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

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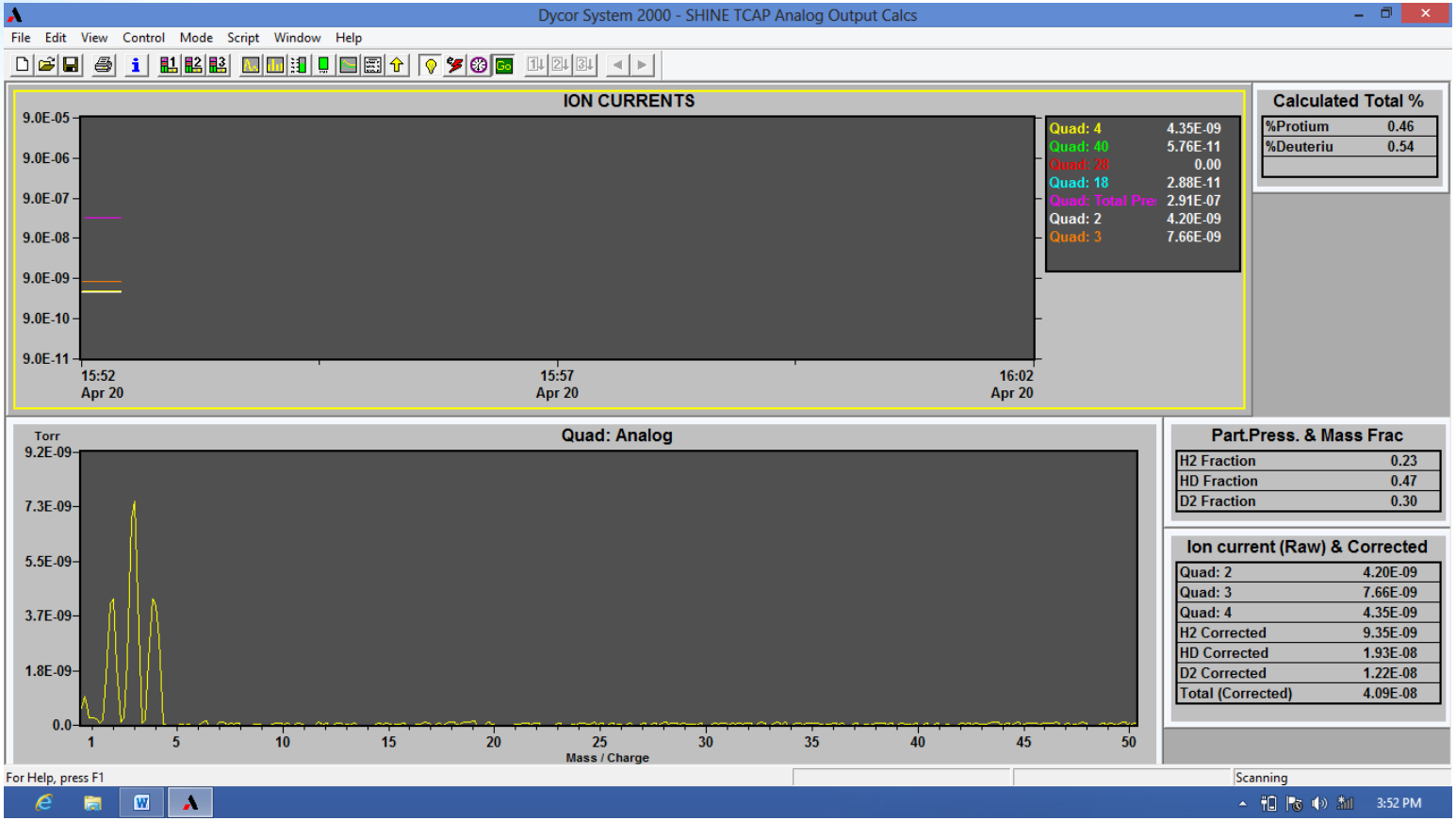
Hydrogen Isotope Measurement

- **Tritium measurement**
  - Ion chamber – gas — 10^{-13} (0.03 Bq/cm^3)
  - Scintillation - solid and liquid — 10^{-14} (1 Bq/mL)
  - Solid state — 10^{-13} – 10^{-15} (0.17 – 33 Bq/cm^2)
- **D/H ratio measurement**
  - RGA (mass spec) – Q_2 and Q_2O — 10^{-4} (100 ppm)
  - High end mass spec — 10^{-10} (100 ppt)
  - GC / DID – H_2 in He — 10^{-9} (< 1 ppb)
  - FTIR – HDO — 10^{-5} (10 ppm)
  - Tunable Laser – HDO — 10^{-8} (22.5 ppb)
  - CRDS – HDO — 10^{-8} (30 ppb)

Residual Gas Analyzer: H_2, HD, D_2



$$\pm 100\ ppm = \frac{10^{-11}}{10^{-7}} \cdot 10^{6} \left({}^{D}/_{H}\ molar\ ratio \right)$$

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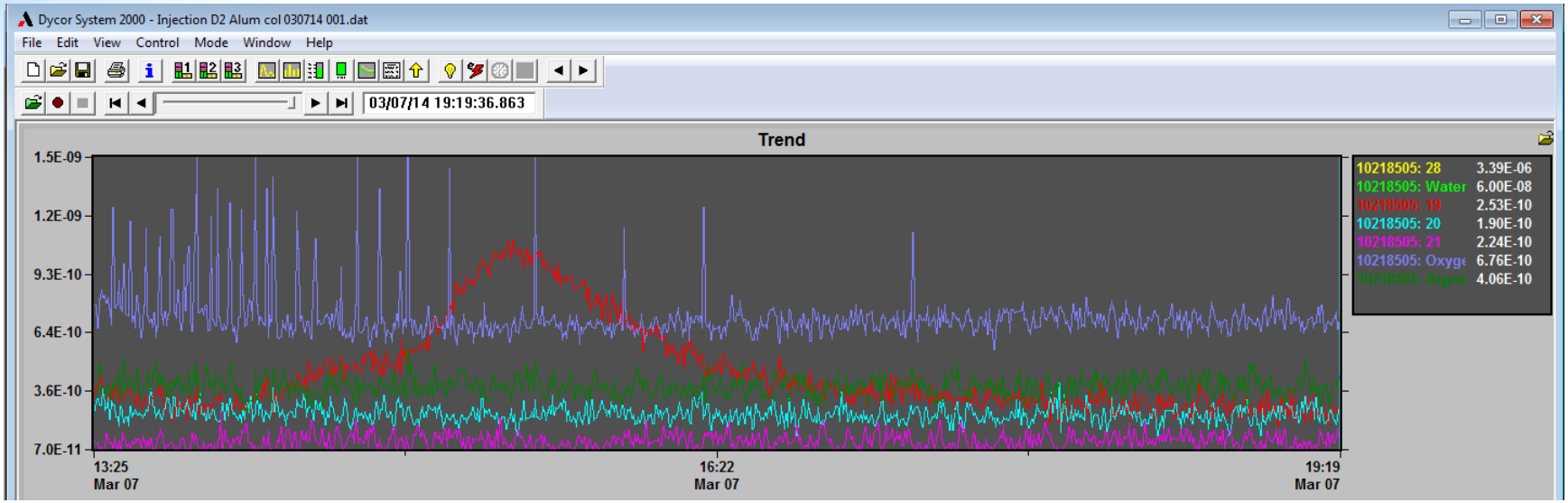
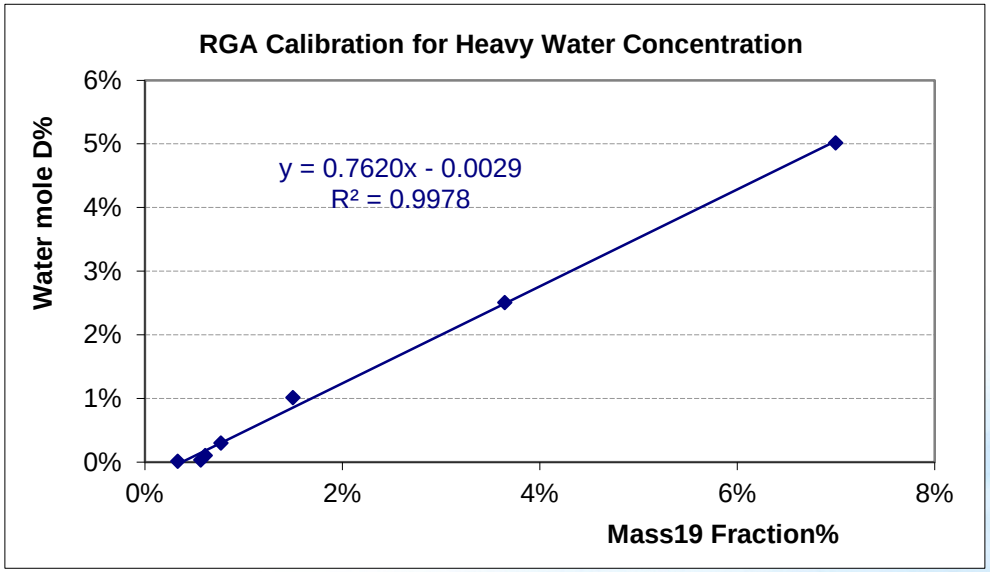
Residual Gas Analyzer: Trace HDO in H_2O



~0.4% over ionization to H_3O^+



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RGA Relative Probabilities of Ionization

Mass number	Species	Probability of ionization
2	H_2	0.44
4	D_2	0.35
4	He	0.15
16	CH_4	1.6
18	H_2O	1
28	N_2	1
28	CO	1.05
32	O_2	1
40	Ar	1.2
44	CO_2	1.4

from PFEIFFER VACUUM MS Catalog

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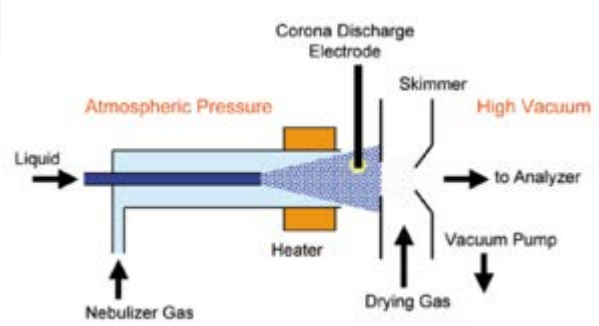
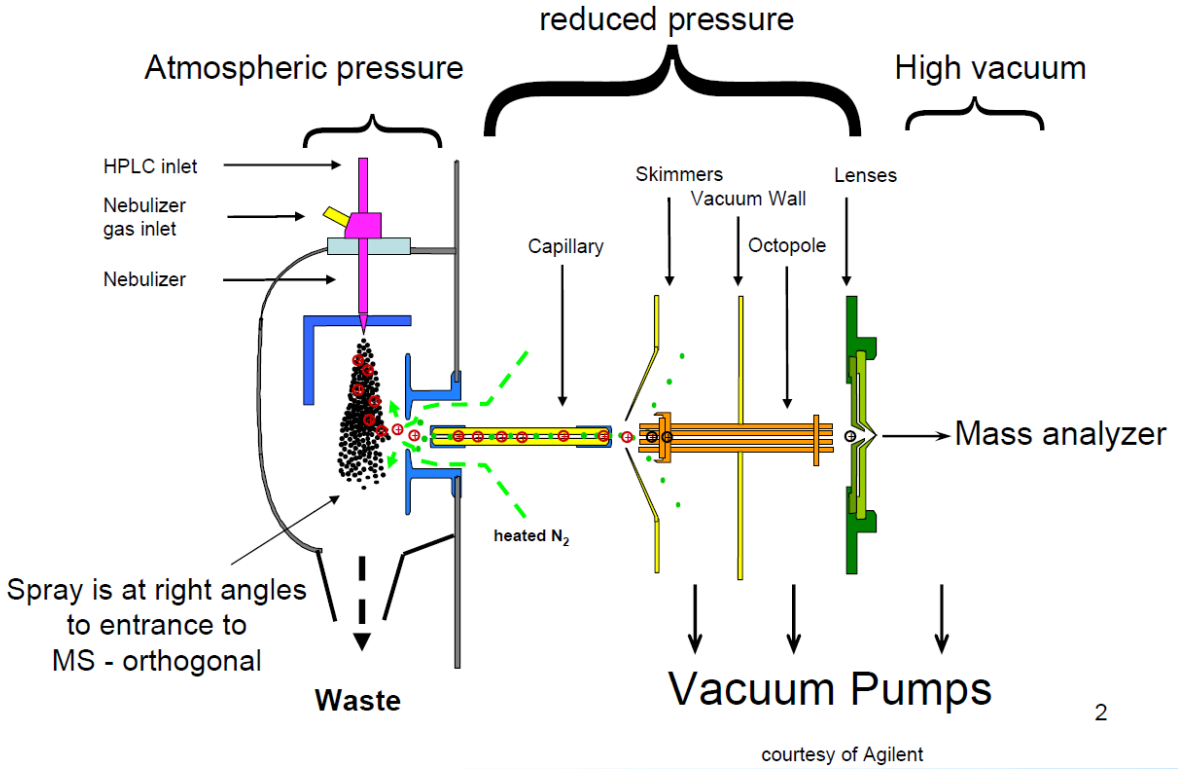
Atmospheric Pressure Ionization Mass Spectrometer



~ 100ppt sensitivity to H_2O, O_2, CO, CO_2, CH_4 and H_2

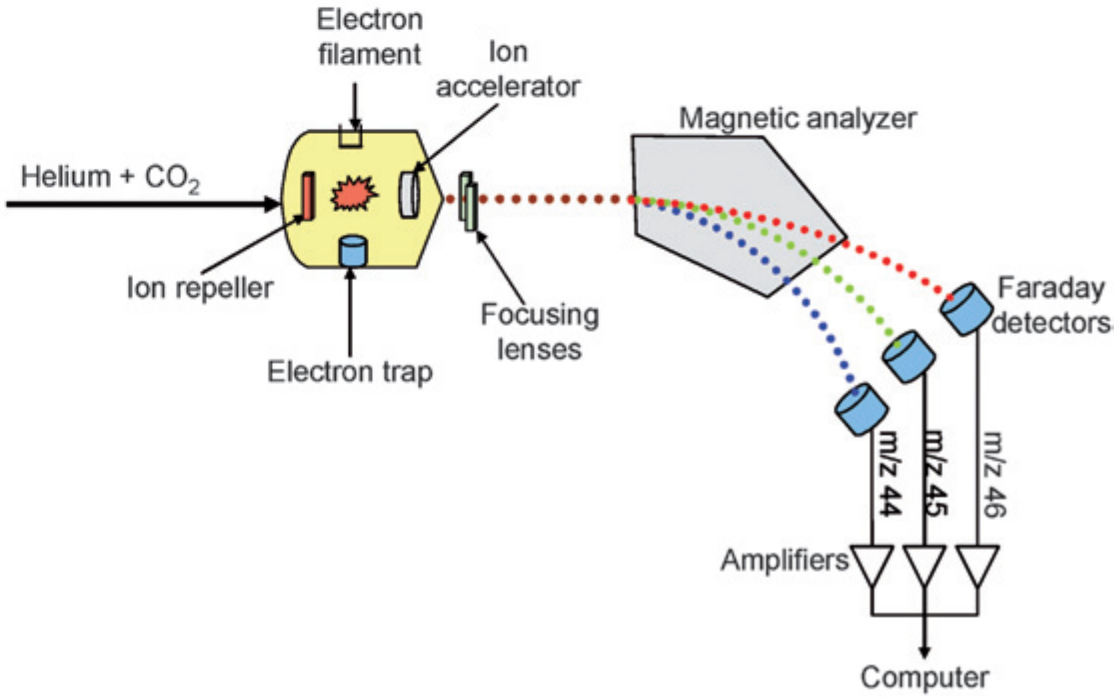
UHP purified gas, calibrated samples with NIST certified cylinders or permeation tubes.

… from SAES



Isotope-Ratio Mass Spectrometry

Isotope Ratio Mass Spectrometer (IRMS)



precision 15 - 300 ppb

M. Gehre et al., "On-line hydrogen-isotope measurements of organic samples …", Anal. Chem., Accepted, DOI: 10.1021/acs.analchem.5b00085, April 15, 2015

Muccio Z., Jackson G.P., "Isotope Ratio Mass Spectrometry", Analyst. 2009 Feb;134(2):213-22, doi: 10.1039/b808232d. Epub 2008 Nov 14.

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More Mass Spec

- **THN 202 double collector HD /H_2 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**

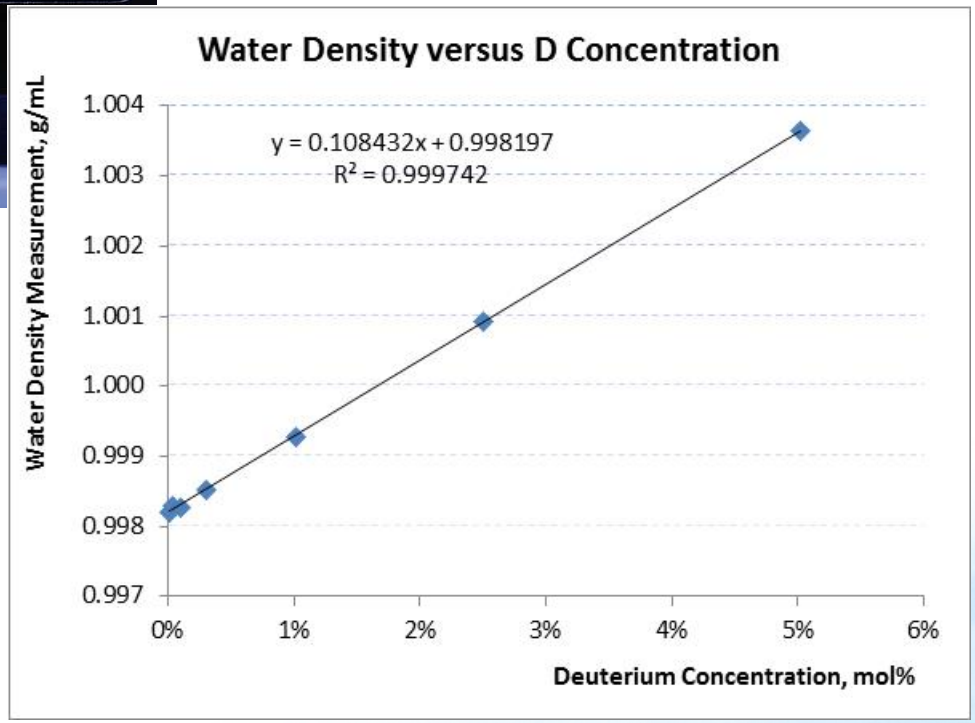
W. M. Thurston, "Steam Film Sampling of Water for Mass Spectrometric Analysis of the Deuterium Content", The Review of Scientific Instruments, (42) 5, May 1971

W. M. Thurston, "Automatic Mass Spectrometric Analysis of the Deuterium to Hydrogen Ratio in Natural Water", The Review of Scientific Instruments, (41) 7, July 1970

Anton-Paar DMA-5000 Precision Densitometer

0.000001 g/cm^3

Temperature: 0.001 °C



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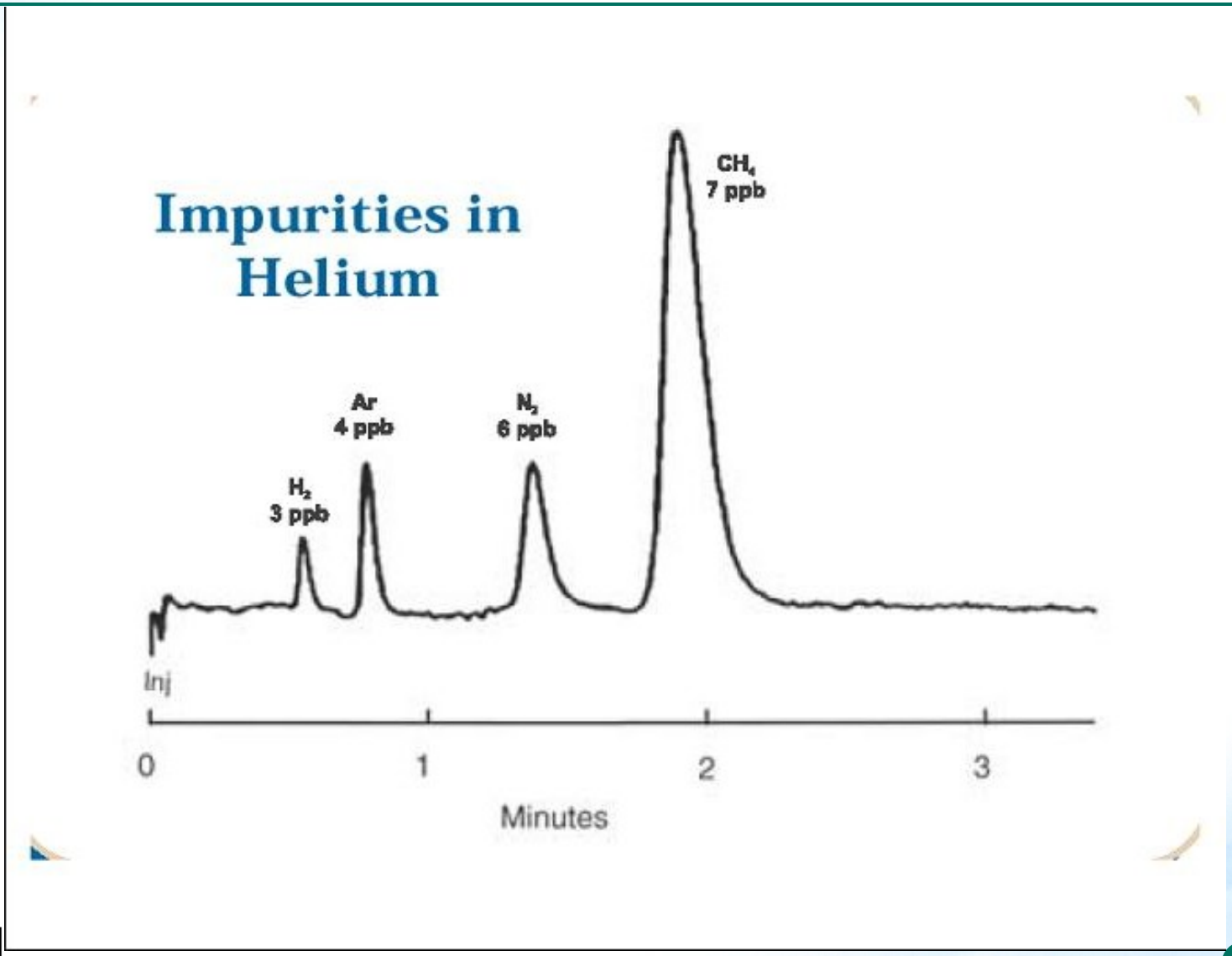
GOW-Mac GC / DID – H_2



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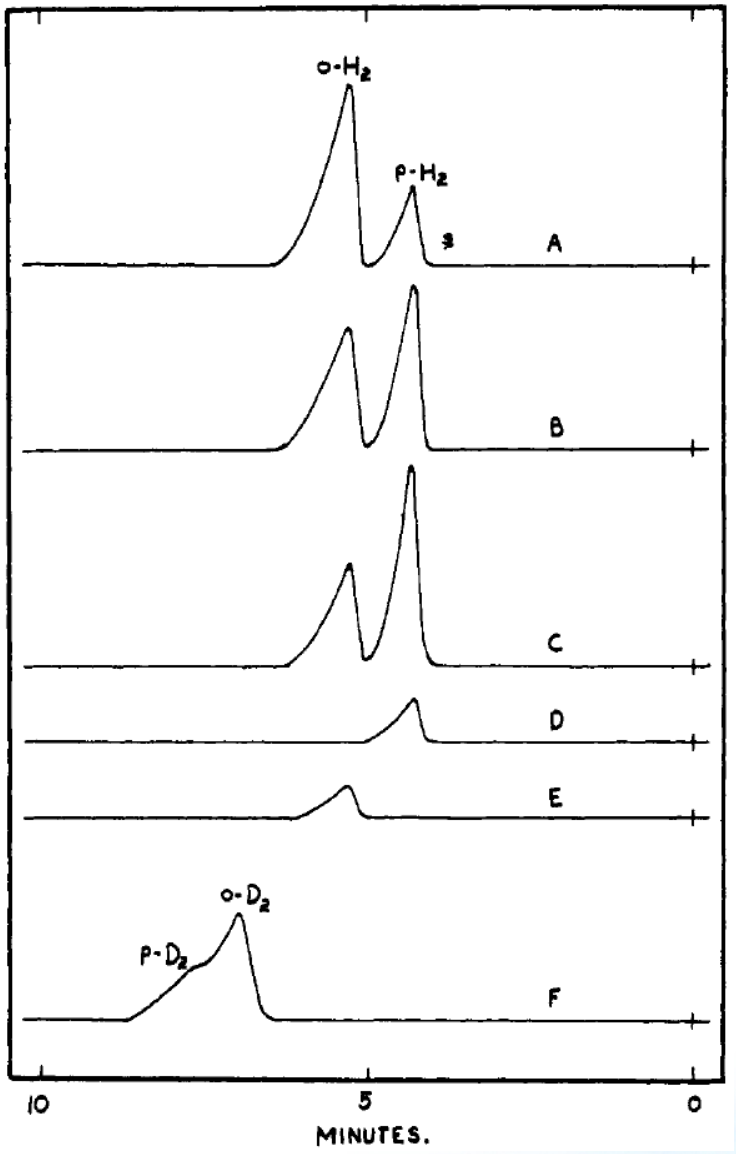
Incredible sensitive detector, pick up almost anything

Cryogenic GC Separation



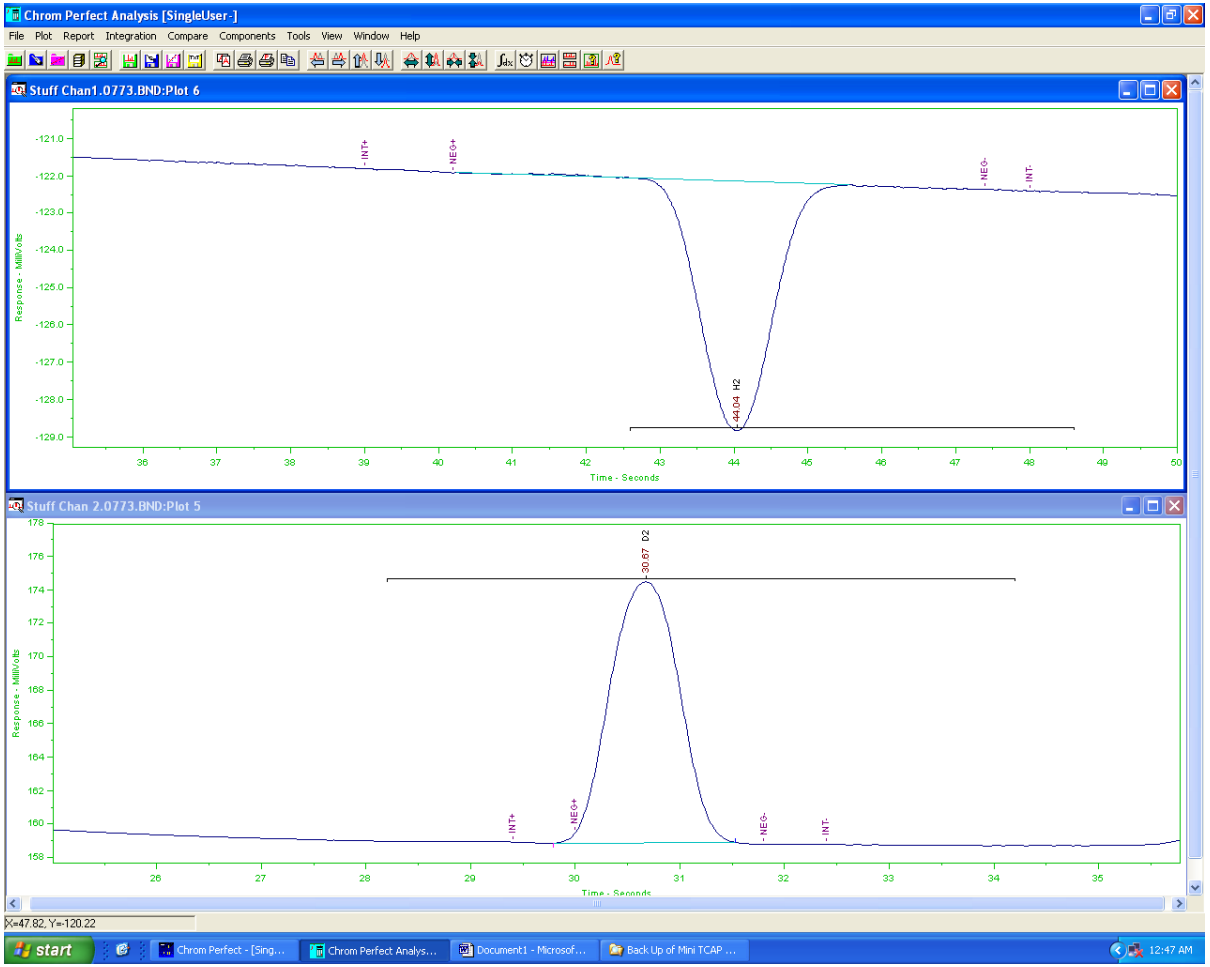
W. R. Moore , H. R. Ward, J. Am. Chem. Soc., 1958, 80 (11), pp 2909

GC with TCD (Thermal Conductivity Detector)

D_2 carrier

10 ppm resolution

H_2 carrier



H. T. Sessions Jr., "Analytical Method for Measuring Total Protium and Total Deuterium in a Gas Mixture Containing H_2, D_2, and HD via Gas Chromatography", presented at Tririum Conference 2007, Rochester, NY

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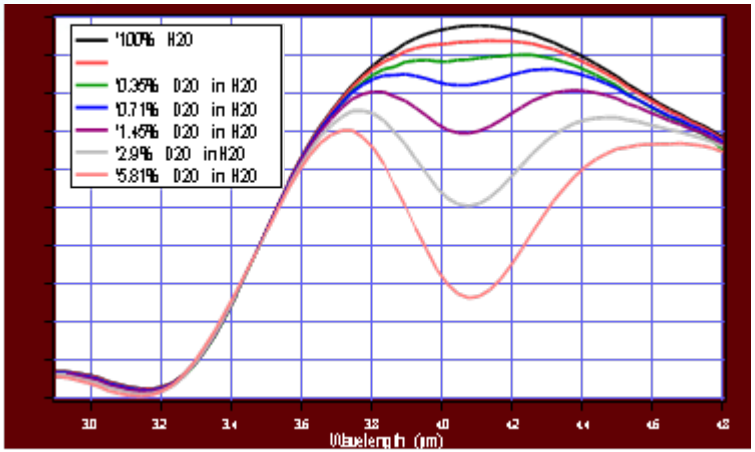
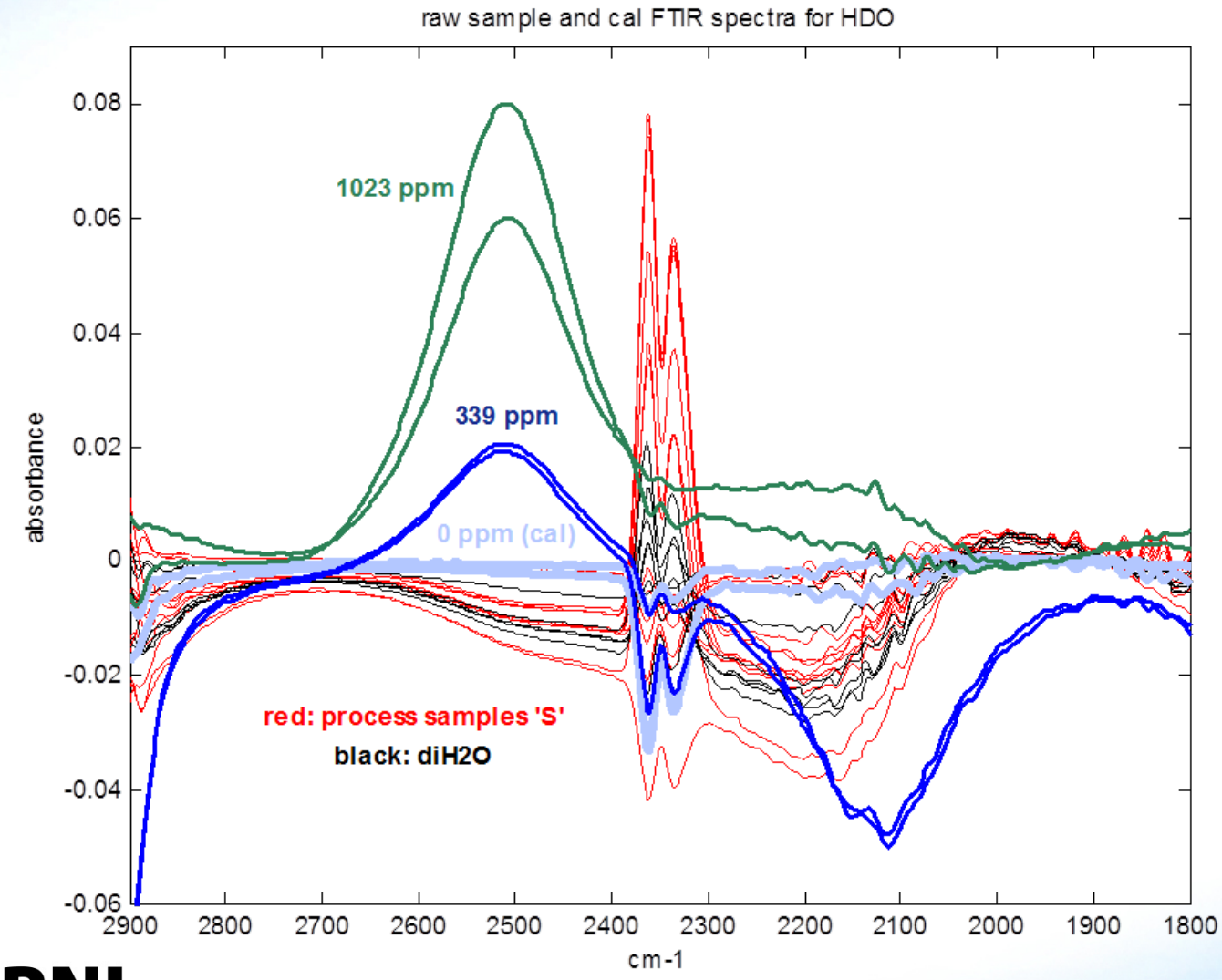
InfraCal IR Spectrometer



0.01 - 5.00% D_2O in water

FTIR Spectrum of Liquid Water



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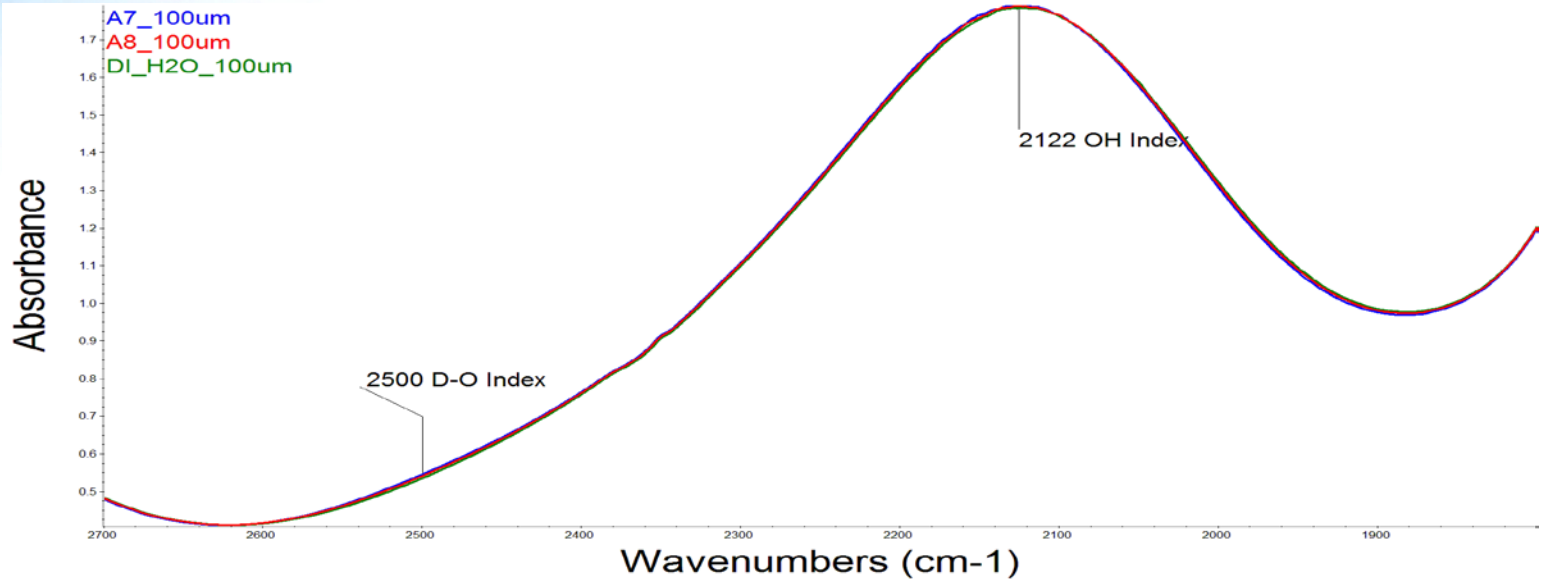
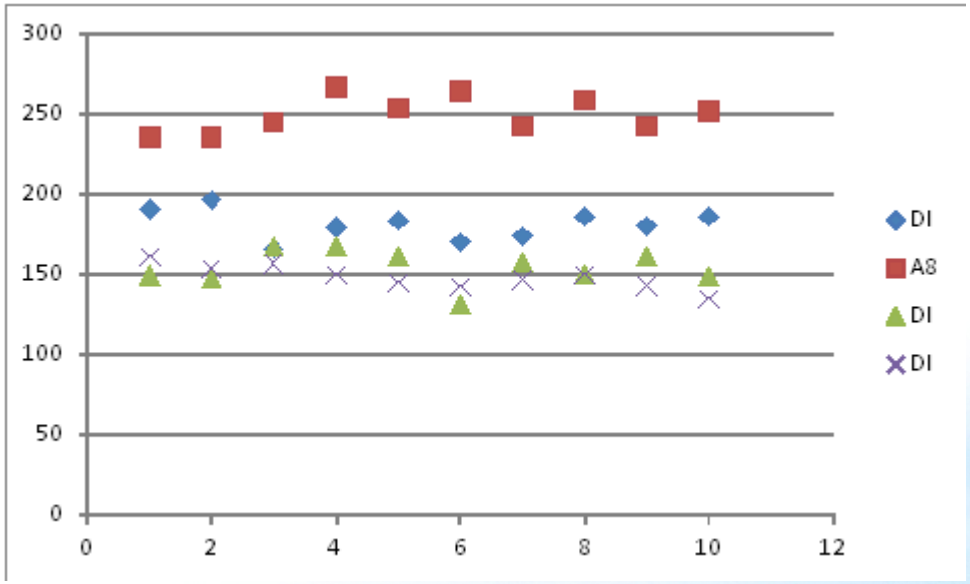
±25 ppm D/H with derivative data processing, ± 80 ppm without

FTIR Spectrum of Liquid Water - TumblIR interface



±10 ppm D/H ratio



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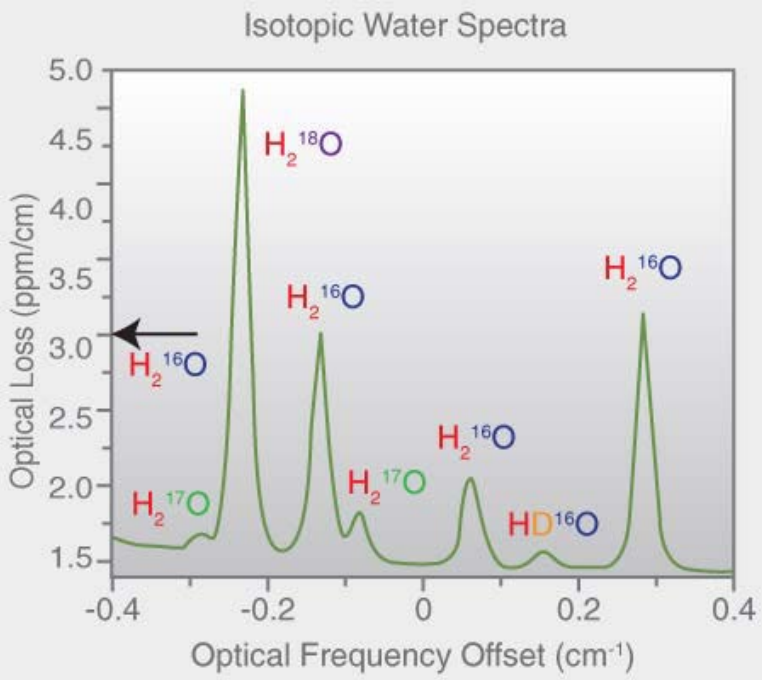
CRDS for Water Liquid / Vapor: Picarro L2130i



±30 ppb (1σ) at 150 ppm D/H ratio

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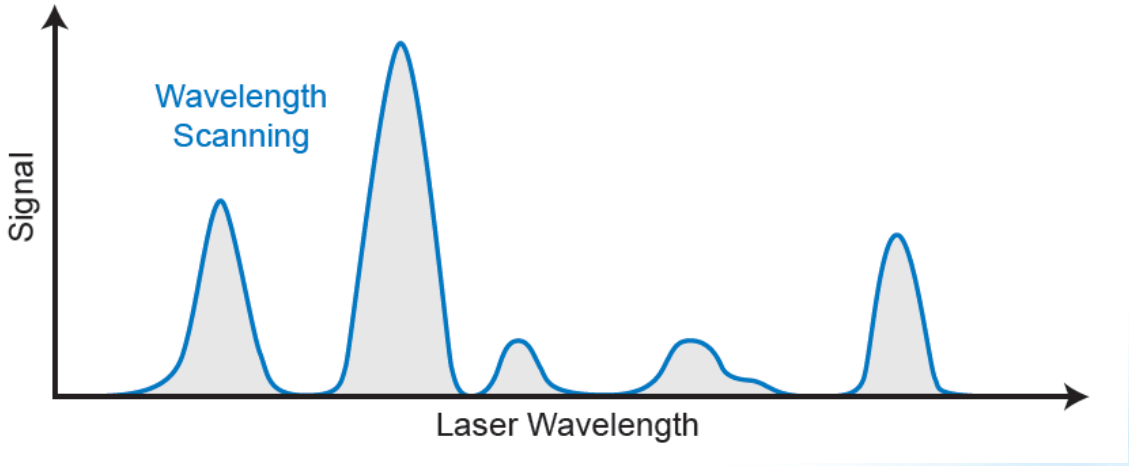
Tunable Laser for Water Liquid / Vapor: LGR TIWA-45-EP

±22.5 ppb (1σ) at 150 ppm D/H ratio



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Summary

- **Tritium detector very sensitive, ~10^{-13} – 10^{-15} T/Q ratio.**
- **Drinking water standard: 6.22x10^{-15} (< 20 pCi/mL).**
- **H and D detection limit ~10^{-4} – 10^{-10} isotope ratio.**
- **Natural abundance D/H ratio ~10^{-4} (150 ppm).**
- **Using H and D surrogates, detection limit desired better than ~10^{-5}.**

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