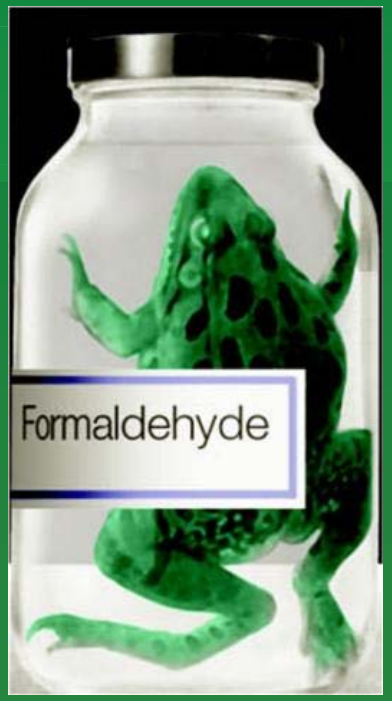
A New Method for Detection of Formaldehyde and Other Volatile Organic Compounds Using a Proton Transfer Reaction - Mass Spectrometer

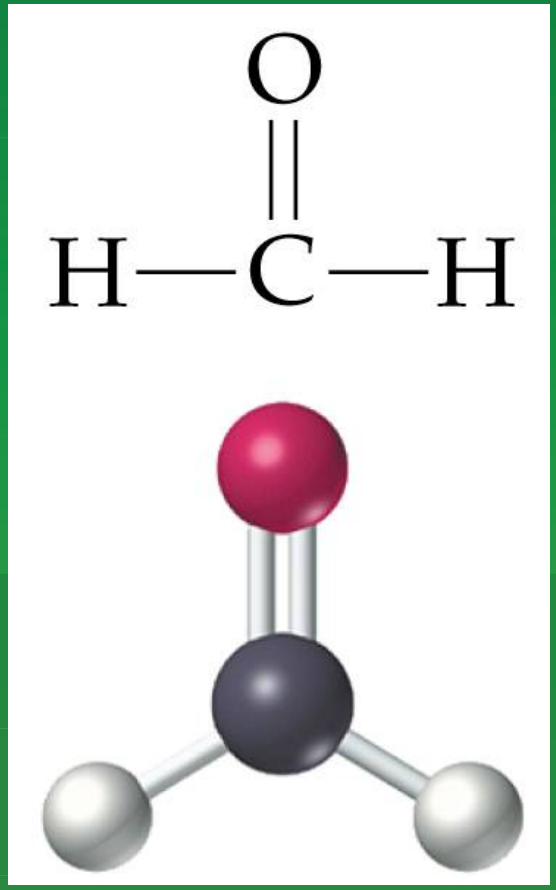
Jacob McCoskey
Tim Olson
Heather Hamilton
Tom Jobson

Laboratory for Atmospheric Research
Dept. of Civil and Environmental Engineering
Washington State University
509-335-7205
jacobmccoskey@gmail.com



Why Do We Measure Formaldehyde (CH_2O)?

- Hazardous Air Pollutant (HAP)
- Primary and secondary sources
- Plays an important role in ozone formation
  - Radical Source



Methods in Development - Proton Transfer Reaction – Mass Spectrometer (PTR-MS)

- Offers real time, pptv measurements of both formaldehyde and an array of other volatile organic compounds (VOC's)
- Allows a method for source proportionment of primary and secondary volatile organic compounds
- Operating Principle

$$H_3O^+ + R \rightarrow H_2O + RH^+$$

Challenges of Measuring Formaldehyde with the PTR-MS

1. **Reduced sensitivity due to back reaction with water**

$$H_3O^+ + R \leftrightarrow H_2O + RH^+$$

1. **Sensitivity is humidity dependent due to ligand switching reactions with water clusters**

$$H_2O \bullet H_3O^+ + CHOH \rightarrow H_3O^+ \bullet CHOH + H_2O$$

$$CH_2OH^+ \bullet H_2O + H_2O \rightarrow H_3O^+ \bullet H_2O + CH_2O$$

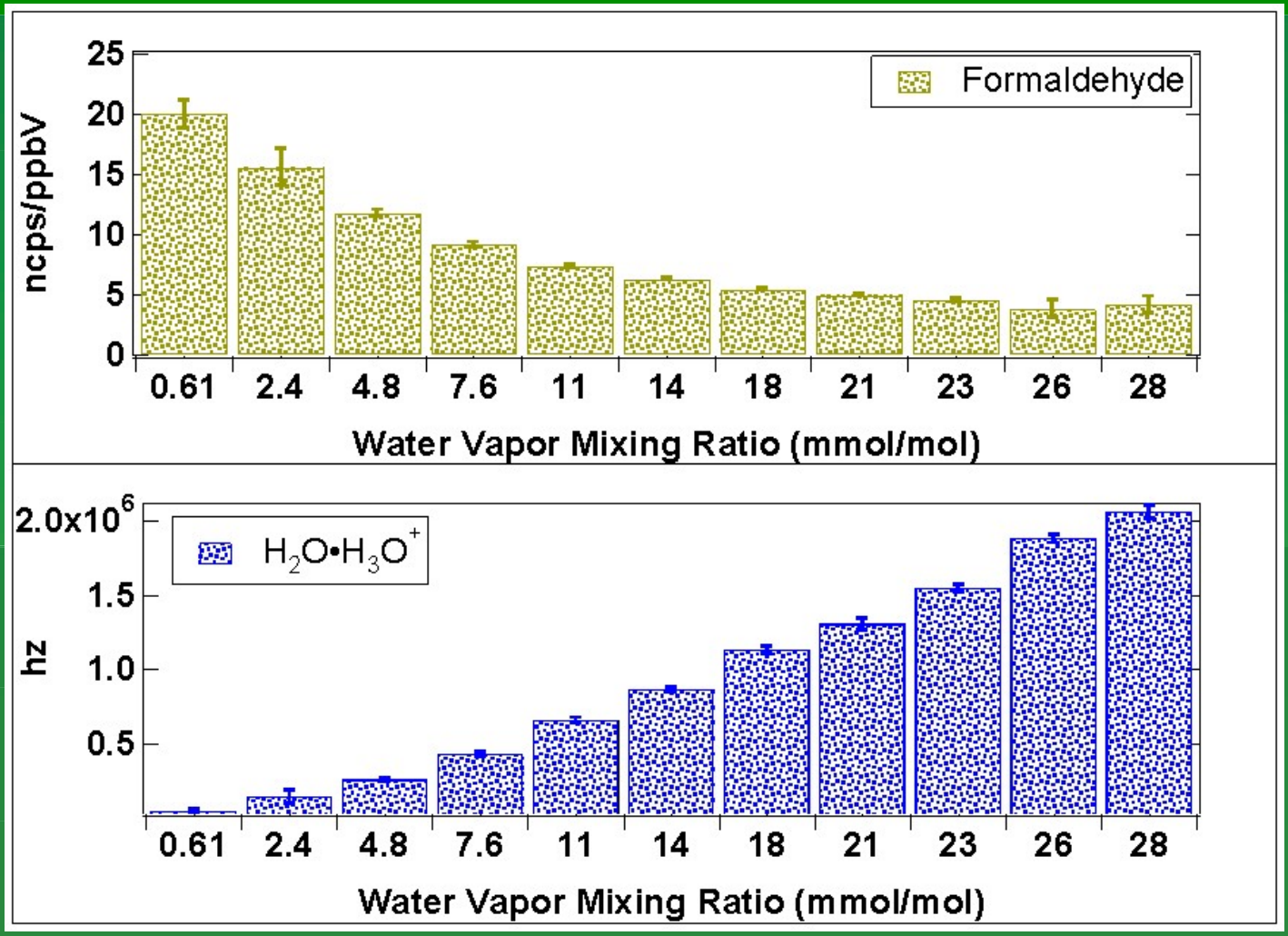
$$CH_2OH^+ + H_2O + M \rightarrow CH_2OH^+ \bullet H_2O + M$$

2. **Interferences from other compounds**
   - Methyl hydroperoxide, methanol, ethanol

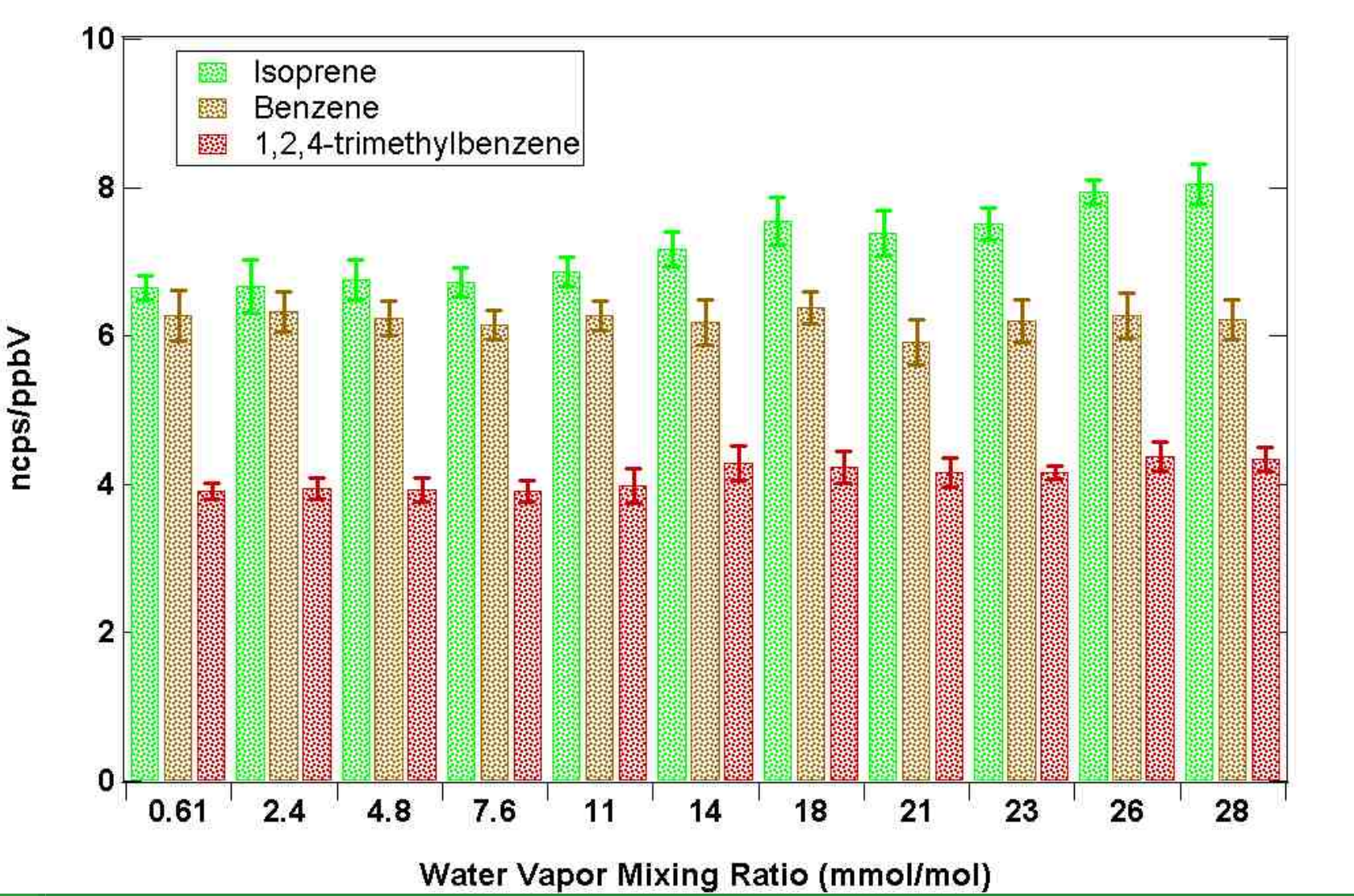
Humidity Effects

Trap Temperature = NA, Flow = 500 sccm

Td = 120, Drift Tube Pressure = 2.1 mbar



Humidity Effects



Current Strategies to Overcome Formaldehyde Measurement Difficulties with the PTR-MS

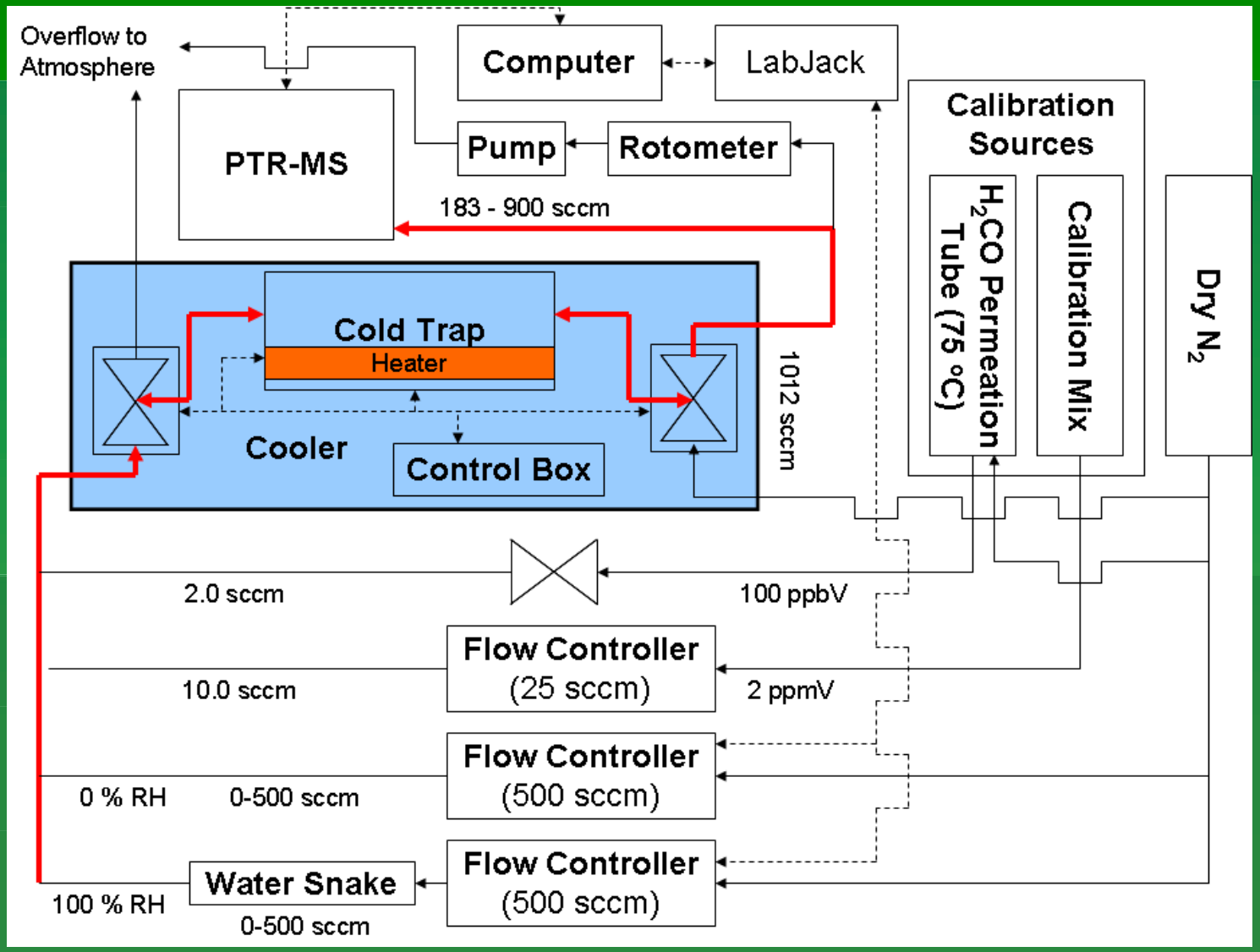
- Correct formaldehyde measurements by applying equations that account for formaldehyde's water vapor mixing ratio dependence

- Current strategies have error greater than **25%**

WSU's strategy for measuring formaldehyde with the PTR-MS

- Use a cold trap to remove water vapor in sample air resulting in increased sensitivity of formaldehyde with little affect on other VOC species
- Hypothesis – VOC's will quickly arrive at equilibrium resulting in little loss of VOC mass to the ice coated walls of the cold trap

Experimental Setup



Experimental Setup cont.

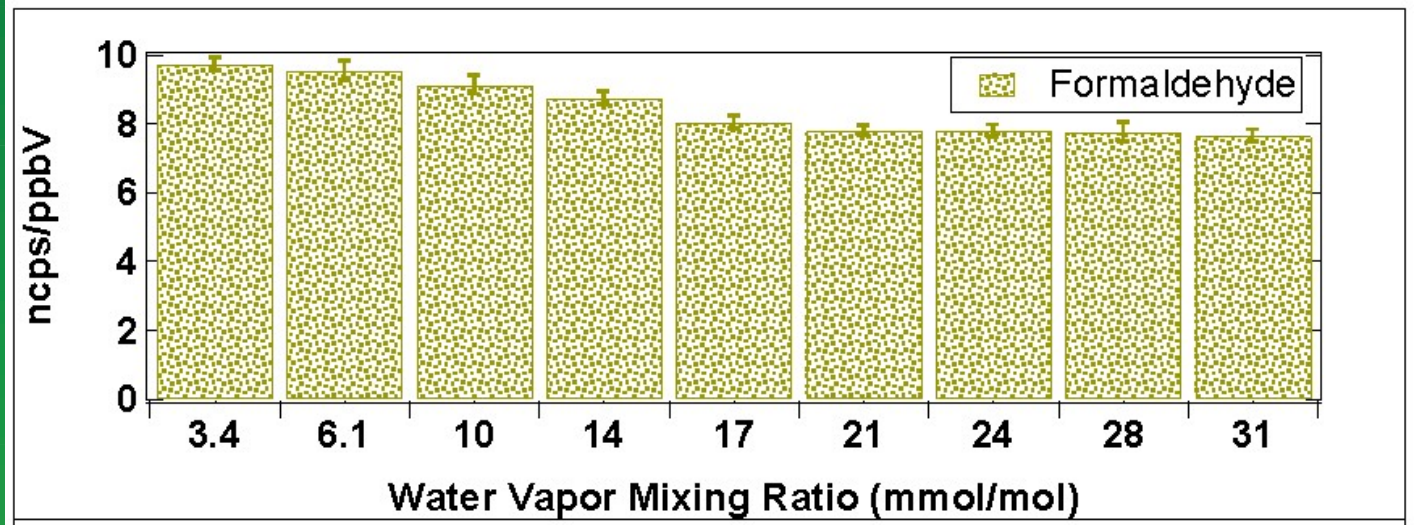
- **Cold Trap Conditions**
  - Flow Varies
  - Temperature Varies

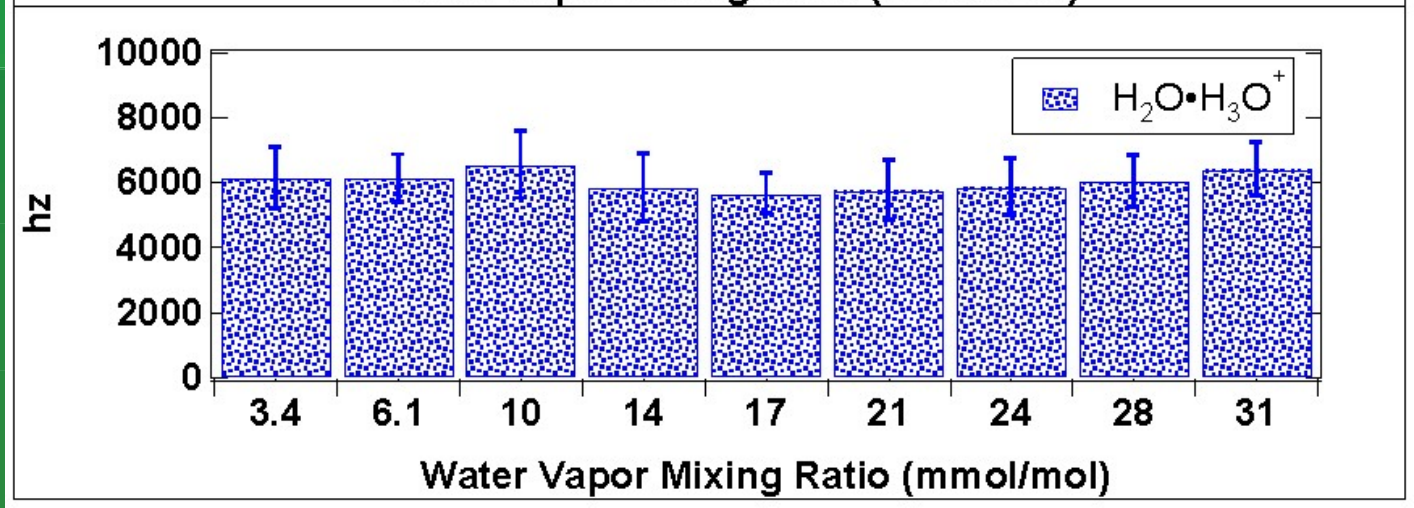
- **PTR-MS Conditions**
  - TD = 108-120
  - Drift Tube Pressure = 2.1-2.4 mbar

Cold Trap Performance

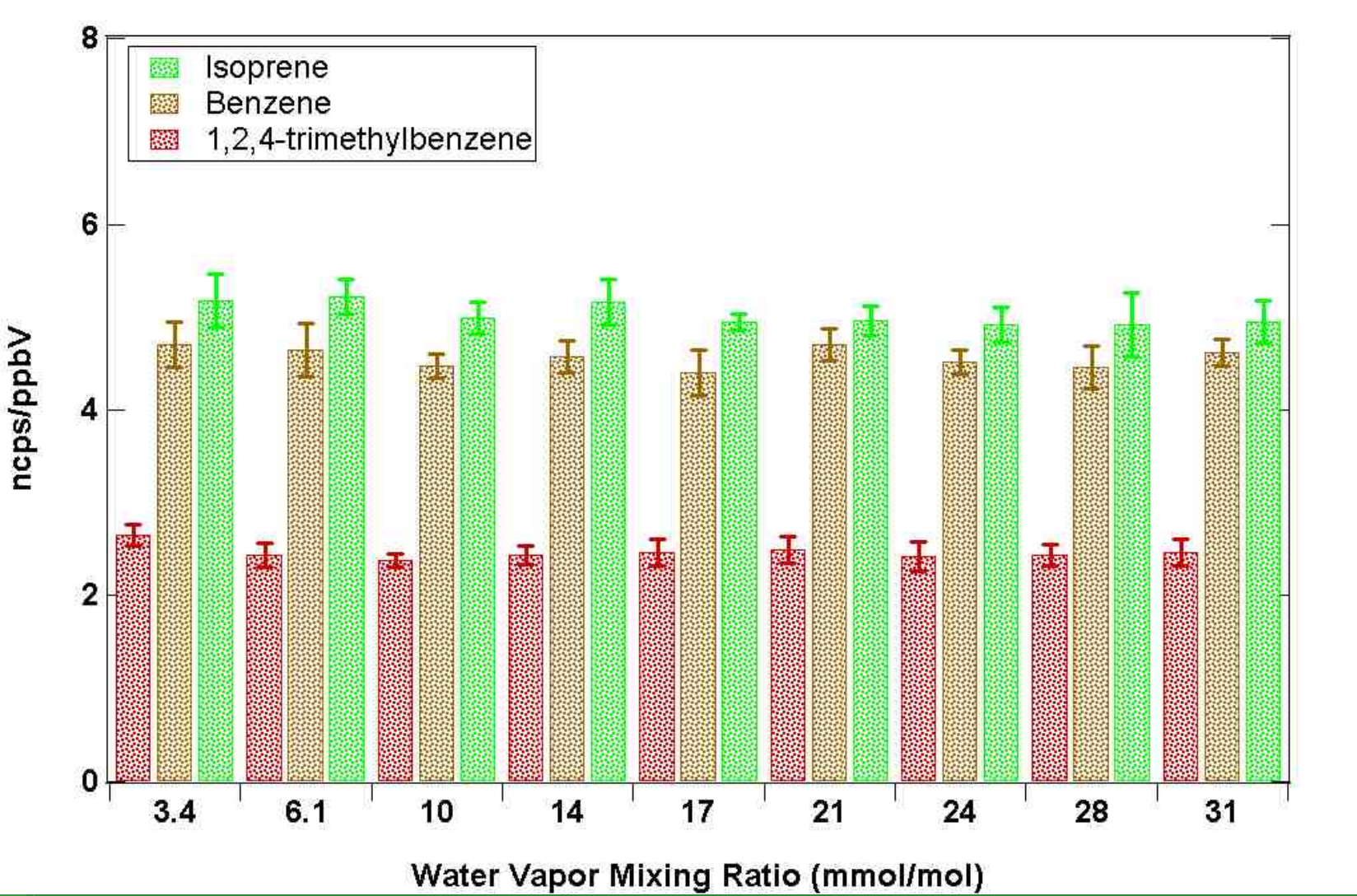
Trap Temperature = - 30 °C, Td = 120,

Drift Tube Pressure = 2.1 mbar Flow = 104 sccm





Cold Trap Performance



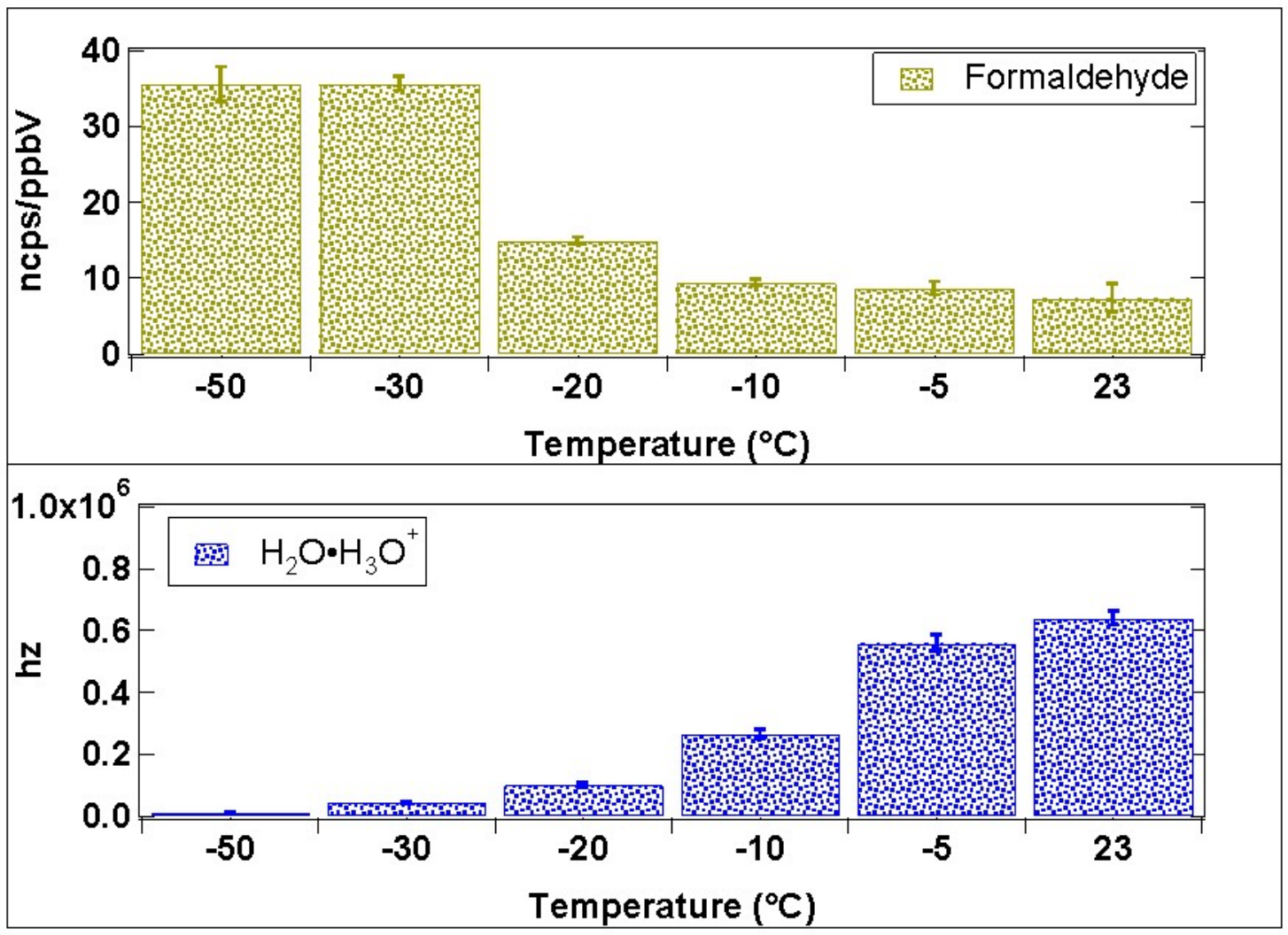
Cold Trap Design - Temperature

- At some point, reducing the temperature produces diminishing returns in the cold trap's drying effect, and consequently instrument sensitivity
- Water vapor always present in PTR-MS due to reagent ion source

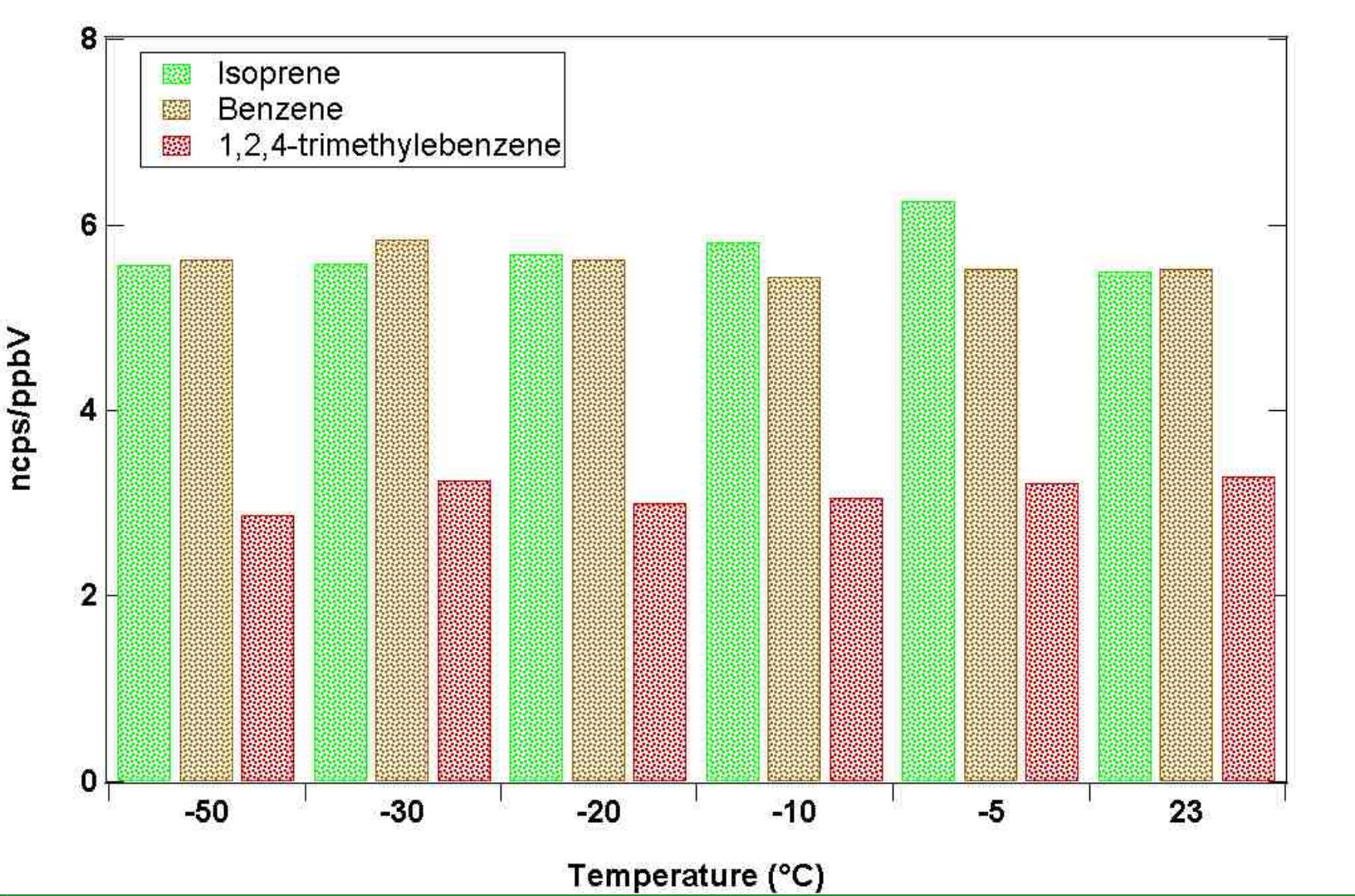
Cold Trap Design –Temperature

WV MR = 16 mmol/mol Flow = 183 sccm, Drift Tube

Pressure = 2.4 mbar Td = 120,



Cold Trap Design -Temperature



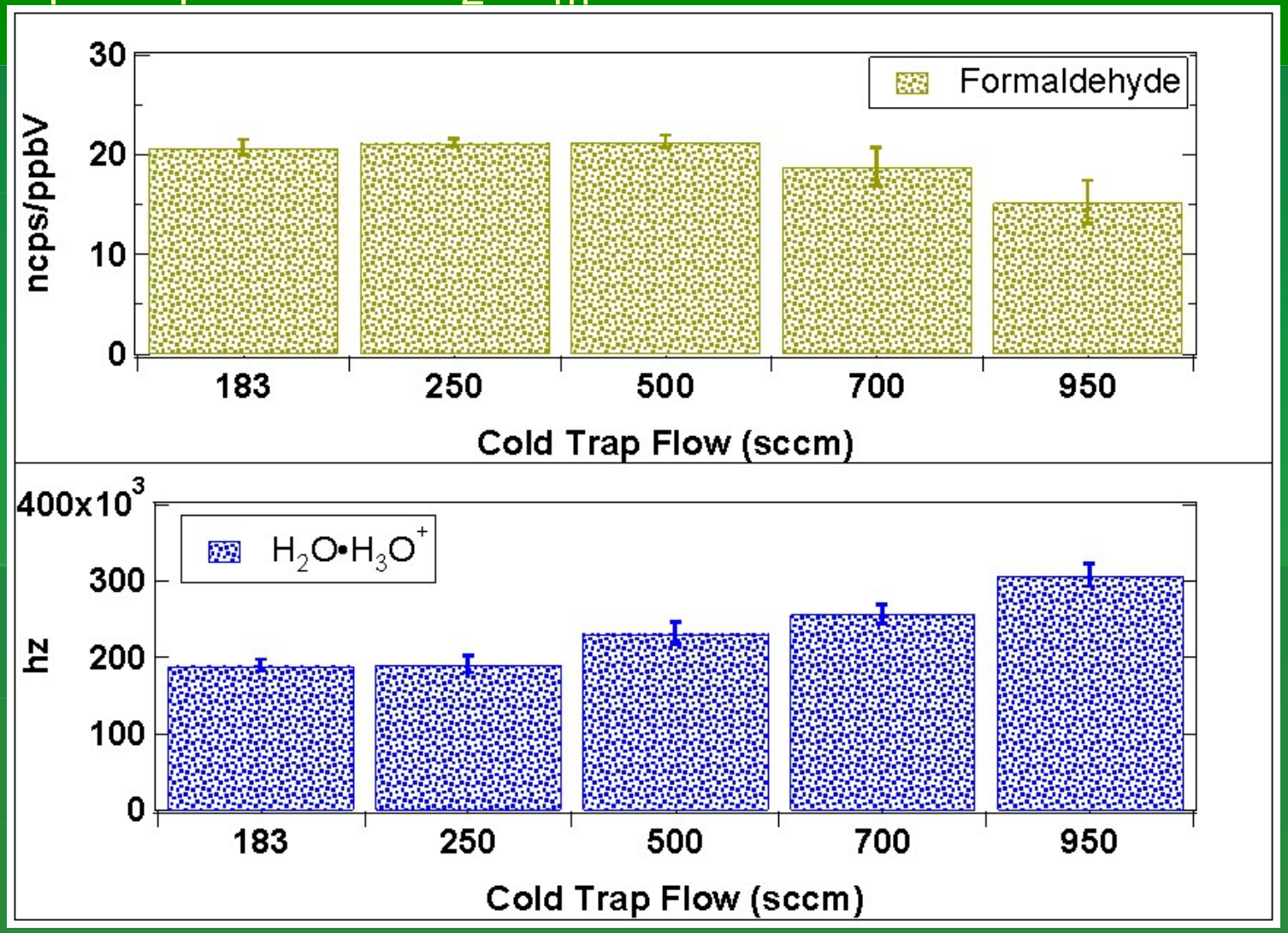
Cold Trap Design - Flow

- **Flow Rate**
  - Influences equilibrium of formaldehyde with ice - coated tube walls
  - Influences water vapor removal

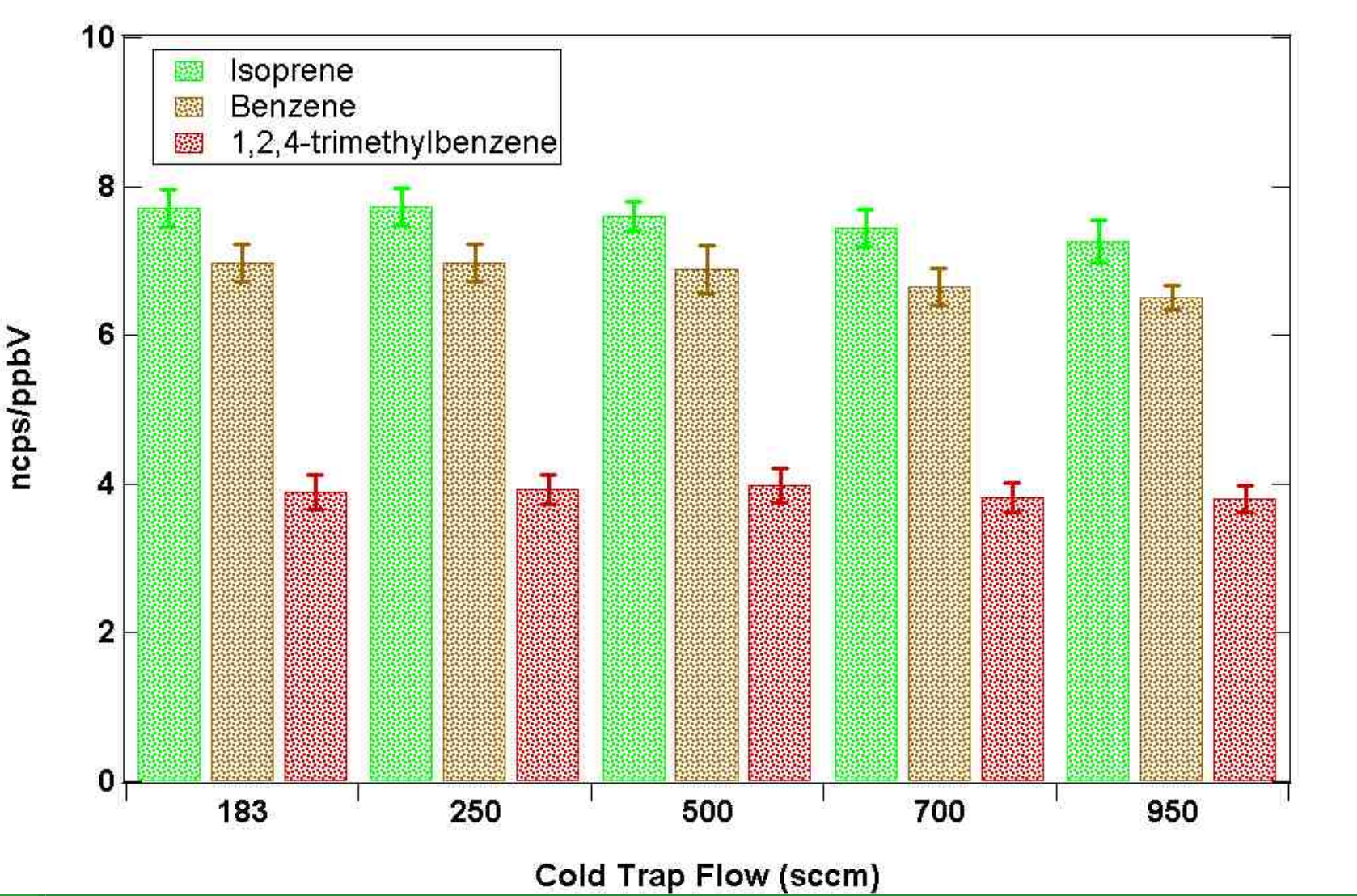
Cold Trap Design – Flow

Trap Temperature = - 30 ºC, WV MR = 16 mmol/mol

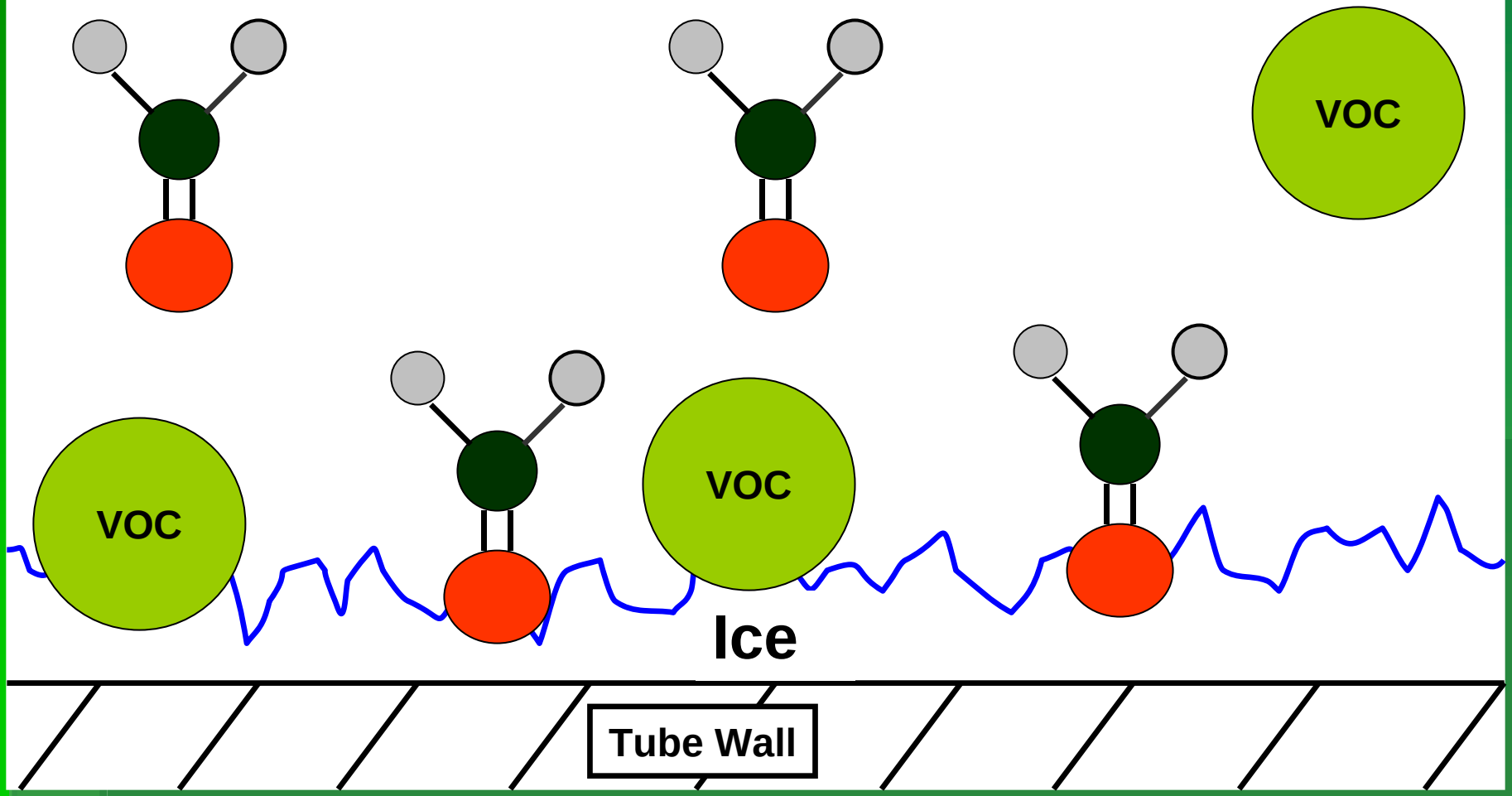
Drift Tube Pressure = 2.4 mbar Td = 120, T = 2 m



Cold Trap Design - Flow

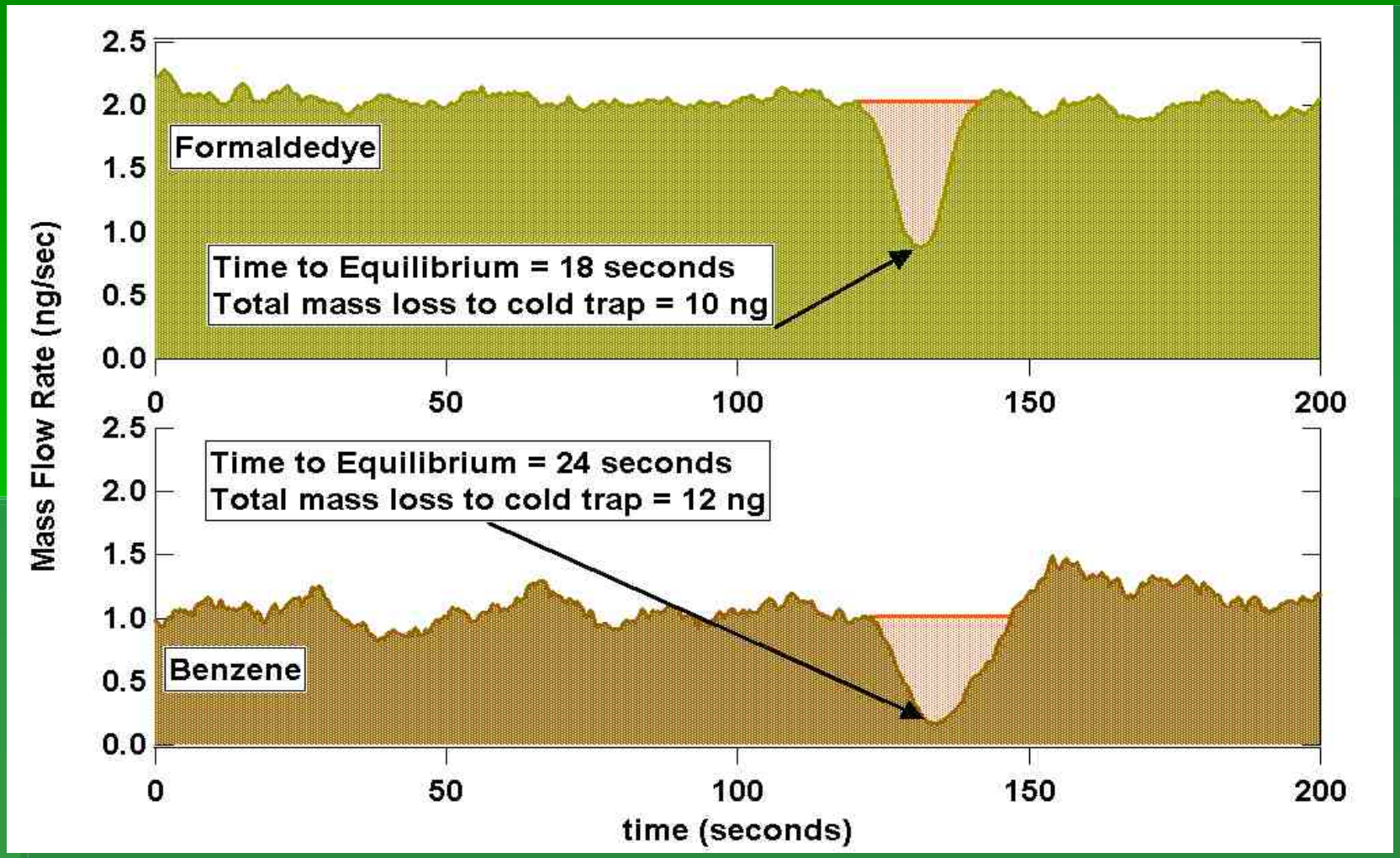


Equilibrium with Ice-Coated Tube Surface



Equilibrium with Ice Coated Tube Surface –

Temperature ≡ - 67 ºC, Flow ≡ 100 sccm



Summary

- The PTR-MS with a cold trap attached to the inlet effectively measures formaldehyde with minimal impact on the measurement of other VOC's
- Once the cold trap reaches equilibrium, fine time resolution measurements can be made that offers a technique for source proportionment of formaldehyde against other VOC's

Questions?

Fire away