FTIR for Emissions Monitoring Applications

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Outline

- General overview of gas measurements using infrared spectroscopy
- Specific issues relating to Fourier Transform Infrared (FTIR) Spectroscopy
- Some issues with ASTM method

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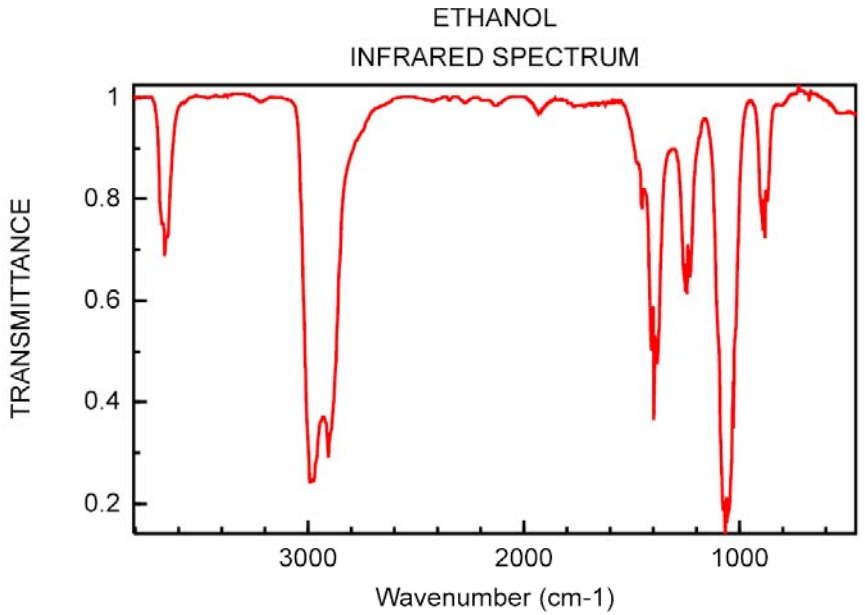
Infrared Spectroscopic Measurements of Gases

- Infrared spectroscopic measurements work by using light to measurement the optical absorption ‘fingerprint’ of the target species.
- In the infrared region the spectroscopic fingerprint of a particular species depends upon the rotational and vibrational modes of the molecule.
- The shape of the absorption features are effected by the ambient conditions and interactions with surrounding molecules.



NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

Principles of Infrared Spectroscopy

- Most molecules possessing a charge asymmetry, or dipole moment, absorb IR radiation
- The IR absorption features are a result of transitions between vibrational and rotational energy levels of the bonds between atoms in the molecule.
- The frequency at which an absorption feature occurs is dependent on the energy separation of the ro-vibrational levels, and is characteristic to the bond within the molecule (eg the ‘C-H stretch’ at ~3 μm)
- Light molecules tend to have fine-scale features with narrow absorption lines.
- Heavy (floppy) molecules tend to have broad spectral features.

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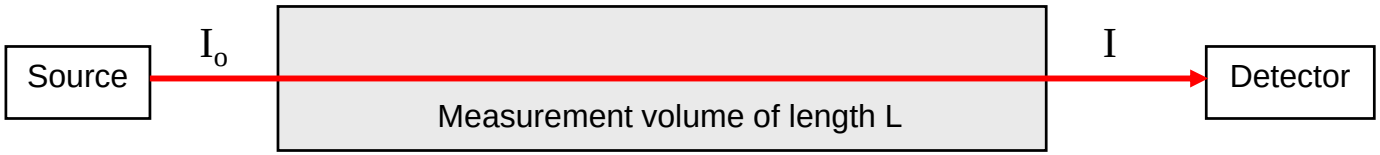
Spectroscopic Measurement Methods

Direct Absorption Spectroscopy

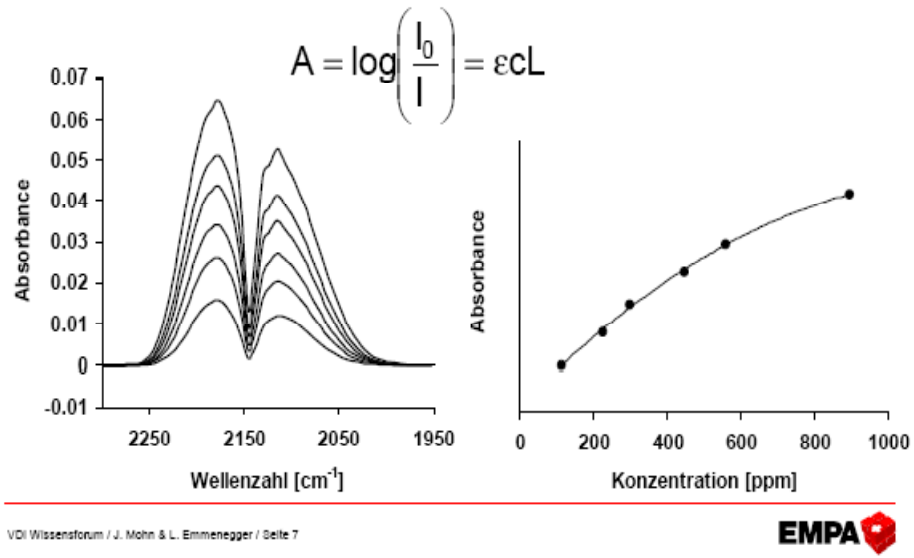


Beer's Law

$$I(\lambda) = I_0(\lambda)\exp(-\alpha(\lambda)NL)$$

where I = measured intensity
I_0 = incident intensity
N = concentration
L = pathlength
α = absorption coefficient

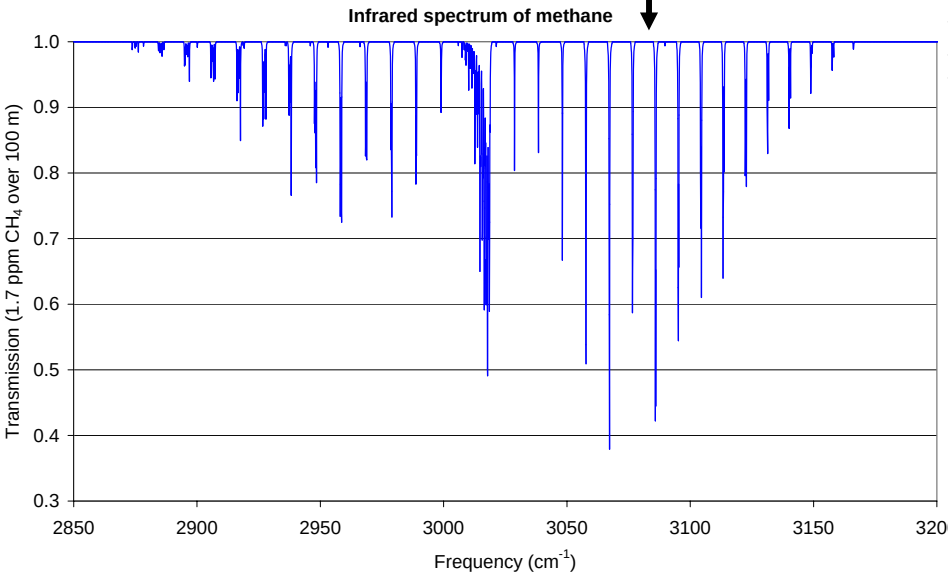
$$N = -\frac{1}{\alpha(\lambda)L}\log\left(\frac{I(\lambda)}{I_0(\lambda)}\right)$$

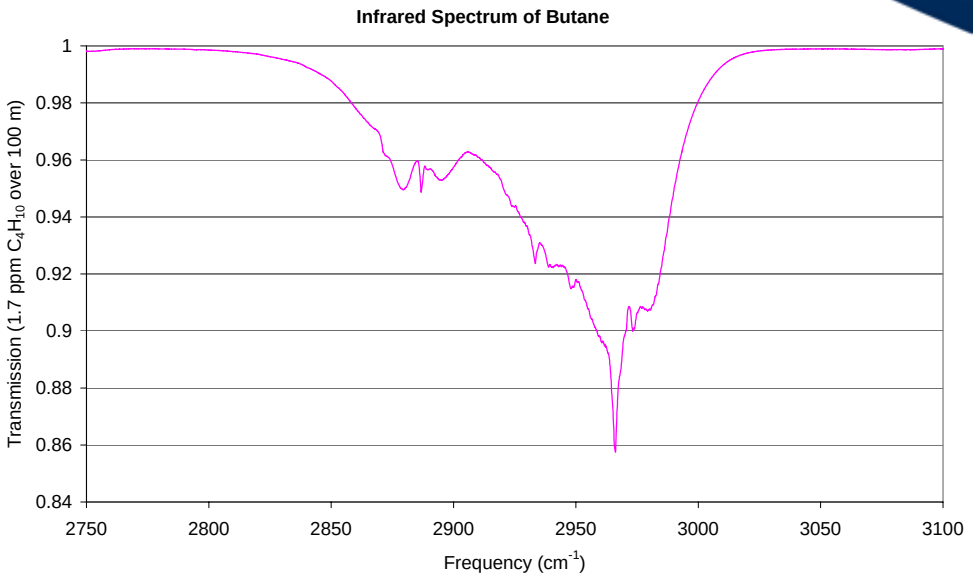


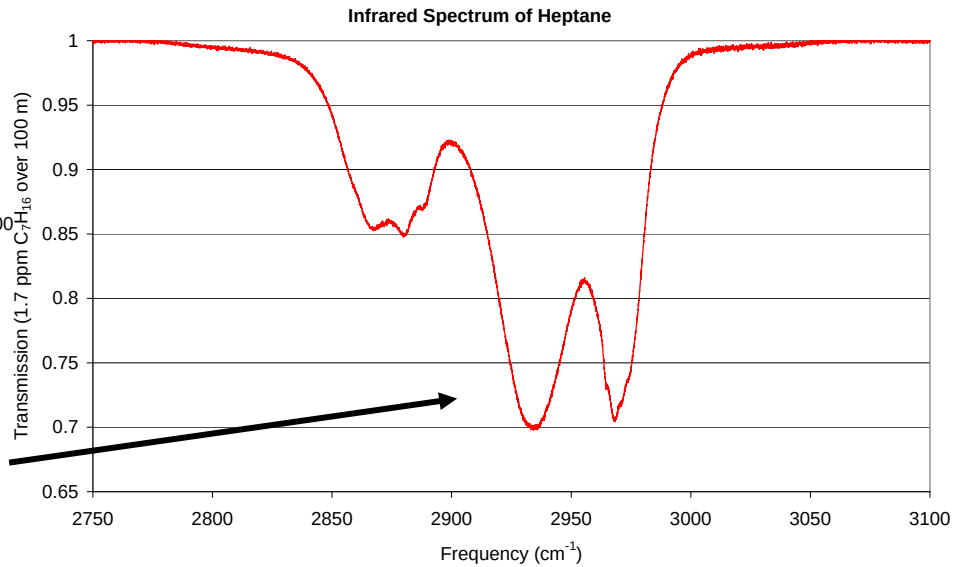
Acknowledgement for this image, Lukas Emmenegger, EMPA,CH

Example Infrared Spectra

Small molecule, sharp narrow features







Small molecule, sharp narrow features

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Advantages of using IR spectroscopy for gas composition measurements

- Potential for simultaneous analysis of many gases
- Non-contact / remote measurements
- Many different measurement geometries possible
- Reduces need for complex sample handling
- Potentially simple calibration chain
- High sensitivity

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Disadvantages of IR spectroscopy

- Need to know absorption coefficient for particular measurement situation.
- Cross-interference from other species (particularly water vapour).
- Non-linear relationship between measured quantity (light intensity) and concentration.
- Instrumental effects on measured spectrum (instrument line shape).
- Some species not detectable (O_2, Cl_2 , etc.)

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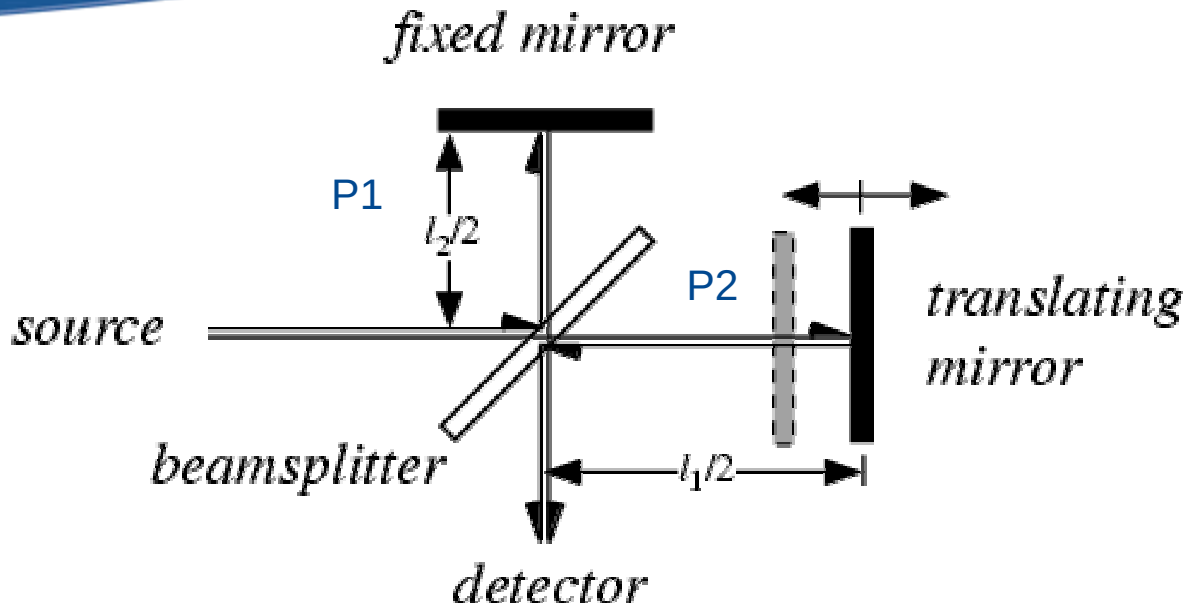
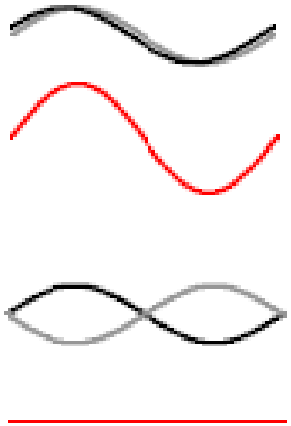
Fourier Transform Infrared Spectroscopy

Fourier transform spectrometer





Based on principle of a Michelson interferometer

Light is split and travels two paths, P1, P2, before recombining at the beam splitter

Depending on the phase it will constructively or destructively interfere

So for a fixed P1 P2, different wavelengths will either constructively or destructively interfere

By scanning P2, an interferogram is recorded.

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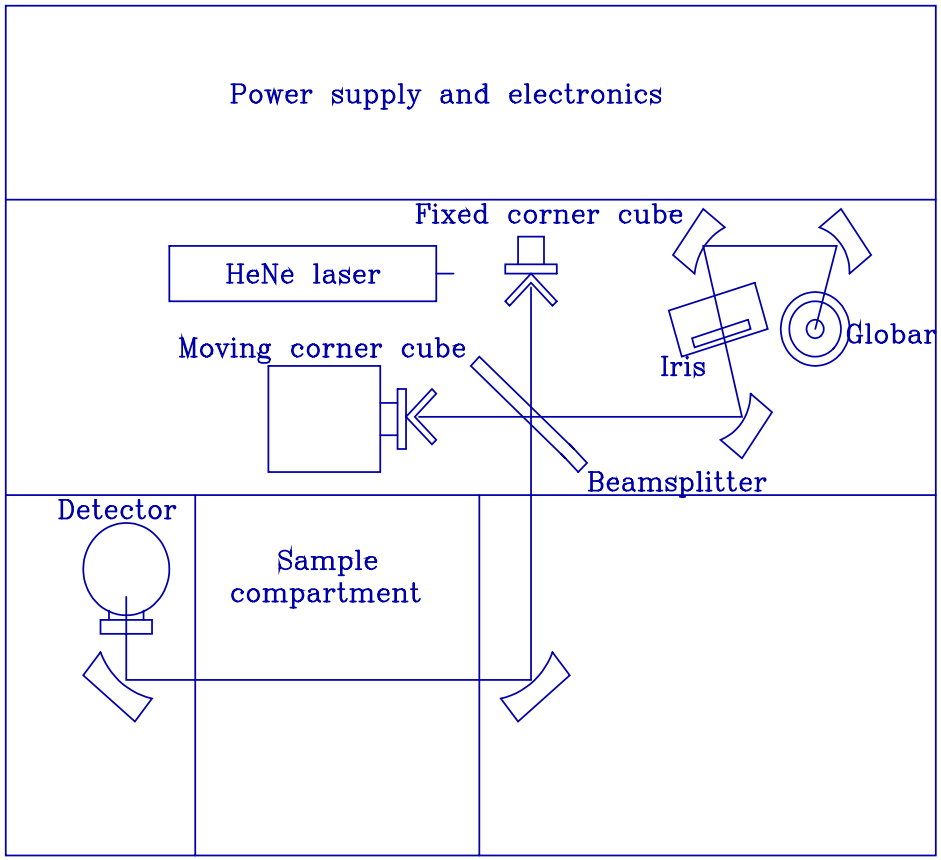
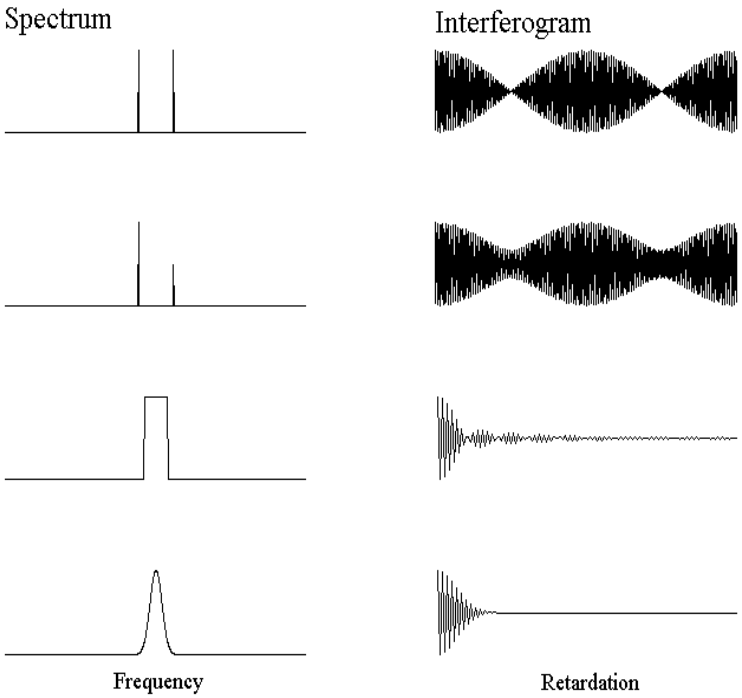
Fourier transform infrared (FTIR) spectrometry

Typical Spectrometer Configuration





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Fourier transform

- FTIR directly measures an interferogram
  - The signal falling on the detector at any time contains information about the whole spectrum
  - This is not the same as instruments which measure the intensity of light at different wavelengths
- To obtain a spectrum software within the FTIR converts it by an inverse fourier transform
- The implications of this are that faults in the FTIR do not have obvious consequences

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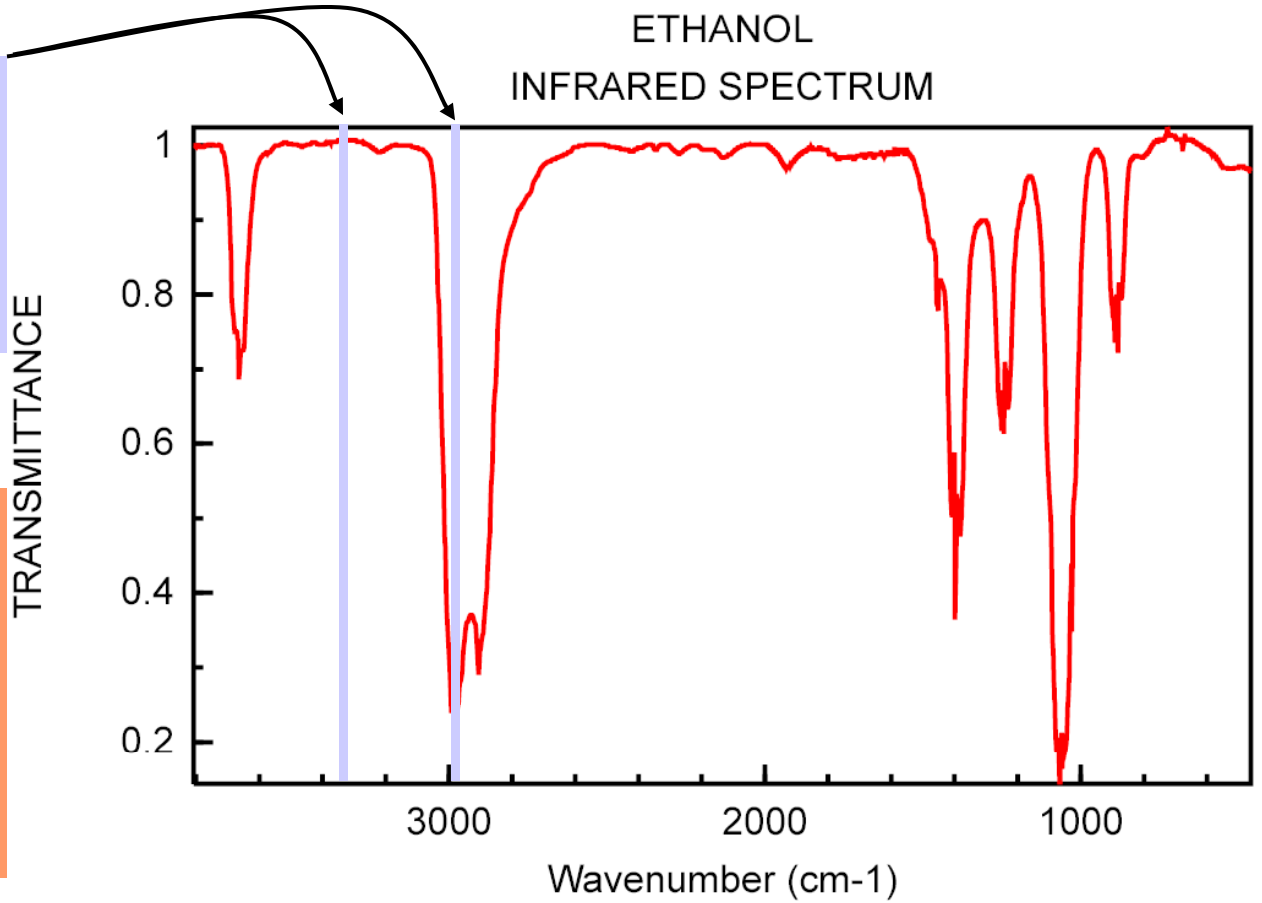
Spectroscopic measurement approaches

Classical two (or multiple) wavelength detection

-measure absorption of light at specific wavelengths

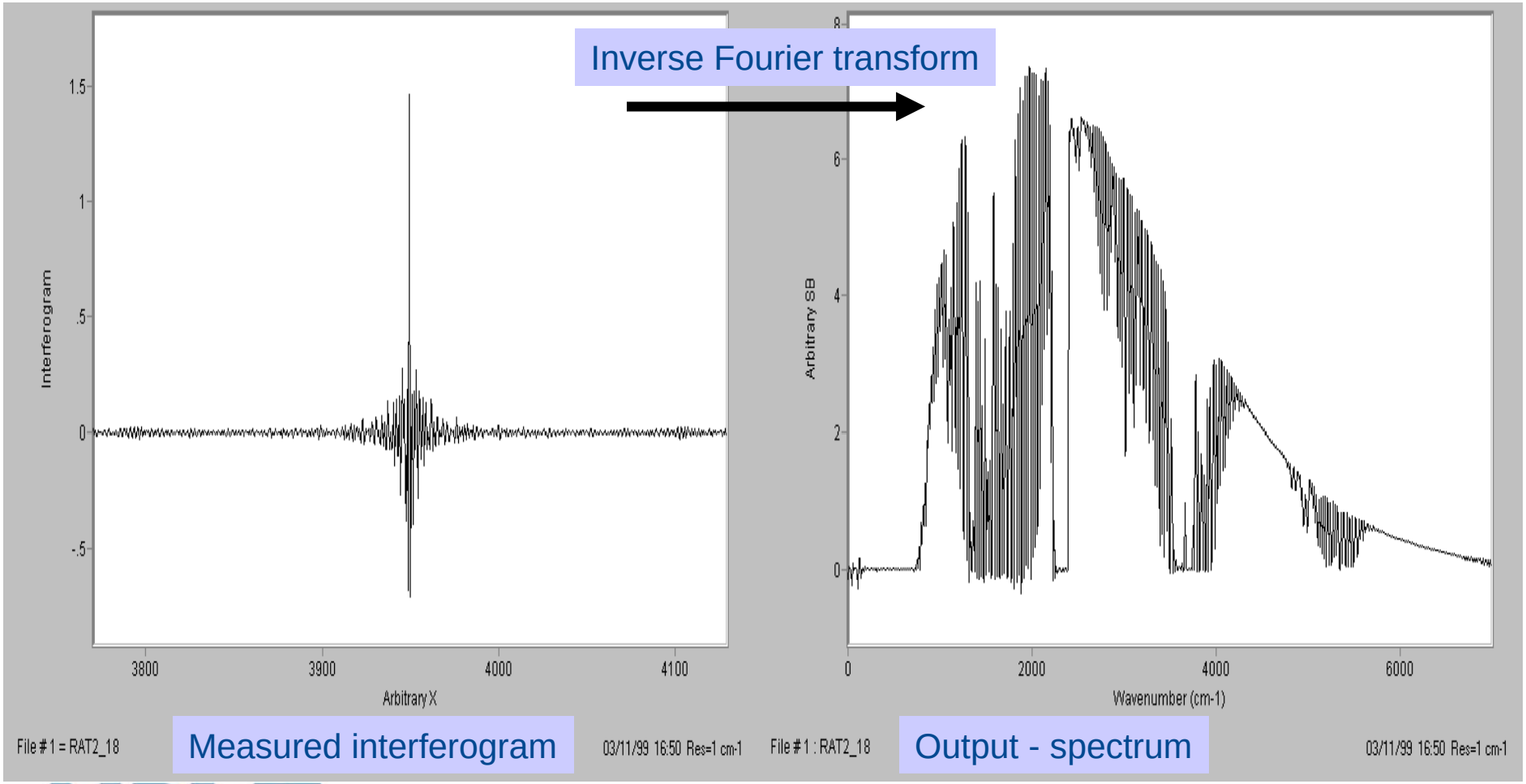
FTIR – measures whole spectrum

So can therefore measure multiple compounds and potentially correct for interference



NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

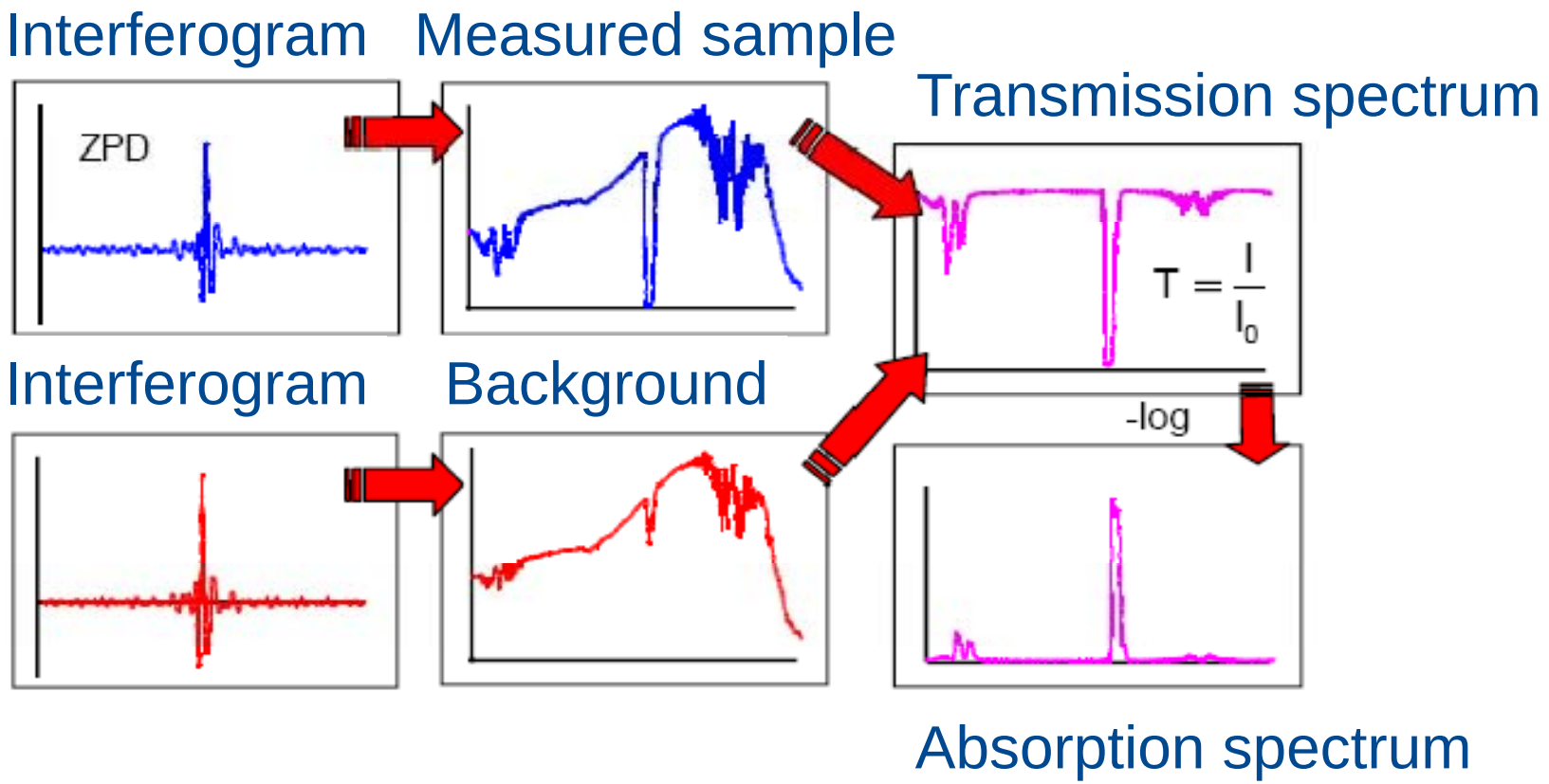
Typical Interferogram and spectrum



Measured interferogram

Output - spectrum

Measurement process



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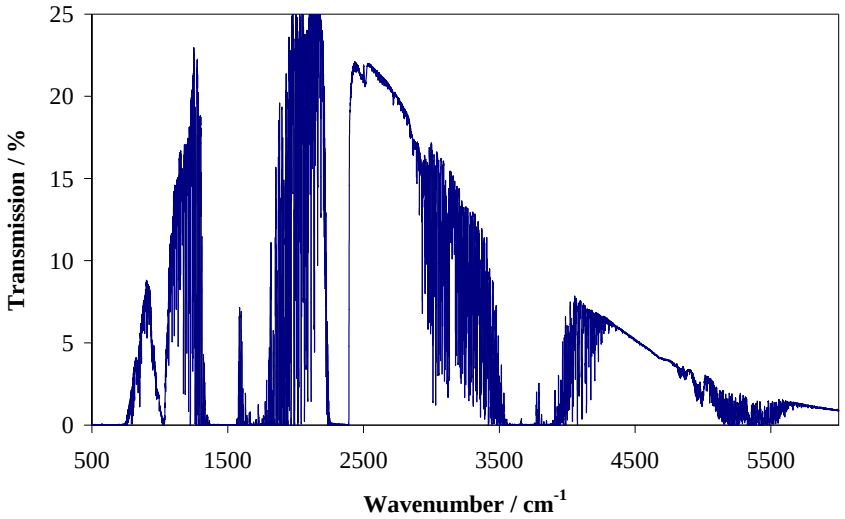
Analysis – simple approach



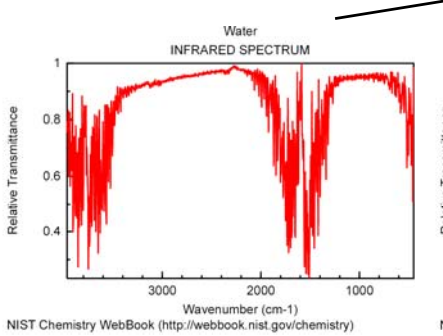
Measured spectra

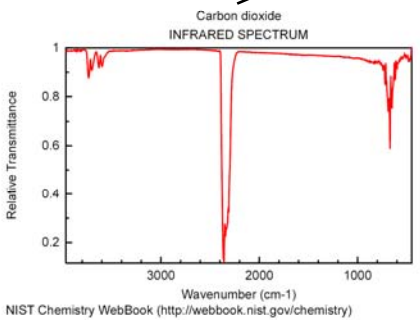
Correct for background
(and source spectrum)

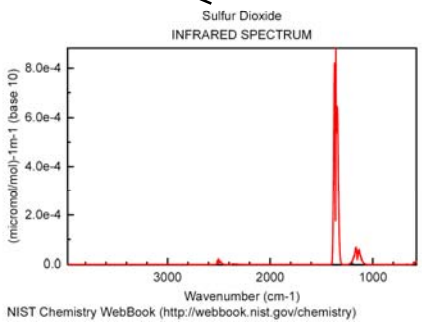
Decide on possible components

Combine various amounts of
each component spectra
Subtract from measured spectra
Adjust till residual is minimised
Possible adding additional compounds

Library spectra







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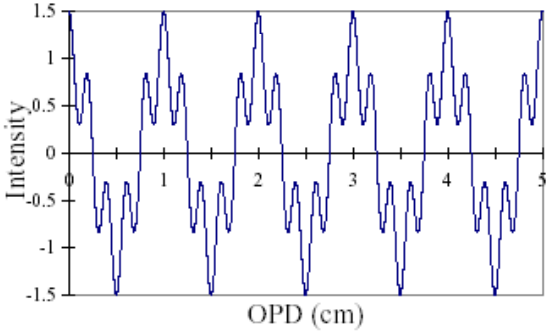
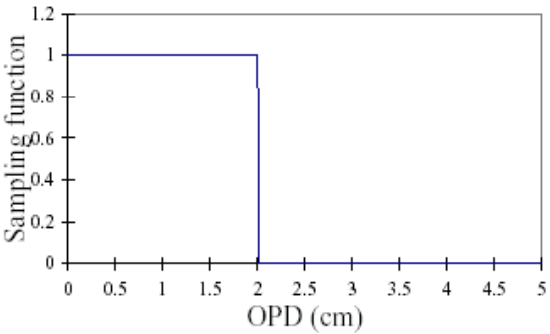
Instrument Resolution

- Scanning mirror can only traverse a limited distance
- Consequently, interferogram only partially sampled
- Same as multiplying length of recorded interferogram by unity, and remainder by zero. Hence, boxcar function
- The fourier transform of a boxcar gives a sinc function
- “Apparent” lines found by convolution of sinc with “true” absorbance lines
- Consequence of limited path difference is broadening and introduction of ringing

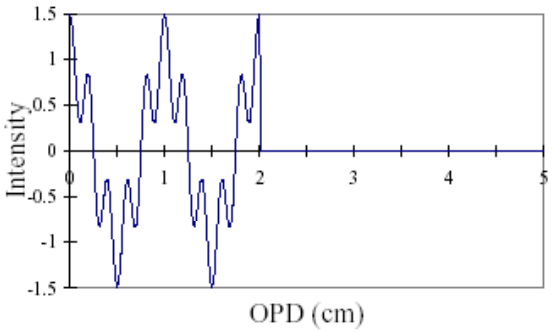
Interferogram Domain



(a) First 5cm of an infinitely long interferogram

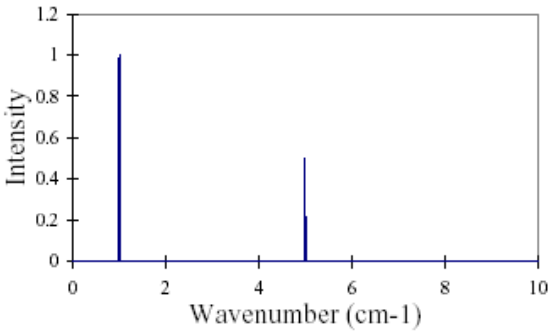


(c) Boxcar sampling function

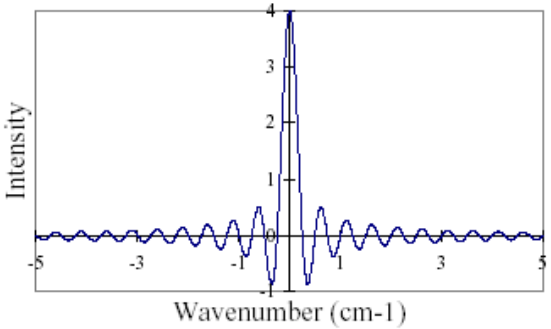


(e) Recorded (finite) interferogram

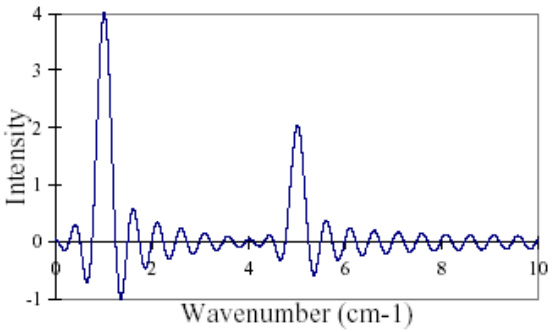
Spectral Domain



(b) FT of the interferogram in (a)



(d) FT of sampling function (sinc)



(f) FT of finite interferogram (spectrum)

Resolution

- Typical emissions monitoring FTIRs have resolutions from 0.5 to 8 wavenumbers
- Better resolution can resolve absorption lines, but instruments will be bulkier and potentially more prone to mechanical noise
- Worse resolution has less noise, more compact, but may have more issues with interference as can’t resolve spectra

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Example of Errors Caused by Deviations from Beer's Law

- Linear least squares quantification techniques rely on absorbance lines following Beer's law ($I=I_0e^{-\alpha cl}$)
- As concentration increases and the true line increases the proportional relationship between the true and apparent lines must remain for linearity to be maintained
- However, at high absorbance values this breaks down and non-linear behaviour can be observed

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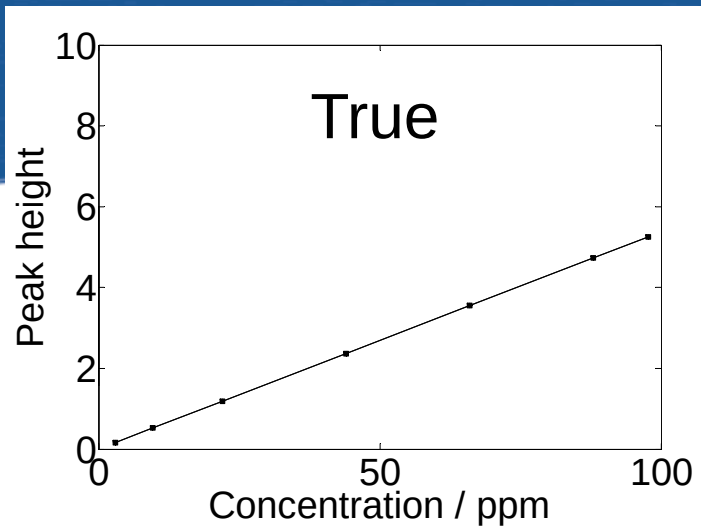
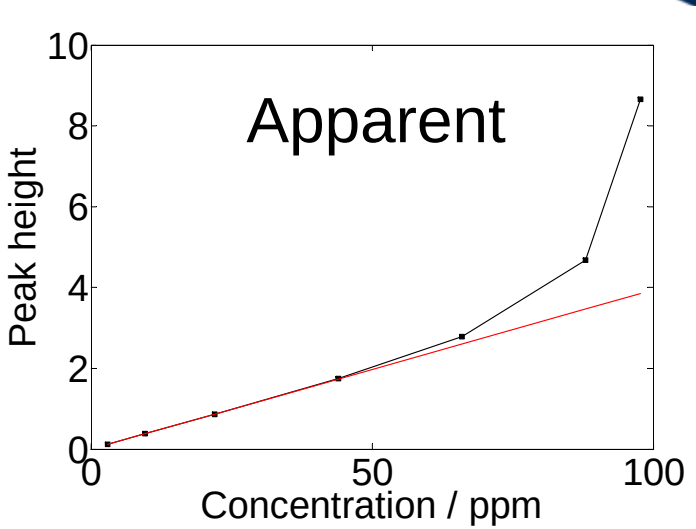
Behaviour of True and Apparent Absorbance Lines with Concentration





- At low concentrations measured line is broadened
- However, as the concentration increases to the point where the true line is very intense the result of convolution and apodization is a narrower, taller apparent line
- The extent to which Beer's law breaks down depends on where the calibration point sits on the linearity plot in relation to the unknown
- **Deviations from Beer's law can produce quantification errors when not properly considered[2]**

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[2] D.J. Brassington, P.T. Woods, *et. al.*, Appl. Opt., **23**, 3, (1984)

Effect of Matrix Gas on Spectroscopic Measurements

- Pressure effects cause a broadened line.
- Overall pressure linewidth is a combination of the pressure linewidths for each gas present, including the target gas itself (self-broadened linewidth).
- Molecules with significant electric fields (polar molecules such as water vapour) have stronger interactions, leading to broader lines.
- Level of effect is not necessarily the same for each absorption line as it depends on the electron transition involved.
- So the overall lineshape is a complex relationship involving the gas mixture present, the temperature of the system and the absorption line being measured.

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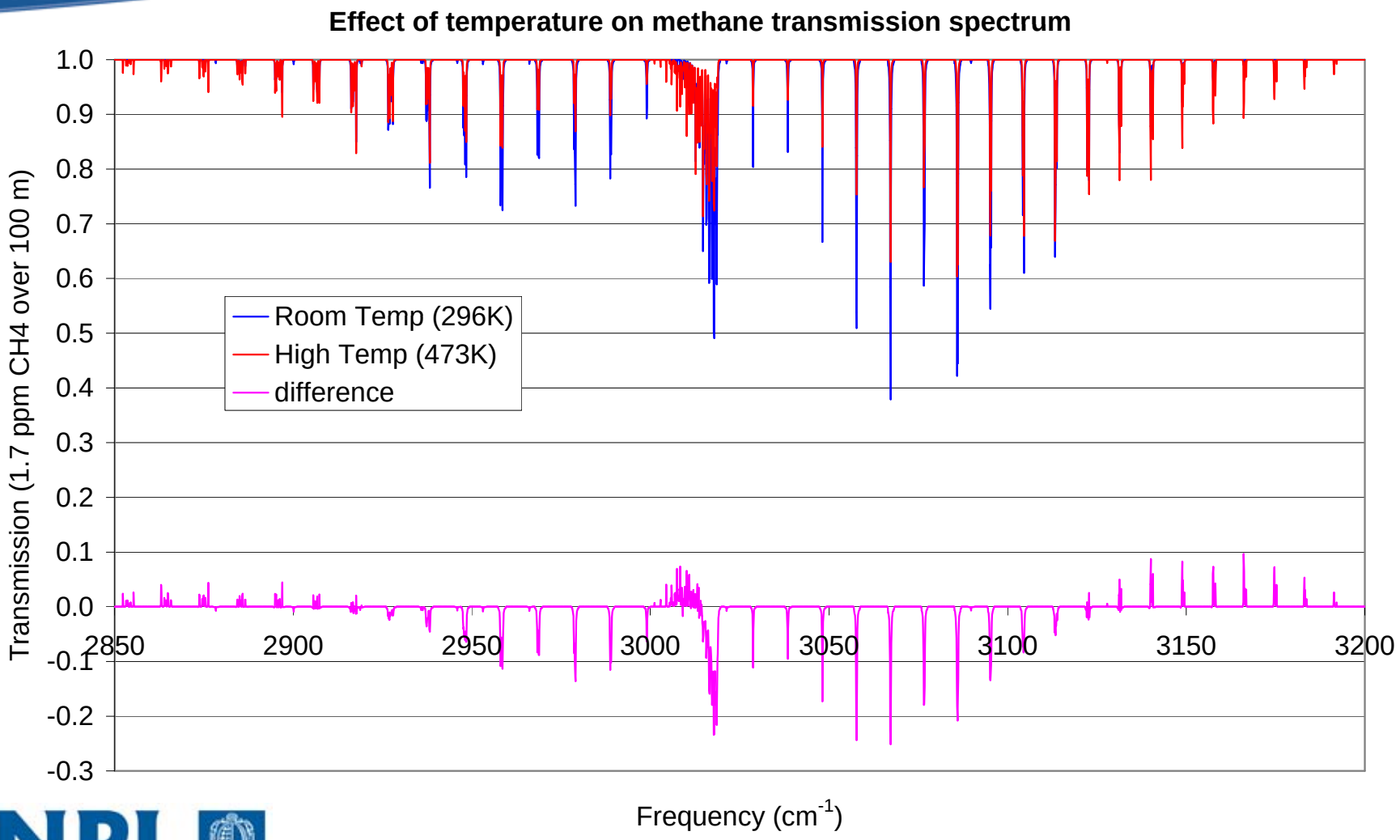
Temperature Effects



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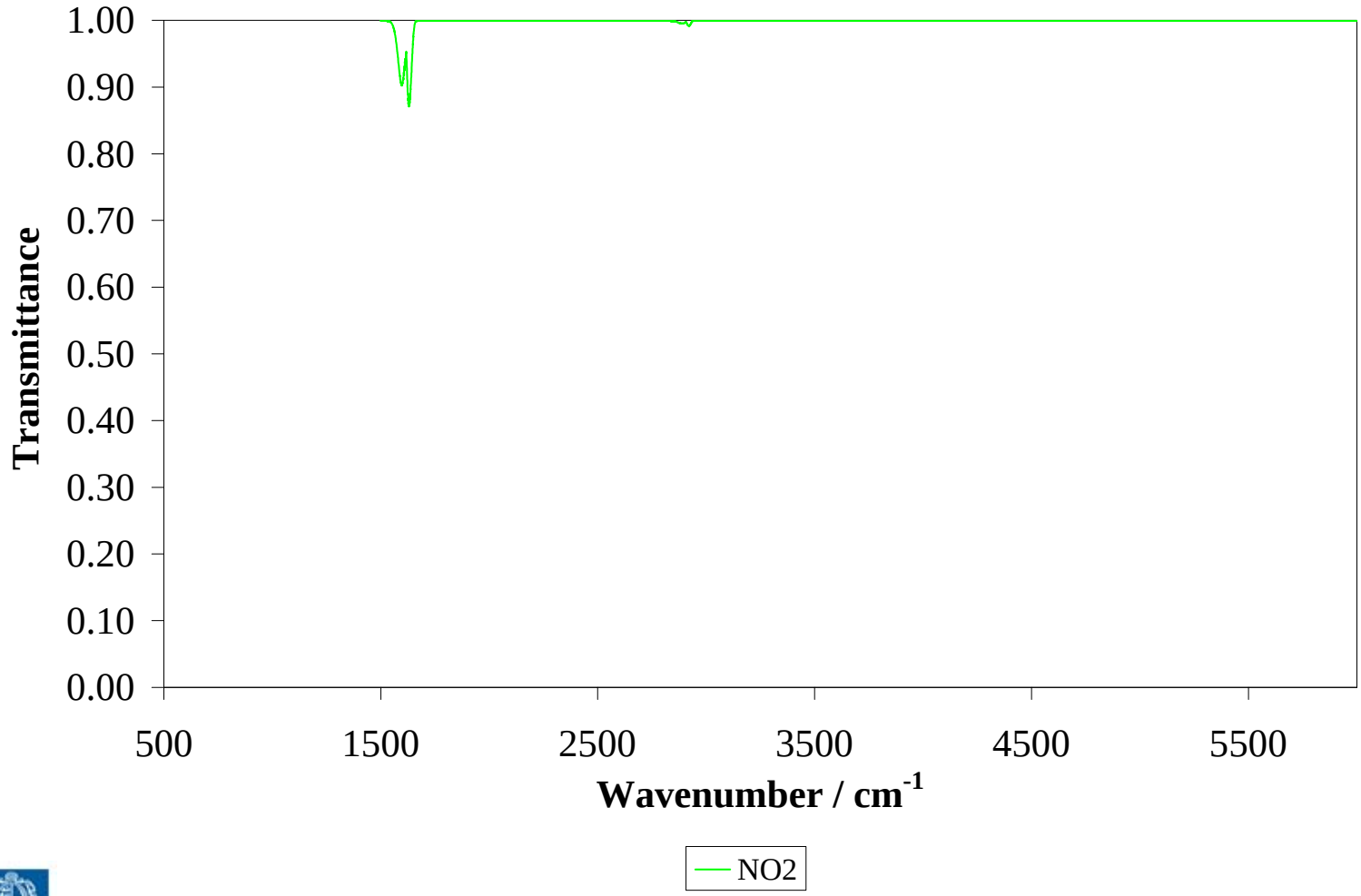
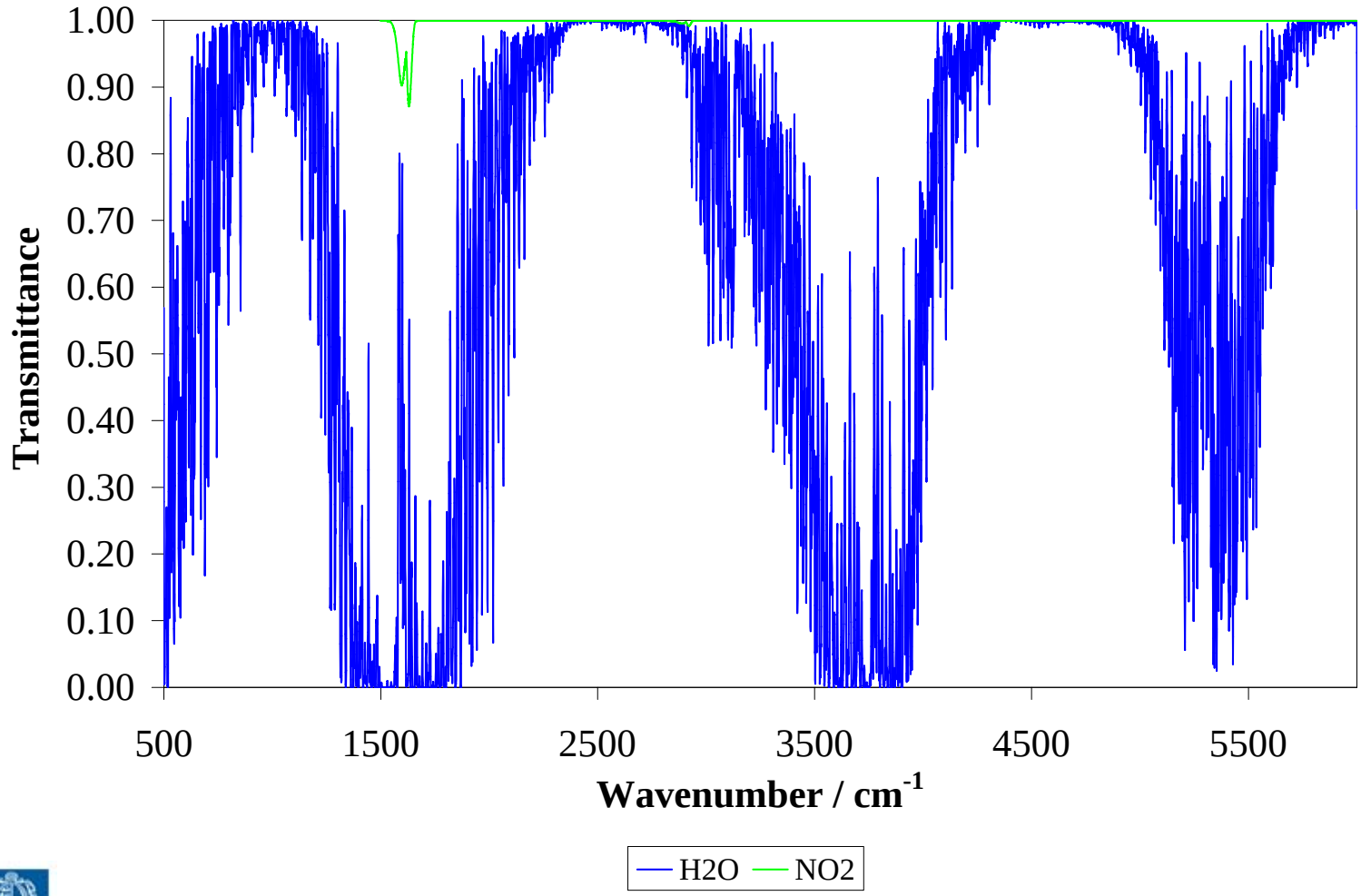
Interference Issues (1)

- Spectra calculated for a 1cm^{-1} resolution, 6.2m pathlength, instrument
- 12ppm NO_2
- Band at ~3000cm^{-1} weak



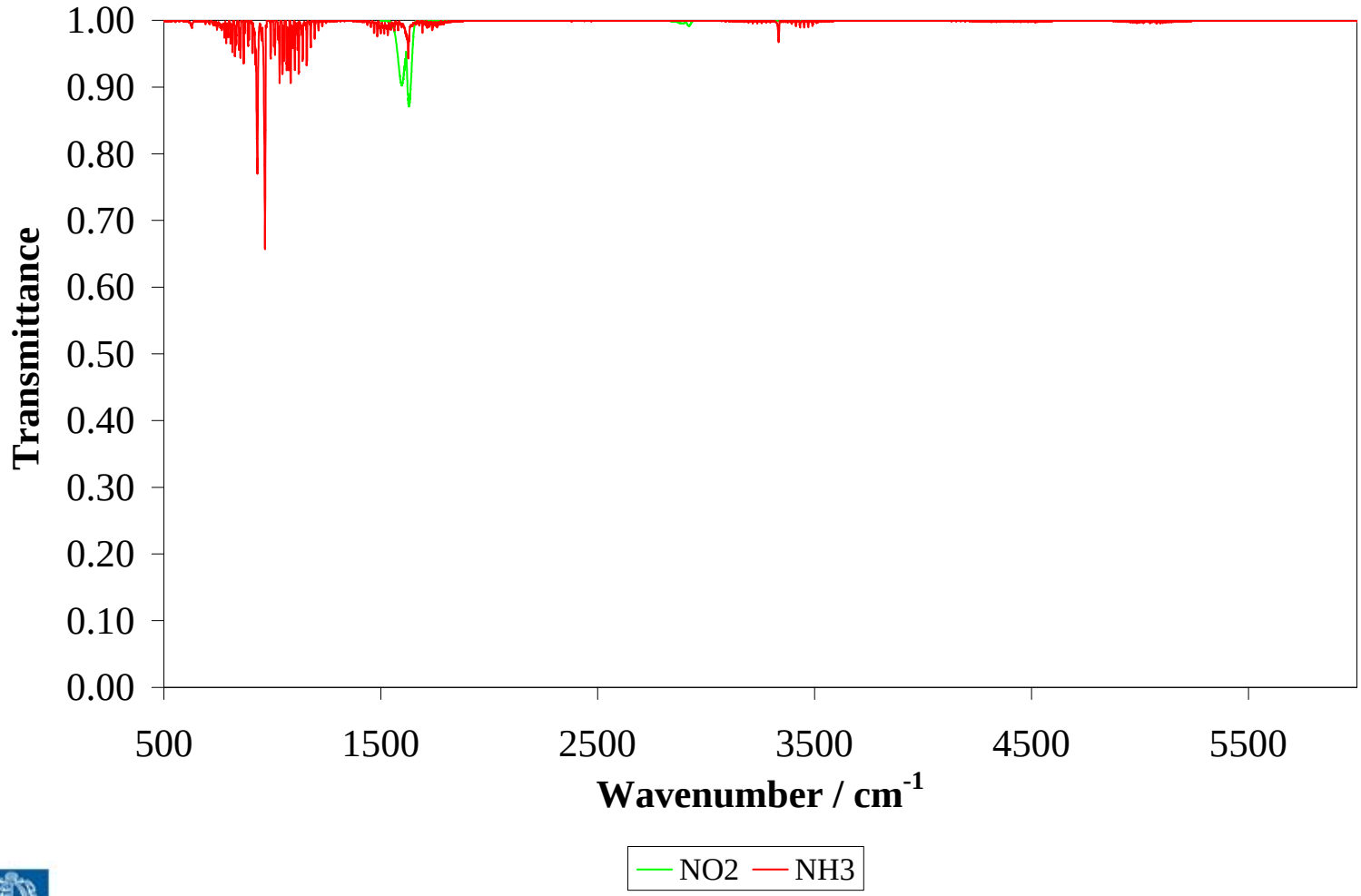
Interference Issues (2)

- 12ppm NO_2
- 22.5% H_2O
- Strong band saturated
- Weak band heavily interfered with



Interference Issues (3)

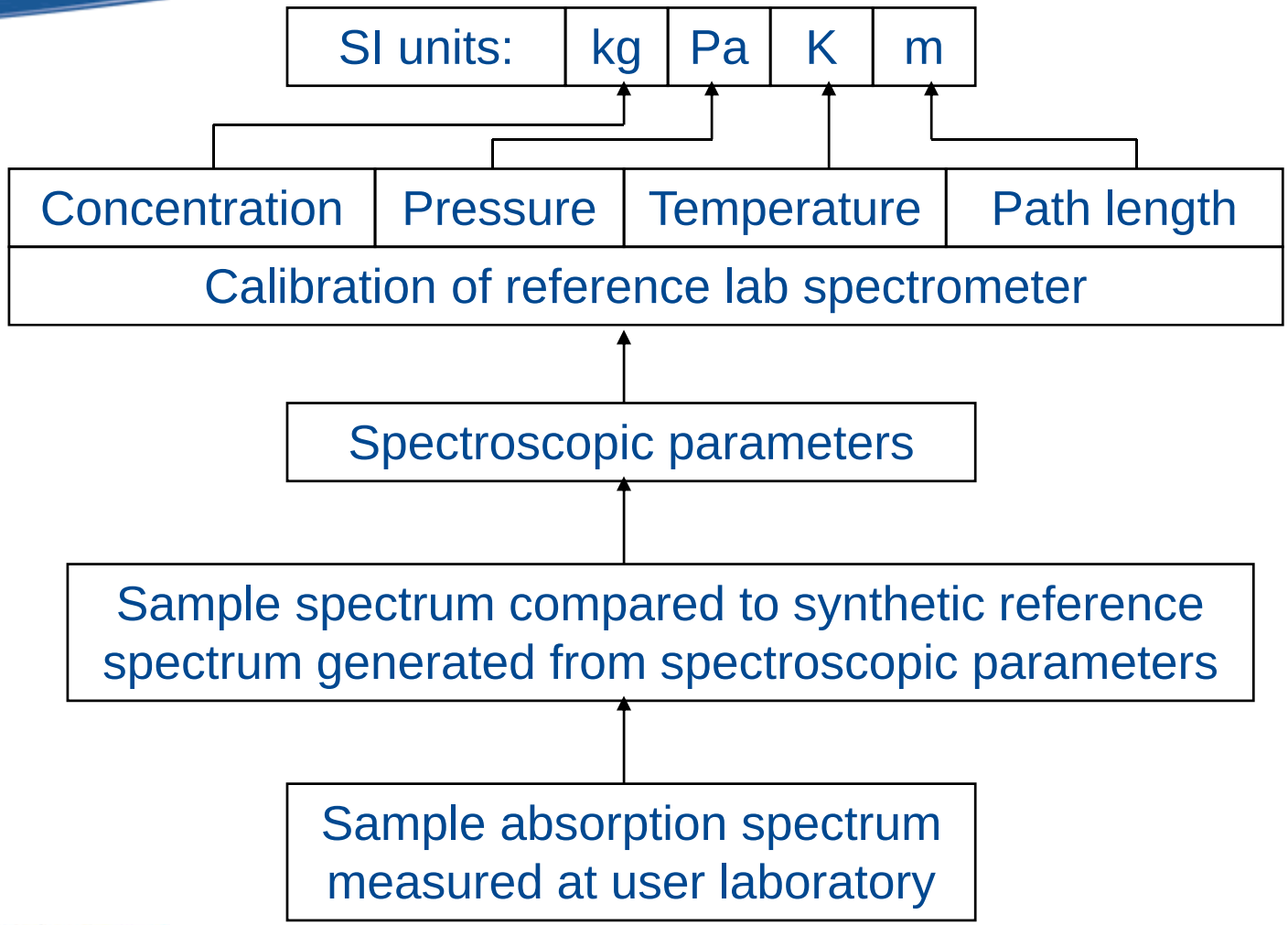
- 12ppm NO_2
- 60ppm NH_3
- Water vapour not the only potential interferent
- Showing that NO_2 can be quantified in presence of water vapour alone does not ensure a robust interpretation algorithm



Some potential interferences

	NH3			N2O			CH4			HCN			HBr	
Interferent	none	some bands	all bands	none	some bands	all bands	none	some bands	all bands	none	some bands	all bands	none	all bands
H2O			x		x				x			x	x	
CO2		x			x		x				x			x
CO	x				x			x		x			x	
NH3					x				x			x	x	
NO		x		x			x			x			x	
NO2		x		x				x			x		x	
N2O		x						x				x		x
HCN			x		x				x				x	
HBr	x				x			x		x				
HCl	x			x				x		x				x
CH4			x		x							x		x
C3H8		x			x				x		x			x
H2CO			x		x				x		x			x
Benzene		x			x				x			x	x	
Toluene			x		x				x			x		x
Xylenes			x		x				x			x		x

Traceability Chain in Spectroscopic Analysis



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Calibration through Modelling Spectrometer

- The ideal case:
  - Database of spectroscopic parameters derived from lab measurements
  - Lab measurements performed where
    - Sample concentration
    - Cell path length, pressure, temperature, etc.
  - Are all traceable back to the SI with known uncertainties
- Using database build a model of the spectrometer where input parameters are also traceable with known uncertainties

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Key Parameters in Calibration

- The list below shows some (but not necessarily all) of the parameters that could be included in a model and require a determined uncertainty
  - Instrument Line Shape
  - Linearity
  - Interferences
  - Sample pressure and temperature
  - Ambient pressure, temperature and humidity
  - Limit of detection
  - Sampling system
  - Repeatability

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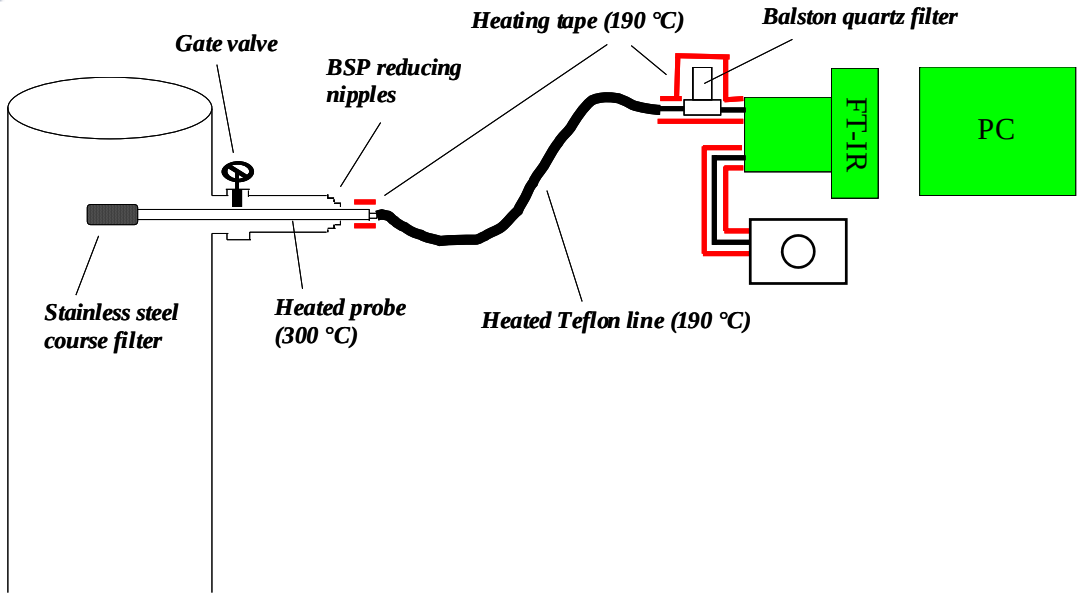
Emissions monitoring configuration



- Extractive configuration
- Have all normal issues of monitoring reactive gases
  - Probe / Sample line losses
  - Avoid condensation in FTIR cell

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Issues with FTIR for stack monitoring

- Measuring complex gas mixtures
- High concentrations of water vapour
- Need calibration of all species measured
- Need to demonstrate no losses in line etc
- Where automatic analysis software is used needs to be under control
- Can ‘over fit’ adding more species to account for noise
- Spectral library used to determine concentrations should be traceable

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Standard methods

- For emissions monitoring
  - EPA Method 320, Performance specification P-15
  - ASTM D 6348
- Open path method for ambient air
  - EN 15483

- ASTM method most commonly used in UK
- Not without problems

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Issues with ASTM D 6348 – 03 (1)

- A2: Three methods for determining Minimum Detectable Concentration
  - A2.2: (MDC1) Noise in a blank as a function of associated reference spectrum and associated concentration
  - A2.3: (MDC2) Using quantification algorithm to interpret a series of blank spectra. 3xSTD of returned concentrations
  - A2.3: (MDC3) Following (1) except using the residual returned by the CLS quantification algorithm. The residual being the result of subtracting the scaled reference spectra from the data spectrum

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Issues with ASTM D 6348 – 03 (1)

- With MDC3 it may sometimes be incorrect to assume the residual contains only noise
- A2.3.2.3: In method MDC3 user is permitted when manually generating the residual to correct for T, P and pathlength differences between the data and reference spectra by using the scaling factor found from
  - (Cd/Cr)(Ld/Lr)(Pd/Pr)(Tr/Td)
  - d=data spectrum, r=reference spectrum
- Cannot reliably correct for such difference by a linear approach
- Although no guidance is provided, the standard appears to allow any one of the three methods to be used

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Issues with ASTM D 6348 – 03 (2)

- A3.3.3: Using a calibration transfer standard cell pathlength determined by
  - Lr=Lf(Tr/Tf)(Pf/Pr)(Cf/Cr){Ar/Af}
  - r=reference CTS spectrum, f=fundamental CTS gas spectrum
- To assume that T, P and peak height/area differences can be accounted for with such a linear approach is incorrect. However, does mention that equation only holds over a limited difference between reference (r) and fundamental (f) values

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Issues with ASTM D 6348 – 03 (3)

- 7.2.2: Calibration assembly at probe outlet for introduction of calibration gases required
- 7.3.1: Calibration manifold for analyte spiking required
- 11.3.5: Analyte spiking procedure required (spiking is not commonly used in UK)
- 11.3.4 & 11.4.1: Measurement of CTS required at start and end of each day

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Current and Future work

- STA FTIR interest group
  - Provides a forum for everyone interested in using FTIR for emissions monitoring
  - Share experiences
  - Develop guidance
  - Enable users and instrument manufacturers to interact

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UK FTIR method

- First task of the group is to develop a UK method for FTIR
  - This will be based on the ASTM method
  - Define a single method for detection limit
  - No spiking but zero/ spans will be required
  - As will demonstration of sample line efficiency
  - Guidance on analysis, with QA/QC checks
  - Two types of user
    - Using FTIR as alternative to SRM
    - Using FTIR as full spectrometer to investigate complex gas mixtures

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Summary

- FTIR is a powerful instrument able to monitor a wide range of species
- Care is needed in applying FTIR for emissions monitoring as a number of pit falls can catch the unwary
- A method is being developed in the UK to try to standardise the use of FTIR and introduce some common QA/QC approaches.

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FTIR Spectrometry at NPL

Application areas at NPL:

- Ground based remote monitoring of the atmosphere.
- Laboratory based certification of reactive gas mixtures
- Purity analysis
- Open-path fence-line monitoring.
- Process and emission gas analysis.

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