Open Path FTIR ambient monitoring - a field experiment

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Outline

- OP-FTIR “Basics”
- Quantification
  - CLS - Classical Least Squares method
- Ambient Monitoring in Seattle
  - Challenges and findings
  - MDL’s
- Next Steps

Advantages with optical remote sensing

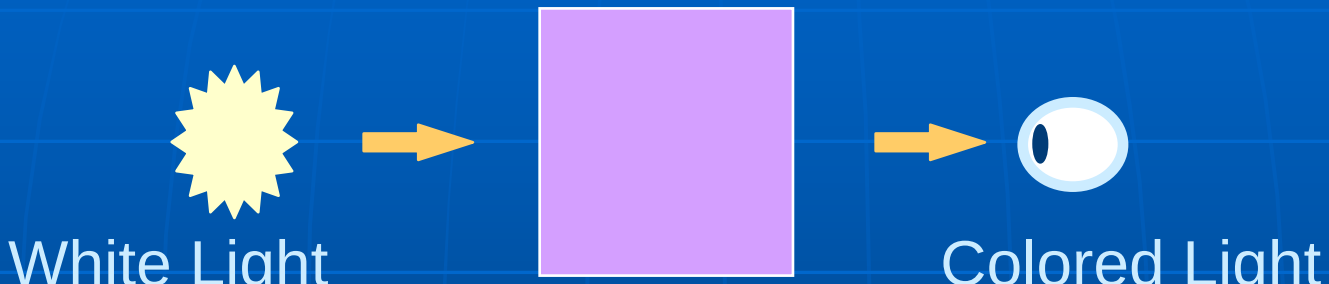
- Multicomponent
- Line/area integrating
- Sensitive
- High time resolution
- Invasive free
- Easily automated
- Rapid deployment
- Cost

Introduction to OP-FTIR

Advantages:

- Rapid Response monitoring
- Rapid, continuous readings
- Multi-compound analysis
- Unexpected compound I.D.

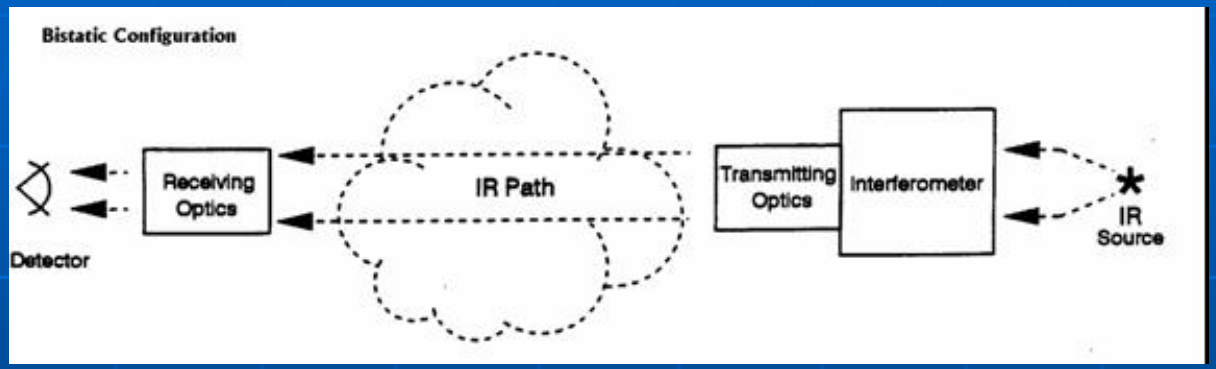
Transmission Spectroscopy



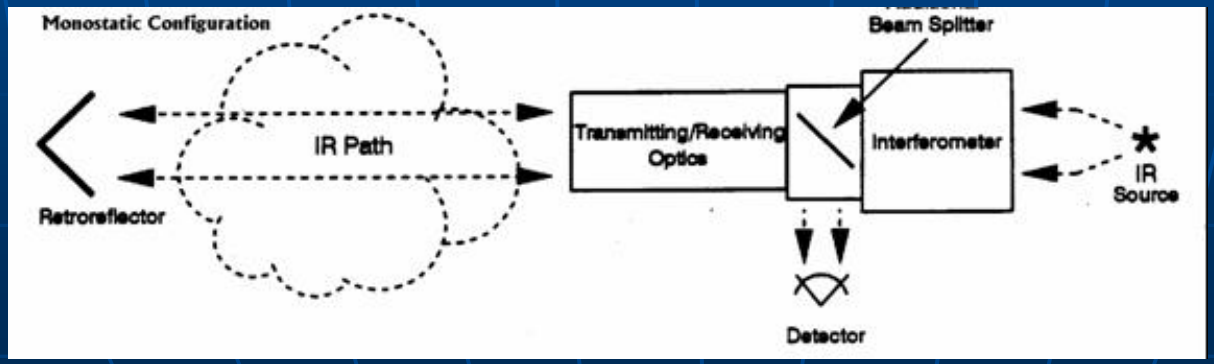
SOURCE OBJECT DETECTOR

- The concept:
- Your eye is an excellent multi-wavelength detector
- Most spectroscopic detectors are not, and need ‘help,’ hence the need for a ‘spectrometer’ to sort wavelengths

Different optical layouts for long path spectroscopy



OUR System: ETG/CEREX Op-FTIR

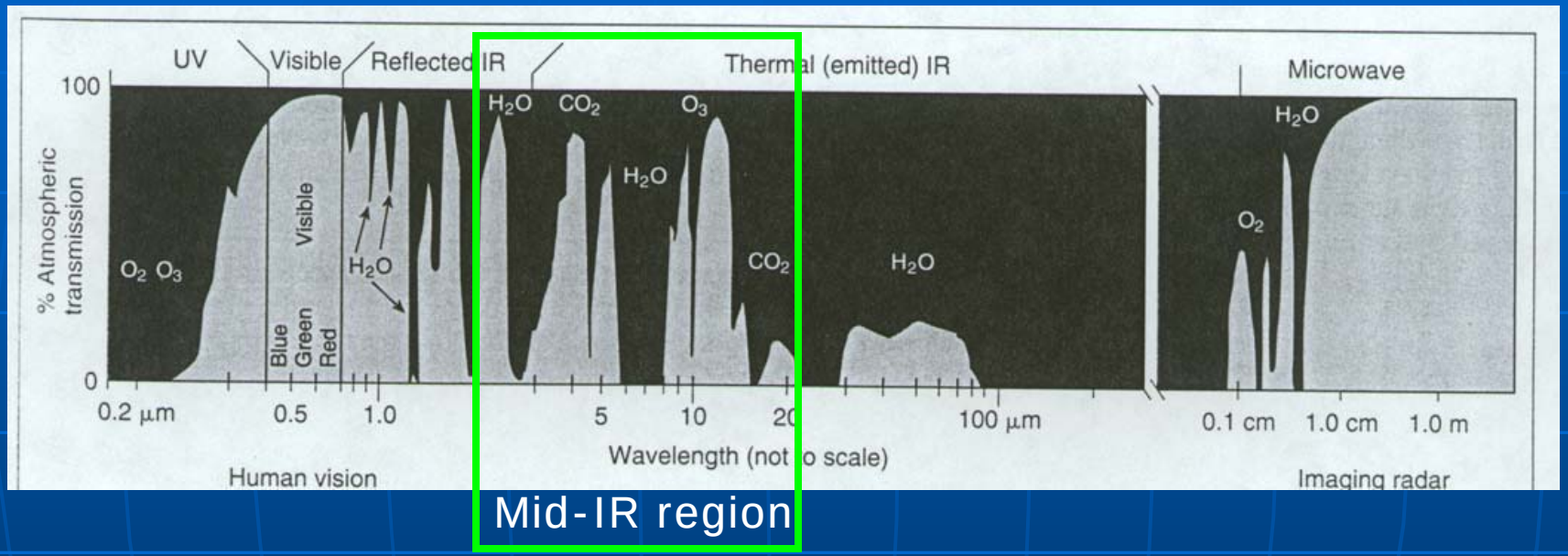


atmospheric windows exploited in remote sensing

- 0.3 - 1.1um UV, visible, near infrared
- 1.5 - 1.8um Mid infrared
- 2.0 - 2.4um Mid infrared
- 3.0 - 5.0um Mid infrared
- 8.0 - 14.0um Thermal Infrared
- (below ozone layer)
- 10.5 - 12.5 Thermal Infrared

OUR System: ETG/CEREX Op-FTIR

Atmospheric transmission



- OP-FTIR operates in Mid-IR transmission bands (light-grey windows
- Significant background from Water and CO_2

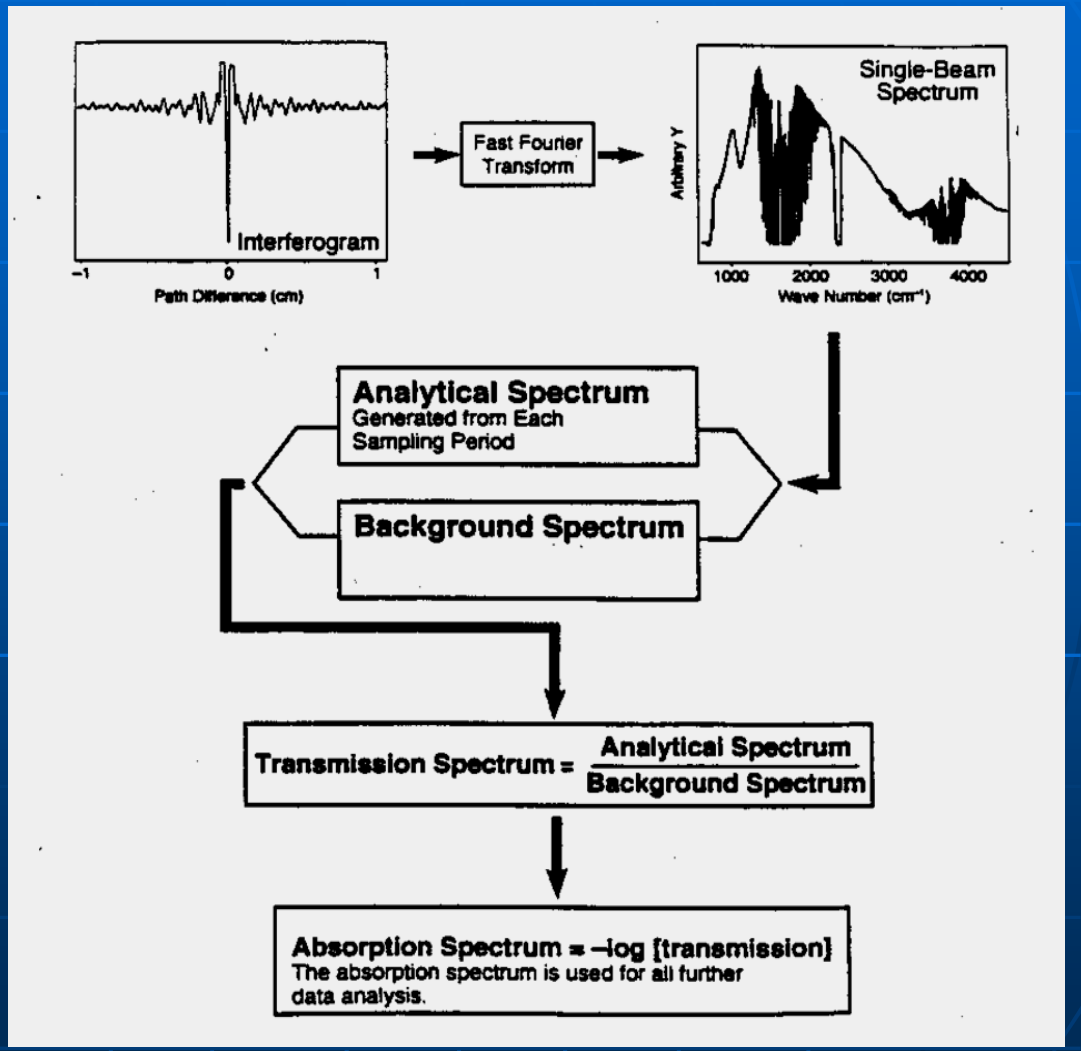
Beer's law

- $I_1(\nu) = I_0(\nu)\exp(-\alpha(\nu)CL)$
- where
  - $I_0(\nu)$ is the intensity of the incident beam measured on the clean background spectrum
  - α is the optical absorption coefficient of the absorbing compound, such as target gases and H_2O.
  - All terms are a function of (ν) which is in wavenumbers, usually in units of cm-1
  - C is the concentration of target compound
  - L is the path length
- The absorbance spectrum, A , due to a specific gas can then be written as:

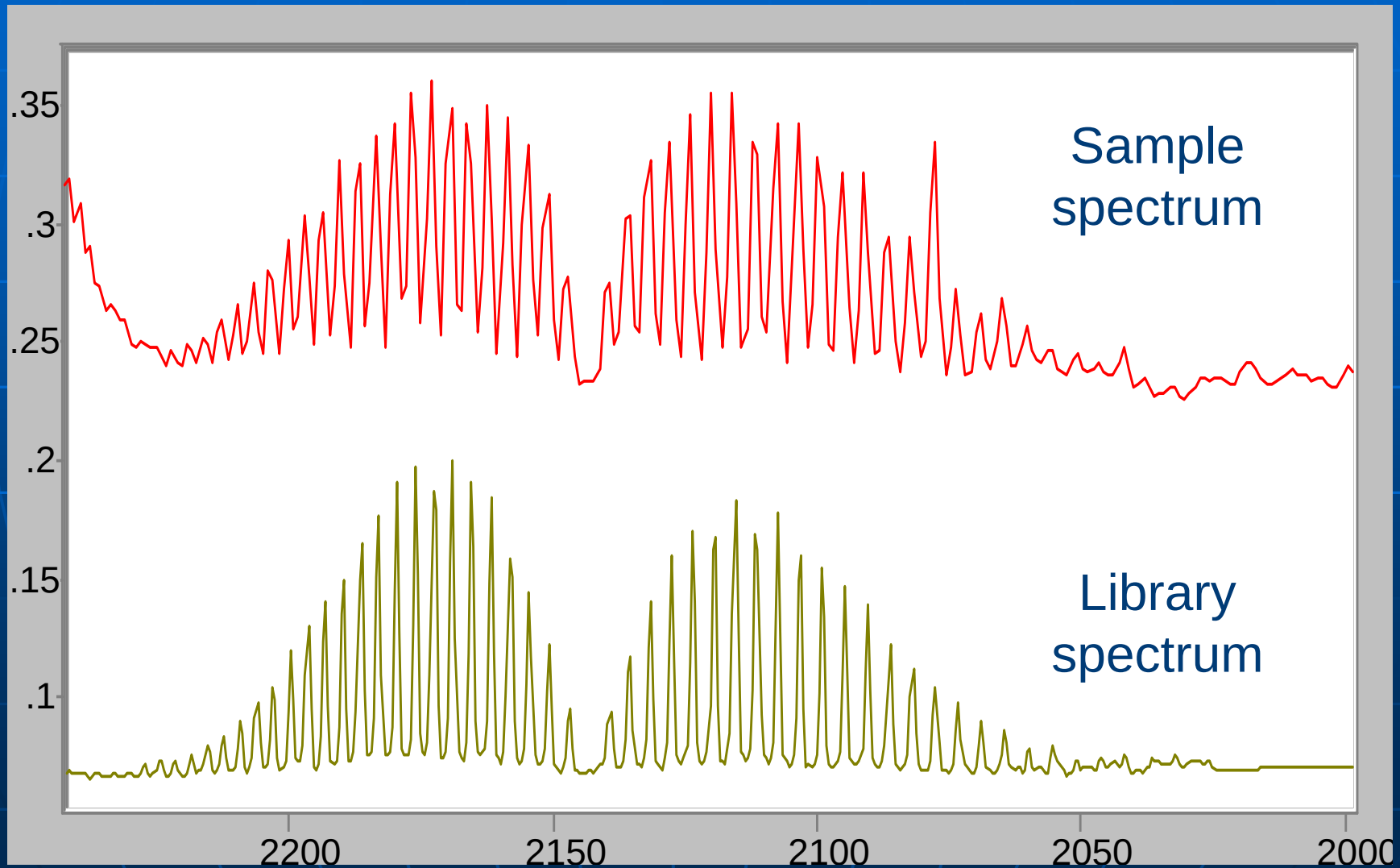
- $A = -\log(I_1/I_0) = -\alpha(\nu)CL$ ← Key Equation

Flowchart of FTIR Data Analysis

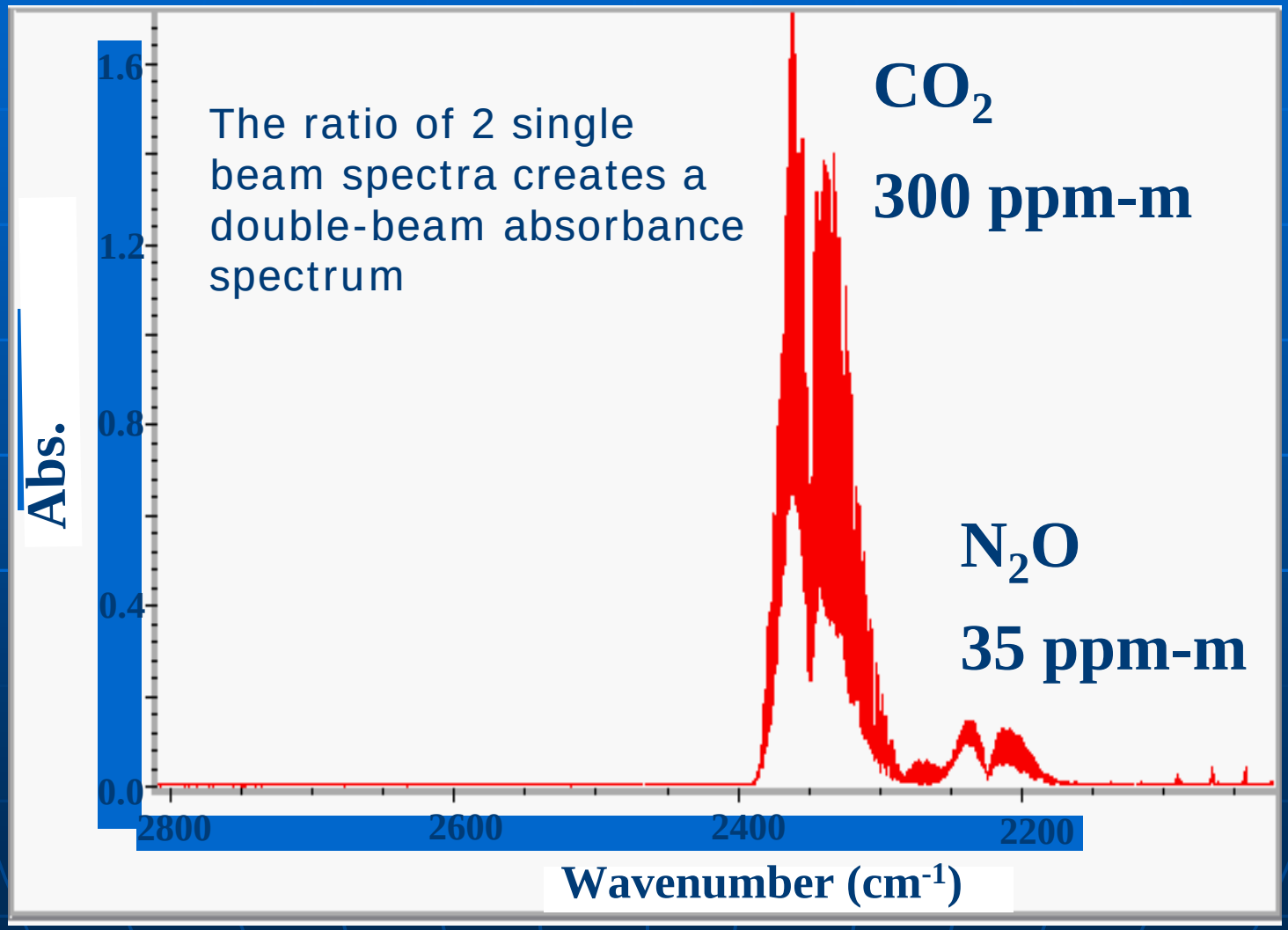
- Compute FFT (Interferogram) = Single beam spectrum
- Ratio (Analytical/Background) single beam to get Transmission spectrum
- Compute Absorbance spectrum:
  Abs = - log(%Trans.) = -*a*CL
- CLS: linear regression (Beer-Lambert Law)
- Average conc. = path integrated beam conc. / path length
  [i.e. (PPM) = (PPM-m) /(m)]



Example: Carbon Monoxide in Car Exhaust

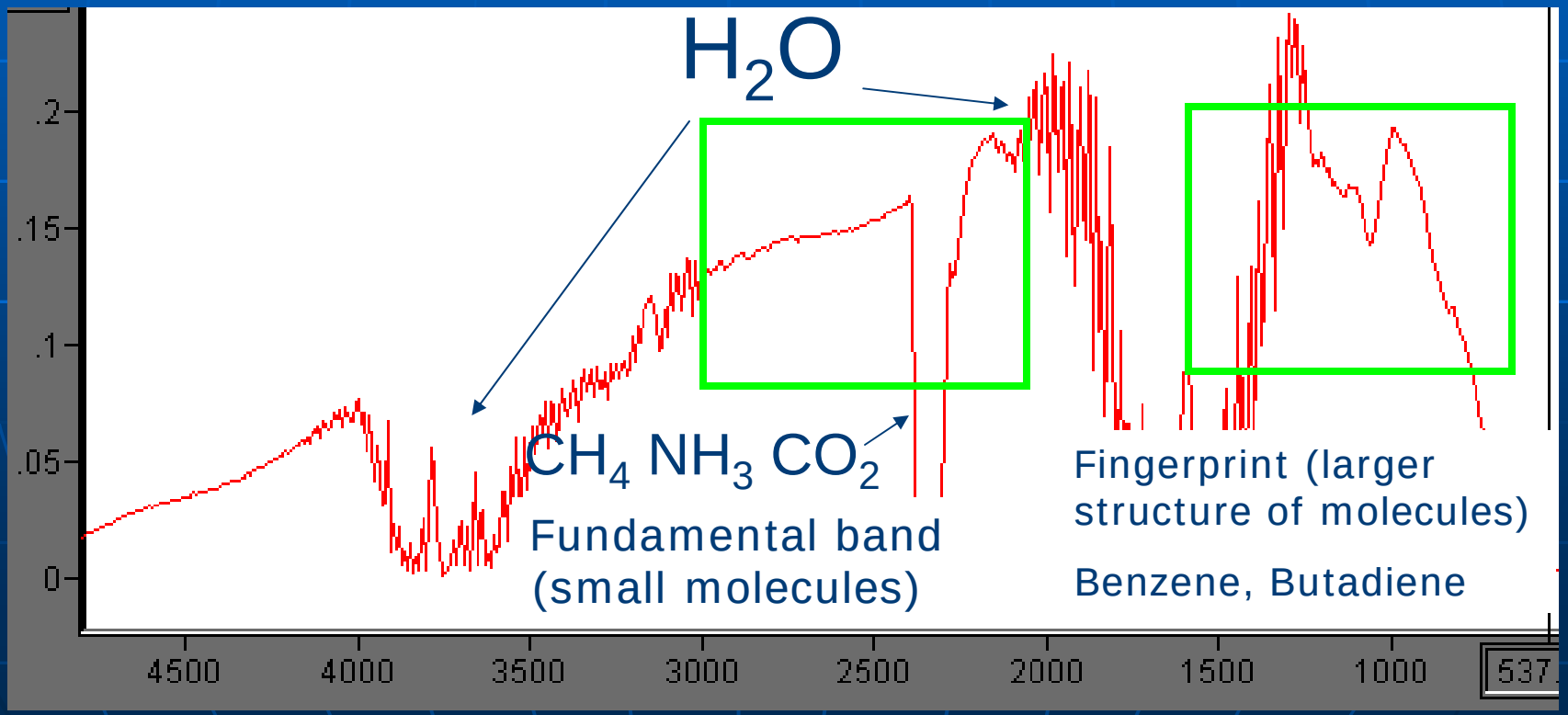


Double-Beam Absorbance Spectrum



Single Beam Spectrum

The shape of the spectrum depends on the black body emission of the source, transmission in the sample, background gases and the detector response

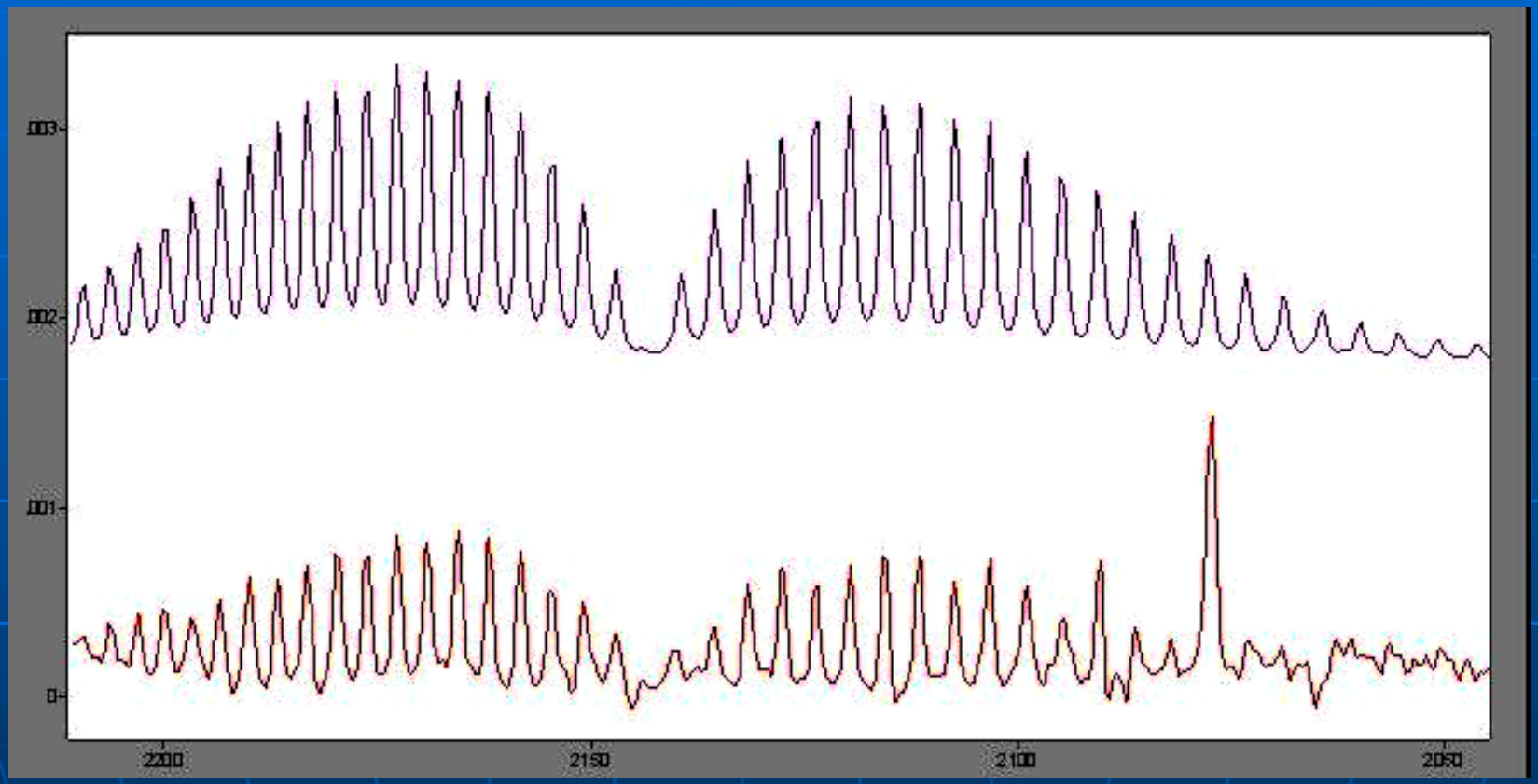


The Duwamish site

<-- Approx. location of 250 m beam path

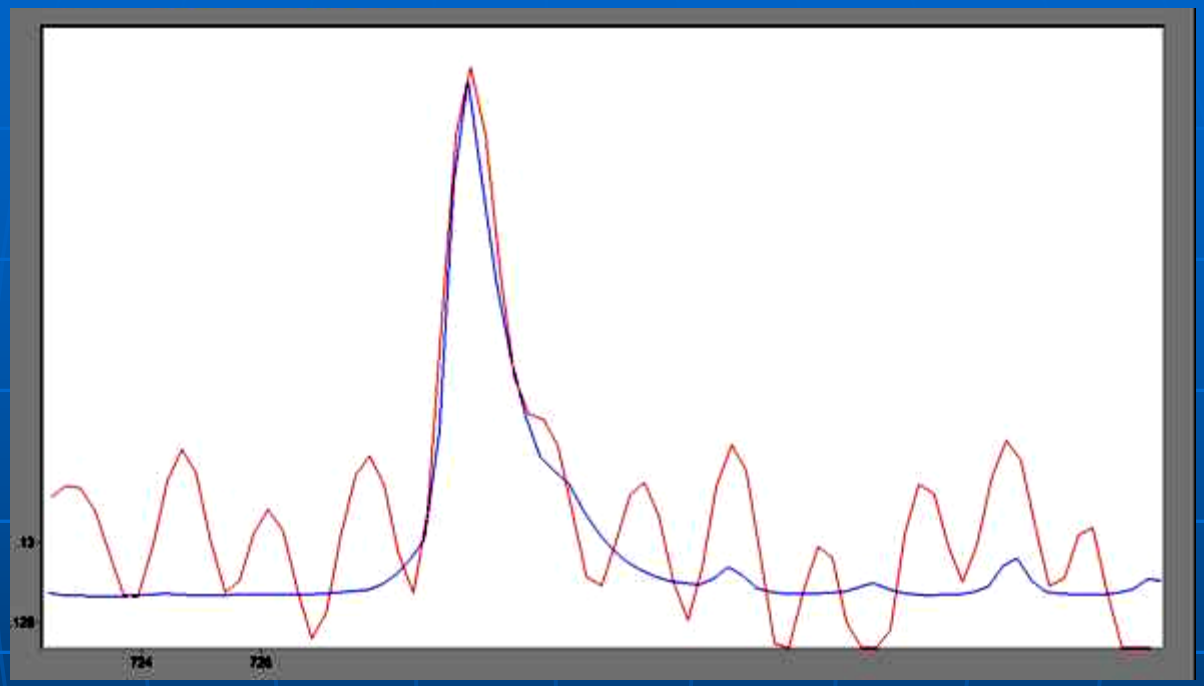
- Data collected at 1 cm-1 resolution
- Logged 5 minute averages
- Spectra collected @ 1 scan/sec

CO at Duwamish site



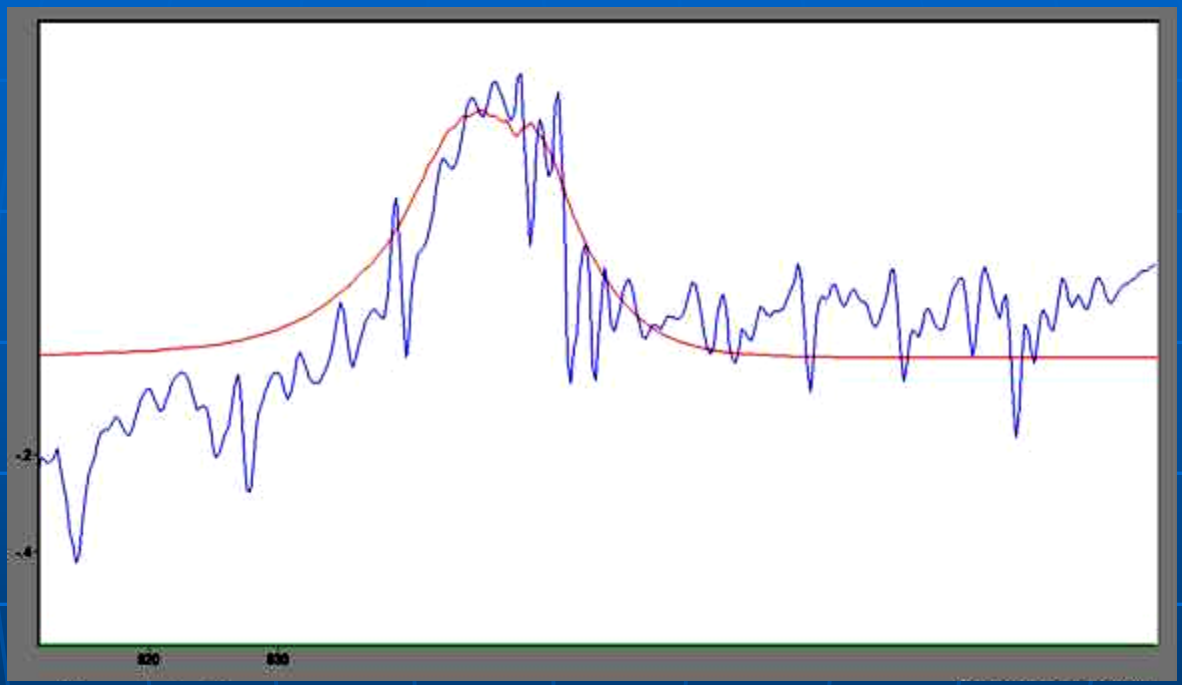
- CO reference (~ 5 ppm-m) (top) & Duwamish spectrum (bottom)
- Height of lines only ~.001 absorbance units and clearly visible!
- Lower trace ~50 ppb based on above reference and 250m path.
- Noise is << .001 absorbance units in above spectrum

Finding unknowns (1)



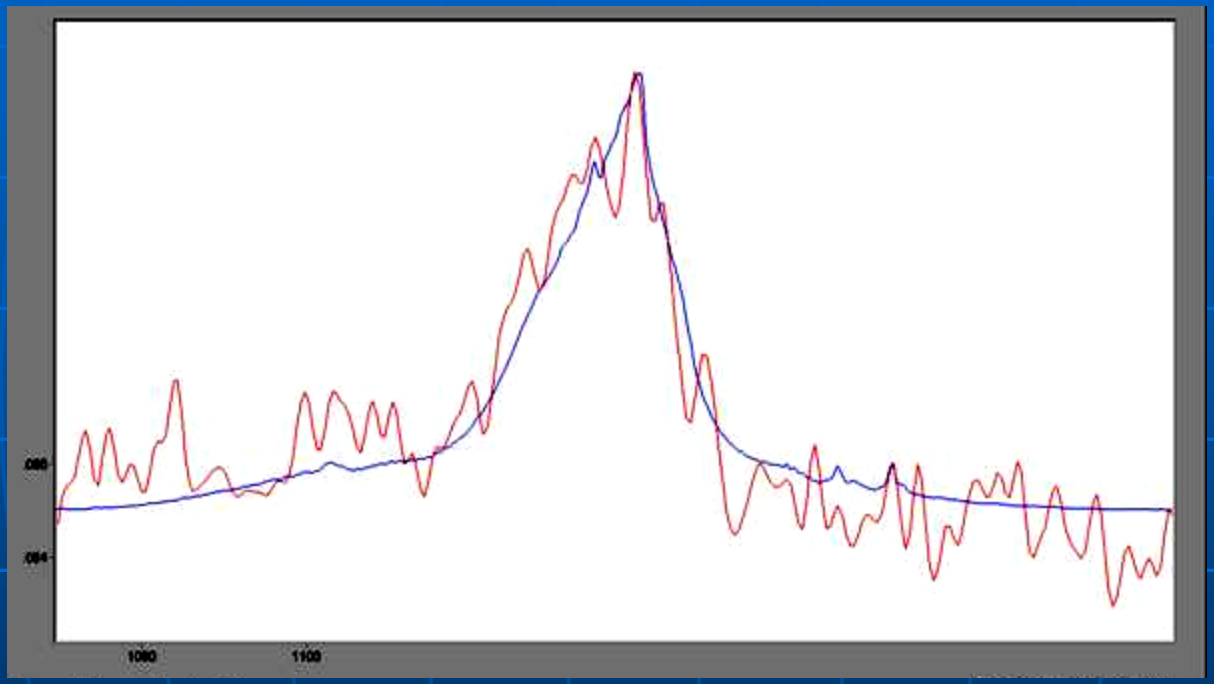
- Comparison of Duwamish Frame 001 to the reference for acetylene (red)

Finding unknowns (2)



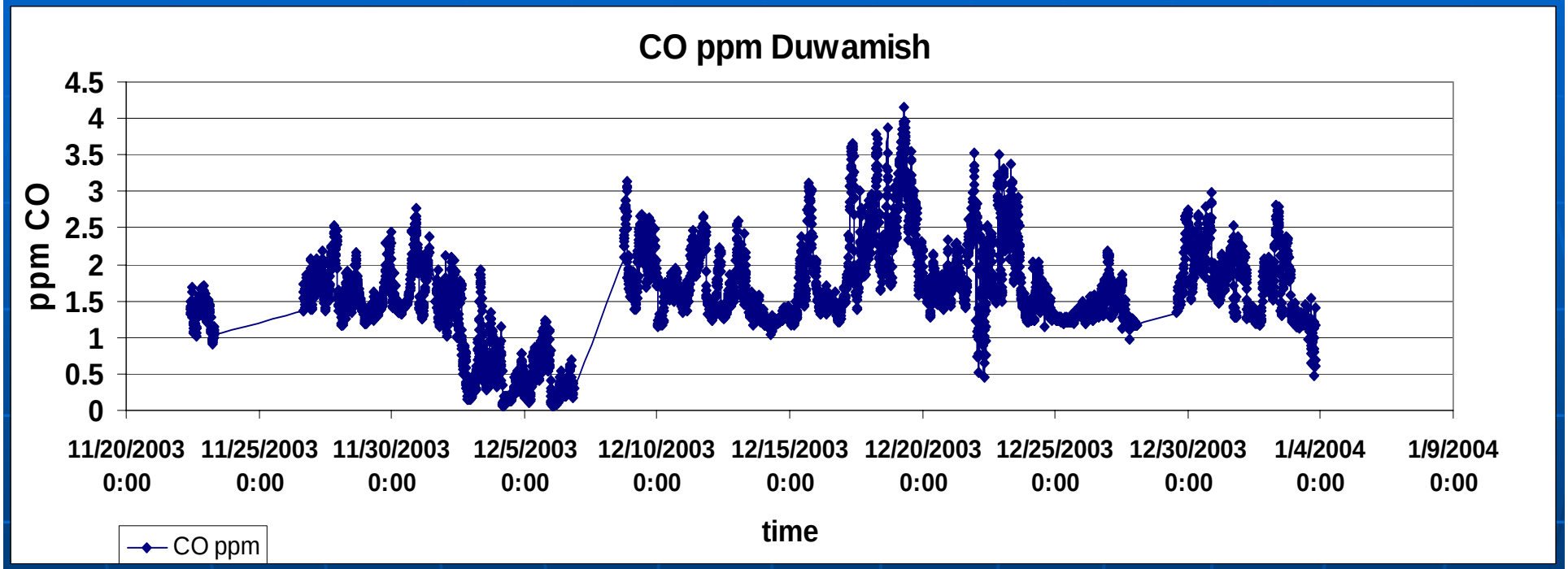
- Average of Duwamish Frames 377, 378, 379 to a reference spectrum of Trichlorofluoromethane (red trace)

Finding unknowns (3)



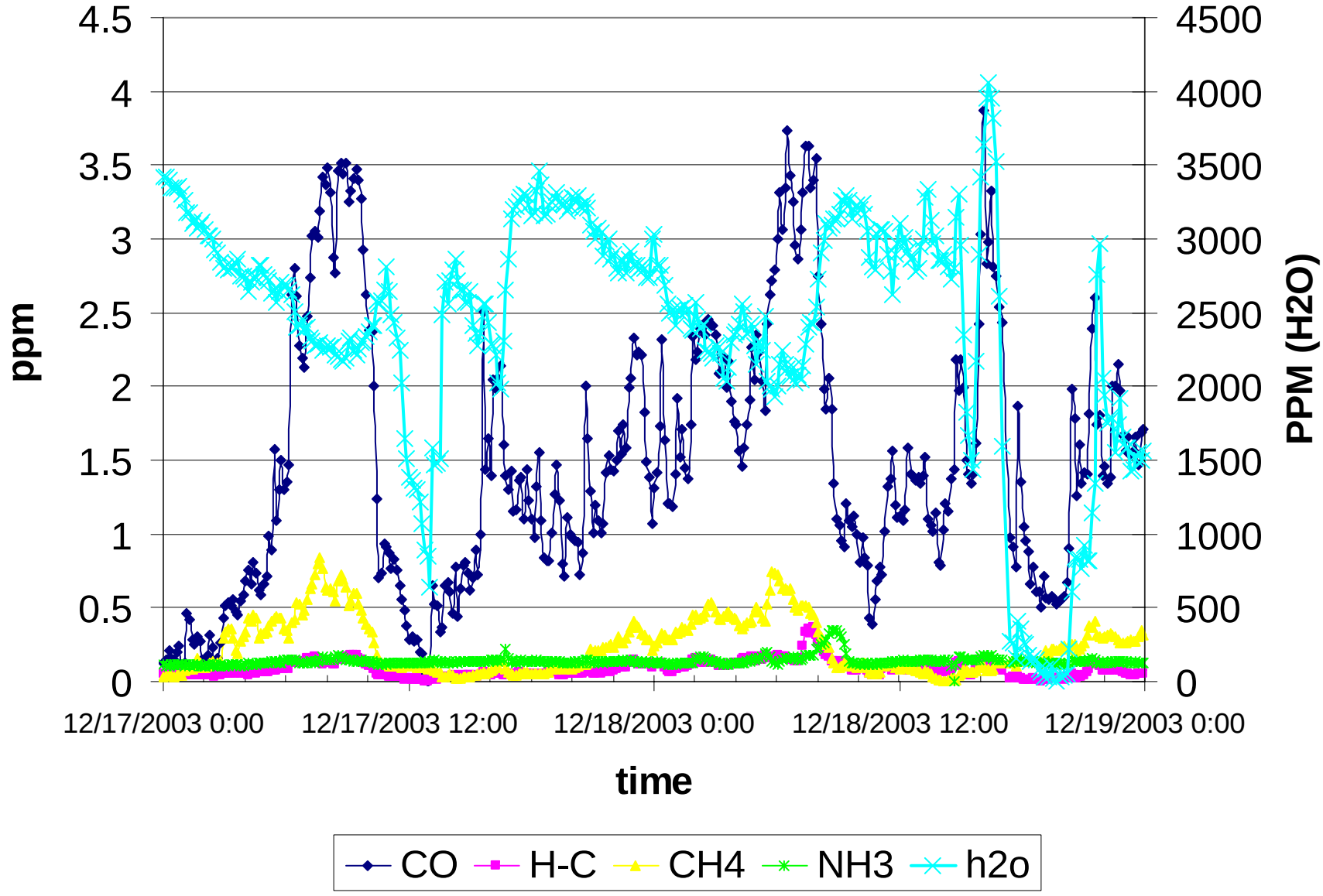
- Lake Forest Park Frame 651 (red trace) to the Reference for 1,1 difluoroethane (blue trace)

Long term Monitoring

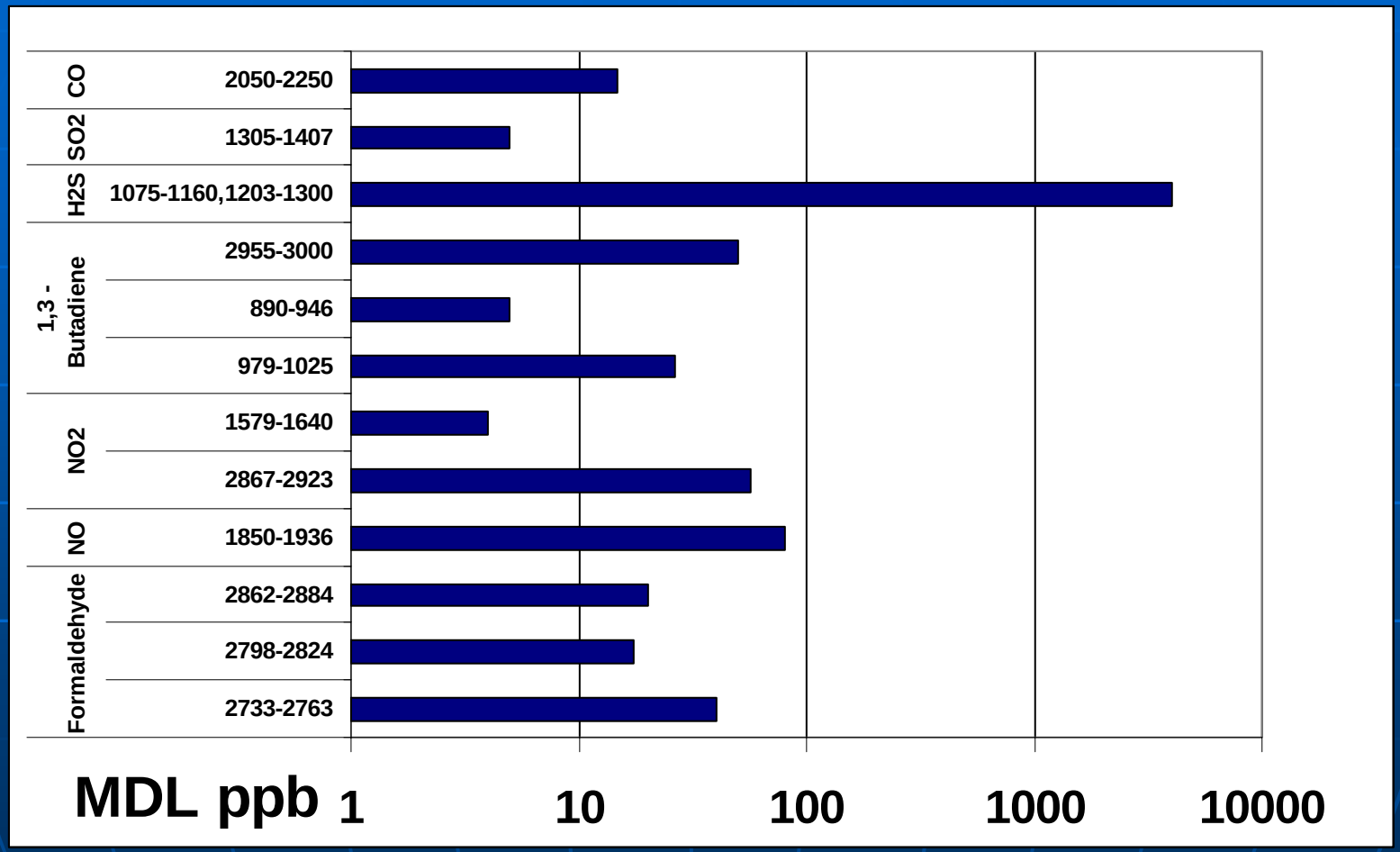


- About 44 days of monitoring data for CO at the Duwamish site
- Gaps (lines) show periods where we had instrument down time

Multi-component analysis of selected days



Some Preliminary Detection Limits



- MDL's based on 250 m path and .001 detectable absorbance (at 3x RMS noise per TO-16 calculations)
- Numbers above are fairly conservative (we could do better!)

Advantages of FTIR spectrometers

- Good signal to noise ratios (>> 200 typical)
- Both identification & quantification of samples
- Searching for Unknowns
  - More than 2000 compounds in readily available libraries
- High Sensitivity compared traditional methods
- Rapid scanning (< 1s / scan)
- High resolution (<1 cm^{-1})
- High wavelength stability & accuracy
- High radiation throughput, no stray radiation

Advantages of FTIR spectrometers

- Disadvantages
  - Moderate-sensitivity compared to Mass spec devices (ppt)
    - (Improves with √# scans)
  - Detector: semiconductor type - LN_2 cooled)
  - Complex interpretation of data
  - Accounting for H2O
  - Need for Software tools to simplify

Next Steps…

- More than 10,000 spectra logged!!!
- Lake Forest Park data not yet analyzed
- Need software tools to screen data
- Water errors contribute significant noise: the instrument noise ~ 10^{-5} AU, so there is great potential to improve MDL's
- Multivariate analysis –> source profiles?
  - PMF
- Aerosol scattering can also be observed in this data.

- Discussion/ Questions?

Quantification: How Much?

Transmission

$\%T = (I/I_0)$

Absorbance

$A = -\log (I/I_0)$

Absorbance = $f(\alpha, C, l)$ - in fact

$A = \alpha Cl$

Chosen to linearize the relationship between the spectrum response, pathlength and concentration of sample

FTIR Spectrometer