Assaying Hydrogen Isotopes with Gas Chromatography

W. T. Shmayda and N. Redden
University of Rochester
Laboratory for Laser Energetics

39th Tritium Focus Group
Oak Ridge, TN
15–17 May 2018
Outline/Summary

- Estimating the thermal conductivity of the hydrogen isotopologues using kinetic theory for monoatomic gas species leads to an error <1.3%
- Estimating the protium content by difference eliminates corrupting the measurements by protium contamination in the sample vessel
- Thermal conductivity and ionization chamber detector measurements are complementary and predict similar atom fractions in H/D/T mixtures
- H/D/T mixtures equilibrate within the sample vessels within 48 h
The hydrogen isotopologues are separated on iron-doped alumina cooled to 77 K

- Minimum aliquot: 1 μL
- Error
  - systematic: 1.2%
  - relative (peak to peak): <0.5%
  - reproducibility: <0.2%

*TCD: thermal conductivity detector
Baseline separation is achieved; H/D/T ratios are calculated from the area ratios

- Neon purge rate: 52.5 scc/min
- Block temperature: 75°C
- Filament temperature: 325°C

5.45% H
60.62% D
33.93% T
Charging cryogenic targets in the permeation cell is a multistep process.
The lighter isotopic species concentrate while charging the permeator in the Tritium Fill Station.

Variation in T/D downstream of the TFS = 1.2%

Composition in %: H/D/T
Tritium decay dominates the decrease in the isotopic ratio of the fuel
“D” and “T” exchange with adsorbed water layers on the inner surfaces of the sample vessel and the process loop

- Direct measurement of the protium content in a gas contained in unconditioned vessels can lead to 300% errors in the protium fraction
Estimating the protium content in the fuel based on the “D” and “T” measurement eliminates vessel contributions.

\[ \%H = 100 - \%D - \%T \]

- Scatter in data < 1.5%

Slope: 0.026 \%/mo
Intercept: 0.52
Start date: 9/24/2014
Quantitative TCD measurements depend on knowing the thermal conductivity of each hydrogen isotopologue.

- Thermal conductivity
  - $\text{H}_2$, $\text{D}_2$ : Saxena*, NIST 12**
  - mixed isotopes interpolated from kinetic theory:
    - for monoatomic gas
      $$k \propto \frac{1}{\sqrt{M}} \rightarrow \frac{k_{\text{H}_2}}{k_{\text{D}_2}} = \sqrt{\frac{4}{2}} = 1.41$$
    - for polyatomic gas†
      $$\text{(polyatomic) } 1 < \varepsilon > 2.5 \text{ (monoatomic)}$$
      $$k \propto \frac{\varepsilon}{\sqrt{M}}$$

- Transit time through detector: 8 s
- Thermal penetration depth in detector: 2 mm
- $\frac{k_{\text{H}_2}}{k_{\text{D}_2}}$ thermal conductivity ratio: 1.33 → 1.37

Expected deviation from theory: 2.8% → 5.6%

---

A 4-cm$^3$ ionization chamber has been deployed to complement thermal-conductivity measurements

Target inventory: 20 $\mu$L
Minimum aliquot: 0.01 $\mu$L

Signal (V)

Time (min)

0 20 40

50% T
91% T

HT
DT
T$_2$

Vacuum
Sample

P
LN$_2$
Fe-doped MS 5 Å

Neon

TCD
TM

TM: tritium monitor
Quantitative measurements of the fuel composition use the TM chromatogram and the equilibrium constants for “H,” “D,” “T”

\[
\begin{align*}
[H_2] + [D_2] &= 2[HD] \\
H_2 + T_2 &= 2HT \\
D_2 + T_2 &= 2DT
\end{align*}
\]

Area ratios:

\[
\begin{align*}
[HT] &= \frac{2A_{HT}}{A_{T_2}} [T_2] \\
[DT] &= \frac{2A_{DT}}{A_{T_2}} [T_2]
\end{align*}
\]

T/D ratios determined by the TCD are systematically 1.3% lower than the TM measured ratios.

The statistical variation in the T/D ratio measured by the two detectors is 0.2%. 

The diagram shows the protium in permeation cell plotted against days since purification. The TCD error is ±1.3%, the TM error is ±1.0%, and the start date is 9/24/2014. The TM data is offset in time for clarity.
Outline/Summary

- Estimating the thermal conductivity of the hydrogen isotopologues using kinetic theory for monoatomic gas species leads to an error <1.3%

- Estimating the protium content by difference eliminates corrupting the measurements by protium contamination in the sample vessel

- Thermal conductivity and ionization chamber detector measurements are complementary and predict similar atom fractions in H/D/T mixtures

- H/D/T mixtures equilibrate within the sample vessels within 48 h
The gas chromatograph has been upgraded to measure the N₂, O₂, CO, and CH₄ content in the DT fuel.
Both CH$_4$/CO are produced inside the process but CO generation dominates.

What is the source: targets or stainless steel?

Concentrations in ppm
Uncertainty:
- CH$_4$—3 %
- CO—17 %
Tritium interacts with the 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