Enhancing Gas Chromatography Performance

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Outline/Summary

• Thermal conductivity and tritium monitor detector measurements are complementary and predict similar atom fractions in H/D/T mixtures within 1%

• Miniaturization of the pressure sensing detector and the effluent isolation valve will reduce DT injection quantities for assay by 60%

• LLE has analyzed two of the three inactive gas samples provided by Sandia National Laboratories as part of the round robin exercise to compare assay results across the complex
Filling cryogenic targets in the permeation cell is a multistep process
The lighter isotopic species concentrate while pressurizing the permeator in the Tritium Fill Station.

Variation in T/D downstream of the TFS = 1.2%
Gas chromatography uses iron-doped alumina at 77 K to separate the hydrogen isotopologues.

Minimum aliquot size: 80 µL

Error:
- systematic: 1.2%
- relative (peak to peak): <0.5%
- reproducibility: <0.2%

MS: molecular sieve
TM: tritium monitor
TCD: thermal conductivity detector
The assaying process requires four steps; first step: evacuate the injection volume
Second step: charge the loop with a predefined aliquot of gas

Minimum aliquot size: 80 $\mu$L
Third step: inject the aliquot into the separation column and detection circuit
Fourth step: sample analysis
The 4-cm$^3$ tritium monitor and thermal conductivity agree within 1% over all T/D ratios.

The minimum aliquot required for analysis by the TM is 0.01 $\mu$L. The gas inventory of a typical target is ~20 $\mu$L!
60% of the gas delivered to the gas chromatograph is not used for analysis

Injection loop volume: 1.5 mL
Pressure transducer and isolation valve volume: ~2.24 mL
Volume injected for assay: 3.74 mL (4.84 Ci)
The volume of the pressure detector and isolation valve assembly has been miniaturized ~200 fold

Injection loop volume: 1.5 mL
Pressure transducer and isolation valve volume: <10 μL
Volume injected for assay: ~1.5 mL (1.9 Ci)
Tritium interacts with stainless steel to generate CH$_4$ and CO

**Impurity growth rate**

<table>
<thead>
<tr>
<th>Vessel ID</th>
<th>CH$_4$</th>
<th>CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>677</td>
<td>21.2</td>
<td>14.3</td>
</tr>
<tr>
<td>624</td>
<td>1.9</td>
<td>6.0</td>
</tr>
</tbody>
</table>

*Time after filling the sample vessel*
“D” and “T” exchange with adsorbed water layers on the inner surfaces of the sample vessel and the process loop

<table>
<thead>
<tr>
<th>Duration since purifying fuel (days)</th>
<th>Protium concentration in fuel (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>600</td>
<td>2.5</td>
</tr>
<tr>
<td>1200</td>
<td>3</td>
</tr>
</tbody>
</table>

- Direct measurement of the protium content in a gas contained in unconditioned vessels leads to 300% errors in the protium fraction.

**Absorbed water layer**

<table>
<thead>
<tr>
<th>Evacuated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baked</td>
</tr>
<tr>
<td>Tritium conditioned</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>H₂O</th>
<th>H₂O</th>
<th>H₂O</th>
<th>M</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>H₂O</td>
<td>H₂O</td>
<td>M</td>
<td>H</td>
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<td>H₂O</td>
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<td>H₂O</td>
<td>H₂O</td>
<td>H₂O</td>
<td>M</td>
<td>H</td>
</tr>
</tbody>
</table>

**Contamination caused by sample vessel**

- Permeation cell
- Assay vessel

- 1.88 %/mo
LLE is participating in the national lab round robin gas-analysis exercise

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Composition</th>
<th>Nominal mixture (%)</th>
<th>Measured value</th>
<th>RSD* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H$_2$</td>
<td>35</td>
<td>42.95</td>
<td>0.11</td>
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<tr>
<td></td>
<td>HD</td>
<td>–</td>
<td>3.01</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td>D$_2$</td>
<td>65</td>
<td>54.04</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>H/D</td>
<td>53.8</td>
<td>80.02</td>
<td>0.16</td>
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<tr>
<td>3</td>
<td>H$_2$</td>
<td>20</td>
<td>30.02</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>HD</td>
<td>–</td>
<td>44.30</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>D$_2$</td>
<td>20</td>
<td>25.50</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>H/D</td>
<td>1</td>
<td>1.10</td>
<td>0.06</td>
</tr>
</tbody>
</table>

*Relative standard deviation
The isotopologue ‘HD’ dominates the H$_2$/D$_2$ spectrum in the Mass Cal Gas sample.
Need to run a calibration gas to confirm the locations of the non-hydrogenic species

Composition of Mass Cal Gas
- $\text{H}_2$
- $\text{D}_2$
- $\text{N}_2$
- $\text{Ar}$
- $\text{CH}_4$
- $\text{CO}_2$

This column cannot identify $\text{CO}_2$
• Thermal conductivity and tritium monitor detector measurements are complementary and predict similar atom fractions in H/D/T mixtures within 1%

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