Detection Limit of H and D for Tritium Process R&D

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Hydrogen Isotope Measurement

- **Tritium measurement**
  - Ion chamber – gas \(10^{-13} \text{ (0.03 Bq/cm}^3)\)
  - Scintillation - solid and liquid \(10^{-14} \text{ (1 Bq/mL)}\)
  - Solid state \(10^{-13} - 10^{-15} \text{ (0.17 – 33 Bq/cm}^2)\)

- **D/H ratio measurement**
  - RGA (mass spec) – Q\(_2\) and Q\(_2\)O \(10^{-4} \text{ (100 ppm)}\)
  - High end mass spec \(10^{-10} \text{ (100 ppt)}\)
  - GC / DID – H\(_2\) in He \(10^{-9} \text{ (< 1 ppb)}\)
  - FTIR – HDO \(10^{-5} \text{ (10 ppm)}\)
  - Tunable Laser – HDO \(10^{-8} \text{ (22.5 ppb)}\)
  - CRDS – HDO \(10^{-8} \text{ (30 ppb)}\)
Residual Gas Analyzer: H₂, HD, D₂

\[ \pm 100 \text{ ppm} = \frac{10^{-11}}{10^{-7}} \cdot 10^6 (\frac{D}{H} \text{ molar ratio}) \]
Residual Gas Analyzer: Trace HDO in H$_2$O

\[ y = 0.7620x - 0.0029 \]
\[ R^2 = 0.9978 \]

\(~0.4\%~over~ionization~to~H_3O^+~\)
# RGA Relative Probabilities of Ionization

<table>
<thead>
<tr>
<th>Mass number</th>
<th>Species</th>
<th>Probability of ionization</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>H₂</td>
<td>0.44</td>
</tr>
<tr>
<td>4</td>
<td>D₂</td>
<td>0.35</td>
</tr>
<tr>
<td>4</td>
<td>He</td>
<td>0.15</td>
</tr>
<tr>
<td>16</td>
<td>CH₄</td>
<td>1.6</td>
</tr>
<tr>
<td>18</td>
<td>H₂O</td>
<td>1</td>
</tr>
<tr>
<td>28</td>
<td>N₂</td>
<td>1</td>
</tr>
<tr>
<td>28</td>
<td>CO</td>
<td>1.05</td>
</tr>
<tr>
<td>32</td>
<td>O₂</td>
<td>1</td>
</tr>
<tr>
<td>40</td>
<td>Ar</td>
<td>1.2</td>
</tr>
<tr>
<td>44</td>
<td>CO₂</td>
<td>1.4</td>
</tr>
</tbody>
</table>

*from PFEIFFER VACUUM MS Catalog*
Atmospheric Pressure Ionization Mass Spectrometer

~ 100ppt sensitivity to $\text{H}_2\text{O}$, $\text{O}_2$, $\text{CO}$, $\text{CO}_2$, $\text{CH}_4$ and $\text{H}_2$

UHP purified gas, calibrated samples with NIST certified cylinders or permeation tubes.

... from SAES
Isotope-Ratio Mass Spectrometry


More Mass Spec

- THN 202 double collector HD /H₂ mass spectrometer by Thomson-Houston (France)
- Sampling techniques for water vapor introduction
- Water vapor reduced over 600°C uranium strips for conversion to hydrogen for Mass Spec
- Precision of ±0.1 ppm


Anton-Paar DMA-5000 Precision Densitometer

0.000001 g/cm$^3$

Temperature: 0.001 °C

Water Density versus D Concentration

$y = 0.108432x + 0.998197$

$R^2 = 0.999742$
GOW-Mac GC / DID – H₂

Impurities in Helium

- CH₄: 7 ppb
- H₂: 3 ppb
- Ar: 4 ppb
- N₂: 6 ppb

Incredible sensitive detector, pick up almost anything
GC with TCD (Thermal Conductivity Detector)

InfraCal IR Spectrometer

0.01 - 5.00% D$_2$O in water
FTIR Spectrum of Liquid Water

±25 ppm D/H with derivative data processing, ± 80 ppm without
FTIR Spectrum of Liquid Water - TumblIR interface

±10 ppm D/H ratio
CRDS for Water Liquid / Vapor: Picarro L2130i

±30 ppb (1σ) at 150 ppm D/H ratio
Tunable Laser for Water Liquid / Vapor: LGR TIWA-45-EP

±22.5 ppb (1σ) at 150 ppm D/H ratio
Summary

- Tritium detector very sensitive, $\sim 10^{-13} - 10^{-15}$ T/Q ratio.
- Drinking water standard: $6.22 \times 10^{-15}$ (< 20 pCi/mL).
- H and D detection limit $\sim 10^{-4} - 10^{-10}$ isotope ratio.
- Natural abundance D/H ratio $\sim 10^{-4}$ (150 ppm).
- Using H and D surrogates, detection limit desired better than $\sim 10^{-5}$. 