Real Time Emission Measurements Using FTIR Spectroscopy (EPA Method 320)

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Presentation Outline

- What is Spectroscopy?
- What is FTIR?
- FTIR Applications
- EPA Method 320

What is Spectroscopy?

Spectroscopy is the study of the interaction between light and matter

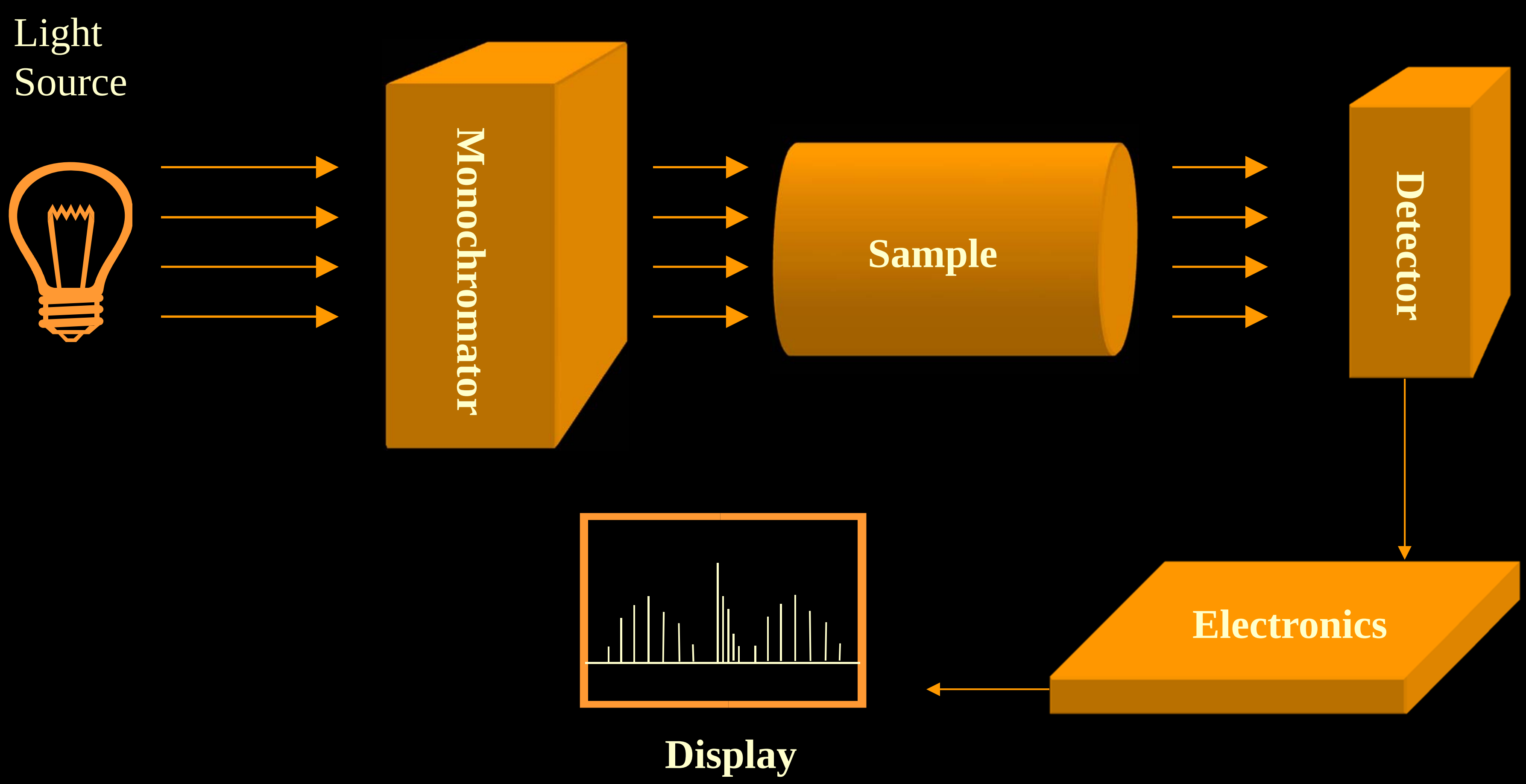
How is this interaction studied?

- Light absorption (most common - FTIR)
- Emission
- Fluorescence
- Light Scattering (e.g., Raman)
- All methods look at light intensity versus wavelength using a spectrometer

Spectrometer Components

- Light Source
- Wavelength Selection Device
- Sample Compartment
- Detector (photoconductive – MCT or pyroelectric - DTGS)
- Signal Processing Electronics

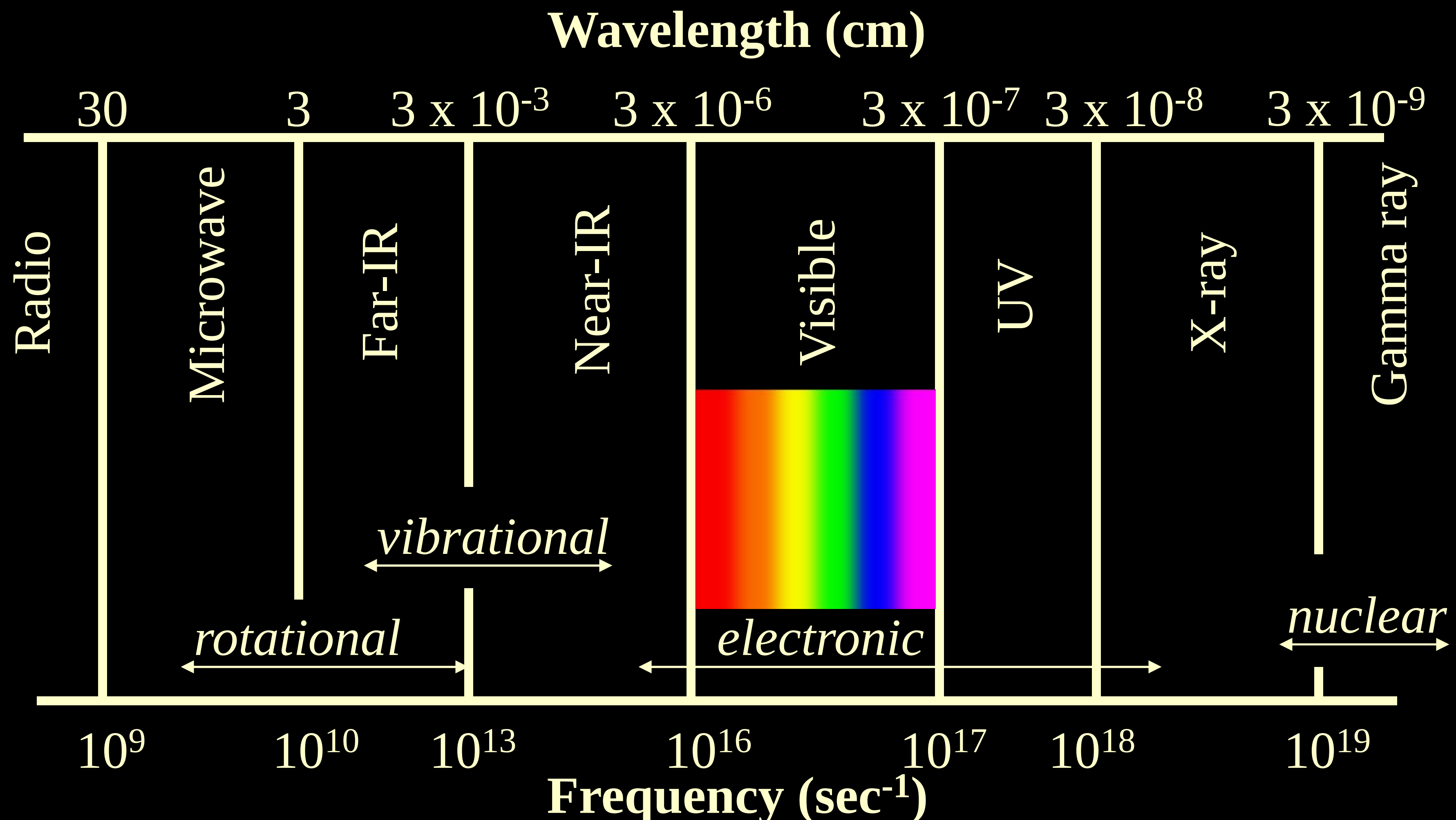
A Simple Absorption Spectrometer



What is the basic response of a spectrometer?

Light intensity versus wavelength

Electromagnetic Spectrum



Infrared Spectroscopy

- IR spectroscopy is widely used for quantitative analysis
- All molecular species except “homonuclear diatomics” (e.g., O_2, H_2, N_2, etc.) are detectable
- IR light absorption due to changes in rotational and vibrational energy in molecule

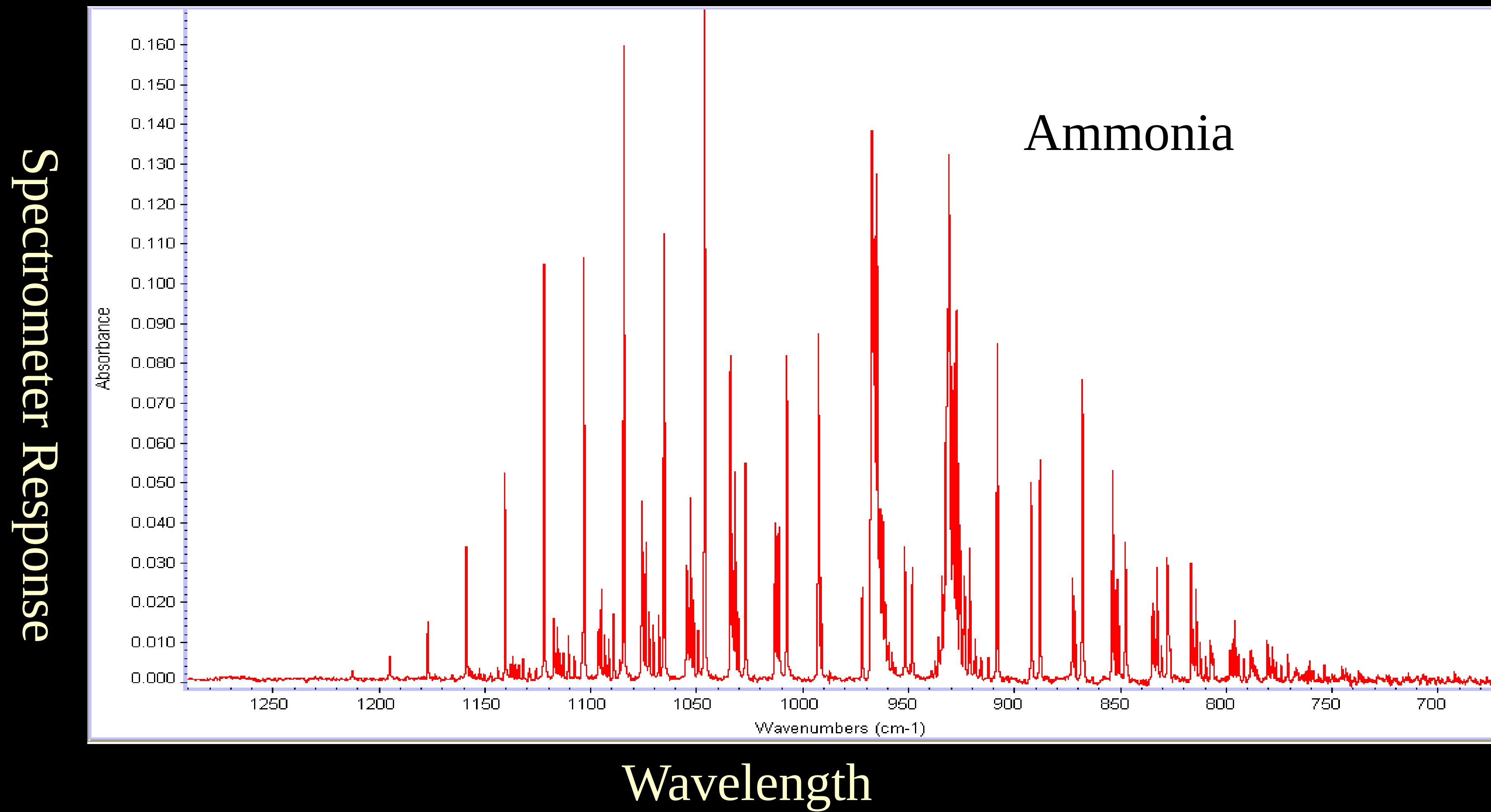
What is a Spectrum?

The spectrometer response versus wavelength

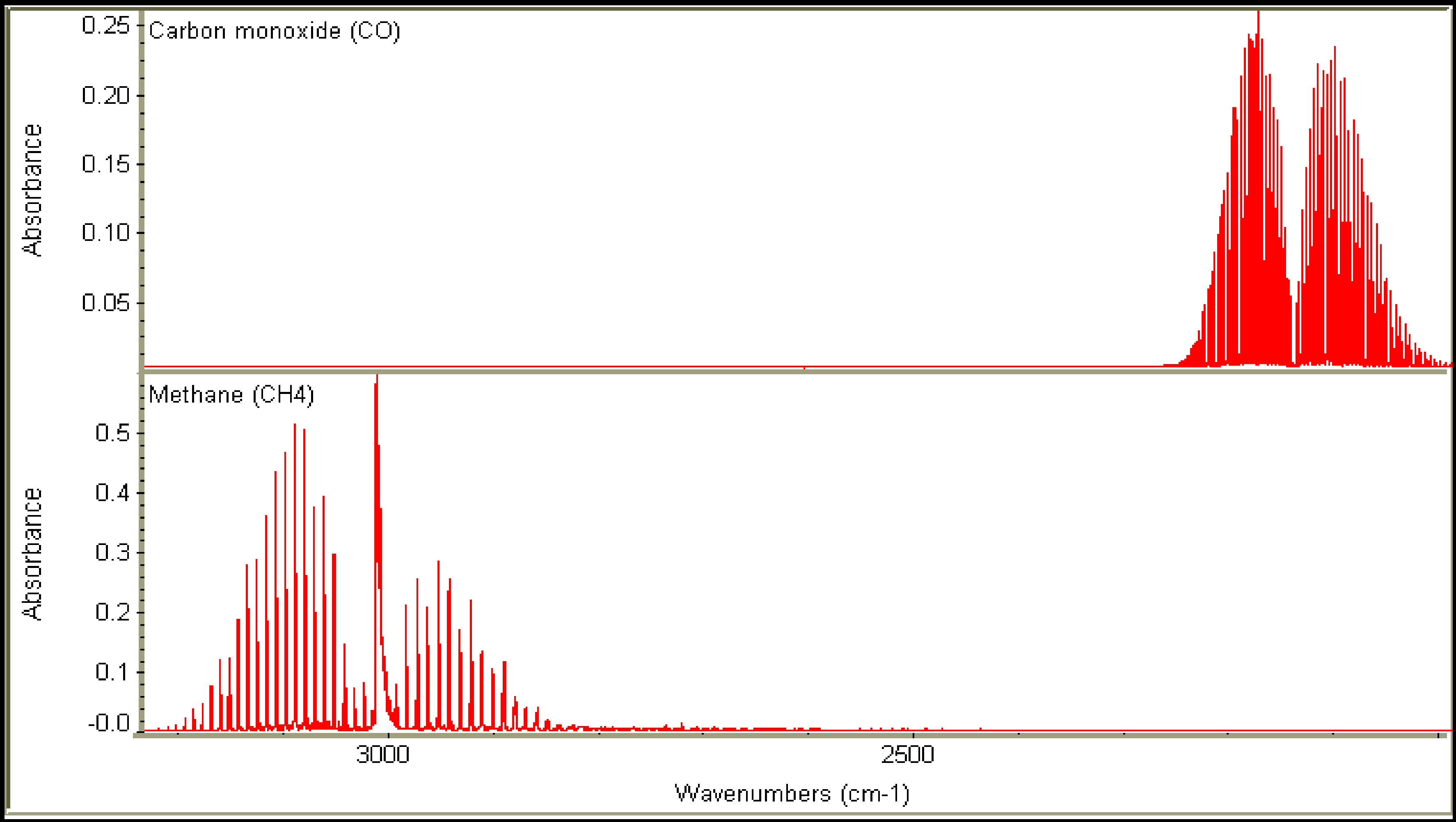
What use is a spectrum?

- It provides identification and quantification information
- No two chemical species exhibit the same spectrum
- The components in a mixture can be identified

Anatomy of a Spectrum



Example Spectra of CH_4 and CO



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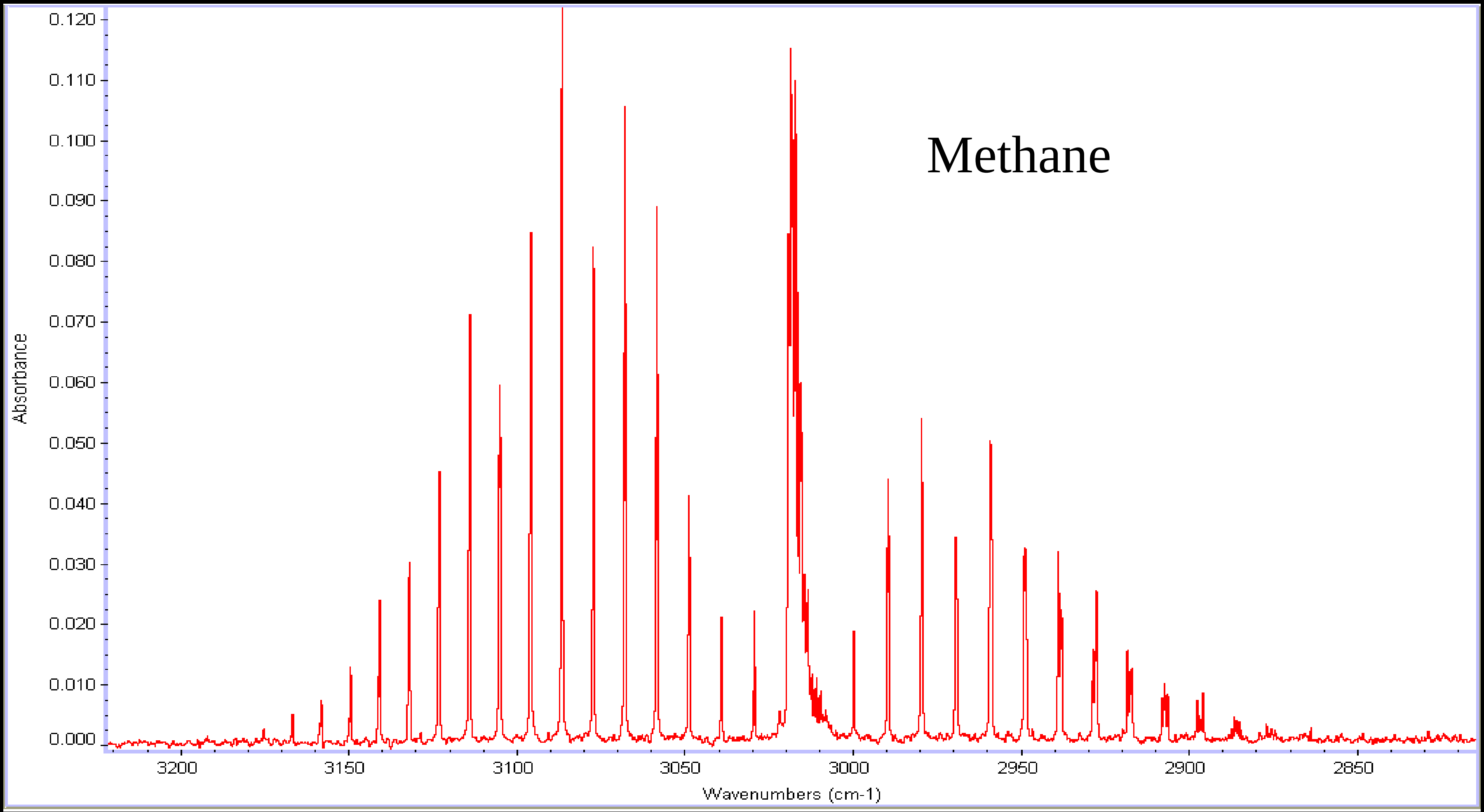
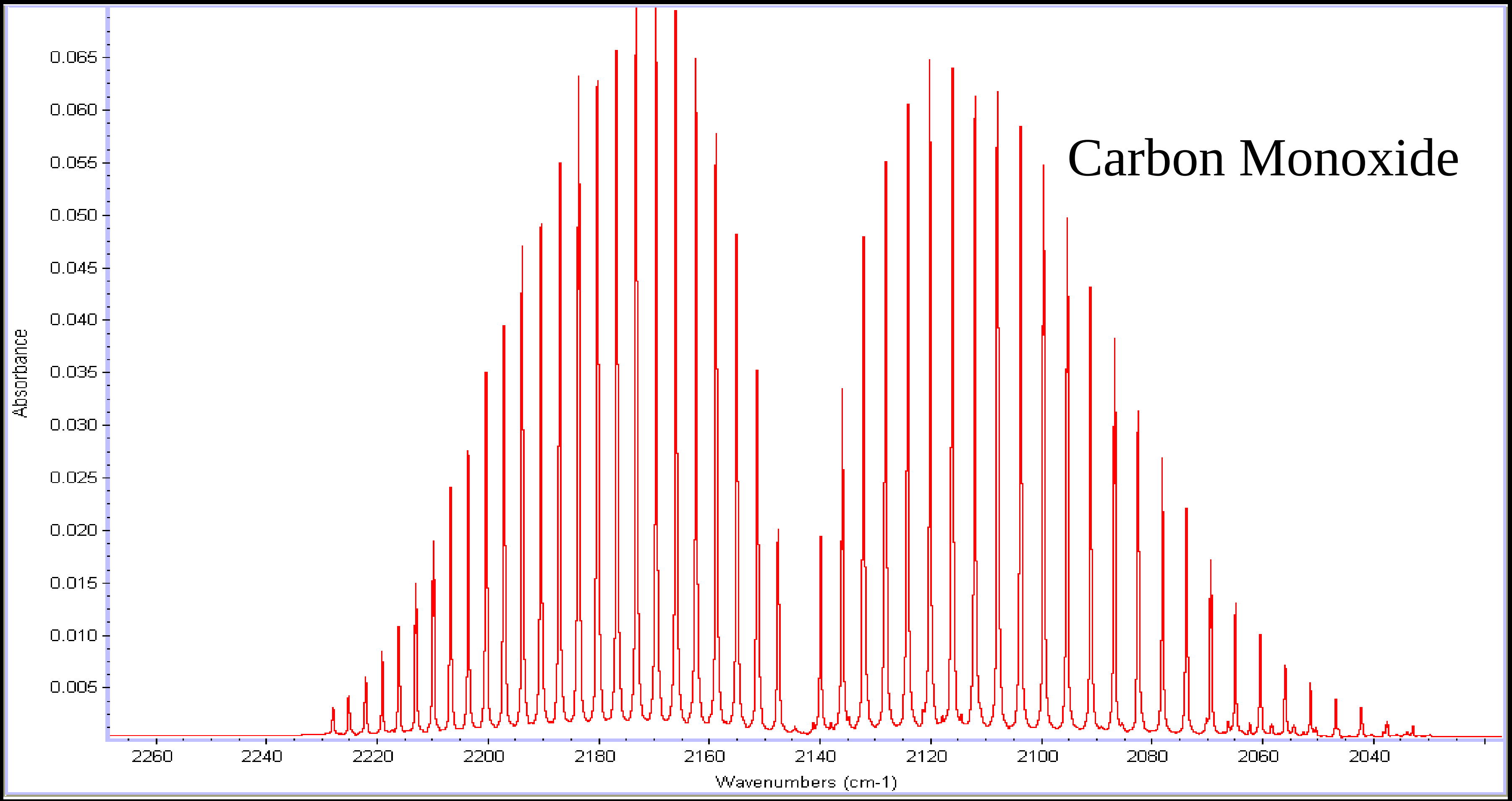
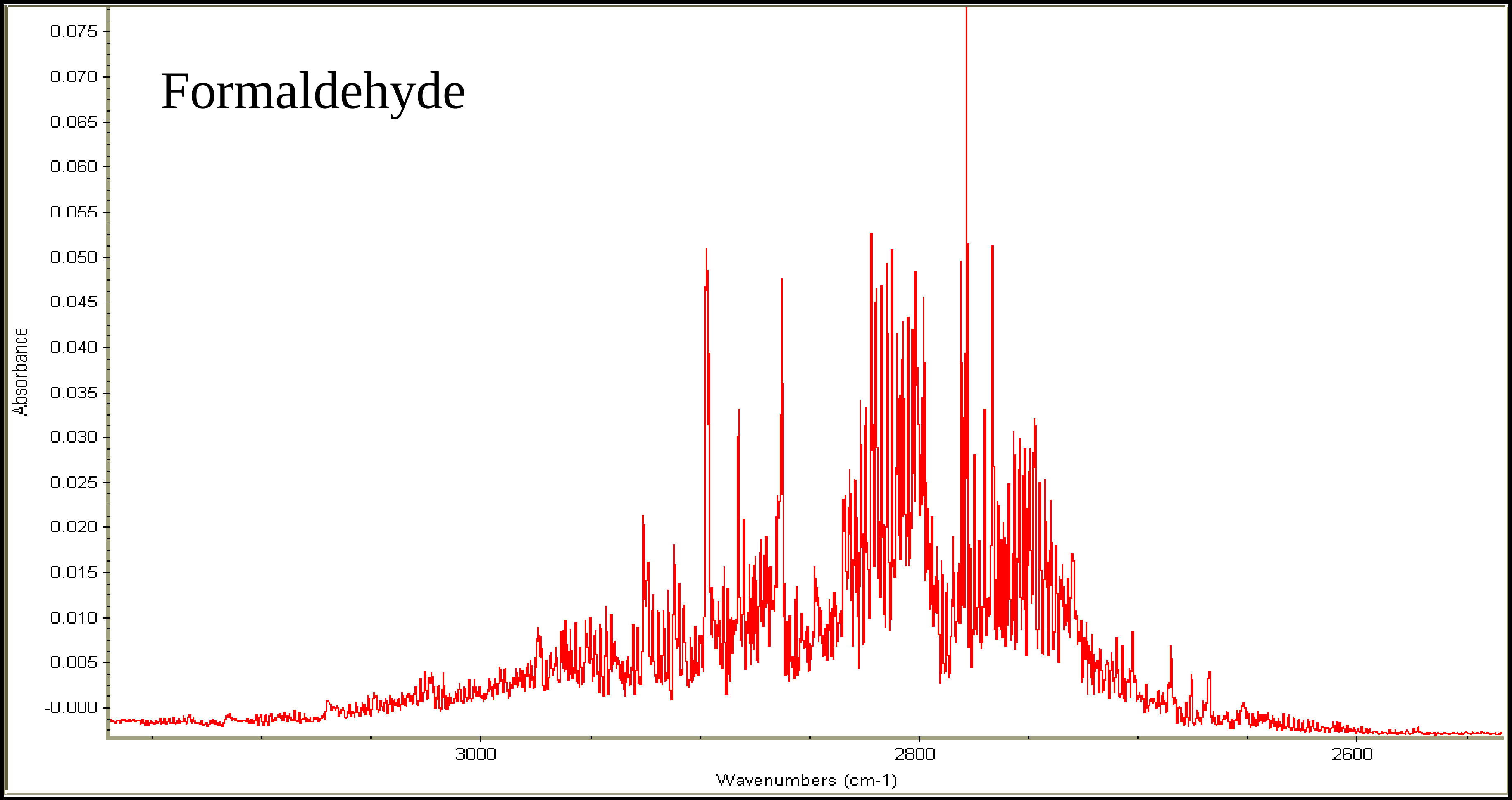
Example Spectrum – CH_4



Example Spectrum - CO



Example Spectrum – H_2CO



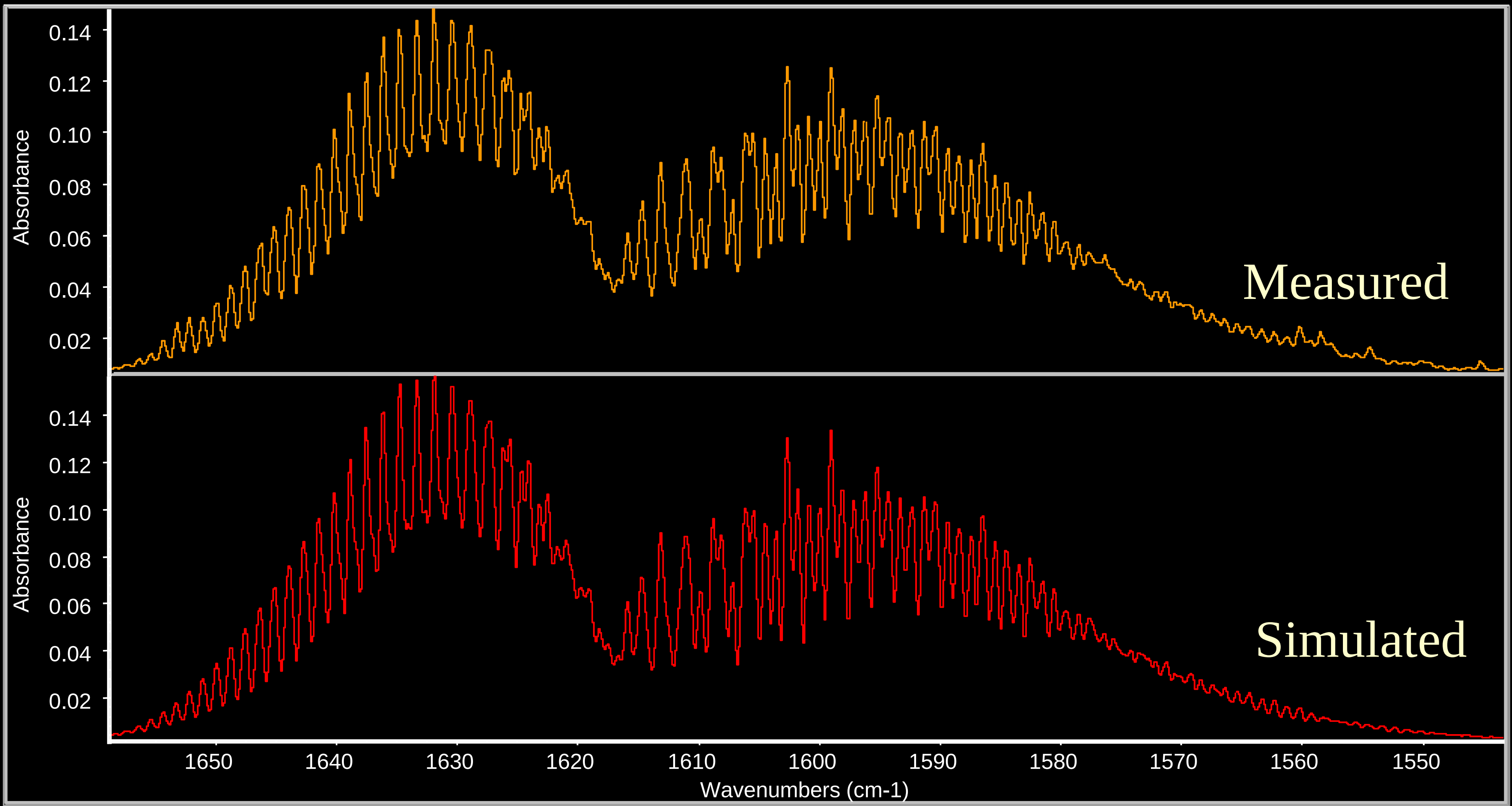
Reference Spectrum

- A reference spectrum is a spectrum of a pure chemical compound measured under controlled laboratory conditions
- Usually utilized as an absorbance spectrum
- Required for quantitative analysis
- “Calibrates” spectrometer for given compound

Reference Spectrum Verification

- Can be verified using quantum-mechanical (QM) simulations of spectra
- QM simulations are highly accurate and noiseless
- Impurities in gas standard can be identified
- Can also verify proper spectrometer operation

NO_2 Synthetic and Actual Spectra



What is FTIR?

- Fourier Transform Infrared Spectroscopy
- Measures amount of light absorbed by sample
- Available since late 1960's
- Application to field since 1970's

FTIR Background

- FTIR is a modern spectroscopic method which operates in the IR (molecular vibrations and rotations)
- The "FT" in FTIR gives the wavelength selection method (Fourier Transformation)
- Prior to FTIR, grating and prism spectrometers were used

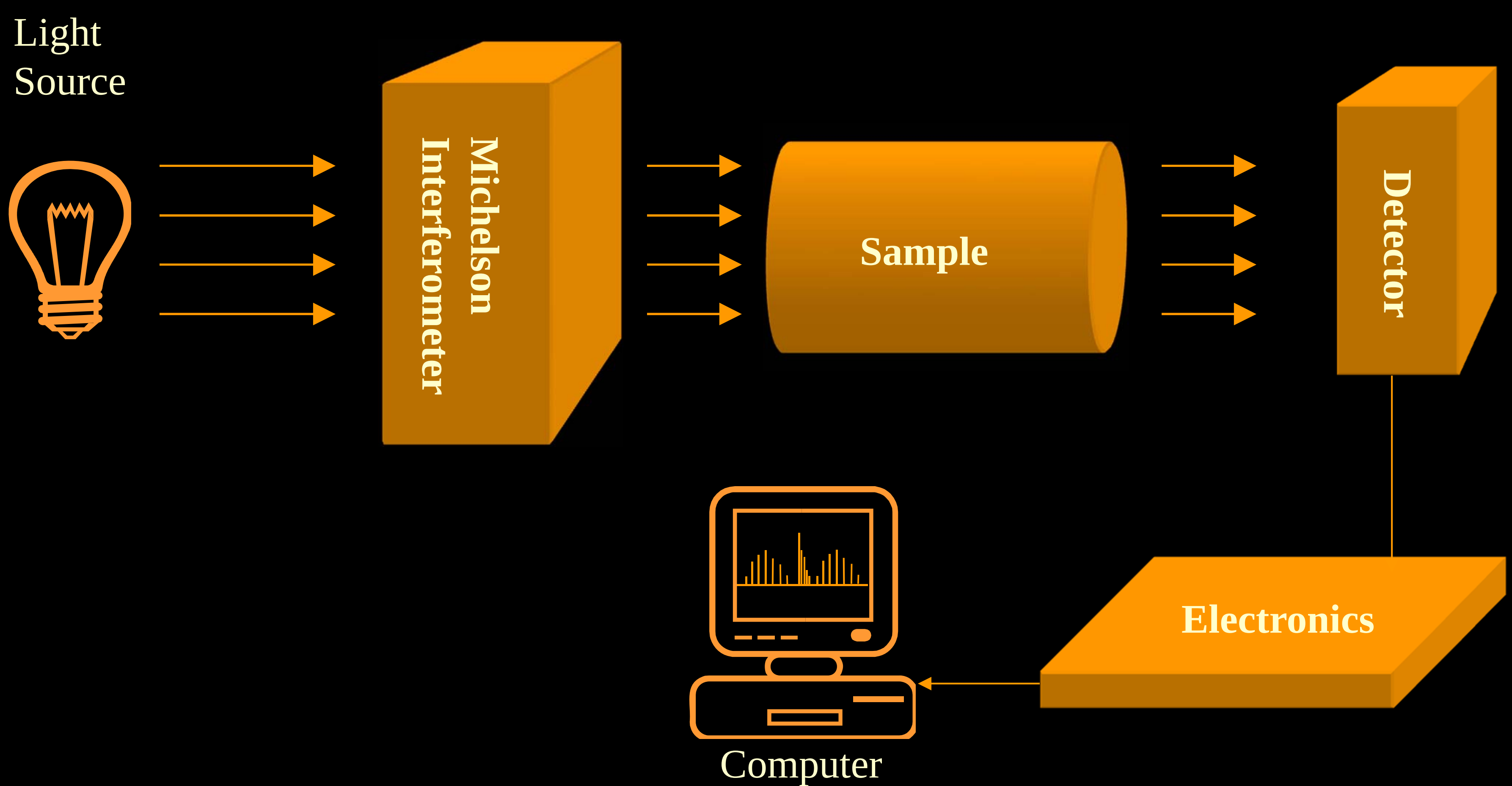
FTIR Background, continued

- FTIR is versatile: can choose many spectral collection parameters unlike any other IR method
- Signal to noise advantage : Fellgett
- Data is subject to Digital Signal Processing (DSP) algorithms
- FTIR is fast: ~ 1 spectrum per second typical

Advantages of FTIR

- Real-time accurate and precise emission data
- Lowest cost per analyte data point
- Off-site re-analysis of spectra for other species not originally targeted

A Simple FTIR Spectrometer



Identification and Quantitative Analysis

- Identification is achieved by a combination of sample chemistry knowledge and in identifying spectral features
- Quantification is carried out by mathematical comparison with reference spectra
- Quantification method depends on application

Quantifying Spectra

- Most common method is called Classical Least Squares (CLS) or Multivariate least squares
- Partial Least Squares
- Neural Networks
- K- or P- Matrix Method
- Principal Component Regression
- Beer's Law

FTIR Sensitivity

- Minimum Detection Limits (MDL) depend primarily on the signal-to-noise ratio (SNR) of the measurement
- Absorption signal can be increased by using a greater optical pathlength
- Noise can be minimized by averaging multiple spectra

Classical Least Squares

- CLS finds the best combination of reference spectra to match the corresponding features in the sample spectrum
- CLS reports an estimated error of analysis for each analyte – can be utilized for MDL measurements
- CLS requires one knows the identity of all detectable species in sample for best results

Common Interfering Species

- Water Vapor
- Carbon Dioxide
- Handled by:
  - Choice of analysis region which contains relatively few and weaker spectral lines of water vapor and carbon dioxide
  - “Windowing” of analysis region
  - Shorter pathlength
  - Sample conditioning

Linearity of Spectral Response

- Due to finite instrumental resolution, moderate strength (A > 0.1) narrow spectral lines begin to exhibit non-linear response.
- Easily modeled and corrected
- Can be modeled from simulated spectra
- Transparent to user
- Not related to detector non-linearity

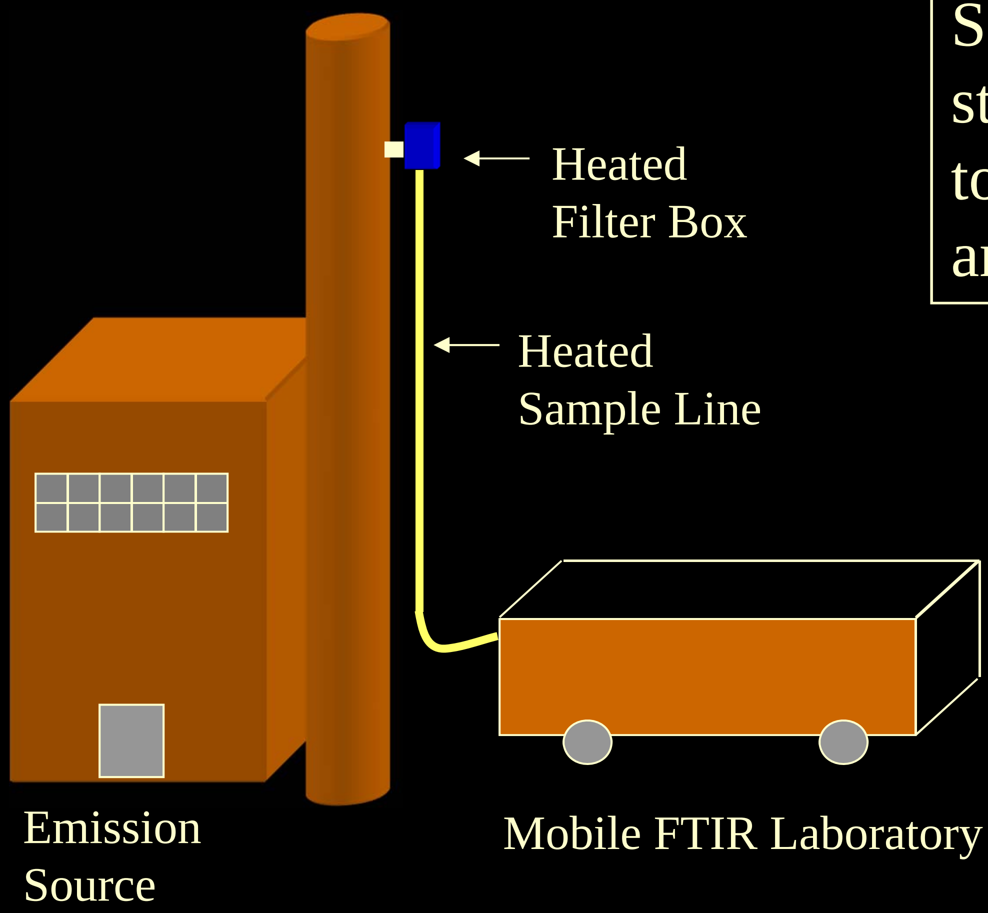
Collecting Field FTIR Spectra

- Spectral data is collected continuously
- Usually a pre-defined number of interferograms are averaged to form a composite which is then processed
- Archived spectral data can be processed later for other species not originally targeted
- Real-time results for multiple species

Application of FTIR in the field

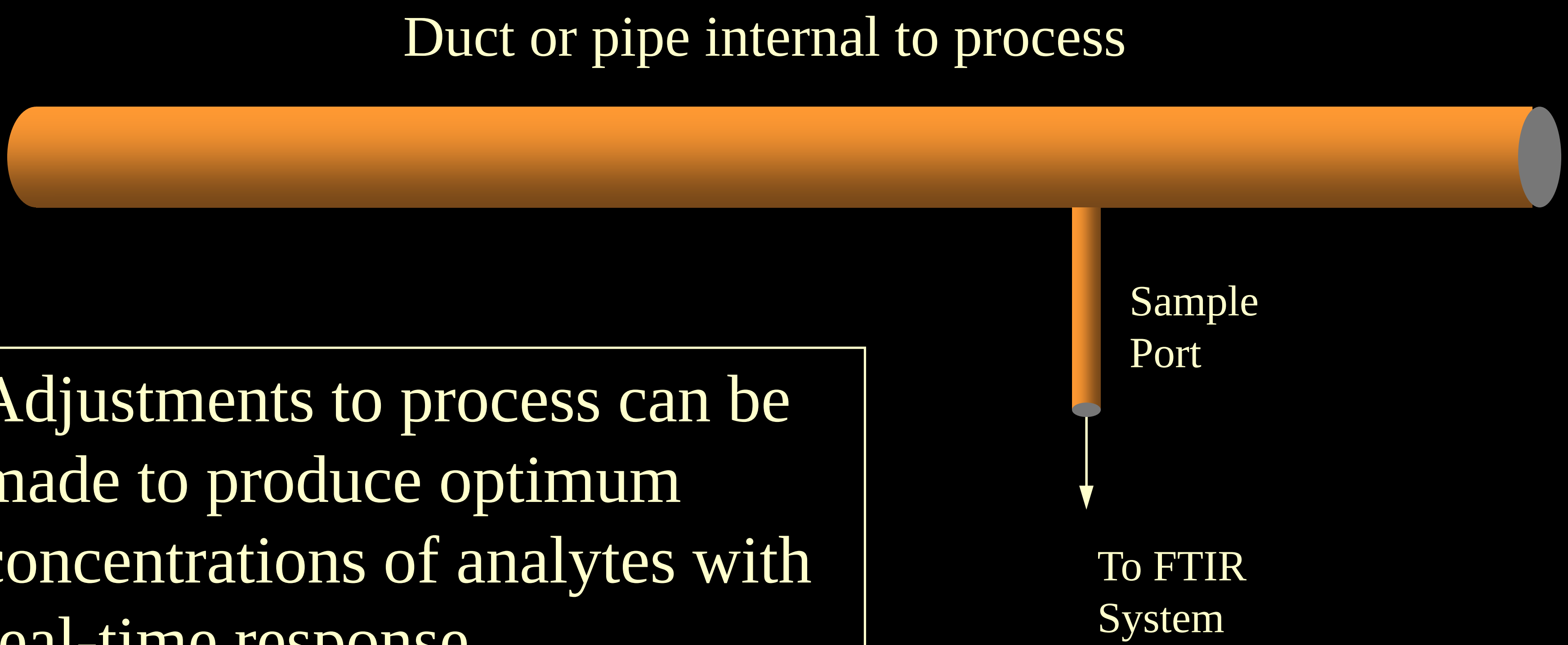
- Point Source (i.e., "stack") Characterization
- Process Optimization
- Ambient Air
- Area Source Characterization and Emission Rates
- Mobile Sources

Source Characterization



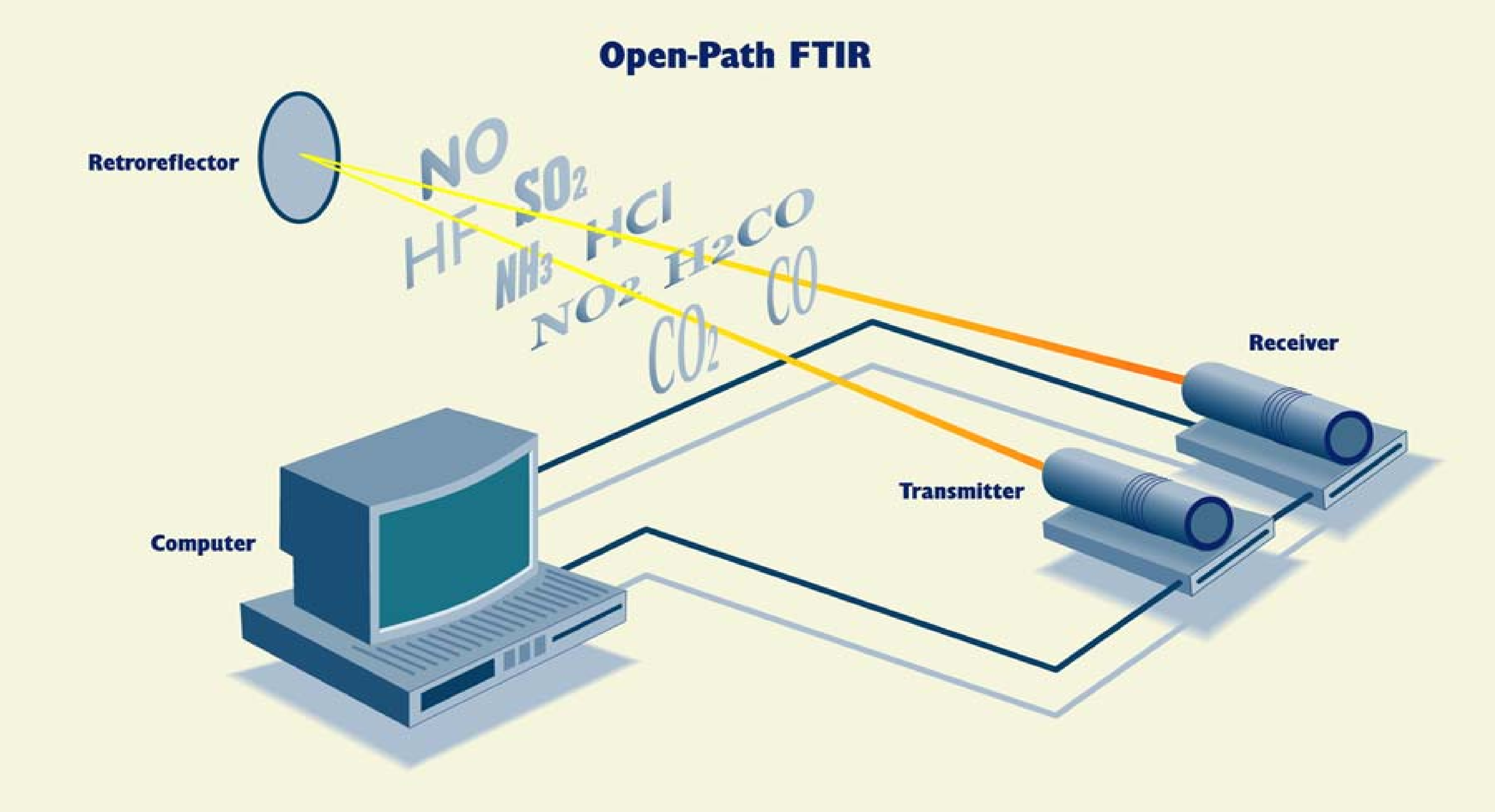
Sample is extracted from stack and transported down to the mobile laboratory for analysis

Process Optimization

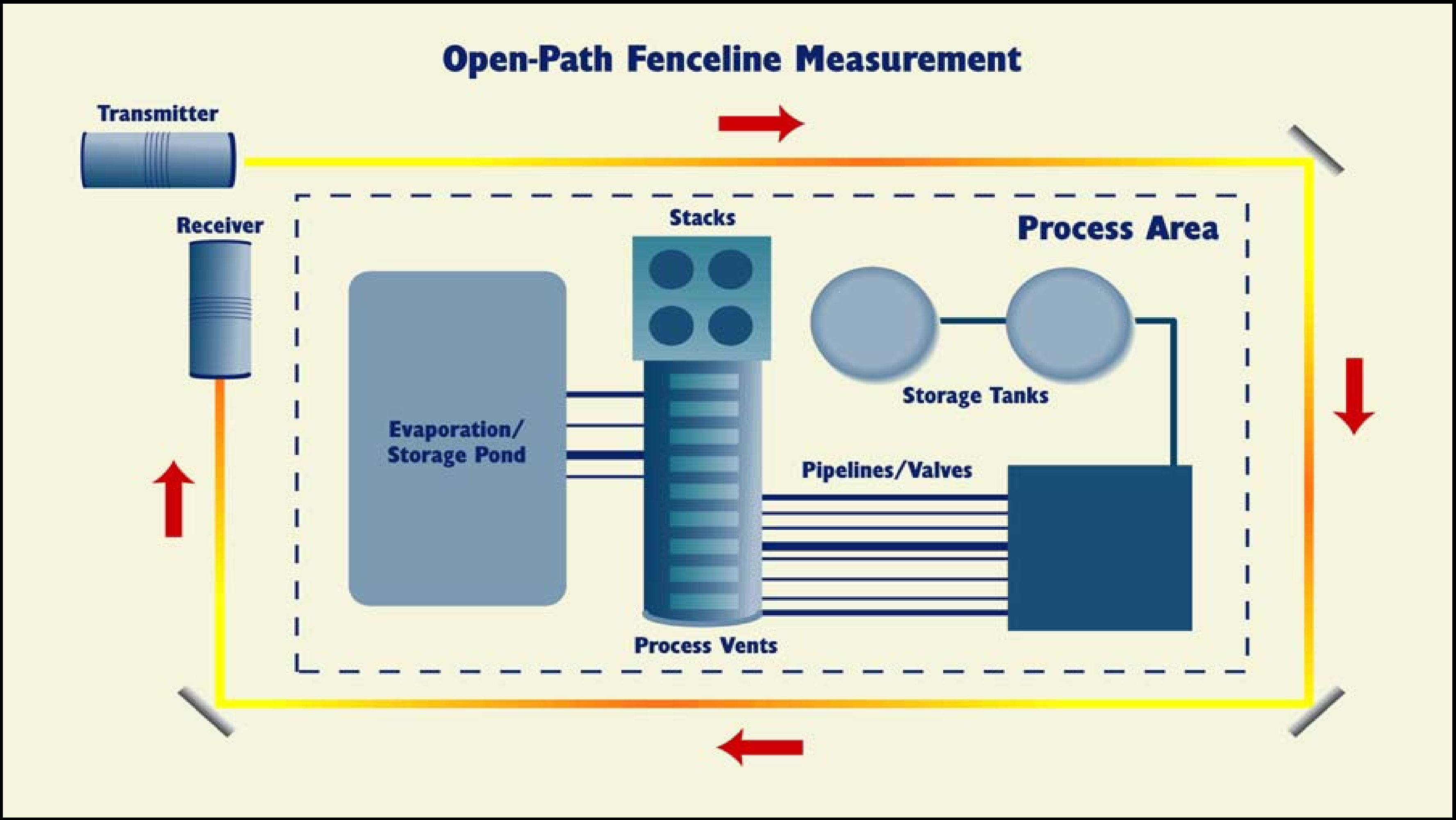


Adjustments to process can be made to produce optimum concentrations of analytes with real-time response

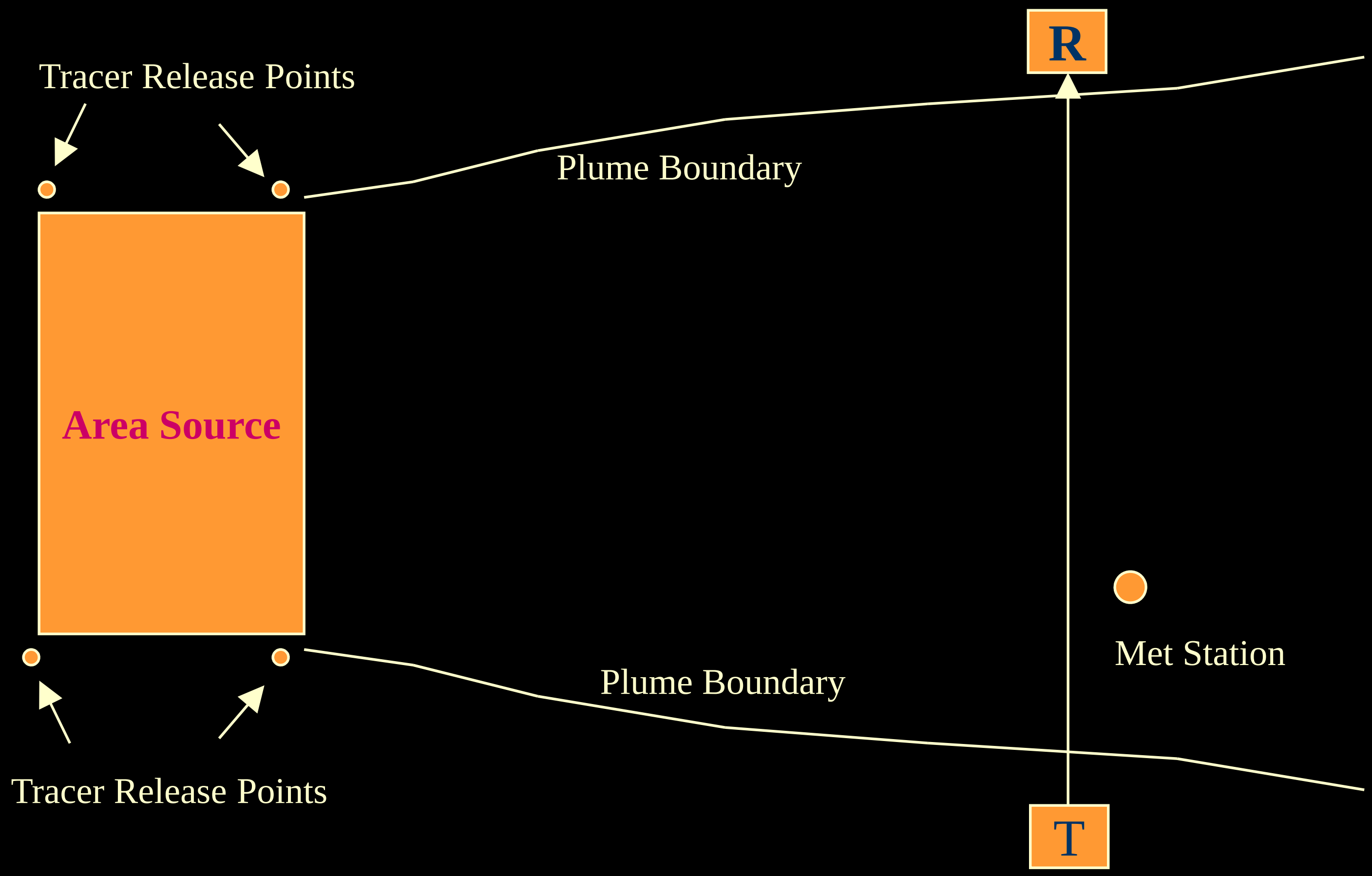
Open-Path FTIR



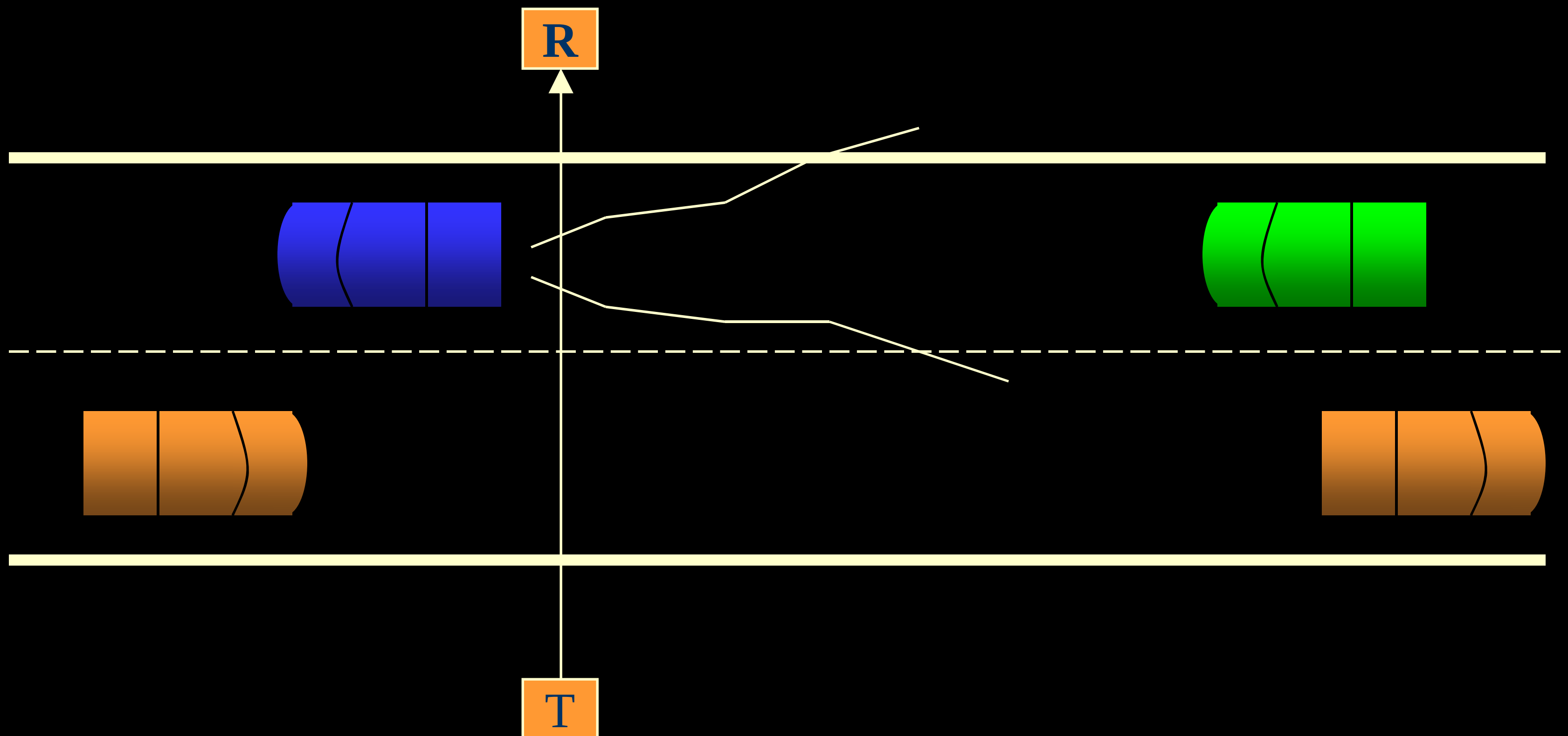
Open-Path Fenceline Measurement



Area Source Characterization and Emission Rate Determination



Mobile Sources



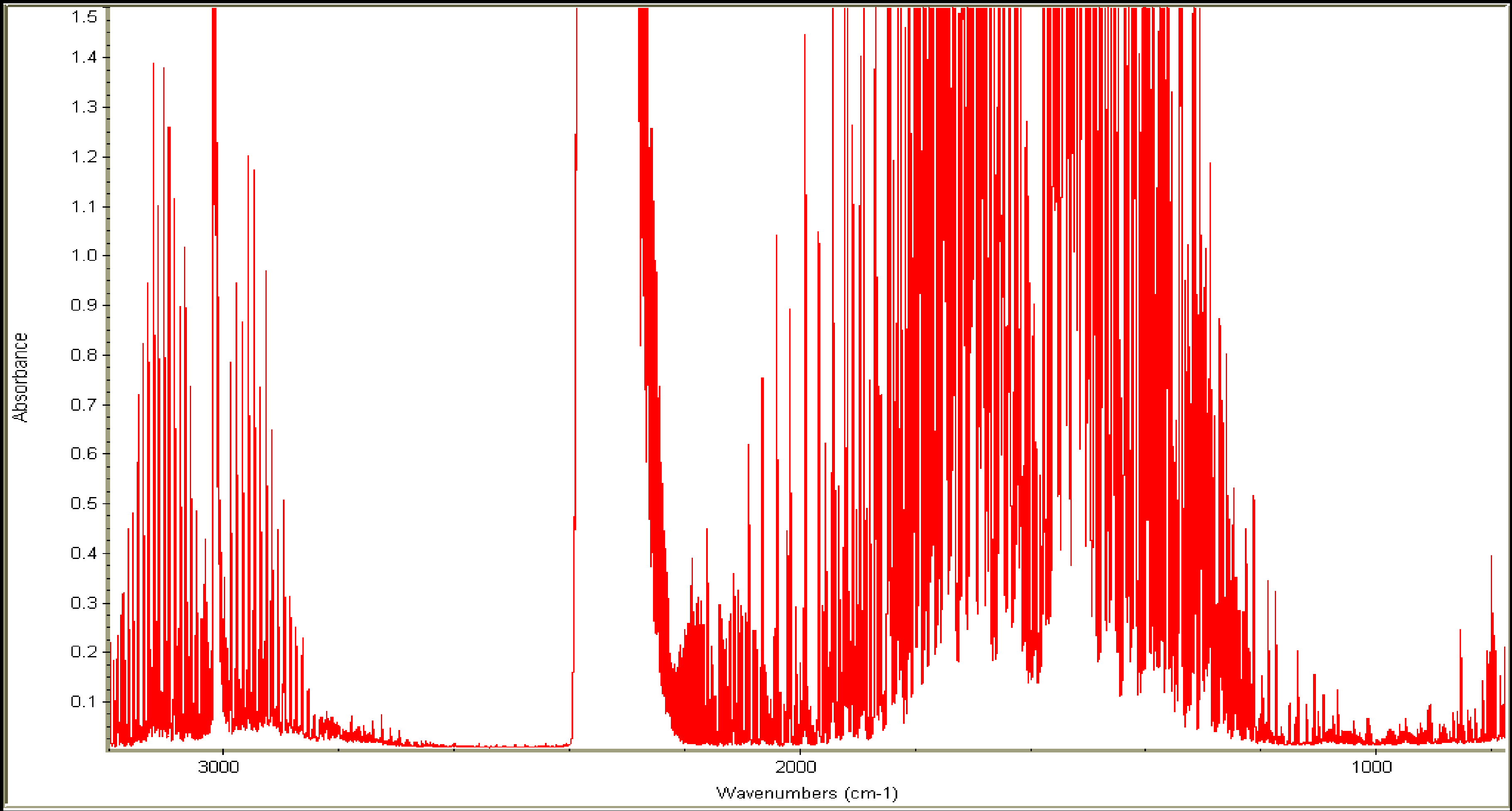
Application to Emission Measurements

- FTIR in regular field use for about 20 years
- Validated (via EPA Method 301) for many source categories
- Formal test procedures: EPA Method 320, ASTM D6348 – 03
- ASTM method acceptable alternative to M320 if ASTM method QA is conducted

Typical FTIR Emission Measurement Applications

- Compliance Testing
- Control device testing (e.g., scrubbers, bag houses, oxidizers, catalysts, etc.)
- Research
- Emissions / process optimization
- Real time gaseous fuel / feedstock analysis

Example Combustion Spectrum



Typical FTIR Detection Limits Combustion Sample Matrix

- Formaldehyde: 0.05 ppmv
- NO: 1 ppmv
- NO_2: 0.3 ppmv
- CO: 0.05 ppmv
- Generally a function of optical pathlength, but also dependent on measurement time (1 minute shown) and sample matrix

EPA Method 320

- Formal Emissions Test Procedure
- Can be applied to any source category with successful validation (i.e., “self-validating”)
- QA/QC via direct instrument and system challenges
- System challenged with key species most difficult to measure

M320, continued

- Supporting calculations from actual data are required (Appendices of Protocol)
- Calculations based on spectral band areas; CLS can directly report measurement uncertainties
- Supporting FTIR protocol document available

M320: First Test of Source

Must conduct Method 301 validation by dynamic spiking of all target analytes

M320 QA/QC

- Involves instrumental and system challenges
- Instrumental: Measurement of a “Calibration Transfer Standard” (CTS) and zero gas measurement for noise / baseline drift
- System: Dynamic spiking before (and after) each testing run - sampling system response time
- Sampling system integrity checks
- Spike should be key species that is most difficult to measure (due to sample matrix or physical properties)

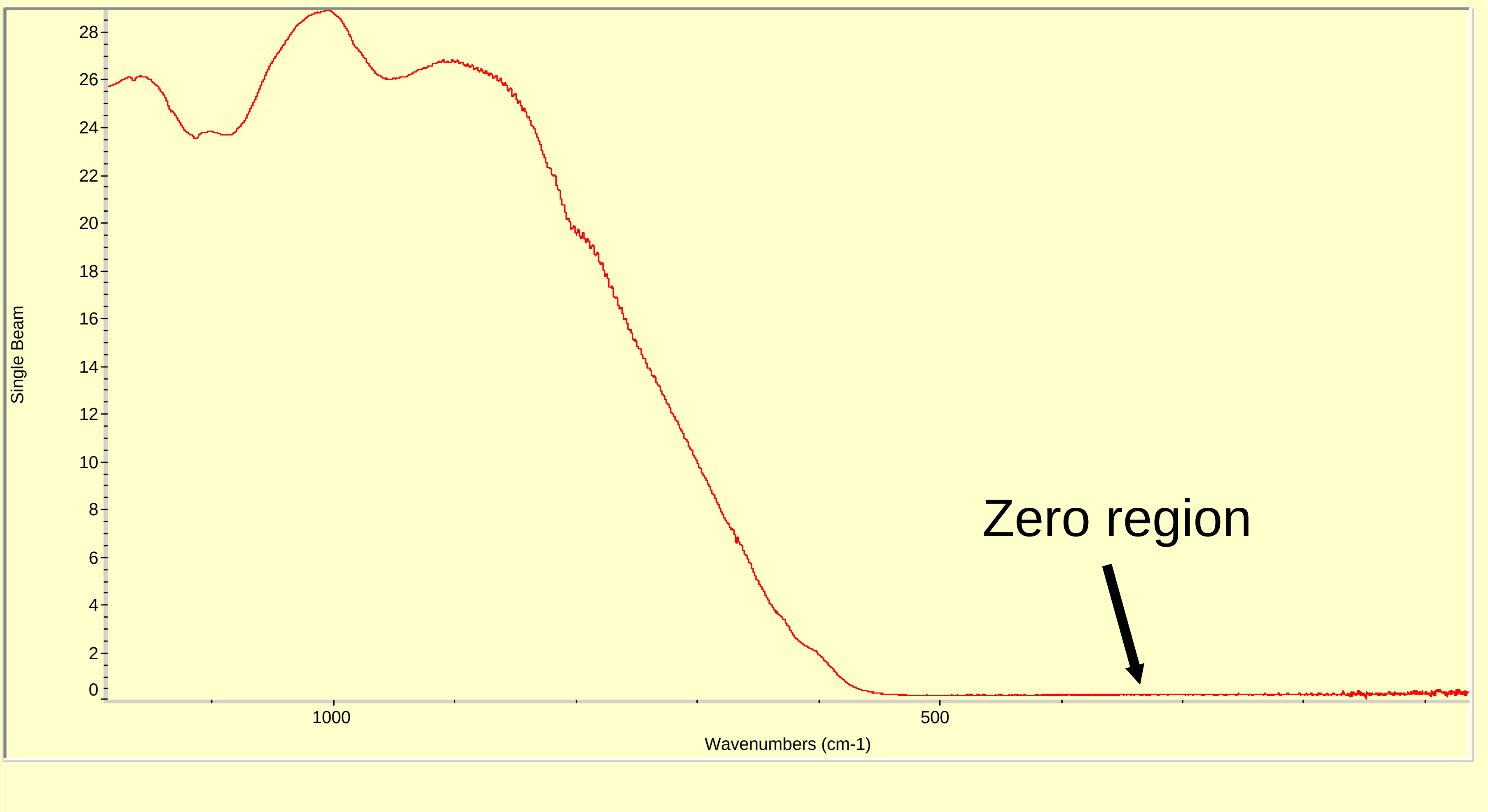
Instrumental Checks

- Detector Linearity (procedure in sect. 8.3.3 most common)
- Optical Pathlength: compare CTS spectrum to CTS of known pathlength
- Cell Leak Check (< 4% of cell volume in measurement period)
- CTS measurements (pre and post)
- Noise / baseline test (zero spectrum)

Detector Linearity

- Once set, rarely requires readjustment
- In test report, a statement that confirms that this was completed is usually considered sufficient
- Can be checked in spectral data by examination of spectrum from 0-500 wavenumbers (should be zero with superimposed noise)

Linearized Detector Spectrum



Pathlength Check

- Measurement of a CTS standard and compared to lab CTS spectrum (appendix H of protocol)
- Tolerance: Within 5 percent of stated ("approximated") pathlength
- Mathematically identical to analyzing CTS standard and quantifying with stated pathlength: agreement to within 5 percent of certified CTS concentration
- Result reported as either actual measured pathlength or % recovery of CTS standard

Cell Leak Check

- Depends on sampling method
- Batch-type sampling (evacuate and fill):
  - Evacuate cell and measure pressure change in 2 minutes
  - Correct to sampling time
  - ≤ 4% volume leak rate in sample period acceptable
  - Repeat with cell pressurized 100 mmHg above ambient

Cell Leak Check

- Continuous sampling (purging) method:
  - Pressurize 100 mmHg above ambient
  - Measure pressure change (loss) in 2 minute period
  - Correct pressure change to sample period
  - ≤ 4% volume leak rate in sample period acceptable

Baseline and Noise Spectrum

- Measurement of zero gas under identical sampling conditions
- Check for baseline drift
- Greater than 0.02 A (5% T) change in baseline requires new background
- S/N ratio must be 10 or greater for minimum analyte peak absorbance
- Modern insturments rarely require new background or baseline corrections
- NEA: < 1 x 10^{-4} in modern instrumentation

Calibration Transfer Standard

- Preserves instrument frequency and intensity calibration at time of reference spectrum measurement
- Ethylene used, but CO, CO_2, CH_4 mixture also used with proliferation of narrow spectral lines in most commonly used spectral regions
- Other species with broad spectral bands used
- Used as an instrumental diagnostic

System Checks

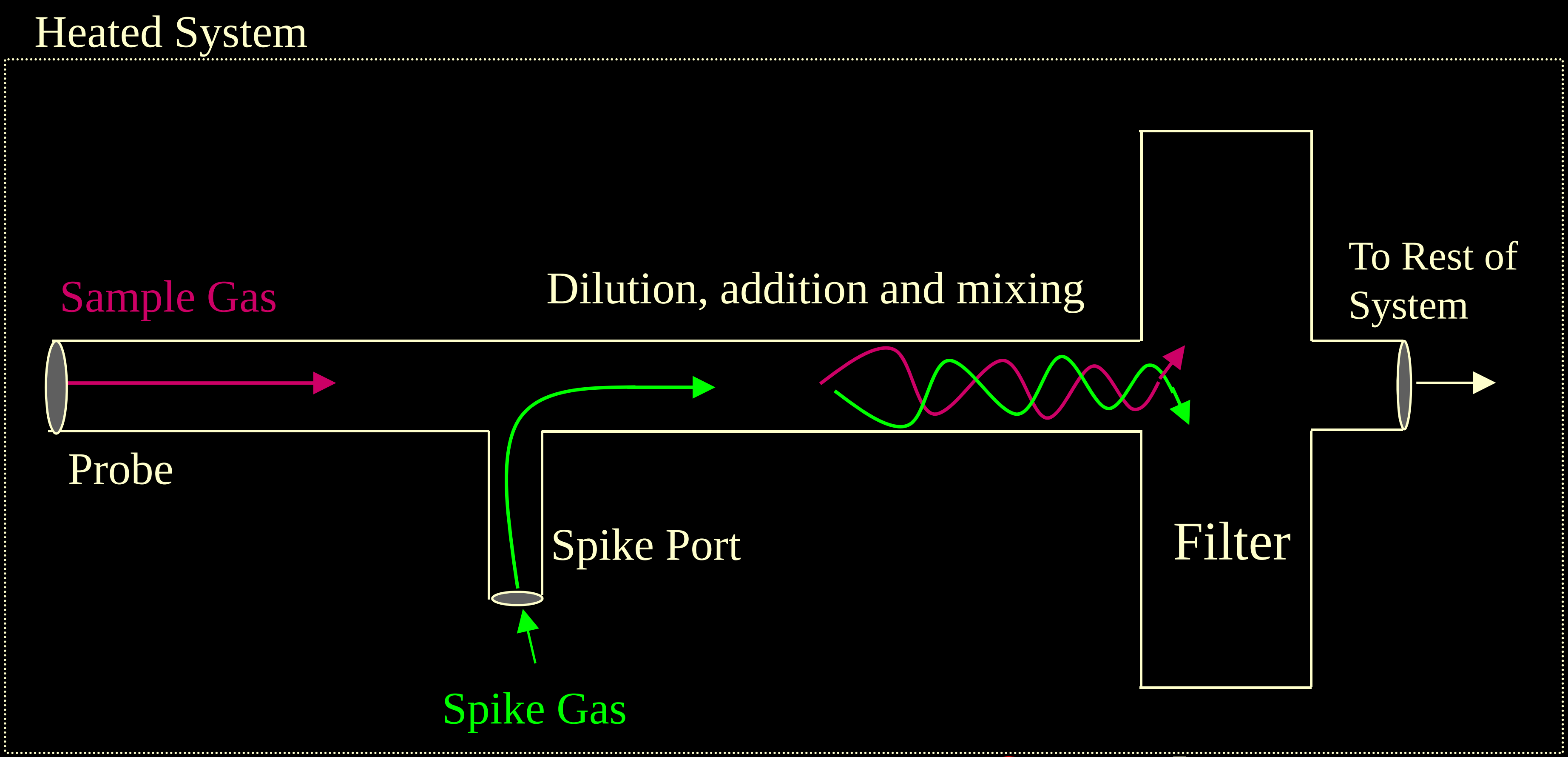
- System Leak Check (< 200 mL/min)

- Dynamic Spiking: System response time and analyte measurement assessment in actual sample matrix

Dynamic Spiking

- Target analyte injected into sampling system at probe (less than 10 percent dilution) with known concentration
- System response measured
- 70 – 130 percent recovery
- Should use target analyte that is considered most challenging to measure (e.g., formaldehyde for natural gas combustion)
- Ethylene is not considered challenging in virtually all expected sample matrices (i.e., non-polar species)

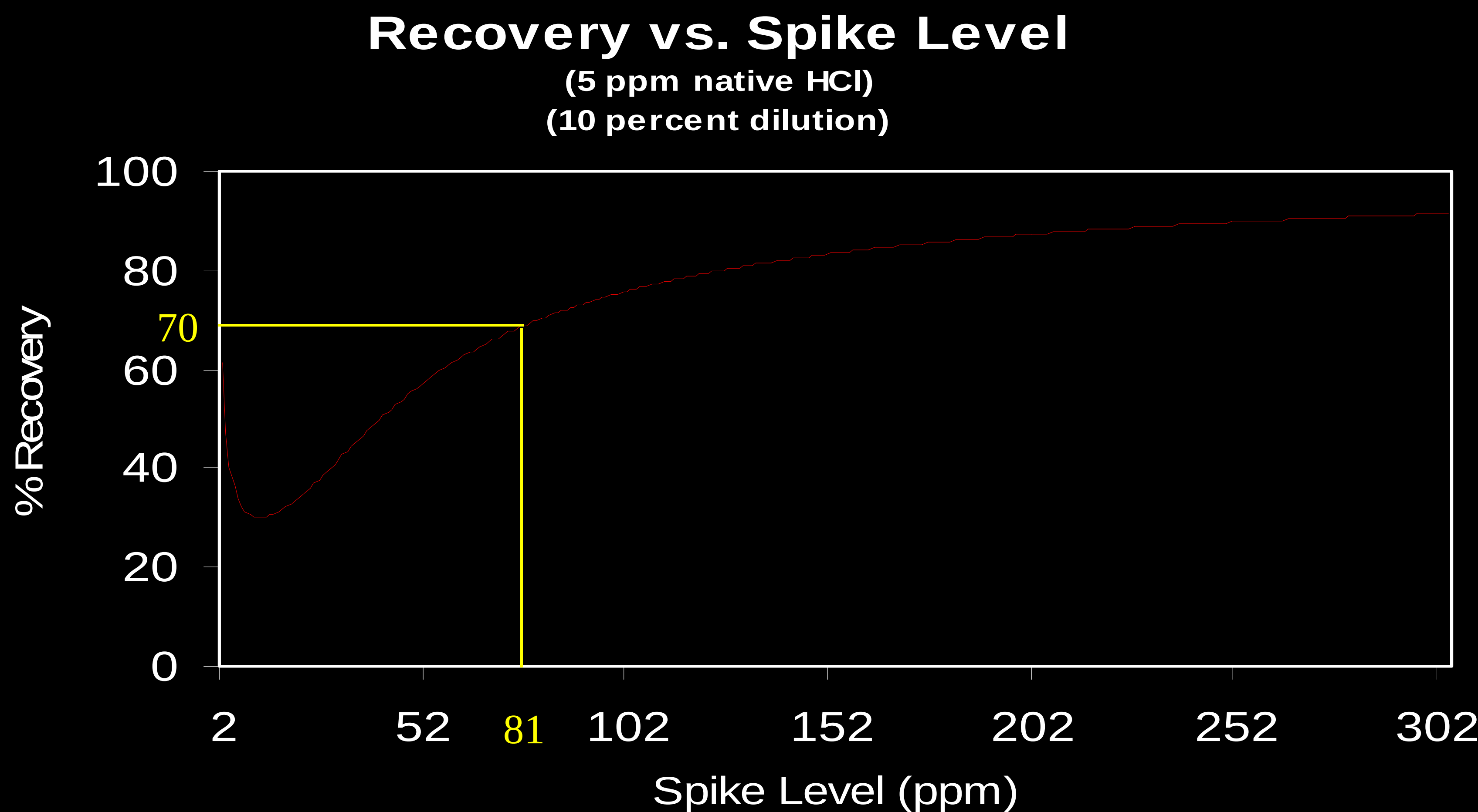
Spike Injection



Spiking into Reactive Sample Matrix

- Very low recoveries may indicate reactive sample matrix
- Example – HCl spike into streams containing NH_3
- Thermodynamic calculations indicate low recovery for moderate level HCl spike
- Confirmed in field by excellent HCl recovery at very low and high spike levels

Simulation of HCl Spike Recovery – 29 ppm NH_3



Sampling

- Batch – evacuate to < 5 mmHg and fill cell with sample
- Continuous Static: Purge cell with 10 cell volumes and isolate
- Continuous – > 5 cell volumes flow per sample period – most common

Questions / Discussion