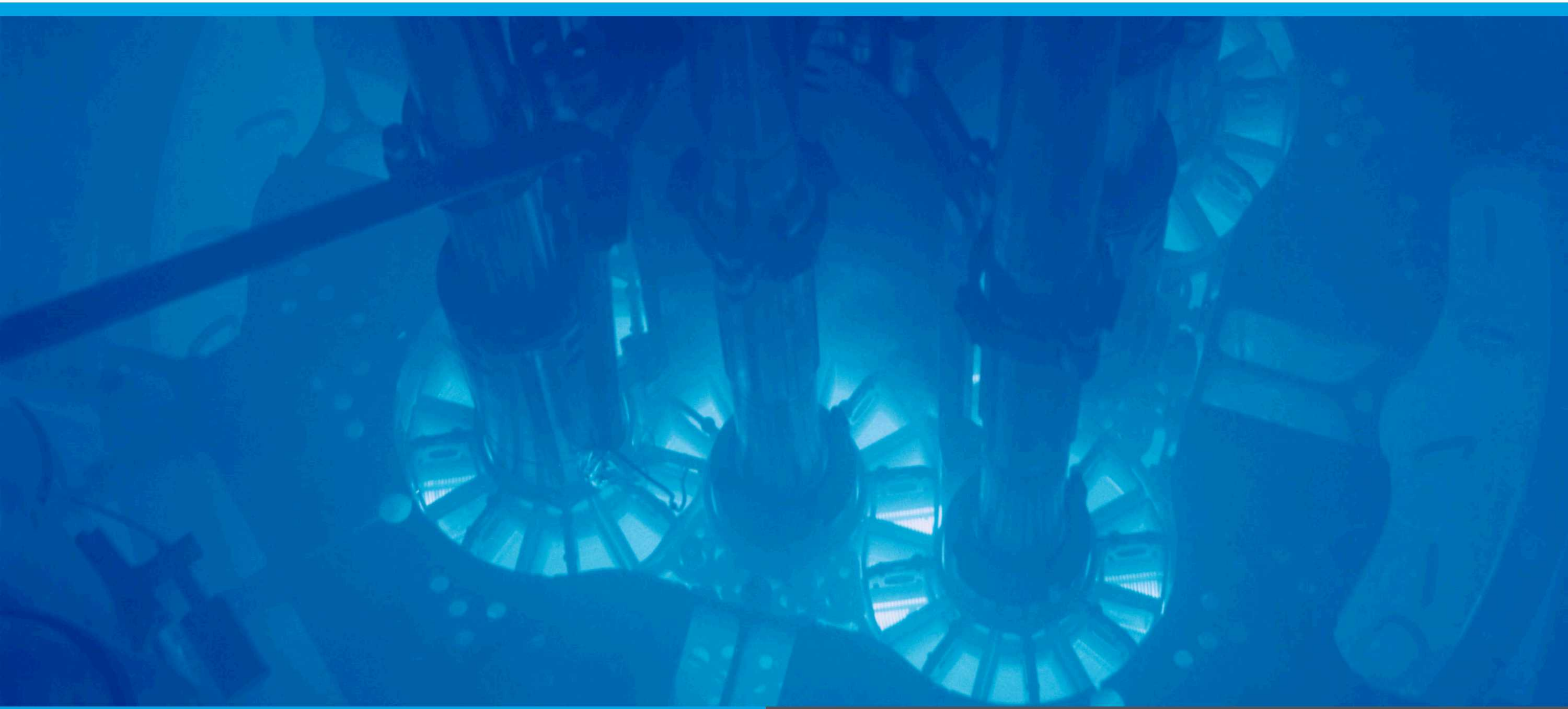
SAND2019-0874PE



High Burn-up Demonstration Cask: SNL Gas Analyses

Charles Bryan, Russell Jarek, Chris Flores, Elliott Leonard

Sandia National Laboratories

ASTM Nuclear Fuel Drying Workshop

January 29, 2019

Overview

- Sample Descriptions
- Gamma Spectroscopy □ ^{85}Kr
- Mass Spectrometry □ O_2, H_2, CH_4 (quant.); H_2O (qual.)
- Water Analysis □ H_2O (quant.)
- Lessons Learned

Sample Descriptions

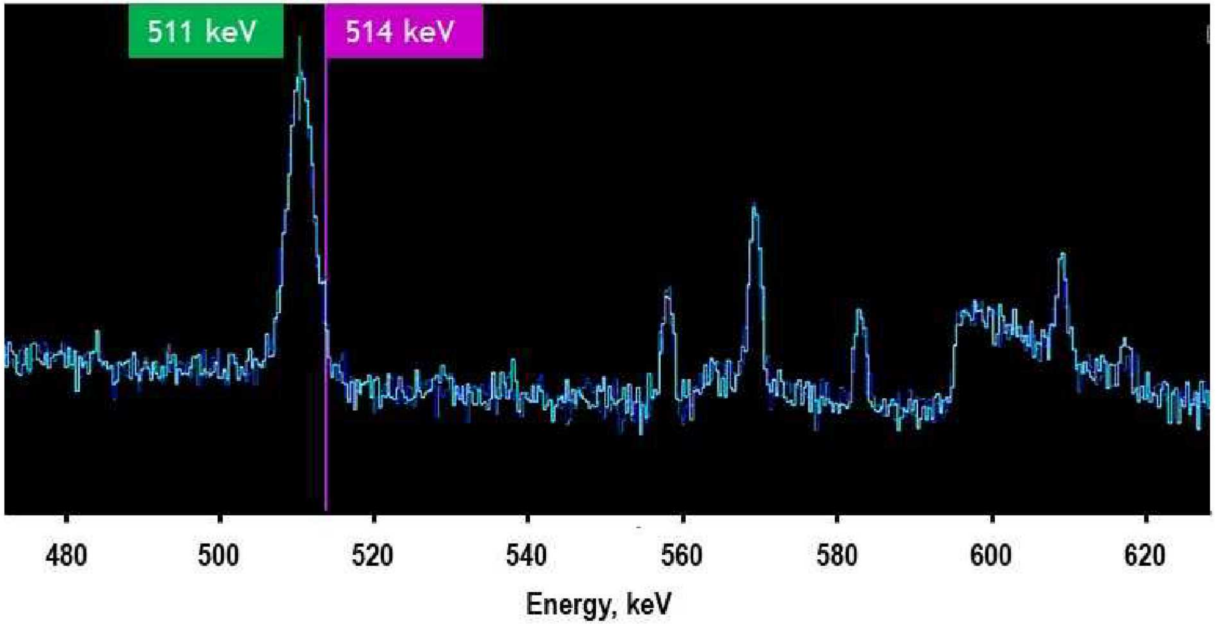
- Sample bottles
  - Sample bottle from Dominion (1L), valved on both ends
  - SNL replaced ¼-turn plug valves with high quality needle valves at cylinder ends, removed septum riser
  - To eliminate sorbed water, bottles heated to 80-90ºC while being pumped at med-high vacuum (nominally 10^{-7} Torr) for 16-24 hours. Water adsorbs strongly to polar surfaces (e.g. metal oxides, glass)
- Three samples delivered. Collection dates:
  - 11/16/17 15:21 (Initial — 4 hrs after sealing)
  - 11/21/17 11:47 (1 week after sealing)
  - 11/28/17 08:34 (2 weeks after sealing)
- Gauge pressures upon delivery recorded as being “about 20 psi”
  - Absolute pressure = 20 psi + 12.5 psi (Abq.) = 32.5 psi (2.24 bar)

Gamma Spectroscopy

- Analyzed at SNL Analytical Services Department
  - Canberra closed-end coaxial high purity germanium detector
  - Highly sensitive for ^{85}Kr — strong gamma (514keV), specific activity ~400 Ci/g, but only 0.43% of decays
  - Not useful for ^{129}I — weak gamma (40 keV), specific activity 1.7×10^{-4} Ci/g
- Initial 12-hour count: No ^{85}Kr observed
- 4.6 day (400,000 sec) extended count
  - Very long counting time yielded a complex background spectrum, including muon interactions with lead shielding(!)
  - No discernable ^{85}Kr peak (but very low levels potentially obscured by nearby $e^{-} – e^{+}$ annihilation peak (511 keV)

Conclusion:
No detectible ^{85}Kr

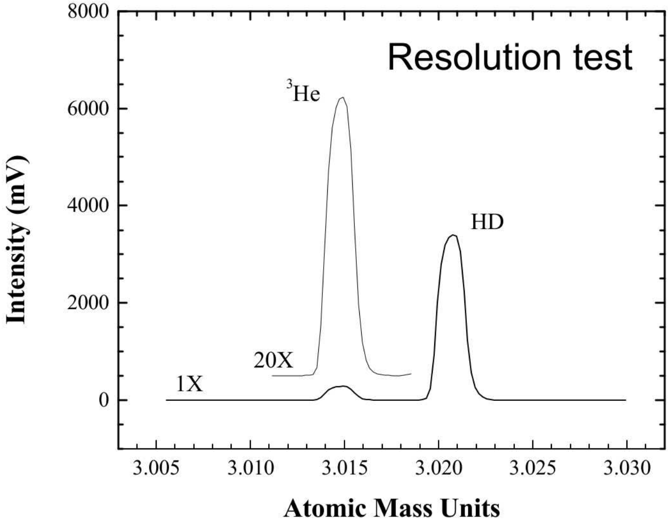
(estimated detection limit of 38 Bq (2.6×10^{-12} g) within the sample bottle)



Mass Spectrometry

- Samples measured SNL Analytical Technologies Department, on a Finnigan MAT 271 high-resolution magnetic sector mass spectrometer with a very stable gas ionization source
- Samples placed on vacuum line with a 50 cc sample vial, pumped overnight to very dry conditions. Valves opened and gas expanded into 50 cc sample vial. Valves shut, 50 cc sample vial moved to mass spec. for analysis
- Mass Spec provides:
  - Concentrations of non-sorbing gases (O_2, N_2, H_2, CH_4) in high to trace amounts (detection limits in the few ppm range)
  - Qualitative estimate of water present (vacuum line sorption/desorption effects limit measurement accuracy)

Finnigan Mass Spec.



Mass Spectrometry Results

Major Gas Species

Gas Species	Sample 1	Sample 2	Sample 3
Sampling date	11/16/2017 15:21	11/21/2017 11:47	11/28/2017 8:34
He	Confirmed balance gas		
H_2O (est.)	0.46%	1.8%	2%
N_2	0.39%	0.07%	0.07%

Trace Level Gases

Gas Species	Sample 1 (ppmv)	Sample 2 (ppmv)	Sample 3 (ppmv)
H_2	46	287	498
CH_4	< 1	9	22
CO	nm	34	25
N_2	off scale	630	680
O_2	680	38	134
Ar	49	8	9
CO_2	103	751	930

nm – not measurable due to large N_2 signal interference.

Trends:

- High N_2, O_2, Ar in Sample 1: Air contamination, likely due to trapped air in the valve; much less contamination in Samples 2 and 3
- Water content low initially (Sample 1), and higher in Samples 2 and 3 (*qualitative*)
- H_2 increases with time, but O_2 changes are small. Hydrogen production by metal corrosion (facilitated by radiolysis)?
- No detectible ^{129}I or Xe isotopes (DL 1-2 ppmv)

Evidence of degradation of organic materials, probably vacuum grease ("dry" pump makes pump oil unlikely):

- CO_2 increases significantly with time (930 ppmV CO_2 = ~**3.5 grams carbon i**n the cask)
- Methane (CH_4) increases with time
- In Sample 3: Trace (low ppmv) levels of ethane/ethene and formaldehyde or alcohol
- In Sample 3: Trace HF (~10 ppmv), possibly due to degradation of perfluorinated pump oil?
- Breakdown of hydrocarbons will produce water via:

$$C_xH_y + (x + y/4)\ O_2 \rightarrow xCO_2 + y/4\ H_2O$$

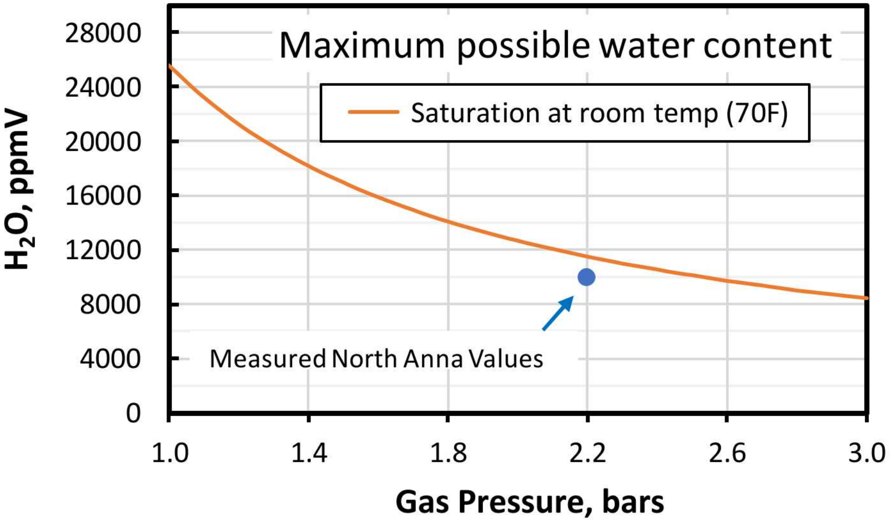
Note: This consumes O_2 (or oxidizing radicals), presumably generated by radiolysis

Water Analysis

Goal: Quantify water in HBU Demo cask

- Water will sorb strongly into sample bombs. Accurate quantification of water requires:
  - Take steps to thoroughly dry out sample bottles—to remove sorbed water—prior to use (heat under vacuum).
  - After collection, water in the gas sample will sorb onto the metal, and sample bottles must be heated during analysis to desorb water.
- Additional concern: Values measured at North Anna were close to saturation at the sample pressure. If samples were saturated, there could be free water in the sample bottles.

Solution: Samples must be heated during analysis to quantify total water, in order to account for sorbed water and potentially, free water.



Water Analysis

First attempt

- Water measured by SNL Materials Reliability Department, using an Agilent gas chromatograph with a pulsed discharge ionization detector
  - Samples measured several times. Results varied greatly, sometimes greatly exceeding saturation at the measurement conditions (P,T)
  - Uniformly heating bottle and instrument lines to desorb water was difficult
  - **Method abandoned**

Subsequent Efforts (SNL Primary Standards Lab)

- Second attempt: Sample bottles placed in a loop in an oven, and gas pumped through heated lines to a RH Systems chilled mirror with an internal pump for measurement.
  - **Results:** Internal pump failed. Sample #1 measured at room temp., but was lost

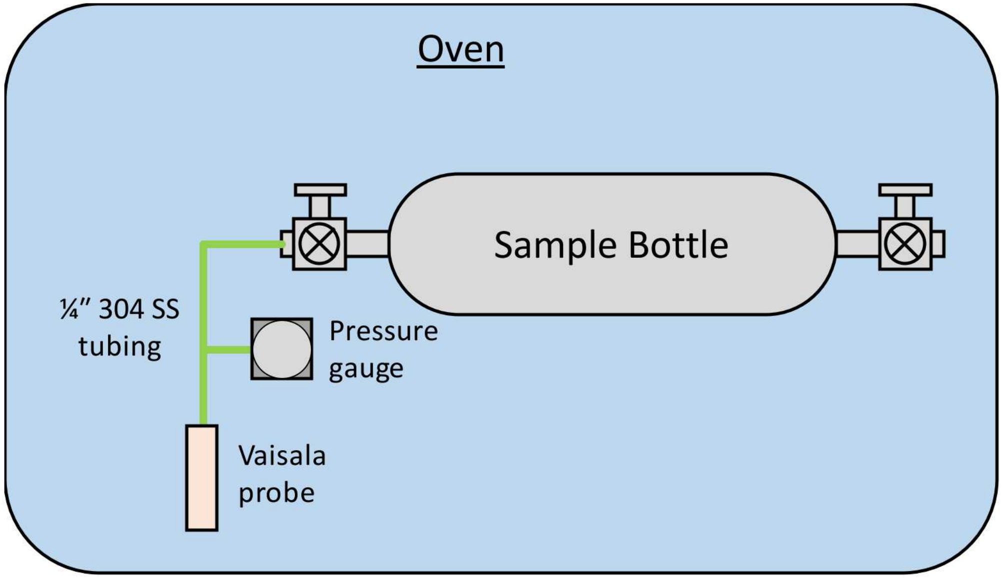
- Third attempt: Similar setup, but gas pumped through a different chilled mirror using an external pump.
  - **Results:**
  - Diaphragm pump immediately failed. Sample #2 partially compromised (static value of 10,500 ppmV H_2O measured, but highly uncertain due to short equilibration time).

Conclusion—needle values on the sample bottles restricted flow greatly, creating back-pressure and damaging pumps. Using existing sample bottles, cannot circulate the gas through a loop.

Water Analysis: Final Method

Final method

- Vaisala temperature/RH probe (model HMP77B, range 0-100% RH, -70ºC -160ºC)
- Measurement done completely within oven. Probe attached to one end of bottle. Sample bottle valve opened and gas allowed to equilibrate.
  - Method worked, but each temperature step required hours to equilibrate, because of restricted flow through the needle valve.
  - Temperatures over 65°C were not used (pressure gauge limited to <80°C).
  - Samples 2 and 3 were analyzed, each taken through 2 temperature ramps.



Water Analysis Results: Sample #1

Sample #1:

- Pump failed, but Sample #1 measured H_2O = 2100 ppmv at ambient temperature (static conditions)
- Roughly consistent with North Anna measurements of ~1630 ppmv
- Sample lost when pump failed, so no temperature ramp data was collected
- A gas standard was measured under the same conditions:
  - Actual: 11,541 ppmv H_2O in nitrogen at 810 Torr
  - Measured: 11,044 ppmv H_2O.

Water Analysis Results : Sample #2

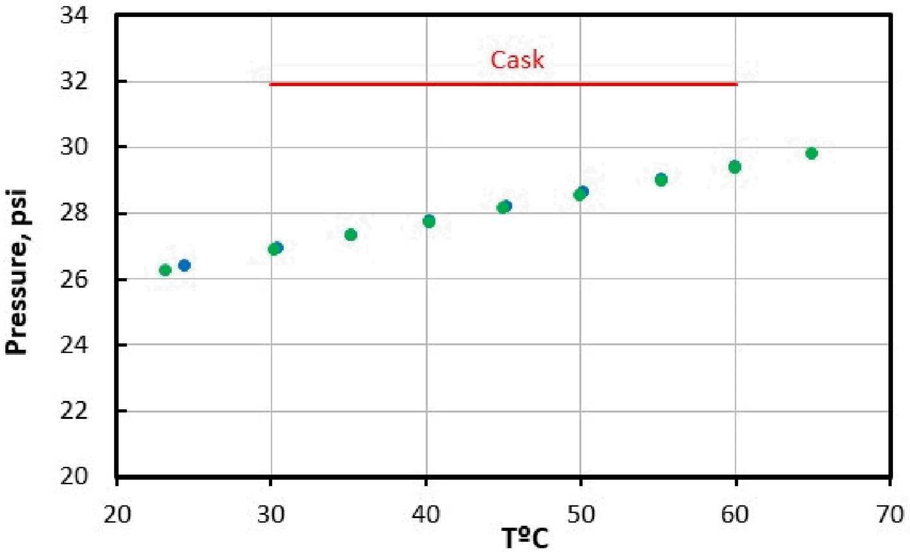
(possibly compromised by earlier effort)

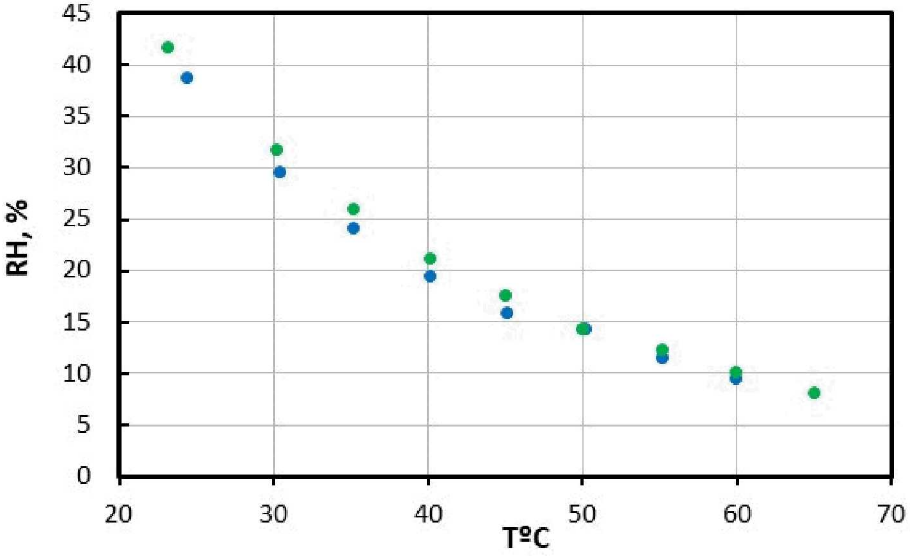
Sample #2:

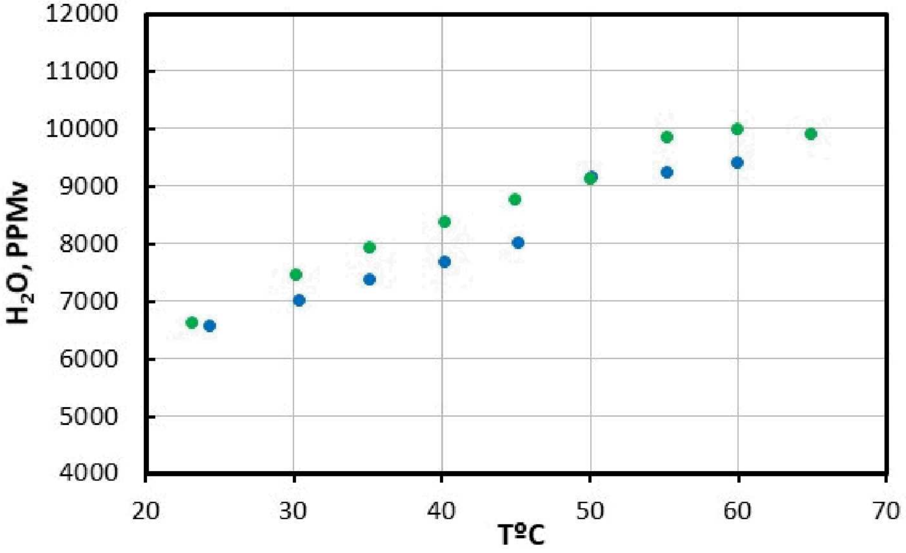
- H_2O ppmv = 6570 at 24.4ºC
  6610 at 23.2ºC
- H_2O ppmv = 9240 at 60ºC
  9970 at 60ºC

Precision ~5% (largely due to variations in equilibration time)

North Anna measured ~8,900 ppmv at ambient T. Why the lower ambient values here? ***Possible water loss due to sorption to the tubing during the previous failed attempt.***





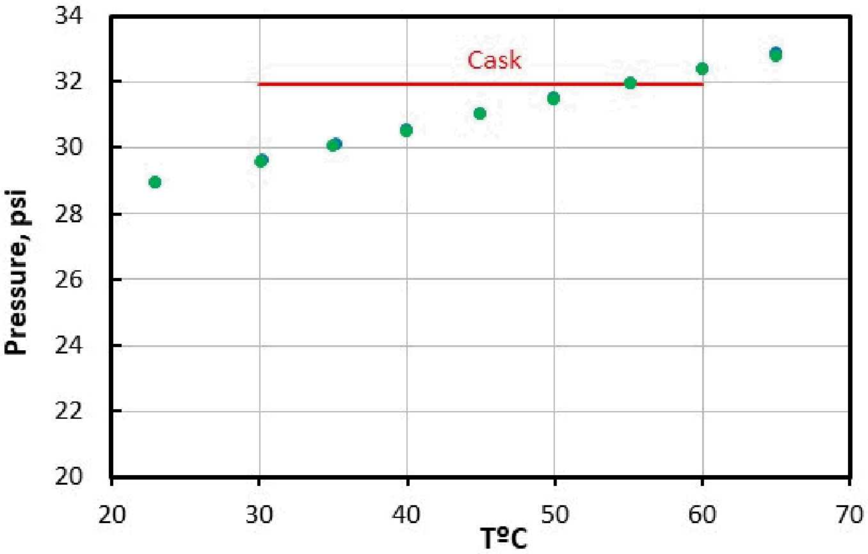


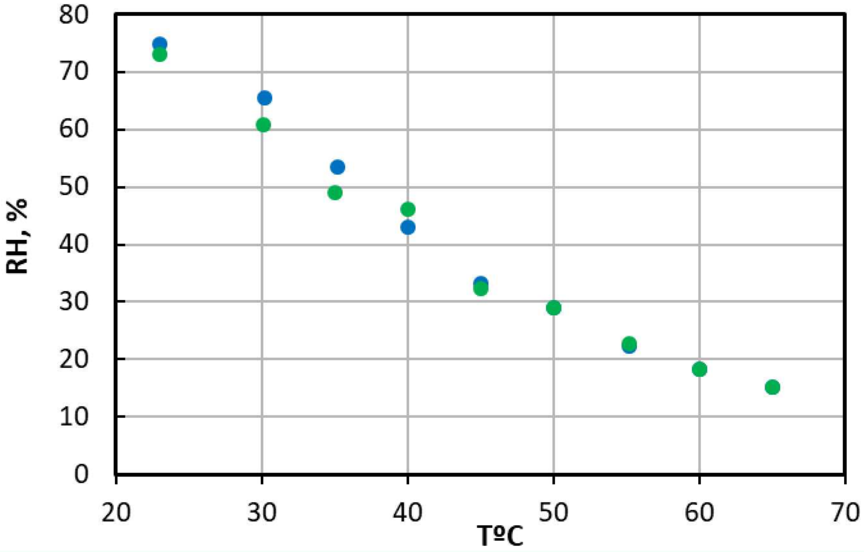
Water Analysis Results: Sample #3

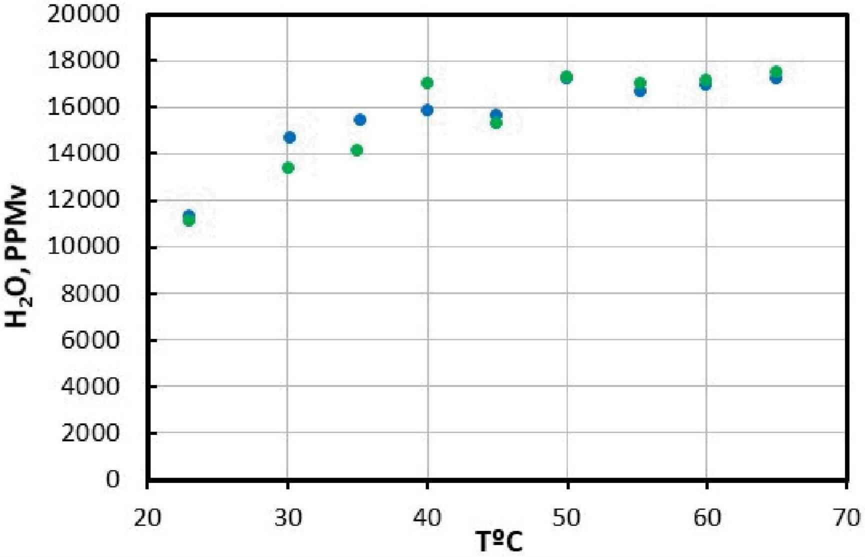
Sample #3:

- H_2O ppmv = 11,340 at 23°C
  11,100 at 23°C
- H_2O ppmv = 17,260 at 60°C
  17,540 at 60°C
- Water content appears to level out over 50°C.

North Anna measured ~8,300 ppmv at ambient T. Ambient values measured at SNL are slightly higher; high temperature values, about double the North Anna values.







Water Analysis: Standard

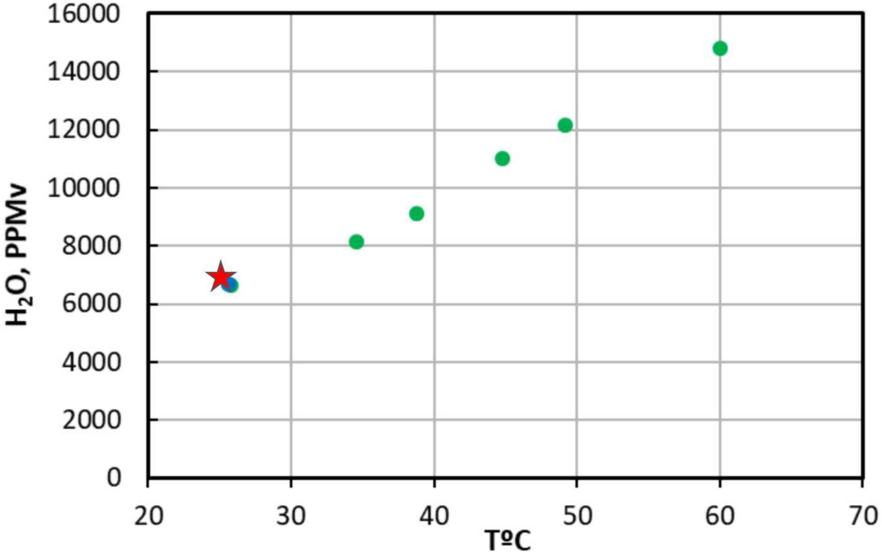
Standard:

- Made by Thunder Scientific, Corp.
- 2.2 bars nitrogen
- H_2O ppmV = 6999 ppmv at 25.5°C

Measured H_2O Values:

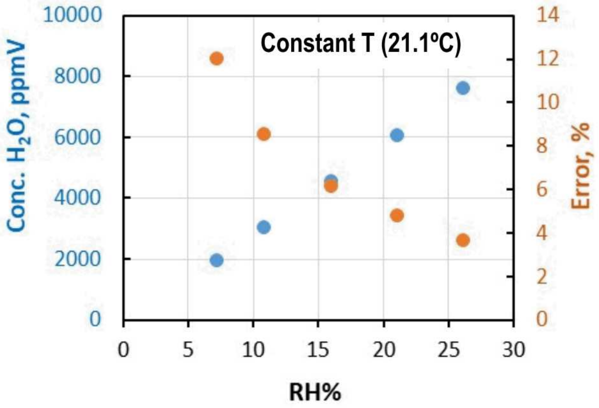
- 6633 ppmv at 25.8ºC
- 6686 ppmv at 25.6ºC
- As with the samples, ramping up temperature resulted in significant increases due to desorption (different response, but different bottle)

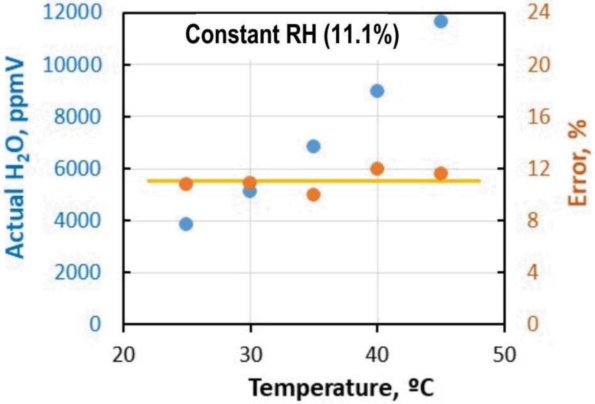
Measured values 5% low



Vaisala probe calibration check:

- At constant T, % error decreases with increasing RH.
- At constant RH (water activity), % Error is constant with Temp.
- **For sample #3 (60-65ºC, 15% RH), measured values should be ~6-7% high.**





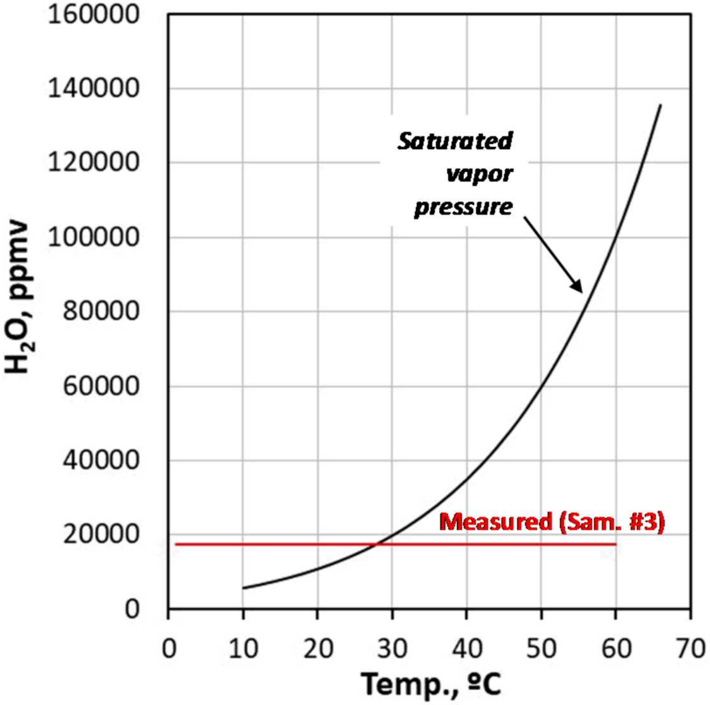
Tests are inconsistent. Rather than attempting to adjust measured values, assume ± 10% uncertainty.

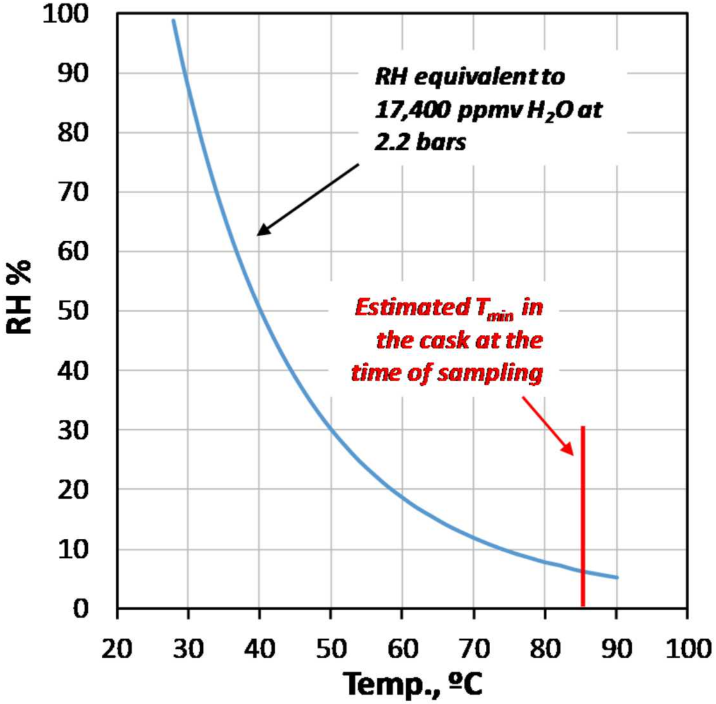
Water Analysis: Implications

Assume Sample 3 water content at 65ºC (17, 400 ppmv ±10%) represents cask gas phase.

- Water content at cask pressure (2.2 bars) is equivalent to saturated water vapor at <30ºC.
- At estimated lowest temperature in the cask (85ºC) at the time of sampling, measured water content is equal to <10% RH.

If the gas phase in the cask is *well-mixed and homogeneous*, then there is no free water in the cask, unless it is trapped in inaccessible locations





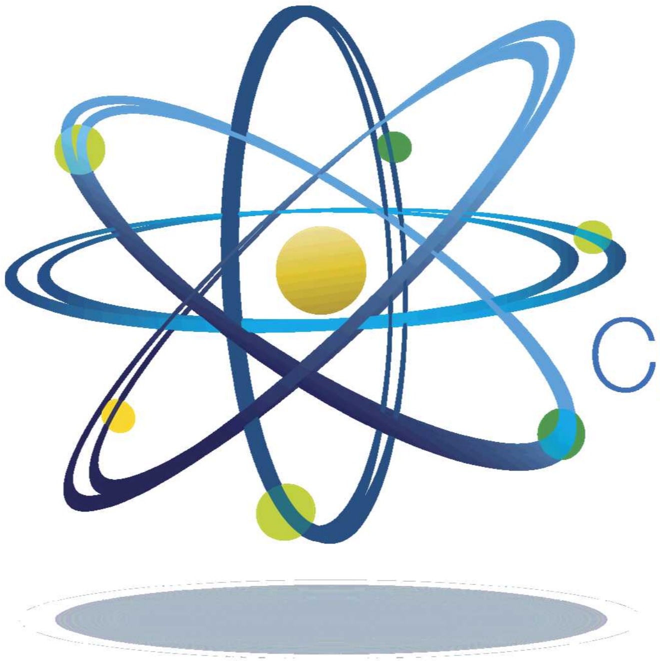
Water Analysis: Lessons Learned

- SNL needle valves preserved sample for long periods, but restricted airflow and constrained possible analytical methods. Depending upon type of analysis and timing of analysis, may be unnecessary.
- Accurate water measurements require accounting for sorbed water within the sample bottles.
  - Heating method straightforward, but cumbersome or impossible for some detection methods
  - Isotopic tracer? Many benefits…
  - For in-line measurement (experimental systems?), recirculate sample through a heated loop allowing equilibration between surface-bound water and the gas-phase, and then measure at that temperature. Requires in-line high temperature water analysis probe like the Vaisala or preferably, chilled mirror instrument (e.g. Mitchell S8000).
- Current method (Vaisala probe) relatively low accuracy. Alternative methods in discussion
  - Cold trap? Simple gravimetric measurement.
  - Isotopic tracer (D_2O spike)? Many benefits.
    - No heating required during analysis.
    - Simple measurement with a portable unit (e.g., Los Gatos Water Vapor Isotope Analyzer).
    - High accuracy, essentially limited to accuracy of µL syringe used to inject the spike through a septum and into the sample bottle.

Conclusions:

- No detectible ^{85}Kr
- H_2 builds up to over 500 ppmV in two weeks. Possible sources:
  - Produced directly by metal reduction of H_2O
  - Produced by radiolysis (also produces reactive oxidizing radicals)
- High CO_2 suggests oxidation of organic material in cask (pump oil) Requires oxidizing compounds produced by radiolysis.
- O_2 variable but low. *Two* sinks for O_2 or oxidizing radials produced by radiolysis: reactions with metal or with hydrocarbon.
- Water:
  - No condensate in sample bottles. Ambient temperature values from SNL are consistent with those measured at North Anna; but sorbed water is very significant, and must be desorbed by heating prior to analysis.
  - Sample #3 values indicate that after 2 weeks, ~17,400 ppmv H_2O (~100 ml) in the cask gas phase.
  - Liquid water in the cask? Probably not, but a topic of discussion.
- Lessons learned:
  - Needle valves preserve sample, but restrict airflow and constrain possible analytical methods.
  - Accurate water measurements require accounting for sorbed water within the sample bottles.
  - Current method (Vaisala probe) relatively low accuracy. Chilled mirror better if possible—good for experimental systems where in-line loop circulation is possible. Alternative methods in discussion.
    - Cold trap?
    - Isotopic tracer (D_2O spike)?

Questions?



Clean. **Reliable. Nuclear.**

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. SAND2018-12583 PE