Trace Water Vapor Analysis Using Cavity Ring-down Spectroscopy, Oscillator Quartz Crystal and Impedance Sensor Technologies

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Overview of Presentation

- Introduction
- Objective
- Experimental Aspects
- Operating Principles
- Results comparing the three techniques
- Summary
- Conclusion and future developments

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Introduction

Why Trace Water?

- Next generation of semiconductor devices requires high purity gases to meet performance criteria
- Trace water impurity measurement needed to meet purity specifications.
- H_2O detection is challenging at low ppb levels
  - Adsorptive properties of water
  - Reactivity and or corrosive properties of gases
  - Strong IR absorption of many matrix gas
- Various H_2O measurement approaches
  - Spectroscopic: FTIR, CRDS, TDLAS
  - Sensors: QCM, P_2O_5 cell, Al_2O_3 impedance
  - Other: APIMS, MS, ion mobility, chilled mirror hygrometry

Objective

- Investigate three techniques for H_2O detection in the concentration range of 0-100 ppb
  - Quartz crystal microbalance (Ametek 5800)
  - Cavity ring-down spectroscopy (Halo, Tiger Optics)
  - Al_2O_3 impedance sensor (Hygrotrace, GE Sensing)
- Performance evaluation for
  - Detection sensitivity
  - Linearity
  - Response time
  - Long term stability
  - Application in inert and hydride gases

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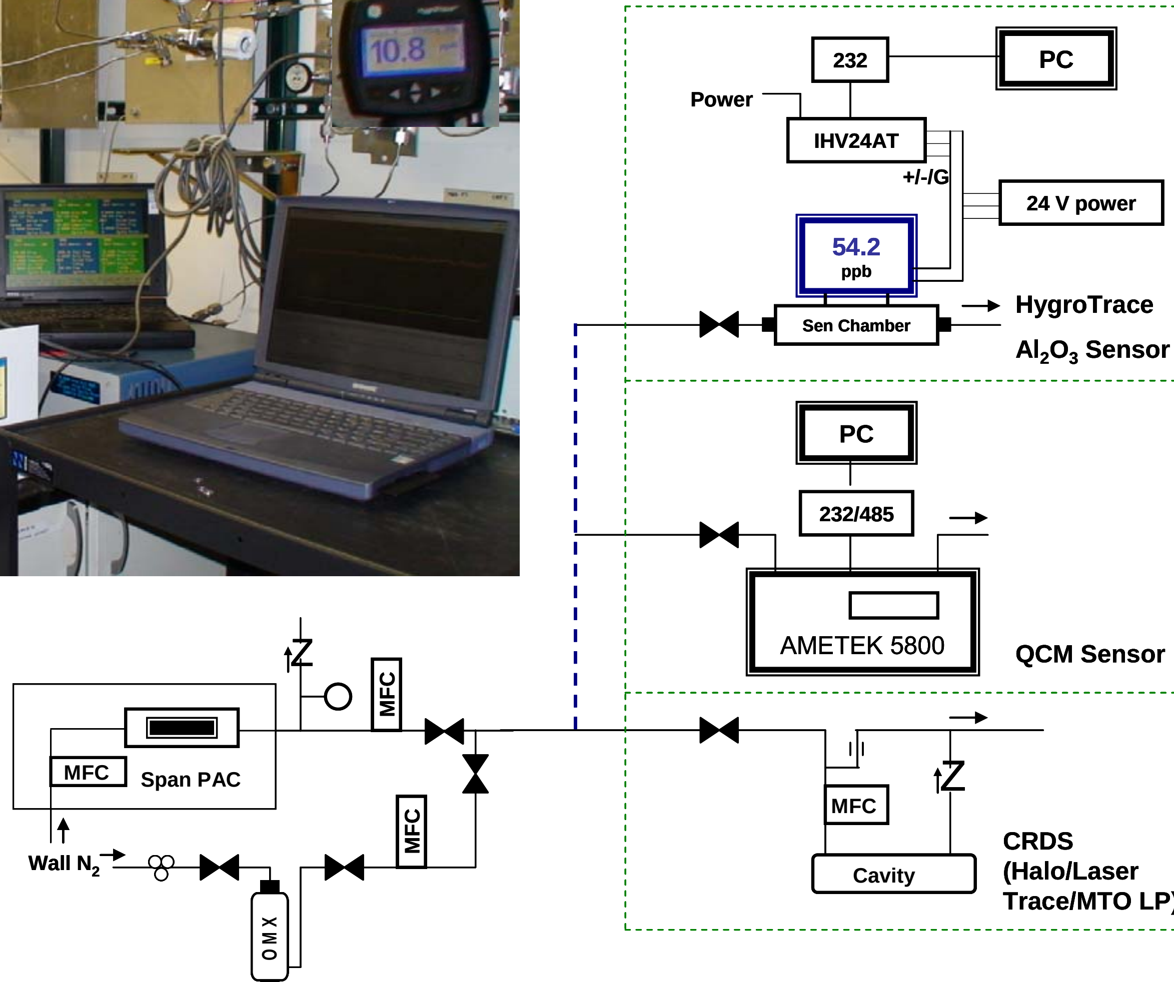
Experimental Set-up



Manifold for trace water vapor measurement using

Span-pac H_2O generator, AMETEK 5800, CRDS and GE HygroTrace Sensor

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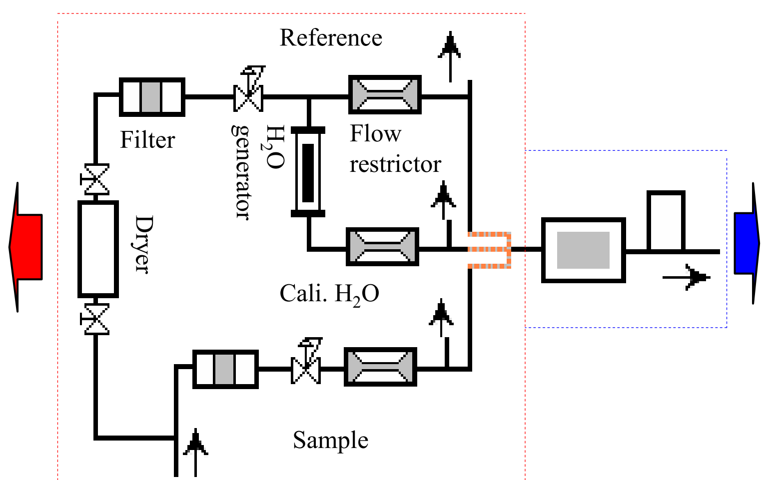
Quartz Crystal Microbalance

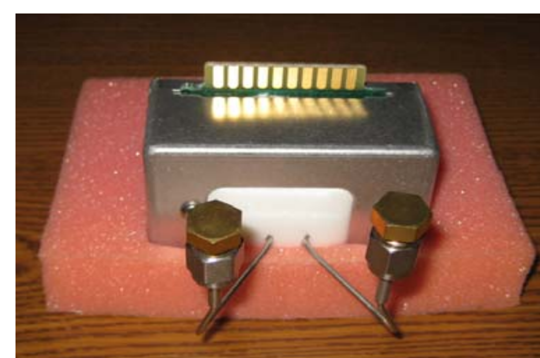
Sensors based on resonating piezoelectric crystals, developed in the 1960s by researchers at ESSO Research and Engineering Co and Dupont Company.

AMETEK Inc and Shimadzu Corp. developed technology for water vapor detection in high-purity gases from ppb to ppm levels.

Sensors are coated with a hygroscopic polymer film to enhance the sensitivity for water sorption. Offers wide operating range and high detection sensitivity [1-4].

1. Sauerbrey, G., Z. Phys., 155, (1959) p 206
2. King, W. H.; Piezoelectric Sorption Detector *Anal. Chem.*, **1964**, *36* (9), pp 1735–1739
3. Guilbault, G.G: Jordan J.M Analytical uses of piezoelectric-crystals – a review CRC Critical Rev Anal Chem 19, 1-28 (1988)
4. Feng, J.; Raynor, M.; Owens, M.; Trace Water Vapor Detection in Pure Arsine Gas Using Quartz Crystal Oscillator Technology, Pittcon 2007 Feb 25- Mar 02 2007, Chicago





Oscillator Quartz Crystal Analysis: Operating Principle

$$\Delta f = -C_m \Delta m$$

Δf – change in crystal resonance frequency (Hertz) is proportional to the change in the mass per unit surface area Δm in grams as a result of H_2O absorption

C_m is a property of the crystal used based on fundamental resonance frequency, the surface area, density of the quartz and polymer properties at constant T and P

Δf measurement relative to a reference cell compensates for temperature drifts.

By alternating flow of wet sample and dry reference gas over the crystal over a set interval, Δf due to H_2O absorption can be determined

$$\Delta f = (f_{sample} - f_{ref.crystal}) - (f_{drygas} - f_{ref.crystal})$$

A microprocessor stores the frequencies and based on the amount of accumulated H_2O during the sampling interval, calculates the H_2O concentration using a polynomial expression obtained from prior calibration.

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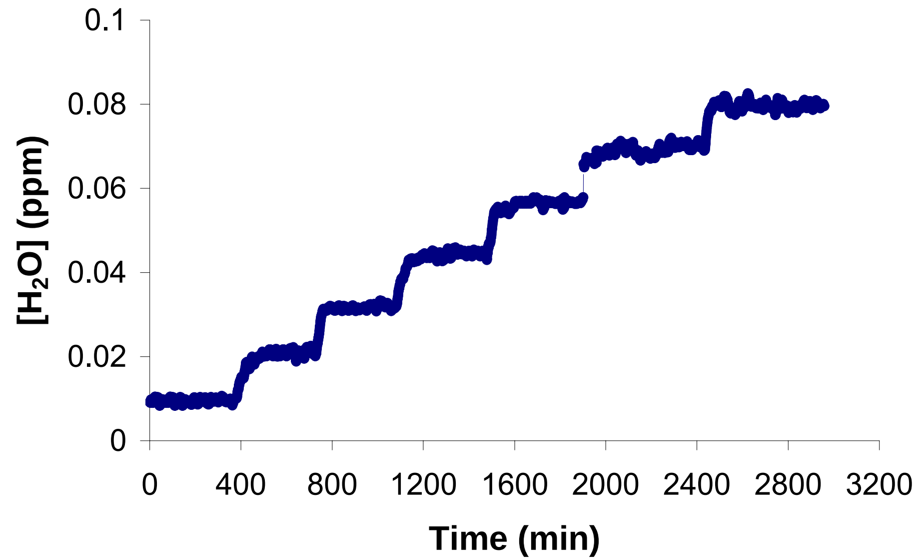
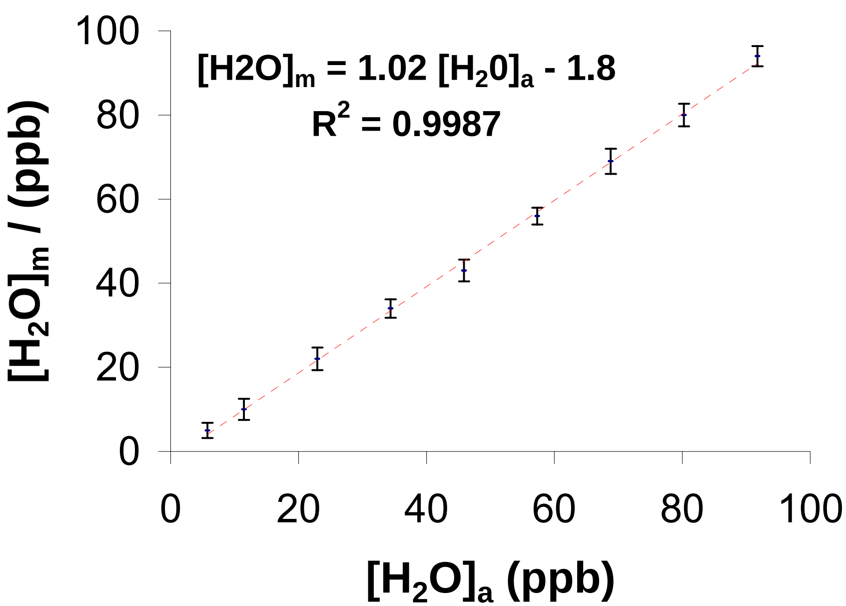
Trace H_2O Addition into Ametek 5800

H_2O measurement with H_2O step-addition in N_2

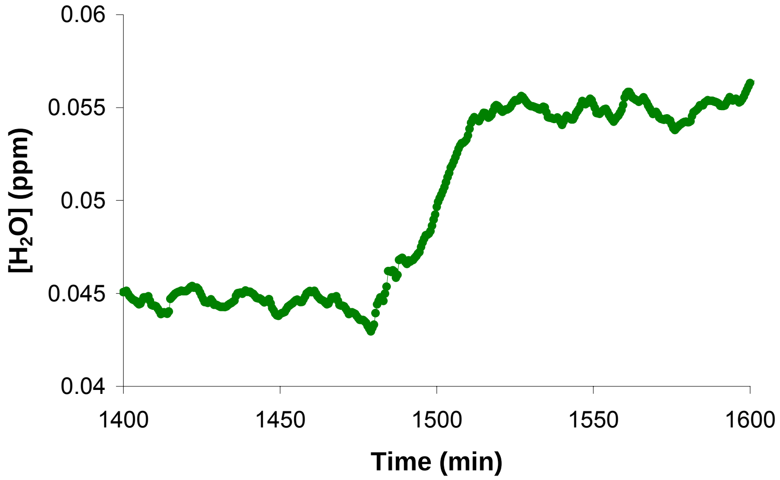


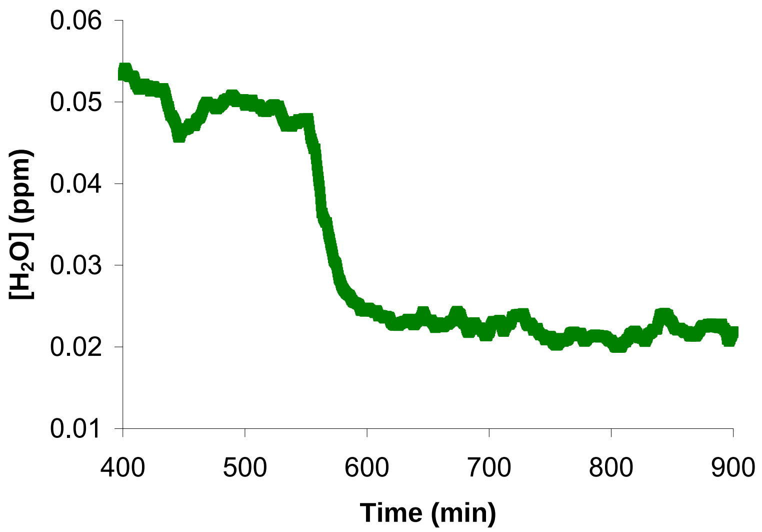


Linearity and correlation between H_2O measured and H_2O added in N_2

Ametek 5800: Response to Changes in Trace H_2O

Water vapor wet-up response in N_2: Ametek took 47 minutes to reach 95% of the final value for the step 44.6 – 55.4 ppb





Water vapor dry-down in N_2: Ametek took 72 minutes to reach 95% of the final value for the step 49.8 – 23.2 ppb

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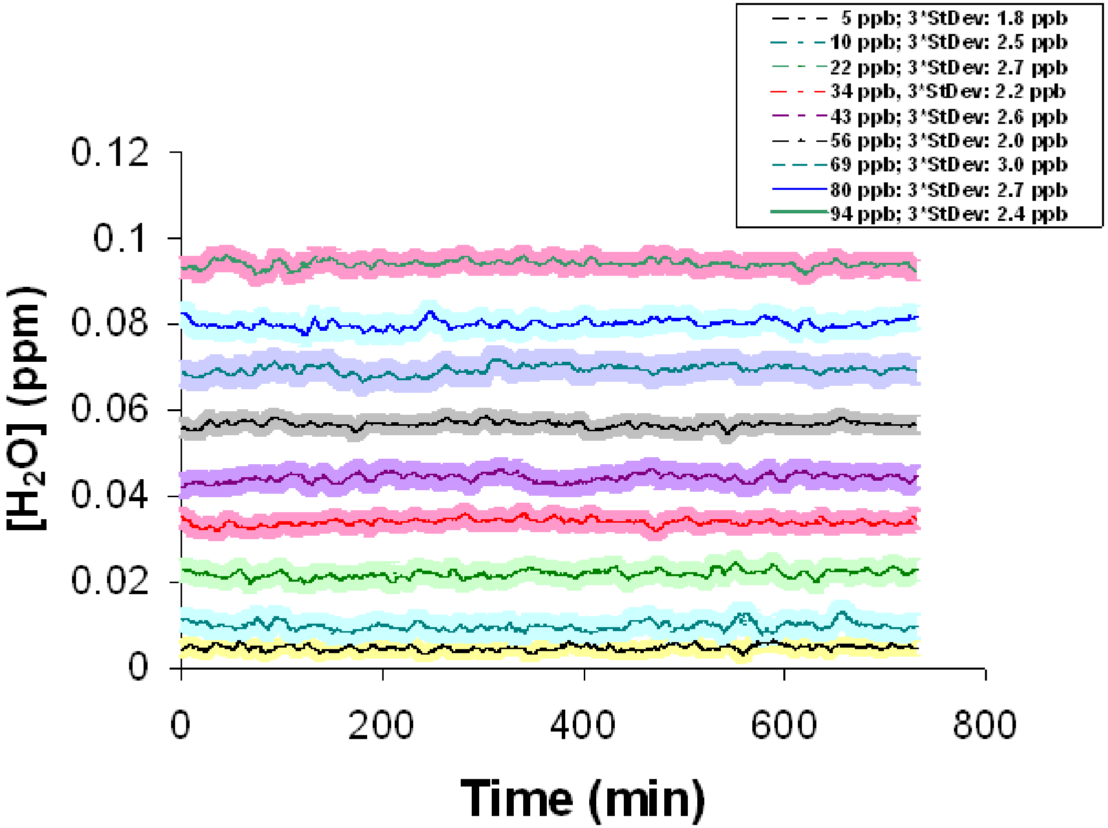
Ametek 5800: Trace Water Vapor Measurement Stability Test in N_2



- Sensitivity is 2.4 ppb (average over 0-100 ppb range)
- Detection limit ~5 ppb in Nitrogen
- MDL dependent on dryness of the reference stream

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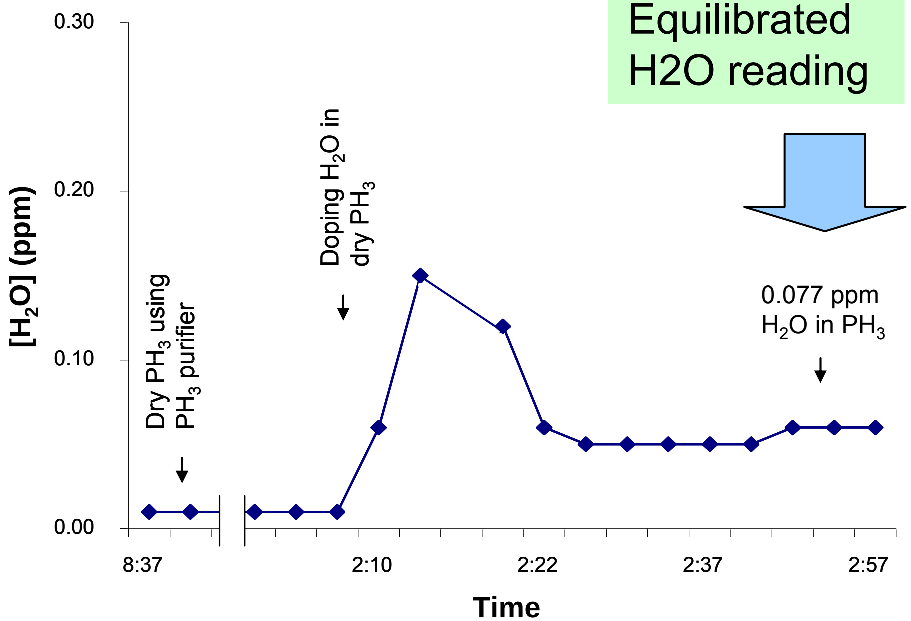
Trace H_2O Analysis in Phosphine

Equilibrated H2O reading



Trace water vapor doping into dry PH_3 using Nanochem PHX purifier

- QCM technology shows capability for measuring [H_2O] in gases such as PH_3, based on frequency difference of sample gas and reference gas line.
- Reference based method
- Issues observed with switching between N_2 and PH_3 references due to equilibrium of purifier
- Difficulties experienced with use of different reference matrix to sample matrix due molecular weight difference.
- Sensor lifetime also affected by gases such as phosphine

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Cavity Ring-down Spectroscopy

- Cavity ring-down spectroscopy (CRDS) [1] developed since late 1980s.
- CRDS uses narrow-frequency, tunable laser diodes with ultra-high finesse optical cells to provide highly spectral resolution (0.0001 cm^{-1})
- The high-reflectivity of the mirrors in the optical cavity results in an effective path length of over 40 km, which enables trace water vapor detection in nitrogen to ppt levels [2].
- Trace water measurements demonstrated in high-purity process gases, such as N_2, HCl, HBr, arsine and phosphine [3].

1. Okeefe, A Rev Sci. Instruments 59, 2544 (1988);
2. Dudek JB, Tarsa PB, Velasquez A, Wladyslawski M, Rabinowitz, P, Lehmann KK Anal Chem 75, 4599-4605 (2003);
3. Feng J, Raynor M Chen Y, *Compound Semiconductor* 13, 31 (2007)

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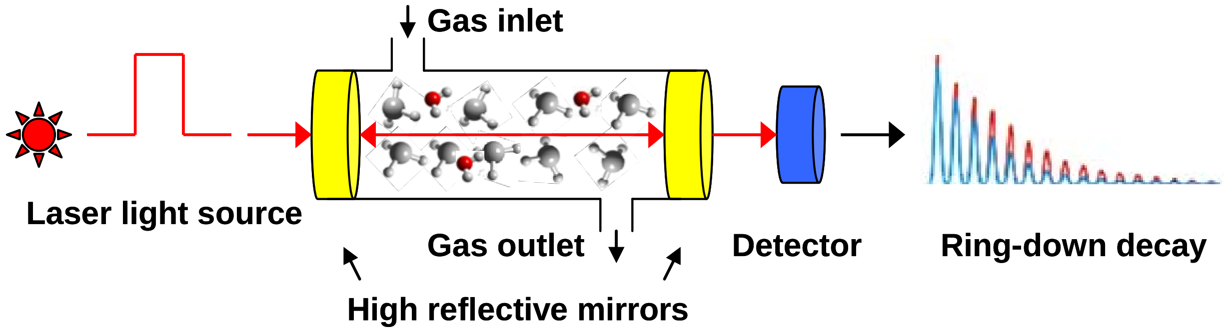
CRDS: Operating Principle



- Light is reflected by the mirrors, leaking out a tiny amount upon each reflection.
- Ring-down signal measured when the light is abruptly turned off. The decay constant increases when light is additionally absorbed by H_2O in the cavity
- Ring-down time of the sample, $\tau(\boldsymbol{v})$ is measured at a strong H_2O absorption line
- The reference ring-down time τ_0 is measured where there are no absorptions
- The H_2O concentration is calculated using:

$$1/\tau(\boldsymbol{v}) - 1/\tau_0 = c\, s(\boldsymbol{v})\, N$$

where: c = speed of light
s($\boldsymbol{v}$) = absorption cross section of molecules that absorbs light at frequency $\boldsymbol{v}$
N = number density (concentration)

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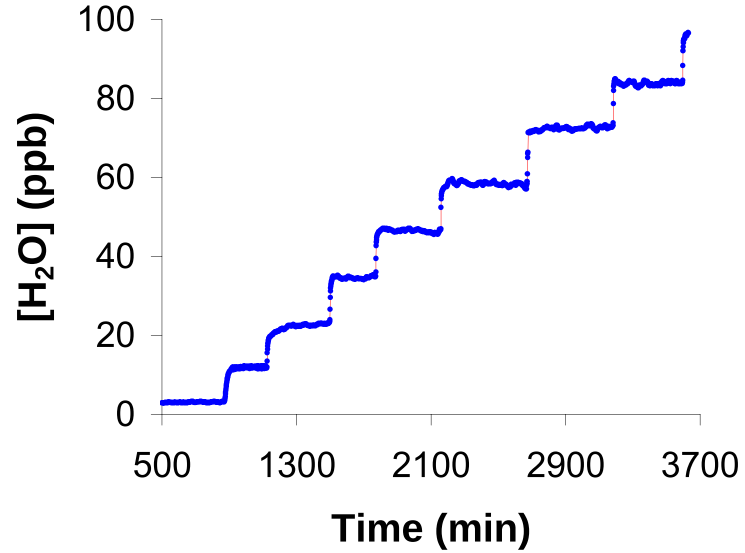
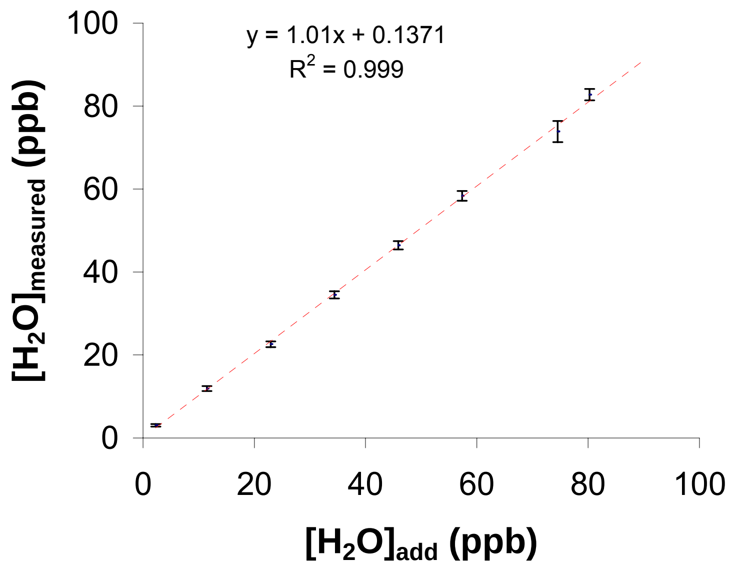
Trace H_2O Step-Addition into CRDS

H_2O measurement as H_2O challenge is increased in steps from 3 ppb to 100 ppb





Correlation of H_2O measured by Halo CRDS versus H_2O added in nitrogen

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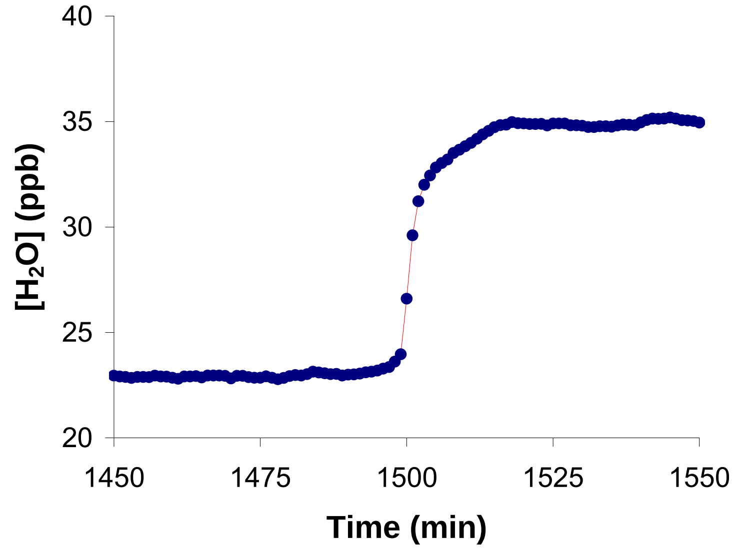
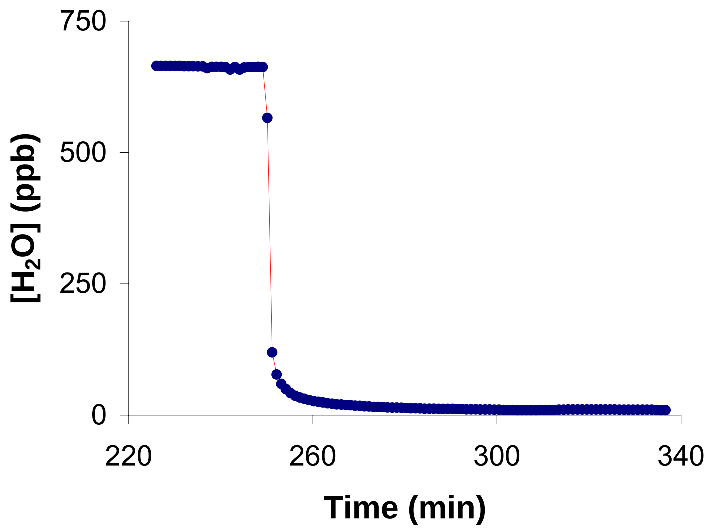
CRDS Response to Changes in Trace H_2O

Wet-up test in N_2: Halo CRDS measured 95% of the step from 23 ppb to 34.6 ppb in 15 min





Dry-down in N_2: Halo CRDS took 8 min to reach 95% of the step from 664 ppb to 0 ppb

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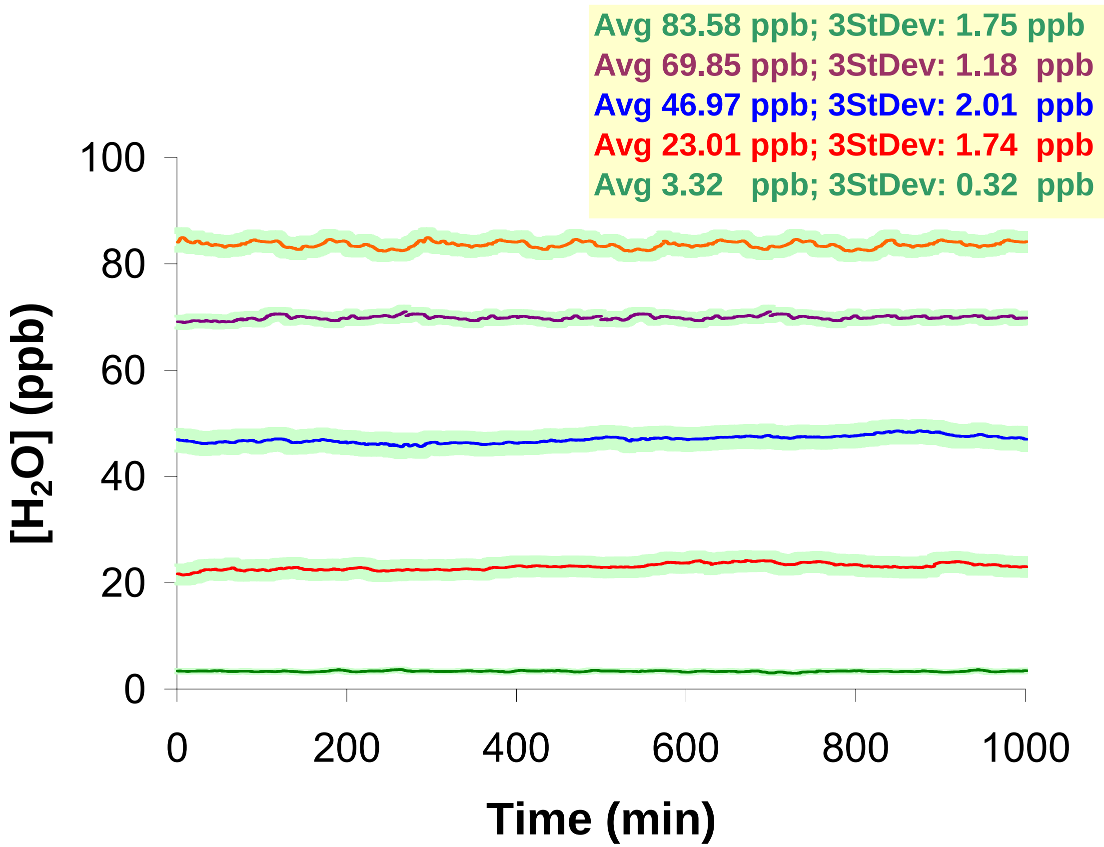
Stability of H_2O Measurements



- Sensitivity is 1.4 ppb (average over 0-100 ppb range)
- Detection limit <2 ppb in Nitrogen

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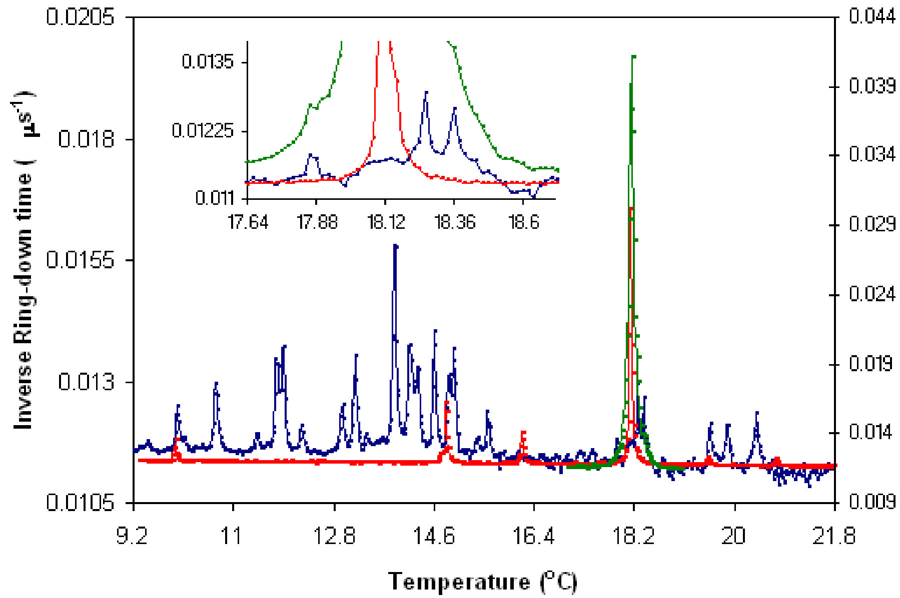
Trace H_2O Detection in PH_3 with CRDS MTO-LP

H_2O has a strong absorption that is sufficiently removed from those of PH_3 to allow detection between 1300-1400 nm at 100 torr

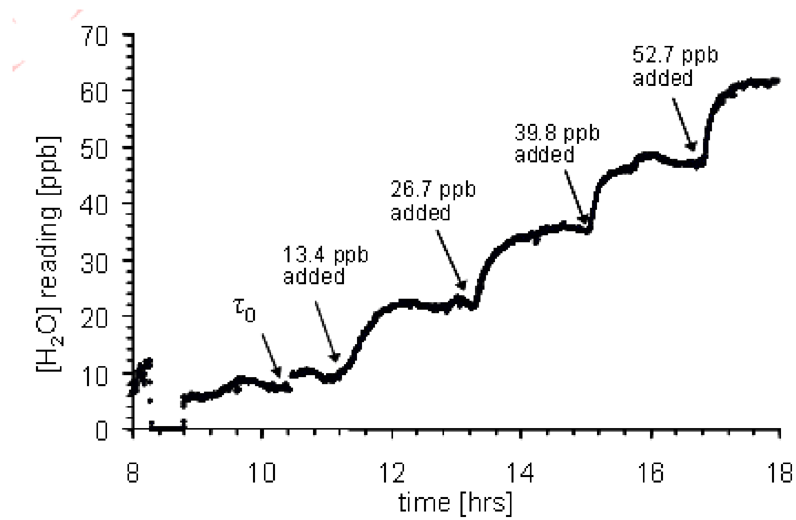
Spectra opposite show: 120 ppb water in N_2 (Red); dry PH_3 (Blue); and 1.5 ppm water in PH_3 (Green)



Sensitivity is 1.3 ppb based on 3std dev of the intercept, for a weighted linear fit.

CRDS response is linear in measured range

Zero offset of 9 ppb is due to the overlapping of PH_3 and residual water background that cannot be distinguished.

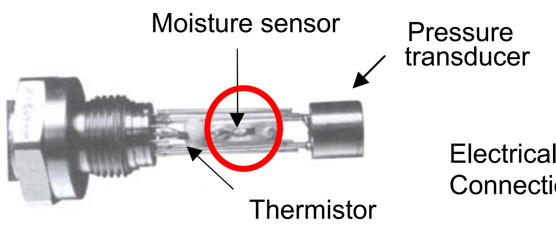


Funke H.H. et al, Applied Spectroscopy, 61 (2007) p 419

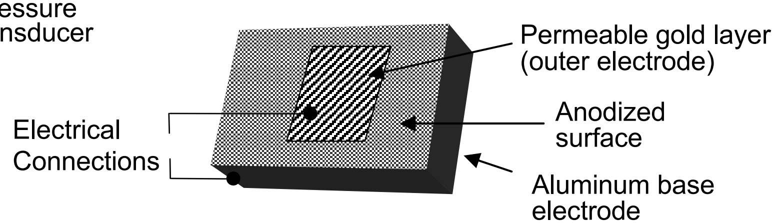
Al_2O_3 Moisture Sensor

- Alumina first proposed for H_2O sensing in 1930s and applied in early 1950s [1-2].
- Based on the correlation of the capacitance / impedance with H_2O adsorption on an Al_2O_3 film. Offers wide measurement range, minimal effects of P and T.
- Technology traditionally suffers from slow response time [3] due to the intrinsic adsorption/desorption properties of this material

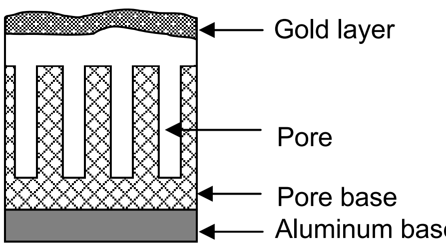
Photograph of Probe Assembly



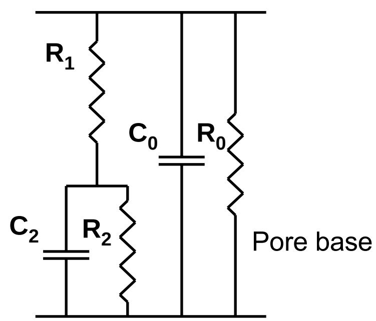
Front View of Al_2O_3 Sensor



Cross-sectional View



Impedance Model



$$C = \varepsilon\varepsilon_0 \frac{A}{d}$$

$$\varepsilon_0(vacuum) = 8.85\times10^{-12} \quad F/m$$

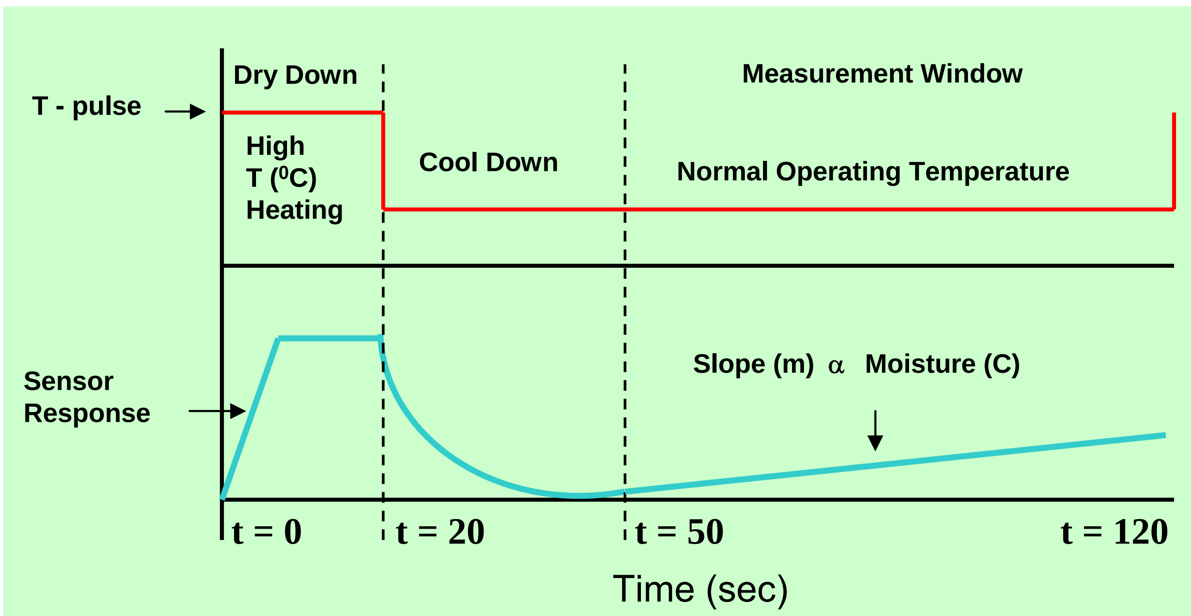
$$\varepsilon(H_2O,\ 20^0C) = 80.4$$

$$\varepsilon(Al_2O_3) \approx 9.3$$

1. Taylor, H.S.; Gould,A.J. *J. Am. Chem. Soc.*, 1934, 56 (8), 1685-1687
2. Weaver, E. R. *Anal. Chem.*, 1951, 23 (8), 1076-1080
3. Basu, S. et.al., Sensor and Actuators B 79, 182-186 (2001)

New Development in Al_2O_3 Sensors

- Al_2O_3 based H_2O sensor with integrated heating element that periodically cycles the temperature developed by GE Sensing [1].
- A temperature pulse is applied to ‘dry down’ the sensor. Then the sensor is allowed to cool down and the H_2O measurement is made based on the wet-up slope and resulting change in impedance



$$Z(f) = R(f) + jX(f)$$

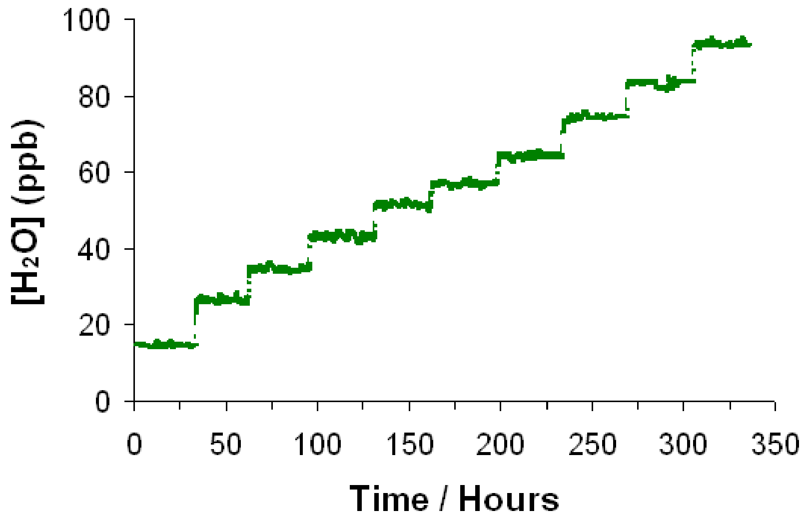
Z: impedance;
R: resistance;
X: reactance;
f: frequency

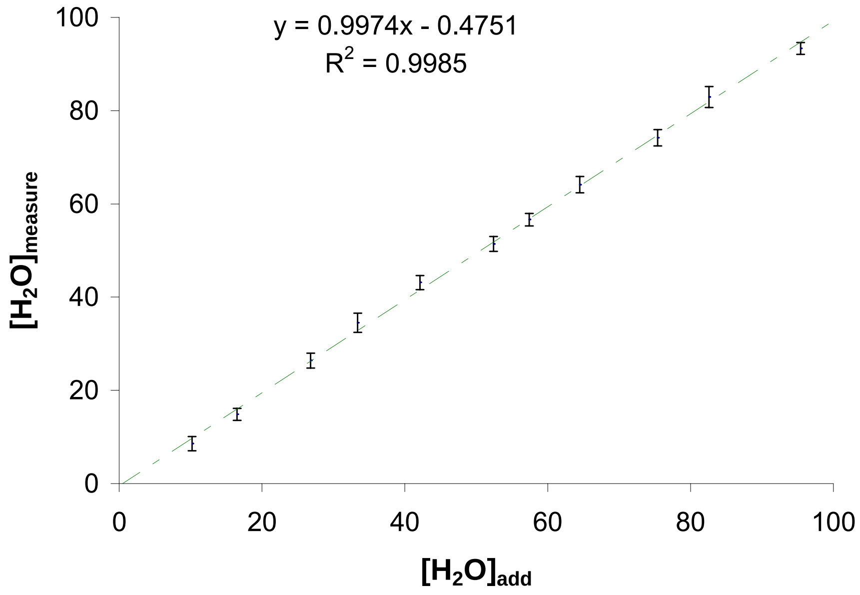
1. Kerney,J. New Method for Trace Moisture Measurement, Advances in Wafer Processing, SEMICON West, San Francisco, California, July 2007
2. Kerney J, ISA 53rd Analysis Division Symposium, Houston TX, 2008

GE HygroTrace Moisture Sensor

Trace H_2O Addition and Response of HygroTrace Sensor

H_2O measurement with H_2O step addition into purified N_2 from 15 ppb to 93 ppb





Correlation of H_2O measured and H_2O added

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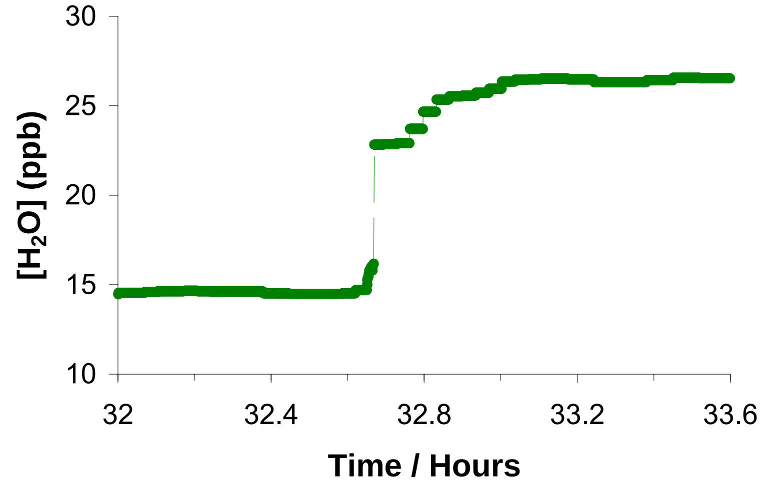
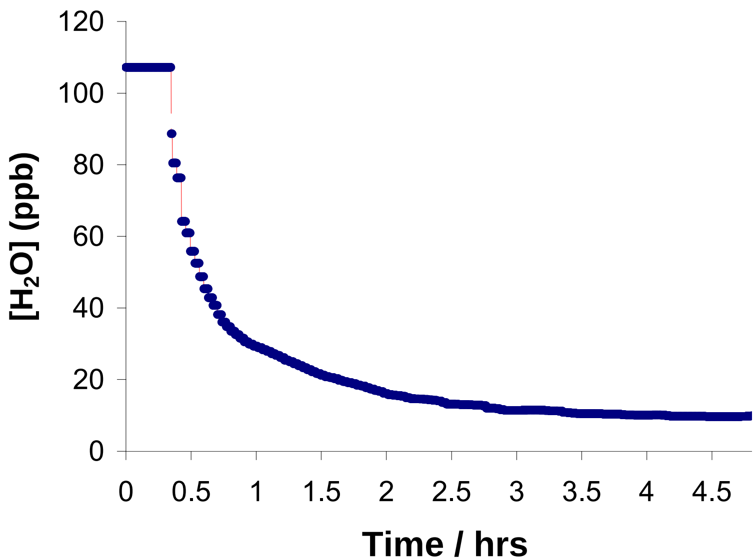
Response of HygroTrace Al_2O_3 Sensor to changes in H_2O

Wet-up Test in PN_2
HygroTrace sensor took 13 min to reach 95% of the final value during the step from 15 ppb to 26 ppb





Dry-down Test in PN_2
HygroTrace Sensor took 108 min to reach 95% of the final value during the step from 107 ppb to 10 ppb

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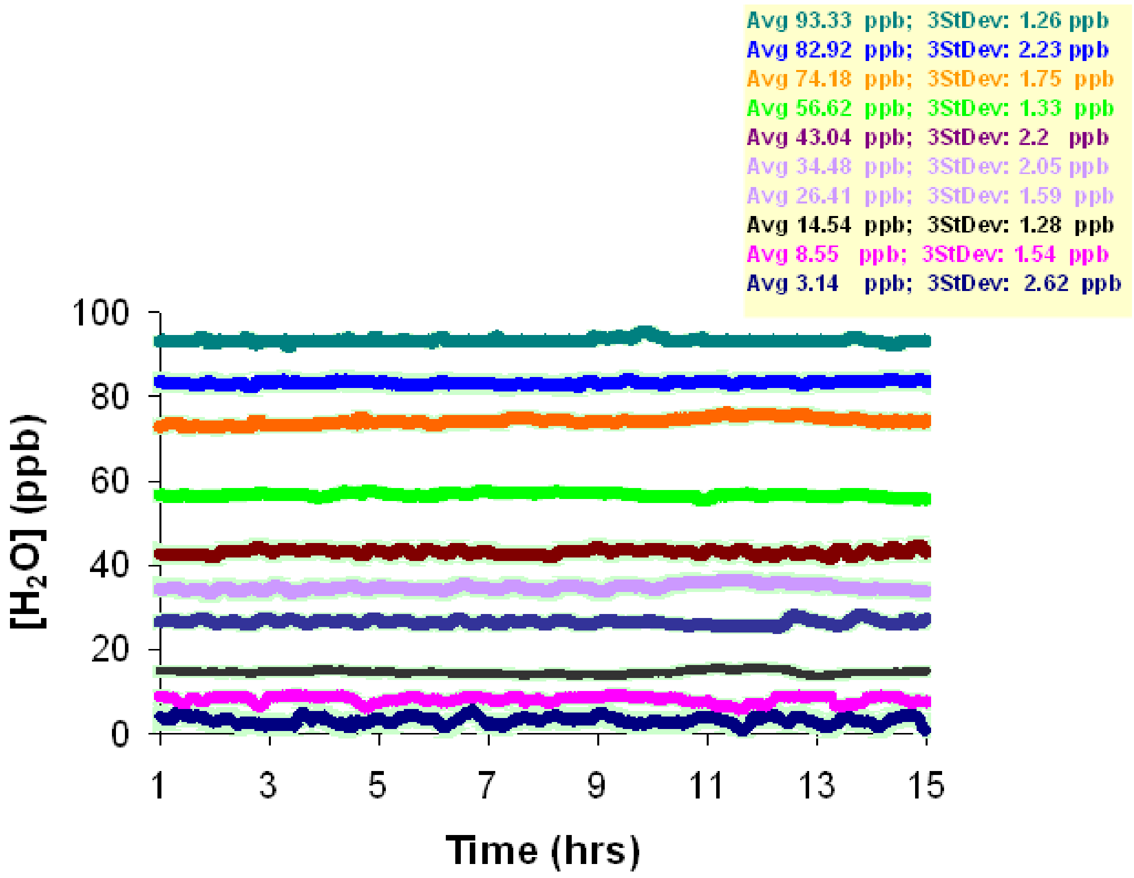
Stability of H_2O Measurements with HygroTrace Al_2O_3 Sensor



- Sensitivity is 1.8 ppb (average over 0-100 ppb range)
- Detection limit ~3 ppb* in Nitrogen (initial 3 months)
- After this DL increased to 10 ppb

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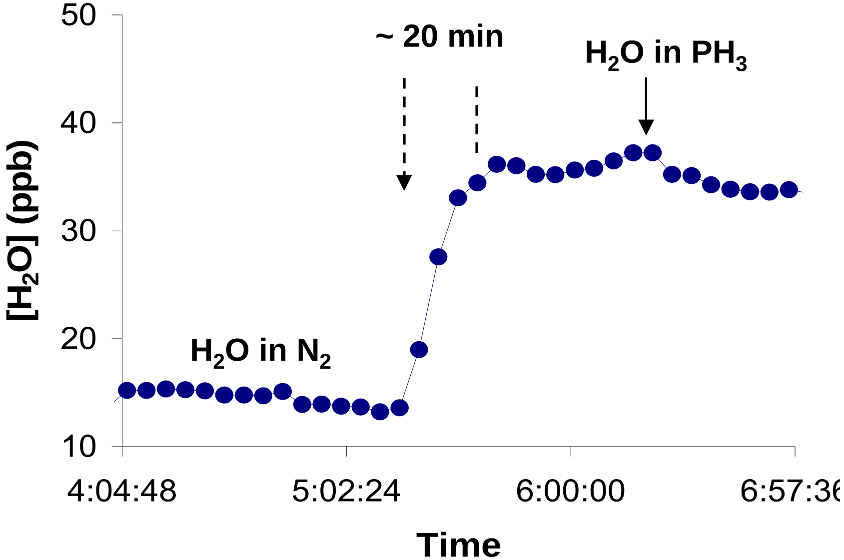
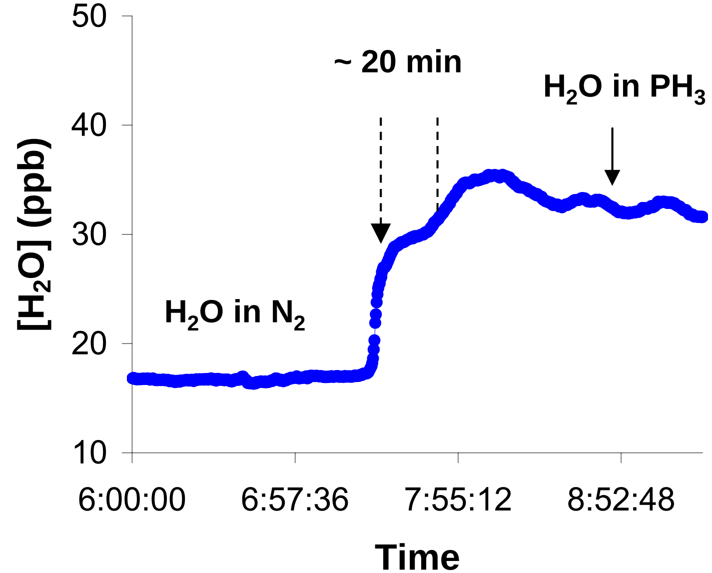
Trace Water Vapor in Ultima PH_3 Cylinder Using HygroTrace Sensor



HygroTrace Measurement



CRDS Measurement

- Preliminary study shows trace H_2O detection feasibility of Hygrotrace Al_2O_3 sensor in PH_3 versus established CRDS method

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Summary of Findings

Parameter	Ametek 5800 QCM	Halo CRDS	HygroTrace Al_2O_3 Sensor
R^2 ($[H_2O]_{measured}$ ~ $[H_2O]_{added}$)	0.998	0.999	0.9985
Sensitivity (Average 3*StDev from 0-100ppb)	2.4	1.4	1.8
Detection limit ppb (in N_2)	~ 5	< 2	~ 10
Wet-up ppb / min	(44.6 → 55.4) / 47	(23 → 34.6) / 15	(15 → 26) / 13
Dry-down ppb / min	(49.8 → 23.2) / 72	(664 → 10) / 8	(107 → 10) / 108
Stability test / min	> 700	> 1000	> 900

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Future Development Trends

Mass-based Sensors

- QCM based sensor: AMTEK moisture analyzer Model 5910 UHP has 100 pptv detection sensitivity and 150 pptv detection limit in inert gases [1];
- CNT mass-based sensor enable potentially ultra-high sensitivity of 10^{-21} g [2].

Laser Spectroscopy

- CRDS, prism CRDS, CEAS [3] , and quantum cascade laser absorption [4] technologies

Electrical Impedance-based Sensor

- Carbon nanotubes may provide new solutions for trace water vapor detection and push sensitivity and detection limits to new levels for electrical impedance measurements.

1. http://www.ametekpi.com/moisture-analyzers/AMETEK-5910UHP-Moisture-Analyzer.pdf
2. Li, Y.; Qiu, X.M.; Yang, F. et.al.; Nanotechnology 19 (2008) 165502
3. Ye, J. et.al.; Science 311, 1595-1599(2006)
4. Provencal R, Gupta M, Owano TG, et al. Applied Optics 44,6712-6717(2005)

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