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Multiplexed Quadrupole Mass Spectrometry for Monitoring of Oxygen and Contaminants in Gloveboxes and Tanks: a progress report

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Outline

- Background
- Project Goals
- Prototype test system
- Time Constants in the Pumping System
- Early Data, Closures/Sensitivities with and without O_2
- O_2 Conditioning
- Recovery-time experiments
- No-emission experiments
- Need for Standards, every cycle
- Path forward, optimization: shorter path lengths, smaller volumes, single orifice, lower source pressure, passivated chamber, different QMS, filament choices
- Summary and Conclusions

Background

- WETF: Category 2 nuclear facility, tritium
- OMS: SS system for worker safety
- prevent flammable gas mixtures in GBs and tanks
- < 5%O_2 (but alarm limit is < 3%)
- 8 Glove Boxes, 2 LPR sample loops, 2 catalytic reactors

How may we provide equivalent or better safety at a substantially lower operational cost?

Existing system

(a)

(b)

(a) Typical O2 cell housing

(b) Glove Box O2 local alarm box

- O_2 sensors sit in glovebox, passive sampling
- alarm boxes inform workers of elevated levels
- other actions (purge) take ~ minutes, may require operator intervention

Existing system

Teledyne Model 3220

- with B-1 or B-3 electrochemical cells

Considerations:

- Mostly specific to oxygen
- Sensitive to pressure
- Accuracy
- Maintenance
- Supply chain
- Mixed waste

Potential QMS system advantages

- Relatively insensitive to pressure
  - eliminate pressure regulation loops?
- Recalibrate without breaching gloveboxes
- *Single unit to serve multiple gloveboxes*
- May quantify multiple species in addition to O_2
- Increased accuracy → less alarm point uncertainty
- Reduced system downtime

QMS system

- Choose consumable parts for long life (e.g., valves > 2M cycles)
- Components should be easy to replace
- Industry standard QMS for first iteration (Pfeiffer QMG 250 PrismaPro)
  - open ion source
  - tungsten filament

Project goals

- Multiplexed contaminant monitoring system
- Sampling of tanks at different pressures
- Interface for status/alarms to the instrumentation and control system (ICS)
- Minimum required measurement time
- Accuracy much higher than electrochemical method, for all sampling conditions

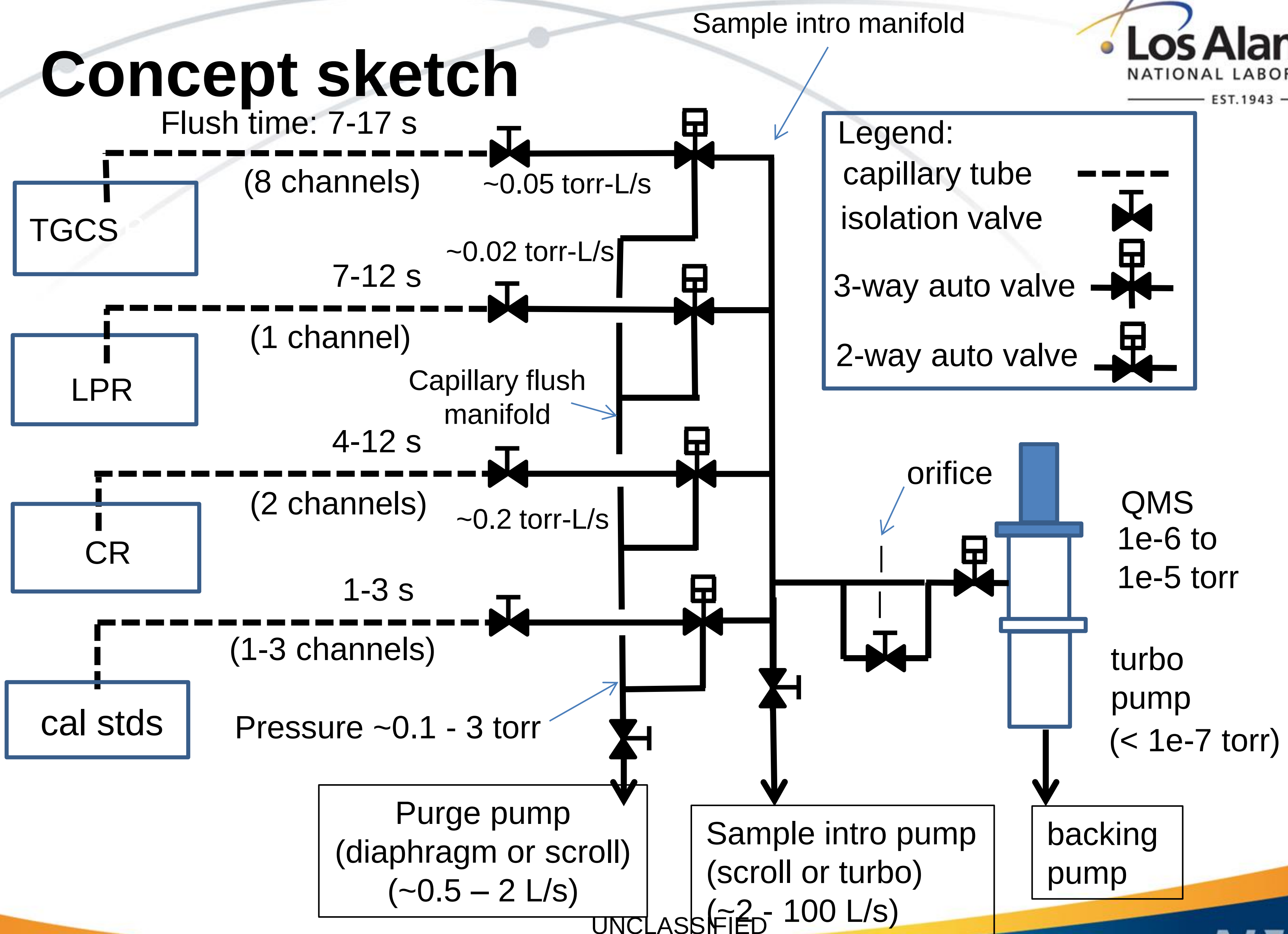
Tasks and deliverables, 1/2

- Determine requirements for performance and interfaces of analyzer and system ✓
- Analyze capillary dimensions required for servicing all gloveboxes and tanks ✓
- Design of sample introduction scheme (orifice, batch inlet volume, etc.) ✓
- Specify RGA/QMS with interface and software to meet analysis and I/O requirements ✓
- Specify valve, pumps, gauges, etc. to multiplexing assembly ✓

Tasks and deliverables, 2/2

- Construction and testing ✓
- "Cold" experiments for performance of different sampling schemes. Software development and interface testing. *in process*
- Optimization of system. Tradeoff of sampling rate vs. accuracy
- Transition to field testing with facility support

Concept sketch



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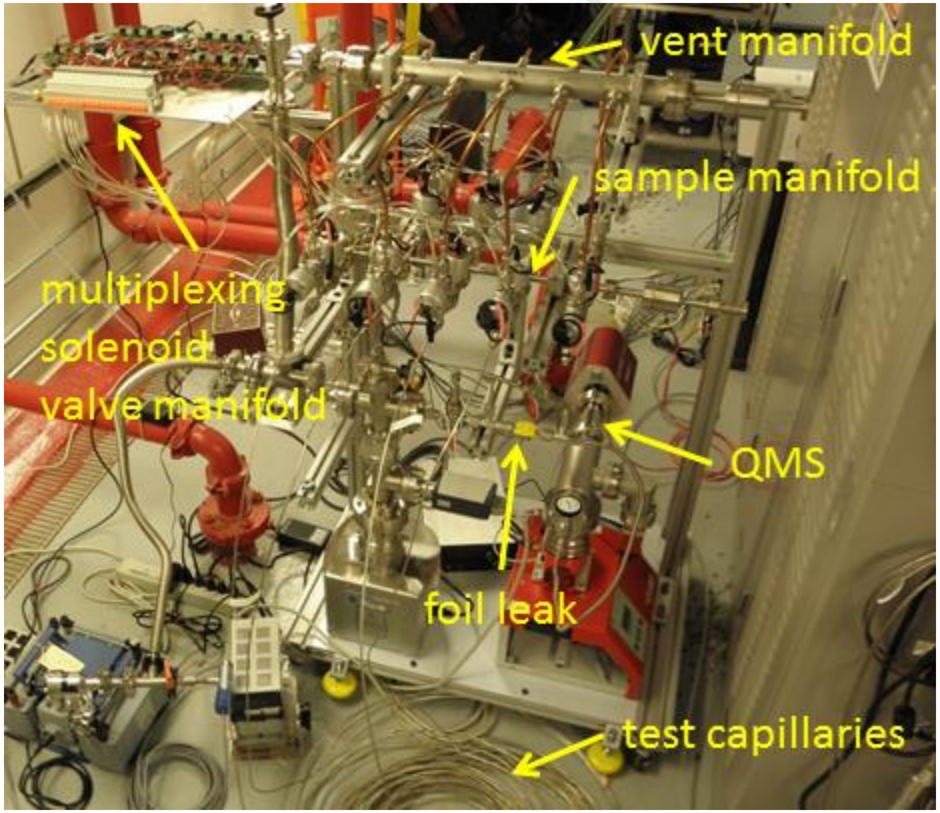
Constructed test system

- Modular
- Reconfigurable
- Solenoid valve control is accessible for testing
- Will be easy to render more compact



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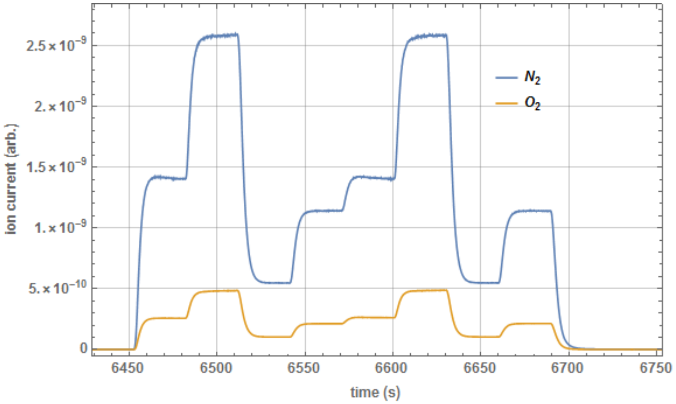
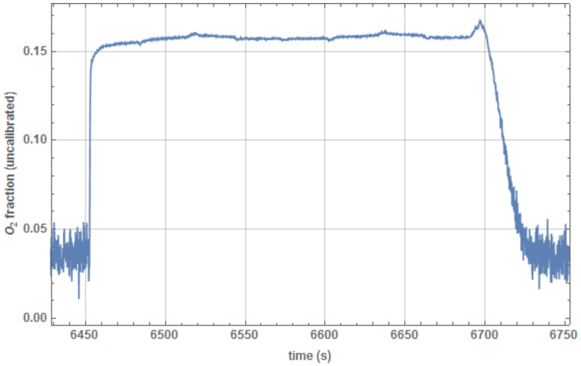
Constructed test system

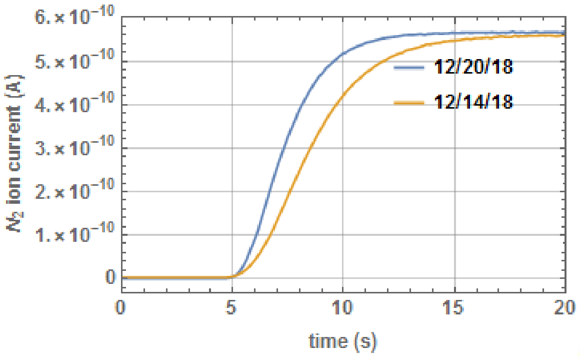
- Gases used:
  - N_2, 2%O_2 (balance N_2), 4%O_2, 6%O_2, air, He
  - O_2 mixtures are known to +/- 10% relative
- Capillaries:
  - 0.015” and 0.020” inner diameter
  - 20’ to 100’ lengths
- 10 sampling ports available on manifold

Early tests

- Sample gas is air
- Check response time of sampling manifold
- Check consistency of O_2 fraction measured for different capillaries







- Response time was improved by reducing volume of fittings in inlet system

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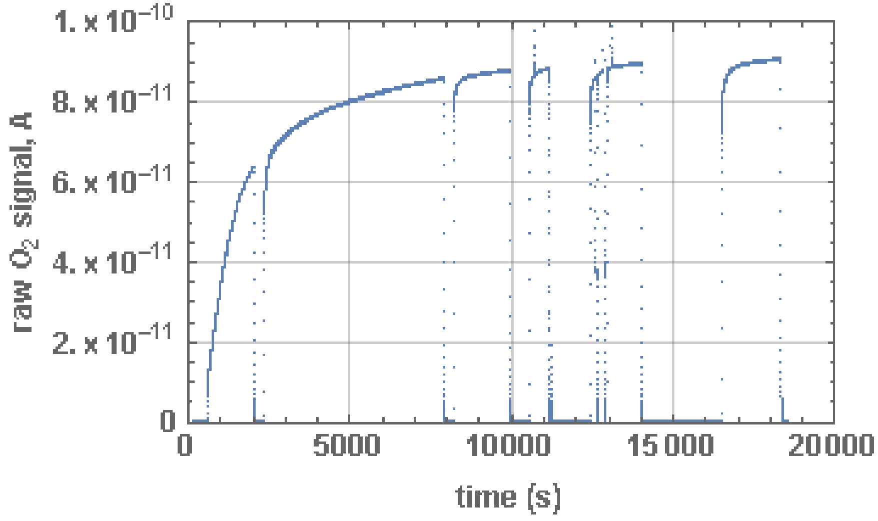
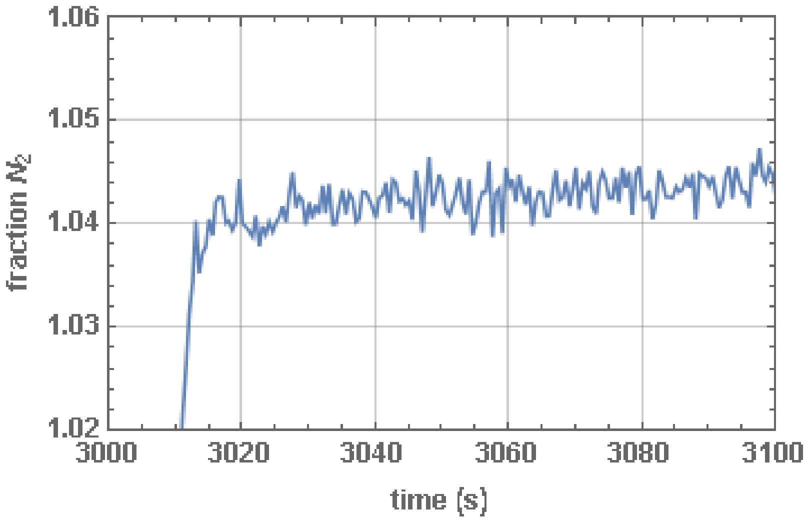
Initial calibration

- Calibrate against air, using accepted values for N_2, O_2, Ar, and CO_2
- Sample for 4-5 h to allow stabilization
- Test pure N_2 ➔ Sensitivity for N_2 is too high, closure ~104%!



(a) sampling air at constant pressure



(b) sampling N_2 at constant pressure

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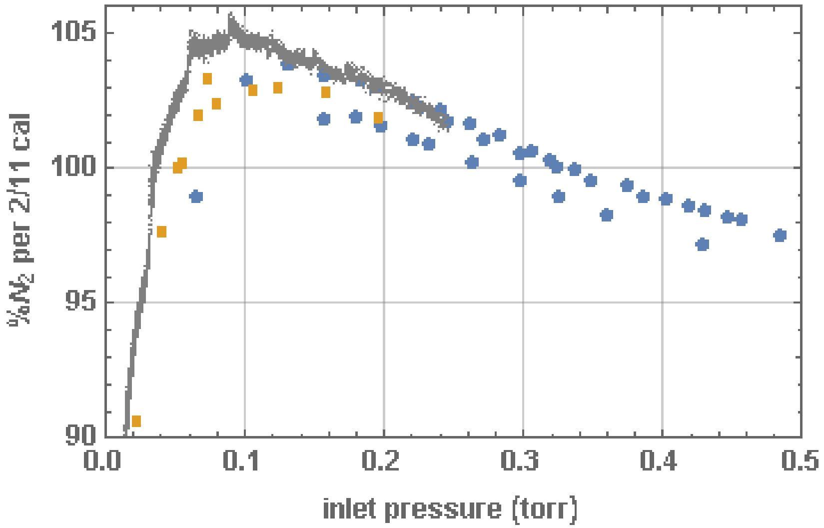
Nonlinearity of sensitivity

- There are some nonlinear effects on sensitivity:
  - Sensitivity is pressure-dependent,
    - depressed by space charge at higher inlet pressures,
    - possible cross-over to transition flow in sample line to QMS chamber
  - Reactive species present (O_2, CO_2, H_2O) may affect sensitivity to other species[1]



1. E.g., C.R. Tilford, Surface and Coatings Technology, 68/69, pp. 708-712 (1994).

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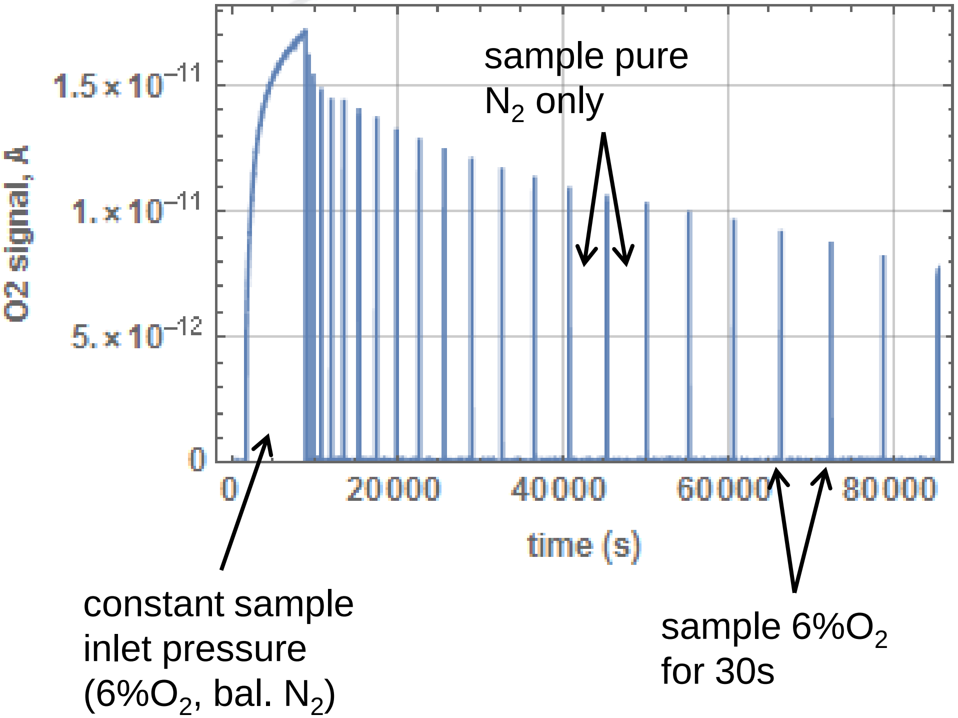
History-dependent sensitivity

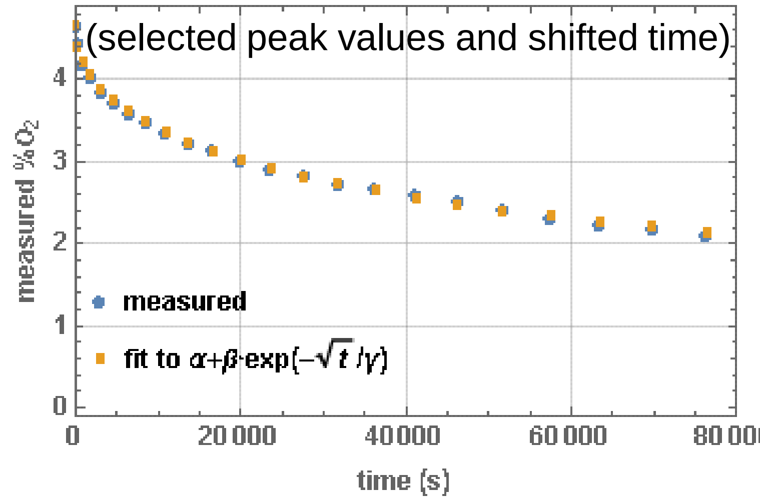
- Sensitivities of non-reactive samples are consistent
- O_2 sensitivity requires conditioning
  - but sensitivity after conditioning appears stable

- Experiment to understand O_2 sensitivity:

1. Sample 6%O_2 mixture for 2 hours.
2. Then switch to sampling pure N_2 instead.
3. Sample the 6%O_2 for 30s after intervals of n*5 minutes.

Long-term decay of sensitivity



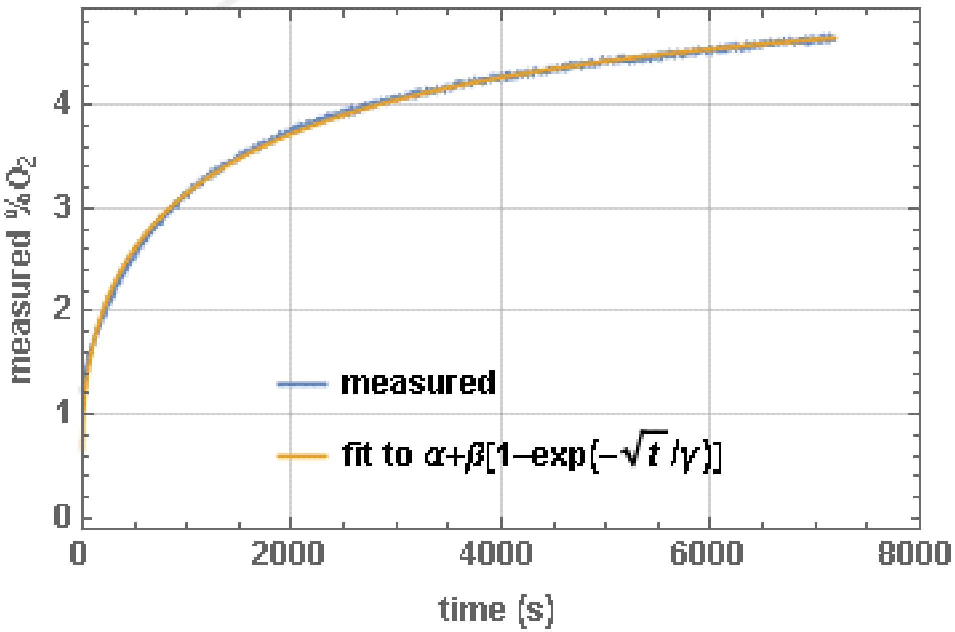


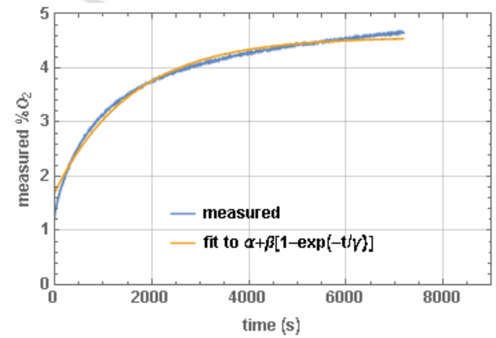
O_2 signal does not completely saturate after 2 hours of conditioning.

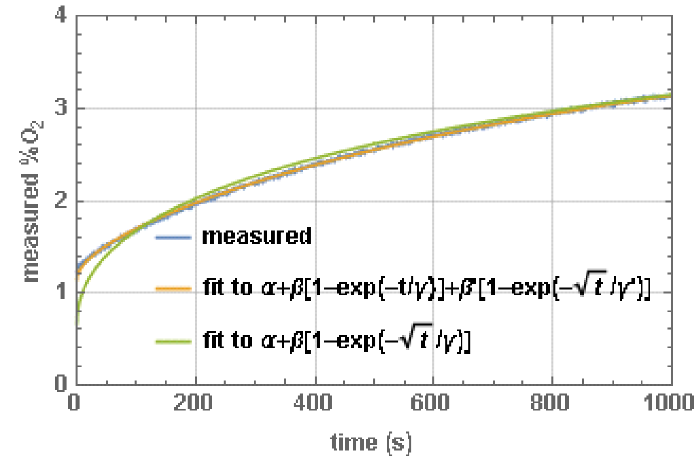
O_2 sensitivity decreases when the O_2 flow is stopped.

Sensitivity decays $\sim e^{-\sqrt{t}/\gamma}$

Rise of sensitivity has two different processes







For the conditioning step of this experiment, the exponential component is needed to fit the short-time behavior

Simple exponential fit alone doesn't work at all

The long-time $e^{-\sqrt{t}/\gamma}$ *behavior is probably due to reactions with surfaces in chamber.*

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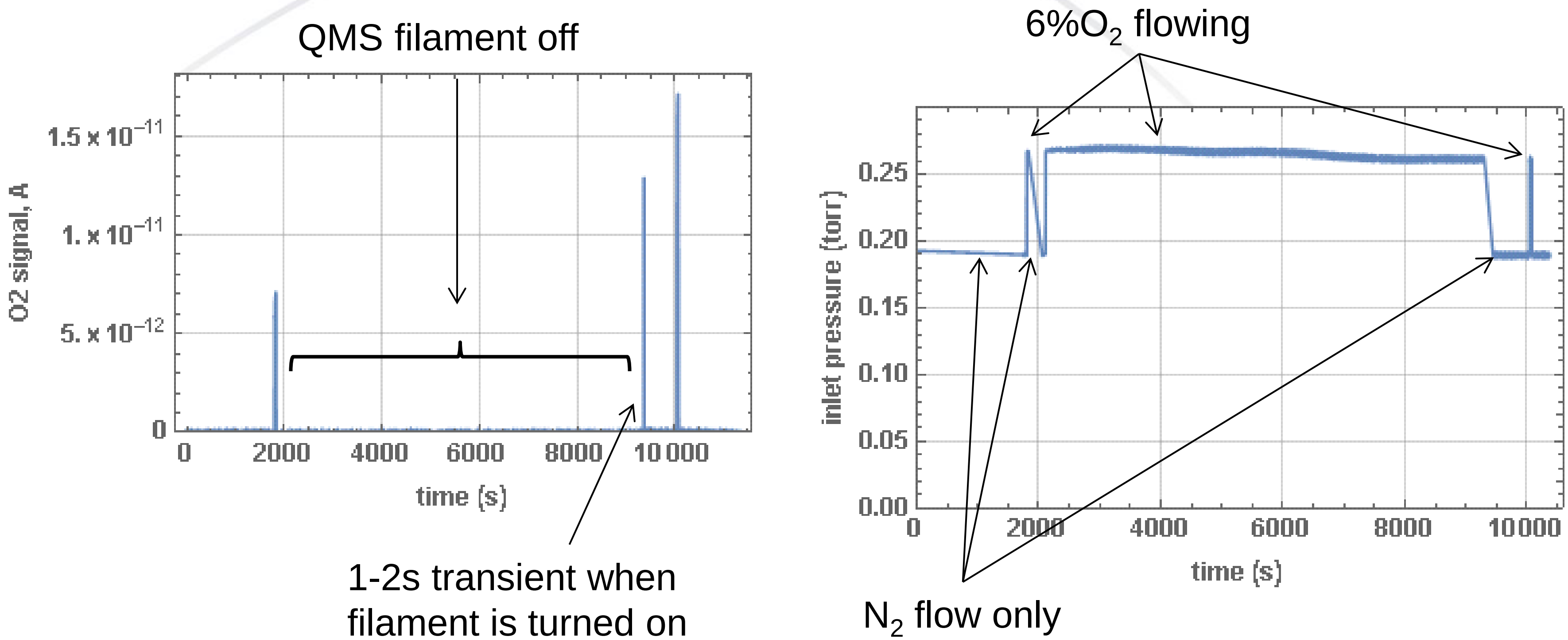
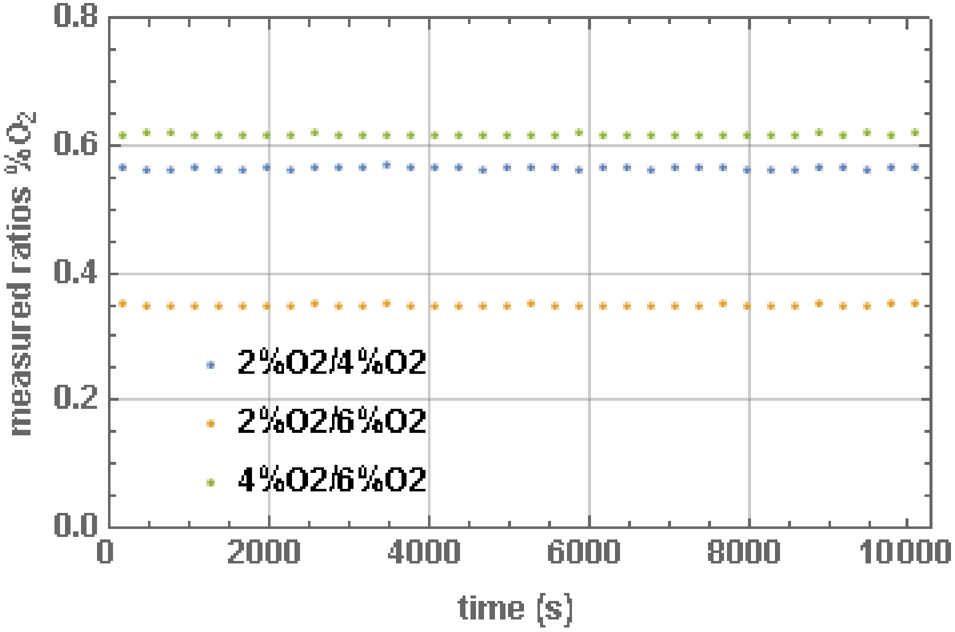
O_2 sensitivity depends on exposure even with filament off

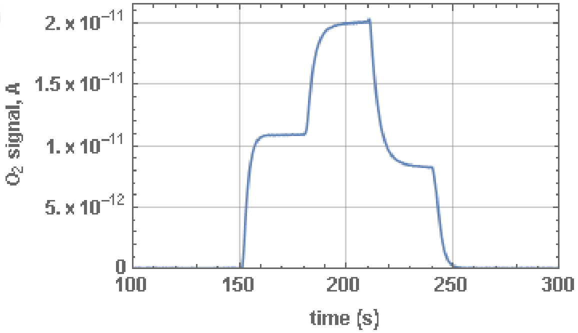


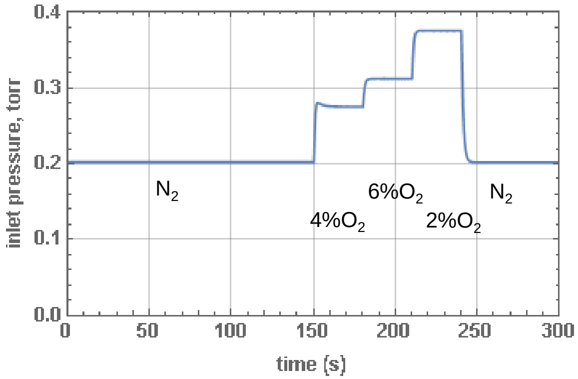
Experiment to test O_2 conditioning of QMS chamber:

- *Sample the 6%O_2 mix before and after 2 hours of O_2 flow*
- *Filament is off during the O_2 conditioning.*

Sensitivity relative to a standard







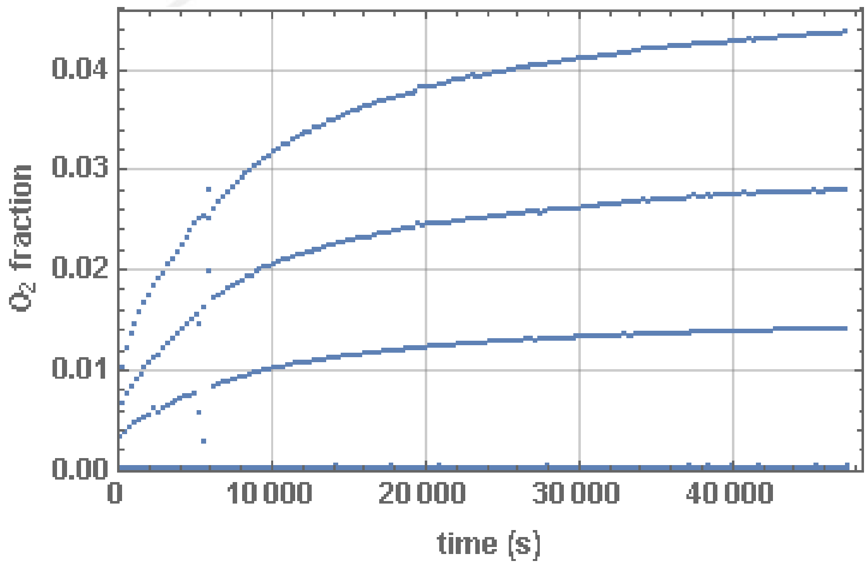
Sensitivity to O_2 may vary in time, but the measured O_2 concentration relative to a recently-measured standard will not vary.

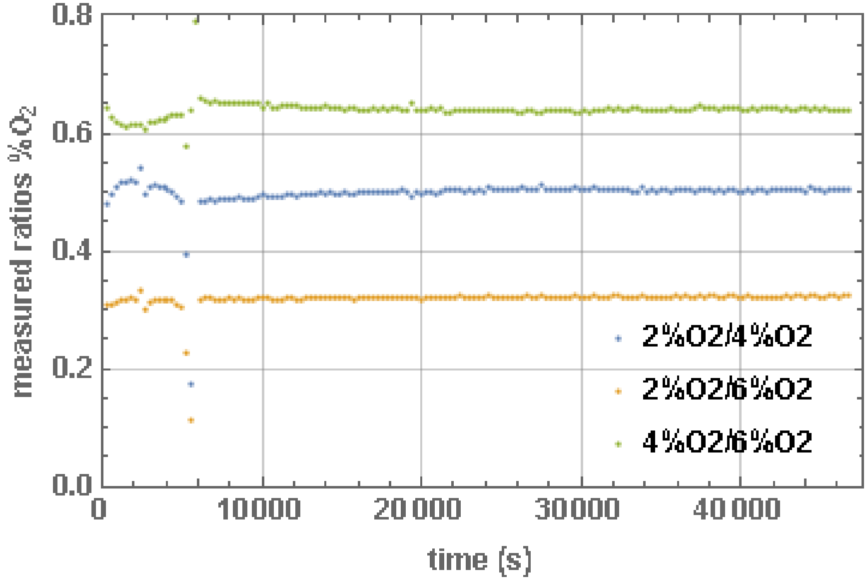
In this experiment, the four gases are 2%O_2, 4%O_2, 6%O_2 (all balance N_2) and pure N_2.

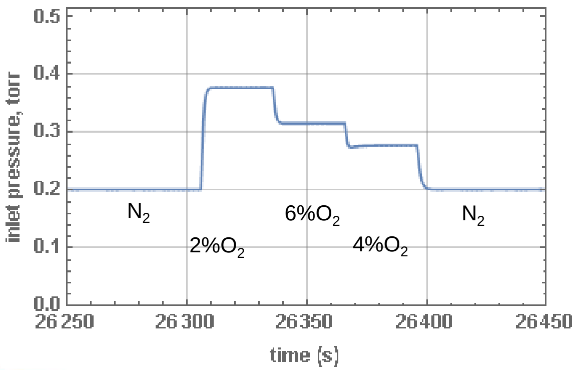
Sample order is N_2, 4%O_2, 6%O_2, 2%O_2, N_2 as shown

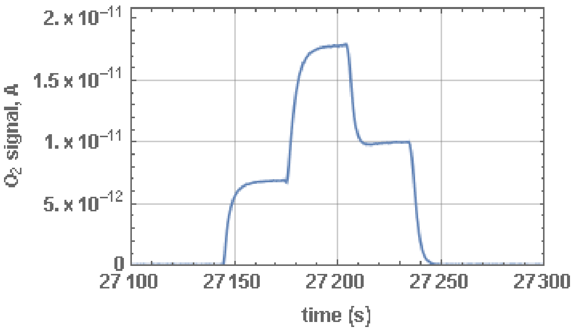
The mixtures are known to +/-10%.

Ratios when sensitivity is changing rapidly









Sensitivity to O_2 changes rapidly when QMS chamber is not conditioned

Even then, the measured ratios of different O_2 mixes are relatively constant

Conclusions

- Response times of 10-20 s are achievable
- Response may still be improved by reducing volume, path lengths
- Long-time rise in O_2 sensitivity may be due to stainless steel surfaces (we will test this)
- Closed ion source may reduce O_2 sensitivity change, at expense of chamber modifications
- Even with O_2 sensitivity drift, real measurements are possible if a standard is regularly sampled

Acknowledgements

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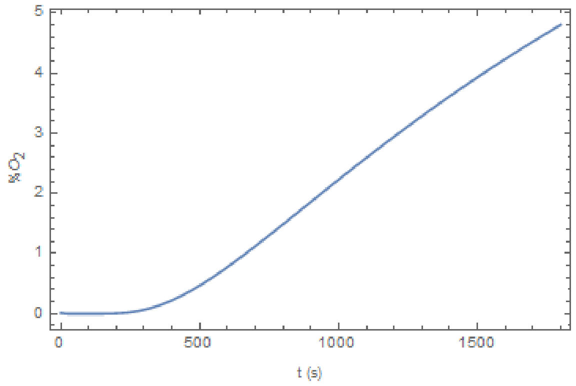
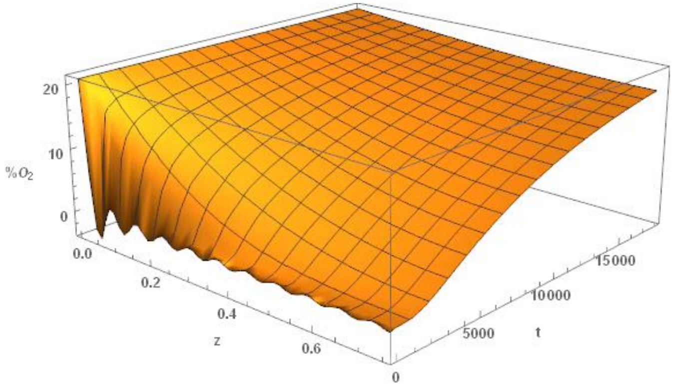
Supplementary Slides

Safety function

WETF DSA:

- "Provide an early warning so action can be taken to prevent a deflagrable gas mixture in the TGCS, and TWTS low-pressure receiver"
  - No rigid requirement on response time
  - Response time may be dominated by diffusion to the sensor or capillary line





Safety function

WETF TSRs (Bases):

- "DSA Section 4.4.6 and the hazards analysis (URS-SMS-TR-11-0003, *Hazards Analysis for Air In-Leakage Events in WETF*) evaluated both slow and fast air in-leakage events. The DSA evaluation determined that the TGCS OMS alarm could only be credited in a slow leak scenario to alert personnel with sufficient response time to initiate ACTIONS to prevent the potential formation of a deflagrable mixture in the TGCS SECTION. In addition, detecting and correcting abnormal oxygen concentrations in the TGCS also prevents oxygen in-leakage to the TGHS and the LPR."
  - No rigid requirement on response time
  - No requirement on continuous measurement

Experiments

- capillaries of varied lengths and flow rates
- standard mixtures, 2-6% O_2 in N_2
- determine accuracy vs. speed of measurement
- measure delay times for capillaries
- test linearity with pressure and concentration
- track calibration drift, determine required recalibration period