsubscript{2}H\textsubscript{6} and C\textsubscript{3}H\textsubscript{8} gas mixtures

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<table>
<thead>
<tr>
<th>C\textsubscript{2}H\textsubscript{6} 4.5</th>
<th>C\textsubscript{3}H\textsubscript{8} 3.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5 % mol/mol</td>
<td>1 % mol/mol</td>
</tr>
<tr>
<td>2000 (\mu)mol/mol</td>
<td>1000 (\mu)mol/mol</td>
</tr>
<tr>
<td>200 (\mu)mol/mol</td>
<td></td>
</tr>
<tr>
<td>25 (\mu)mol/mol</td>
<td></td>
</tr>
<tr>
<td>2.5 (\mu)mol/mol</td>
<td></td>
</tr>
</tbody>
</table>
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Weighing process

- Syringe method - Introducing the liquid into a cylinder
- Two x 20 μmol/mol nominal mole fraction of iso-pentane, n-pentane and n-hexane were prepared
Filling process

- Transfer of target component to the cylinder
- MDV - minimise loss during transfer
Analytical conditions

Experimental conditions for C₂H₆ and C₃H₈

- Detector (FID); 380 °C
- Oven temperature: 120 °C for C₂H₆ & 200 °C for C₃H₈
- Carrier gas: Helium
- Sample loop: 1 mL and 250 µL
- Column: Molecular sieve 5A-C₂H₆ Porapak Q (80/100 mesh, 2m)- C₃H₈
- Sample flow: 100 ml/min
- Run time: 2 minutes
Results - C₃H₈

- Internal consistency study
- The four gas mixtures were analysed using A-B-A method
- One gas mixture was used as the reference
- Drift during analysis ≤ 0.25 %
- Model equation:

\[ C_{\text{sample}} = \frac{A_{\text{Sample}}}{A_{\text{Reference}}} \times C_{\text{reference}} \]

<table>
<thead>
<tr>
<th>Cylinder number</th>
<th>Concentration (µmol/mol)</th>
<th>Means</th>
<th>%RSD</th>
<th>Sensitivity</th>
<th>Sensitivity ratio</th>
<th>%Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>M9 3862</td>
<td>1003.3</td>
<td>31851</td>
<td>0.194</td>
<td>31.73</td>
<td>1.0000</td>
<td></td>
</tr>
<tr>
<td>M9 3831</td>
<td>1000.3</td>
<td>31715</td>
<td>0.260</td>
<td>31.71</td>
<td>0.9993</td>
<td>0.071</td>
</tr>
<tr>
<td>M9 3799</td>
<td>998.8</td>
<td>31730</td>
<td>0.186</td>
<td>31.77</td>
<td>1.0020</td>
<td>0.204</td>
</tr>
<tr>
<td>M9 3910</td>
<td>1000.1</td>
<td>31702</td>
<td>0.188</td>
<td>31.70</td>
<td>1.0003</td>
<td>0.032</td>
</tr>
</tbody>
</table>
Results - $\text{C}_3\text{H}_8$

- Sensitivity ratio graphs - internal consistency study
- % Difference between sample and reference mixture
# Results- C\textsubscript{2}H\textsubscript{6}

- Four x 2.5 µmol/mol C\textsubscript{2}H\textsubscript{6} in N\textsubscript{2} gas mixtures
- Repeatability results

<table>
<thead>
<tr>
<th>Cylinder number</th>
<th>Mole fraction µmol/mol</th>
<th>Means</th>
<th>% RSD</th>
<th>Sensitivity</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>M51 8159</td>
<td>2.513</td>
<td>792.8</td>
<td>0.16</td>
<td>315.5</td>
<td></td>
</tr>
<tr>
<td>M51 8152</td>
<td>2.512</td>
<td>786.5</td>
<td>0.16</td>
<td>313.1</td>
<td>0.7 %</td>
</tr>
<tr>
<td>M51 8259</td>
<td>2.512</td>
<td>792.4</td>
<td>0.19</td>
<td>315.5</td>
<td>0.03 %</td>
</tr>
<tr>
<td>M51 8078</td>
<td>2.507</td>
<td>781.8</td>
<td>0.11</td>
<td>311.8</td>
<td>1.23 %</td>
</tr>
</tbody>
</table>
Analytical conditions

- Methodology $C_5H_{12}$ and $C_6H_{14}$

Analytical method

- Detector (FID); 175 °C
- Temperature program: 80 °C for 5 min, 180 °C for 2 min at 20 °C/min
- Carrier gas: Hydrogen
- Sample loop: 1 mL
- Column: HP-PLOT Al$_2$O$_3$ S
- Sample flow: 35 ml/min
- Run time: 12 minutes
**Results - C₅H₁₂ and C₆H₁₄**

- GC results using one cylinder as a reference cylinder
- % Drift during analysis ≤ 0.7 %

<table>
<thead>
<tr>
<th>Cylinder number</th>
<th>Component</th>
<th>Mole fraction µmol/mol</th>
<th>Means</th>
<th>%RSD</th>
<th>Sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>M51 8085</td>
<td>i-pentane</td>
<td>20.4</td>
<td>76.5</td>
<td>0.29</td>
<td>3.75</td>
</tr>
<tr>
<td></td>
<td>n-pentane</td>
<td>20.8</td>
<td>74.7</td>
<td>0.28</td>
<td>3.59</td>
</tr>
<tr>
<td></td>
<td>Hexane</td>
<td>22.5</td>
<td>88.4</td>
<td>0.36</td>
<td>3.92</td>
</tr>
<tr>
<td>M51 8073</td>
<td>i-pentane</td>
<td>20.1</td>
<td>75.6</td>
<td>0.23</td>
<td>3.76</td>
</tr>
<tr>
<td></td>
<td>n-pentane</td>
<td>20.5</td>
<td>73.9</td>
<td>0.26</td>
<td>3.60</td>
</tr>
<tr>
<td></td>
<td>Hexane</td>
<td>22.3</td>
<td>87.7</td>
<td>0.20</td>
<td>3.94</td>
</tr>
</tbody>
</table>
Results $\text{C}_5\text{H}_{12}$ and $\text{C}_6\text{H}_{14}$
Conclusion

- Sensitivity ratio difference $\leq 0.25\%$, mixtures prepared showed good internal consistency
- Analysis drift $\leq 0.25\%$
- Combined expanded uncertainty $\leq 0.5\%$

\begin{itemize}
  \item [C_3H_8]
  \begin{itemize}
    \item Sensitivity ratio difference $\leq 0.25\%$
    \item Analysis drift $\leq 0.25\%$
    \item Combined expanded uncertainty $\leq 0.5\%$
  \end{itemize}

  \begin{itemize}
    \item % RSD $\leq 0.2$ and analysis drift $\leq 0.5\%$
    \item More development work required
  \end{itemize}

  \begin{itemize}
    \item % RSD $\leq 0.4$ and analysis Drift $\leq 0.7\%$
    \item Improve analysis method- improve repeatability
  \end{itemize}
\end{itemize}
Acknowledgements

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Co-Supervisor: Dr. James Tshilongo
Gas team
THANK YOU
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