Real-time ppb CO_2 Impurity Detection by an Advanced FTIR-UVF System

Presented at the BevTech Conference, Albuquerque, NM 2018

by

Charles M. Phillips Ph.D., Max Analytical Technologies

Mark Taylor, Vice President, Airborne Labs International

Ideal Objectives for a Beverage-Grade CO_2 Purity Analyzer System

1) Fast
2) Accurate
3) Sensitive
4) Robust – Interference free
5) Ability to measure many analytes simultaneously
6) On-Line / Continuous

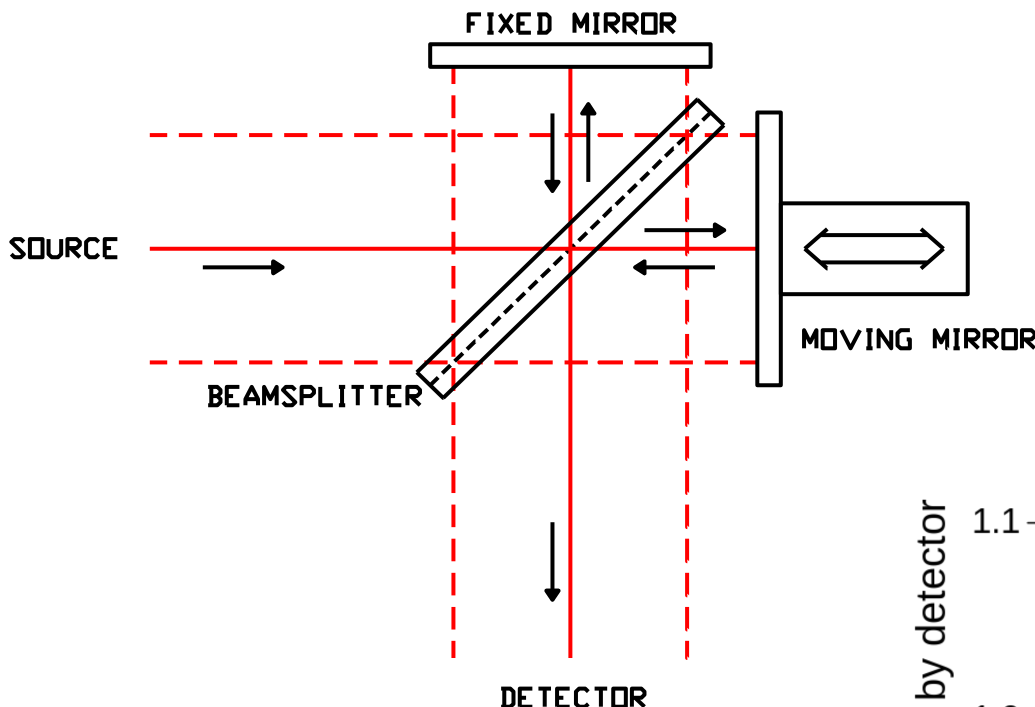
Recent Improvements in FTIR & UVF technologies appear to be able to meet these goals

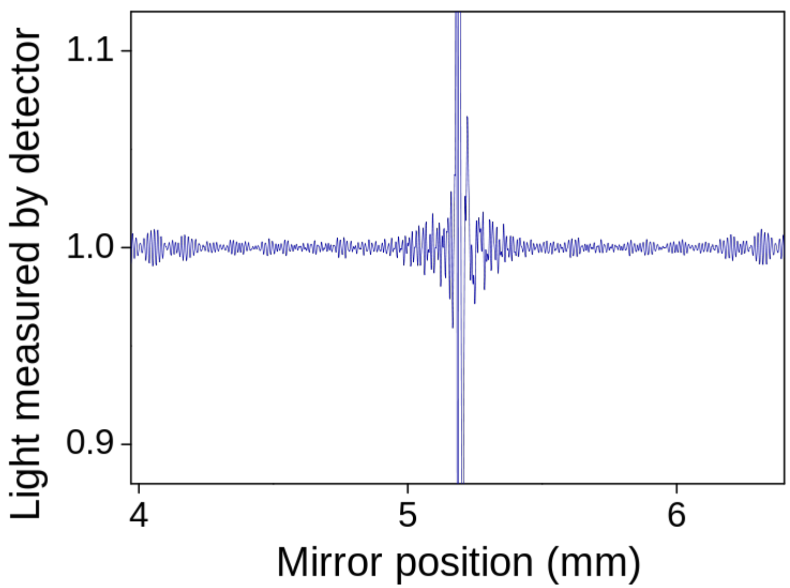
What is FTIR?

Fourier Transform Infra-Red Spectrometry

- All modulated frequencies detected simultaneously
  - The resultant pattern is called an interferogram (signal vs time)
  - Which is a sum of an infinite number of cosine waves vs time
- Fourier transform calculates spectrum from interferogram
- FTIRs have numerous advantages
  - High signal-to-noise and spectral resolution are possible
  - Fast scanning, can collect full spectrum in less than 1 sec.
  - Calculated spectra for each molecule can be a constant

The Michelson Interferometer
(most common type used in FTIR gas analyzers)





Short wavelengths modulated at
high frequencies - Long wavelength modulated
At low frequencies - ∑ (sum) together to create
interferogram

international society of beverage technologists

Single Beam & Absorbance Spectra

Single Beam Spectrum

Voltage vs Frequency

FT (Igram) = Single Beam Spectrum

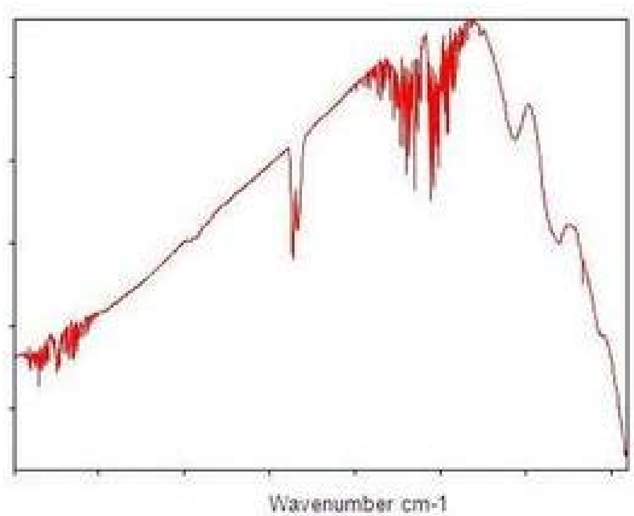
Features are gaseous absorptions

Absorbance Spectrum

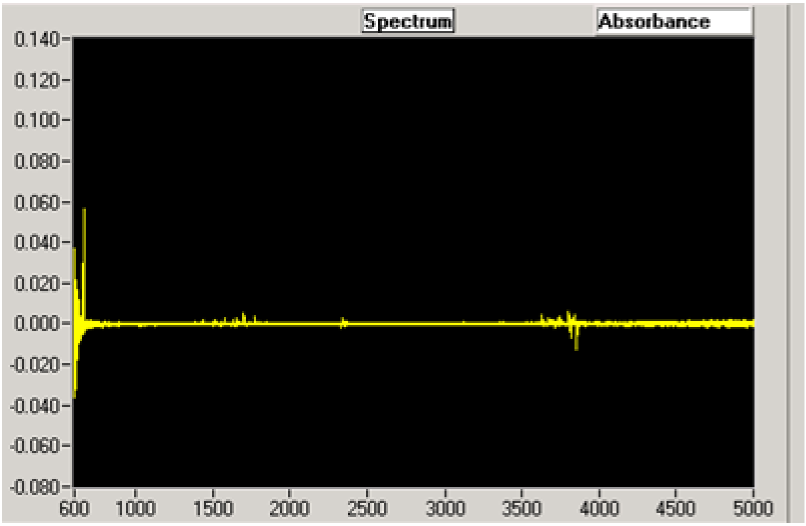
Abs. vs Frequency

$$A = -\log_{10}[I/I_o] = \varepsilon \bullet l \bullet c$$

Voltage



Wavenumber (cm^{-1})



Absorbance

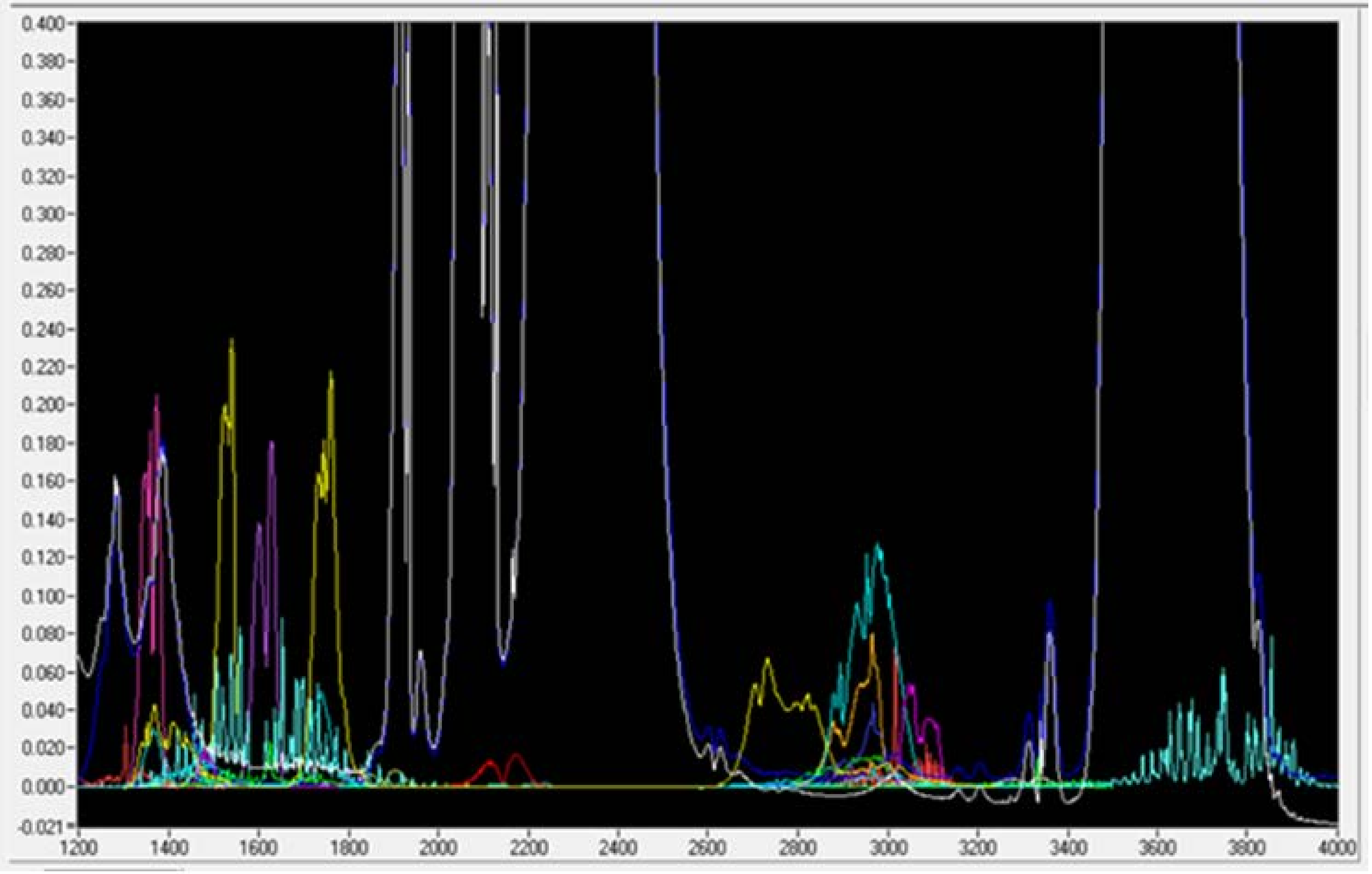
Wavenumber (cm^{-1})

(Ratioed /Subtracted Single Beam Sample – Single Beam Reference)

isbt international society of beverage technologists ®

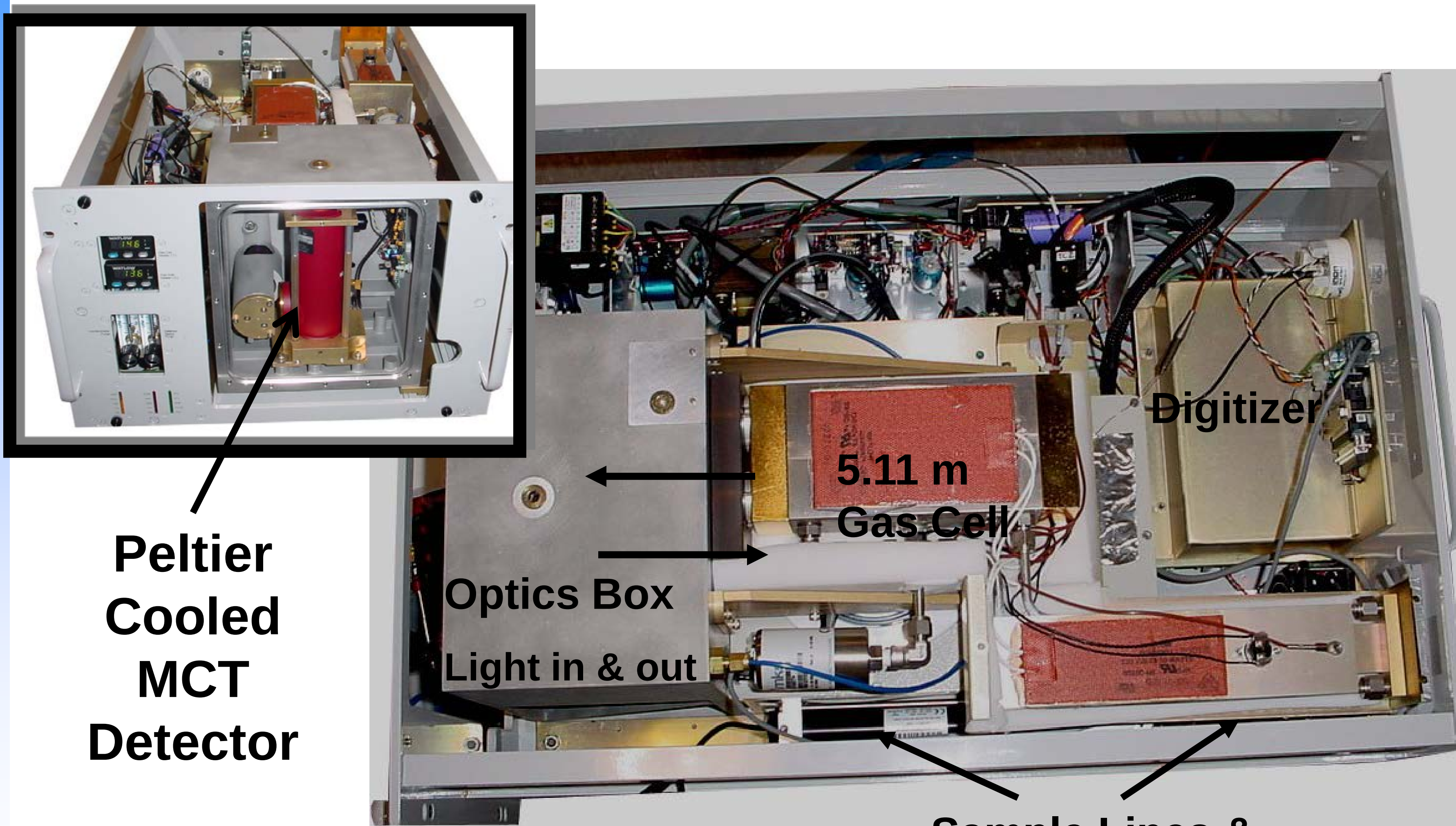
Complex FTIR Spectra from ISBT Listed CO_2 Impurities

(Each color is a different impurity gas + CO_2 Bands)



isbt | international society *of* beverage technologists ®

FTIR Gas Analyzer Layout



Peltier Cooled MCT Detector

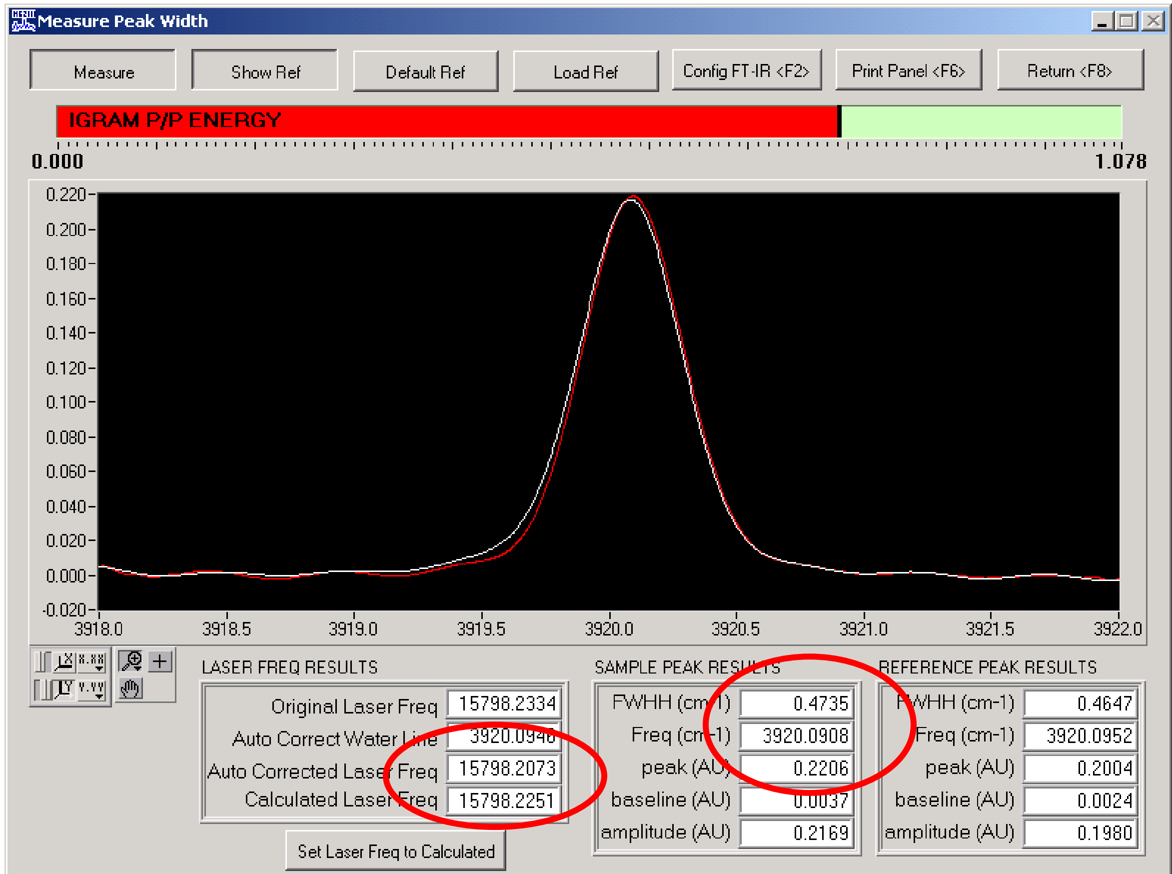
Sample Lines & Pressure Transducer

Technical Improvements in FTIR (Sensitivity & Selectivity)

$$A = -\log_{10}[I/I_o] = \varepsilon \bullet l \bullet c$$

1. Use TE cooled quantum detector (MCT) - Sensitivity
2. Resolution and Frequency Precision - Selectivity
3. Run at lower resolution (4 cm^{-1}) - Sensitivity
4. Quant region selection / “Picket Fencing” – Selectivity & Sensitivity
5. Increase pressure / molecular number density - Sensitivity
6. Multi-pass gas cell with high throughput - Sensitivity

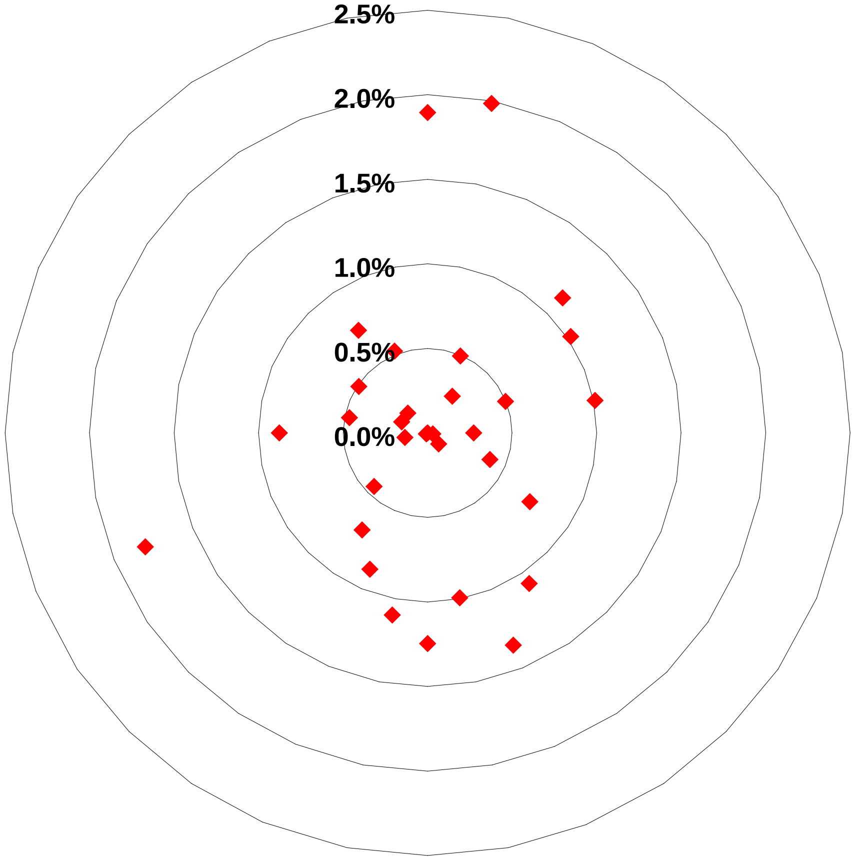
FTIR Calibration
(Instrument Independent = Physical Measurement)



All analyzers are tuned to have the same resolution & optical frequency in order to achieve the same calibration response for all impurities

isbt international society of beverage technologists ®

Analyzer Independent Impurity Calibrations



Instrument-to-Instrument Variation Based on Ethylene Measurements

Easily able to transfer calibration factors from one instrument to another

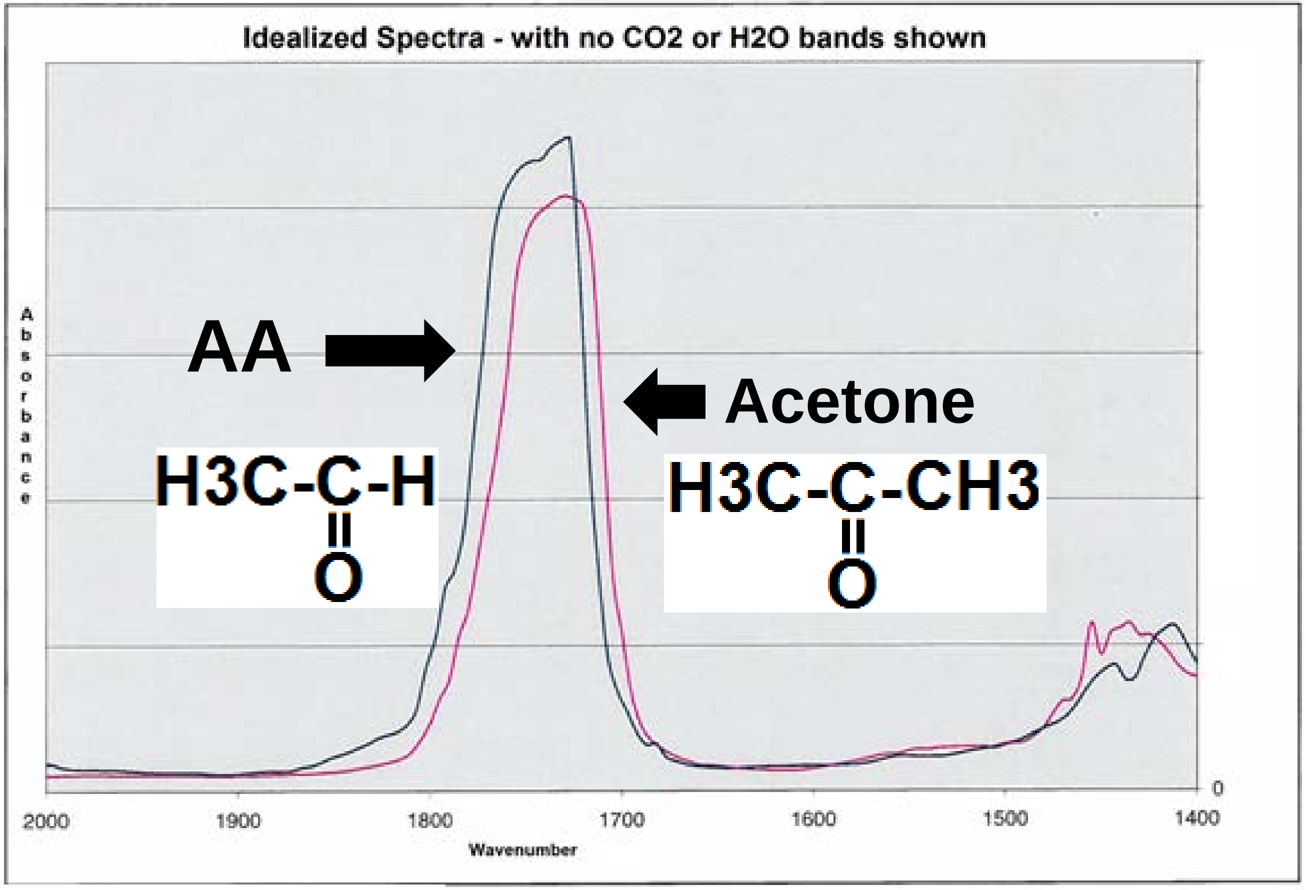
This means an FTIR analyzer should not require impurity re-calibration by a user – only periodic response verification is recommended

All Different FTIR Gas Analyzers and none were calibrated for Ethylene

isbt international society of beverage technologists®

The Challenges of IR Measurements in CO_2

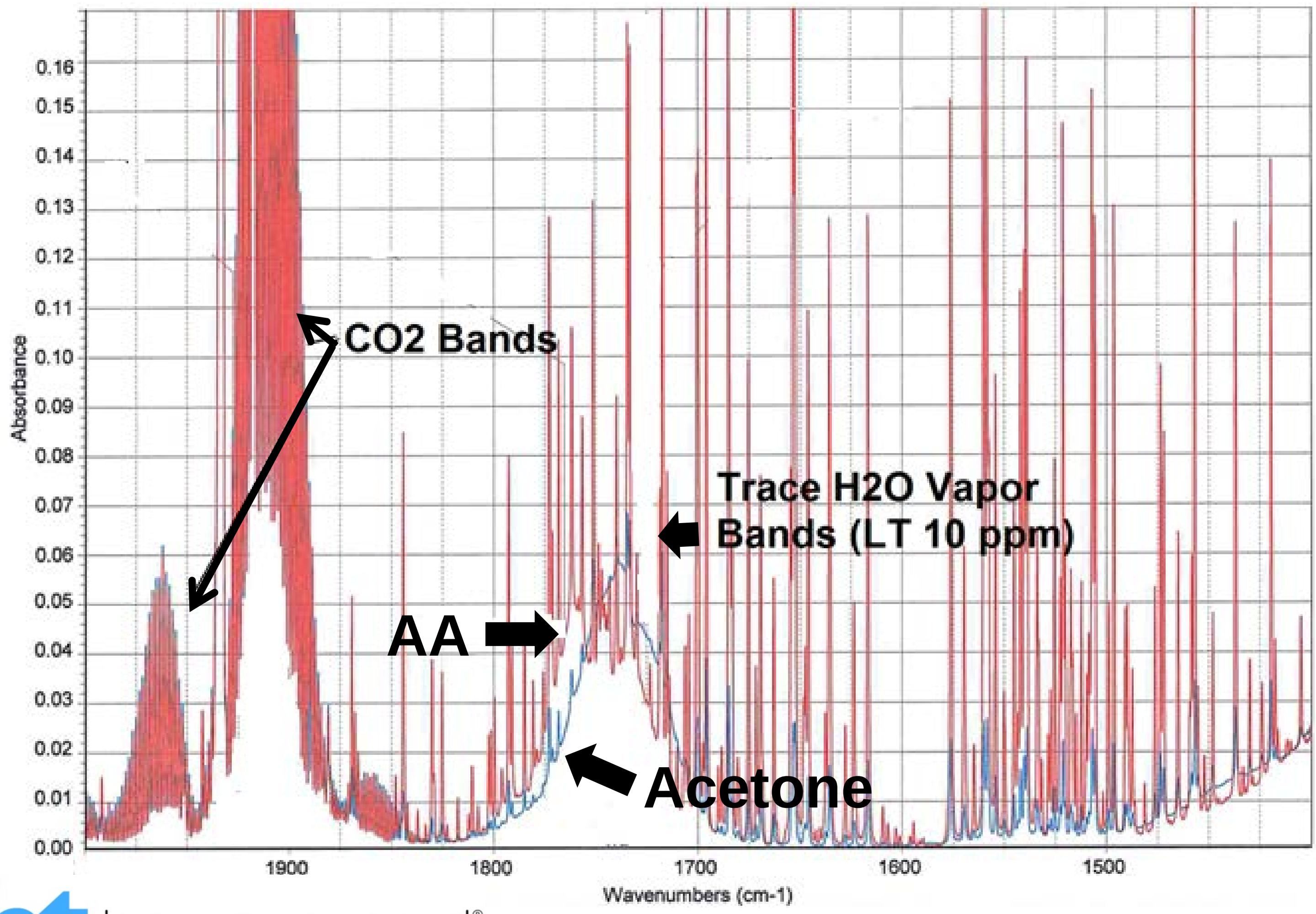
- *High AA is a common source of odor complaints & an ISBT Target Impurity*
- *AA is common in Fermentation & Combustion Feed Gas Sources*
- *Acetone is also a common impurity – but NOT an ISBT listed Target*



international society of beverage technologists

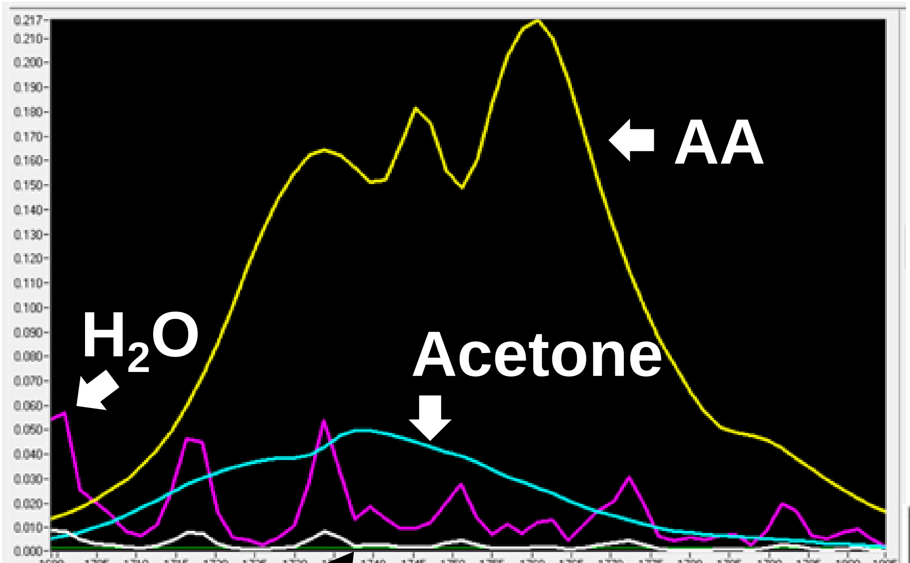
The Challenges of IR Measurements in CO_2

Real World Issues



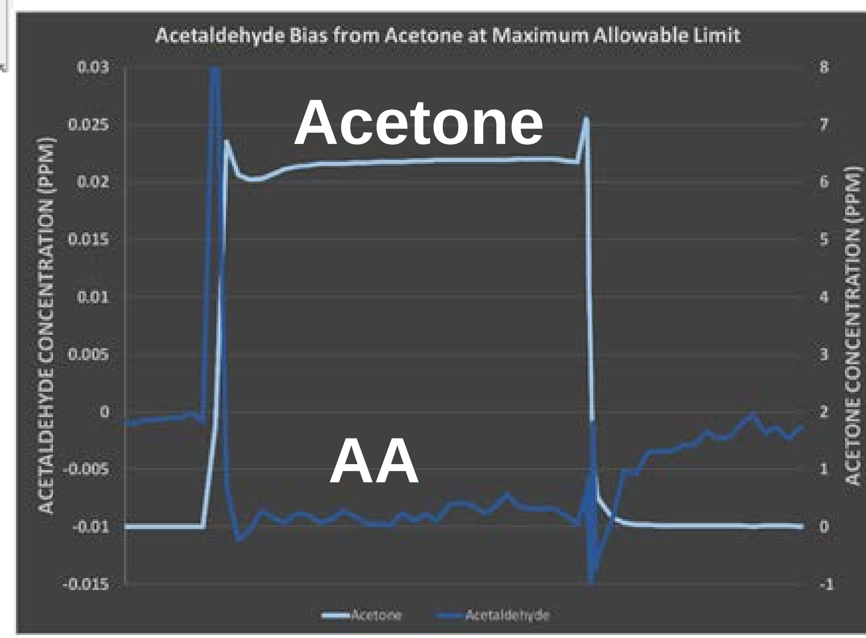
isbt international society of beverage technologists®

Acetaldehyde (AA) False Positive Error Potential when Acetone is present



Sample

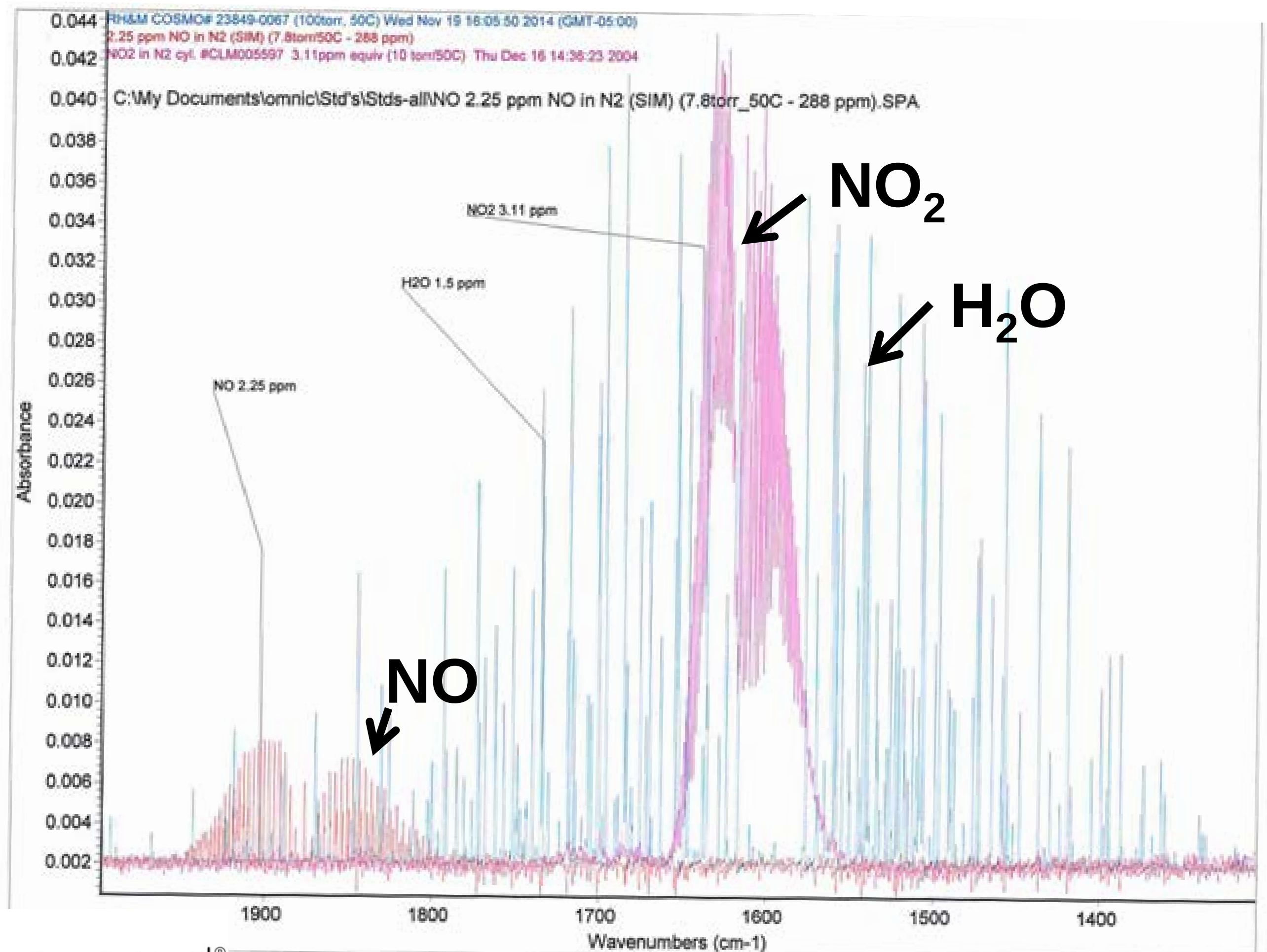
Corrected Result After “Picket Fence” Signal Processing



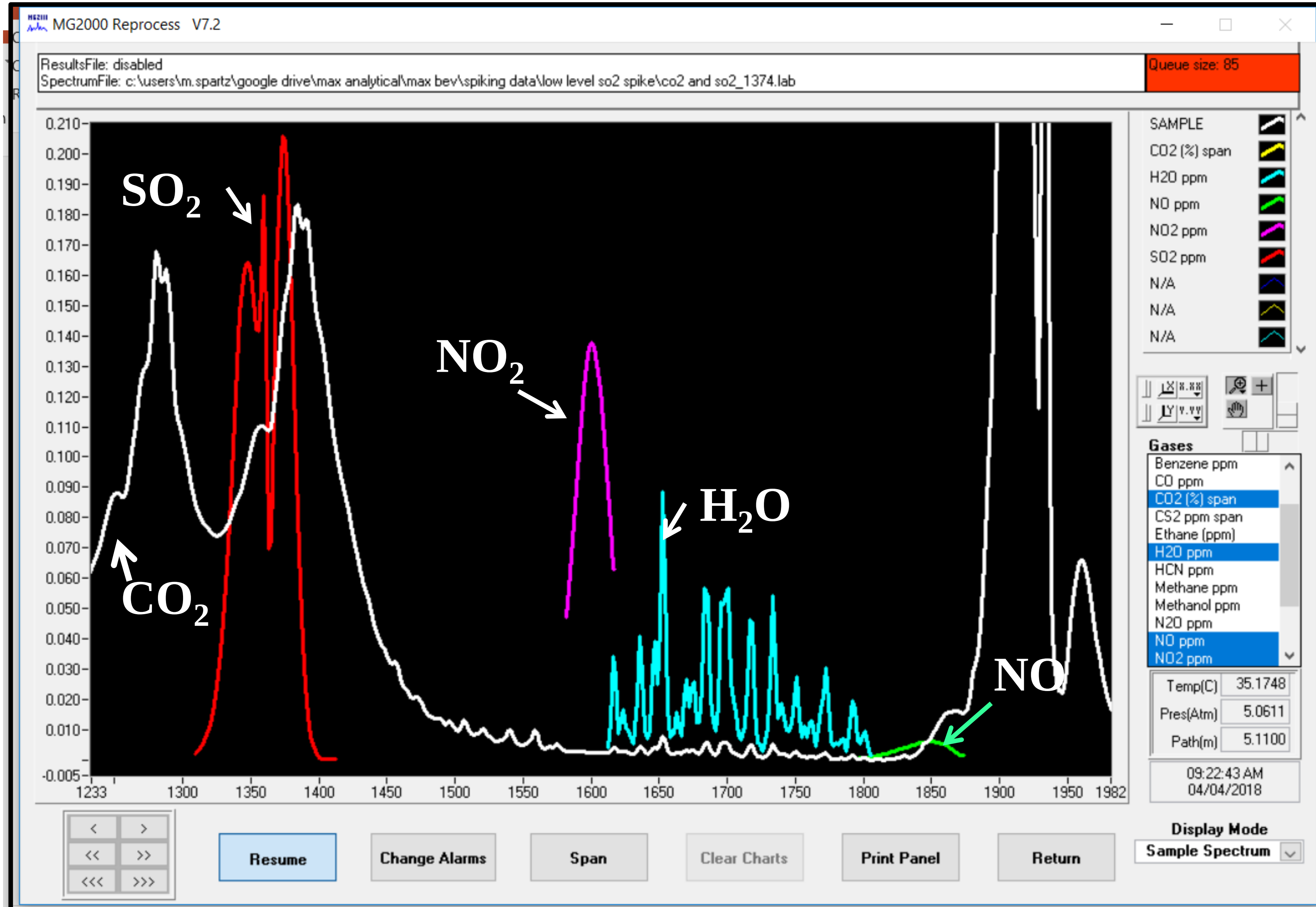
international society of beverage technologists

The Challenges of IR Measurements in CO_2

- ***NO & NO_2 (NO_x) are ISBT Target Impurities***
- ***NOx is common in Fermentation & Combustion Feed Gas Sources***
- ***NO & NO_2 IR bands are superimposed by H_2O vapor bands***

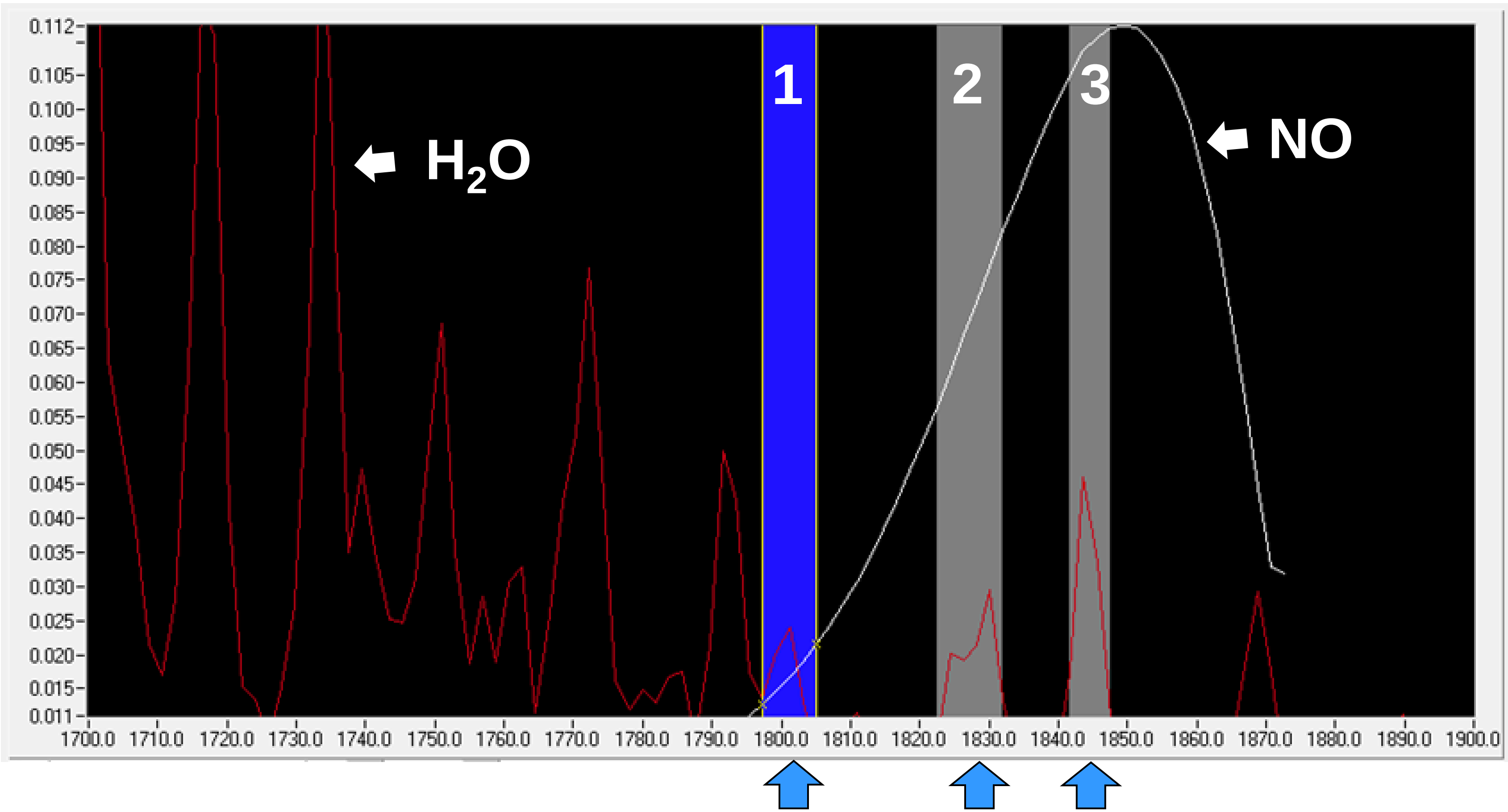


SO_2, NO and NO_2 with H_2O & CO_2 interference

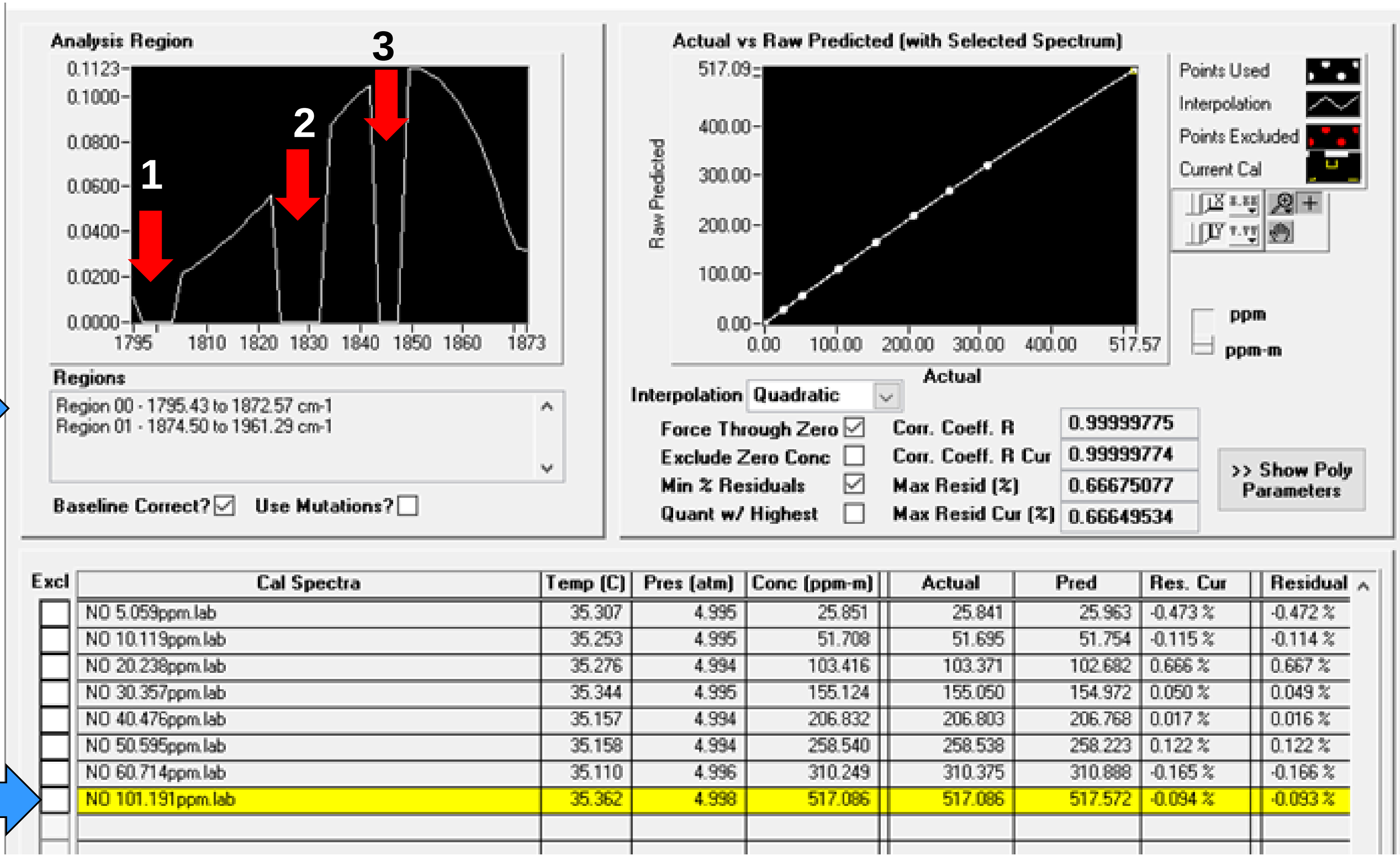


“Picket Fencing” the Desired Data

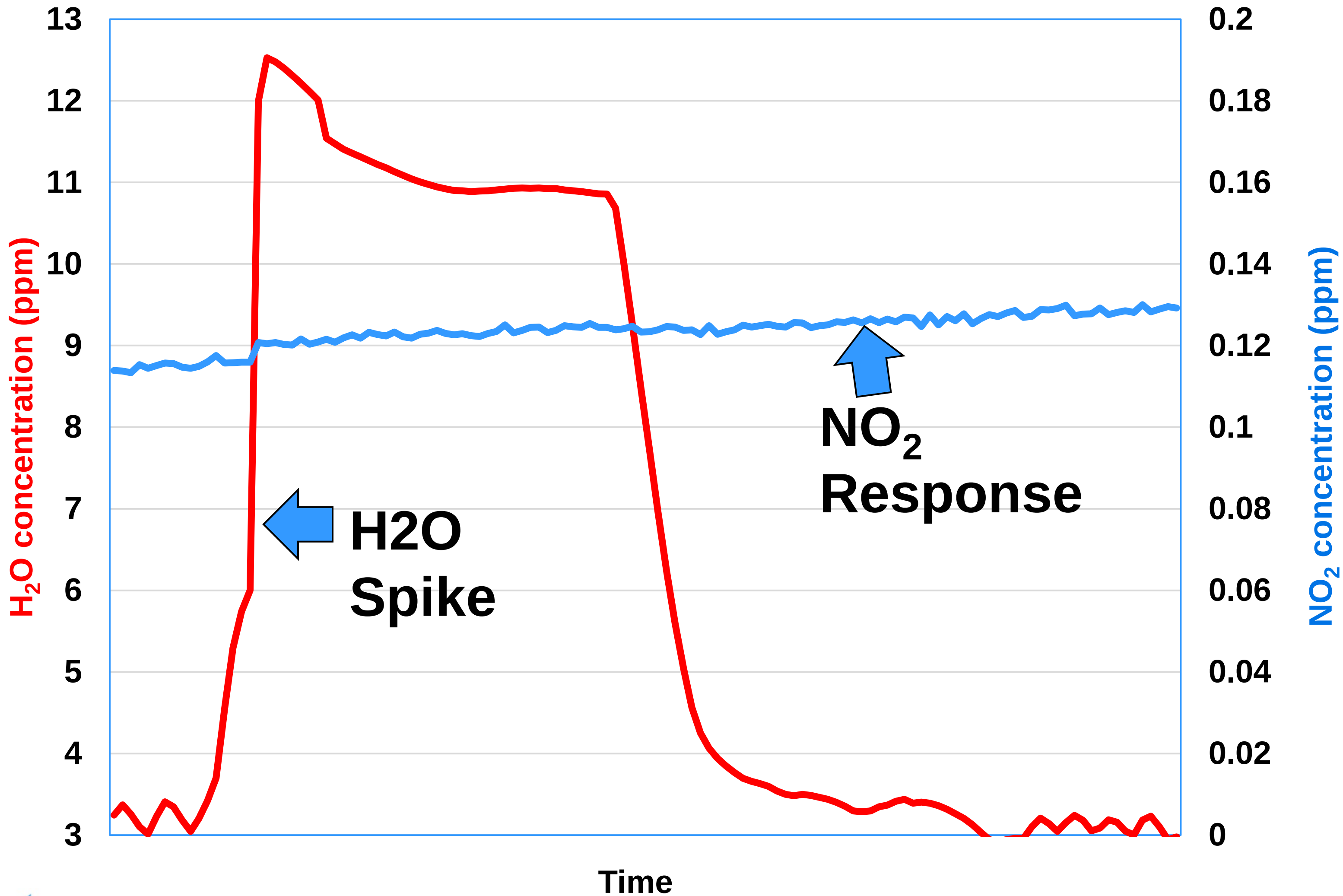
Nitric oxide (NO) analysis in presence of H_2O



Corrected NO Result after "Picket Fencing" & Other Spectral Corrections Applied



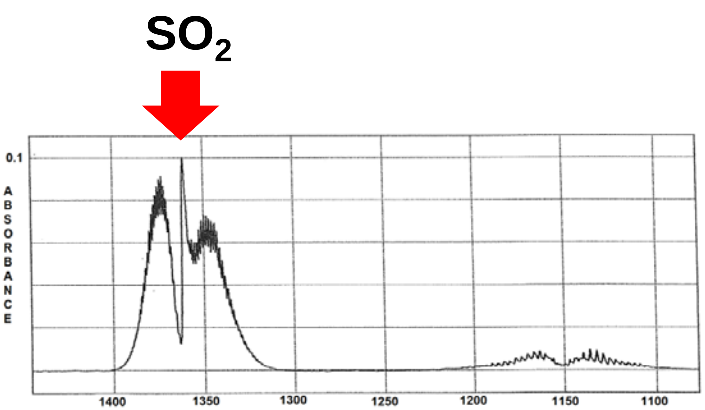
Effect of H_2O on NO_2 FTIR detection



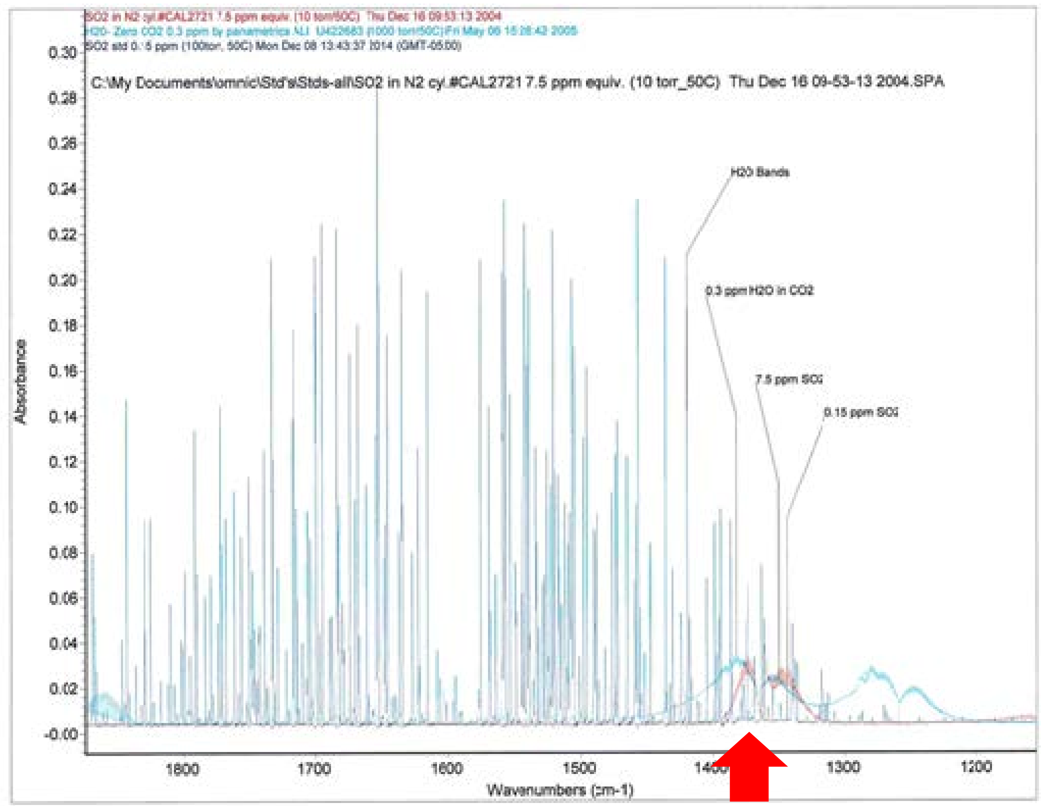
international society of beverage technologists

The Challenges of IR Measurements in CO_2

- ***SO_2 is an ISBT Target Impurity***
- ***SO_2 is common in Combustion Feed Gas Sources***
- ***SO_2 IR bands are superimposed by H_2O vapor bands***



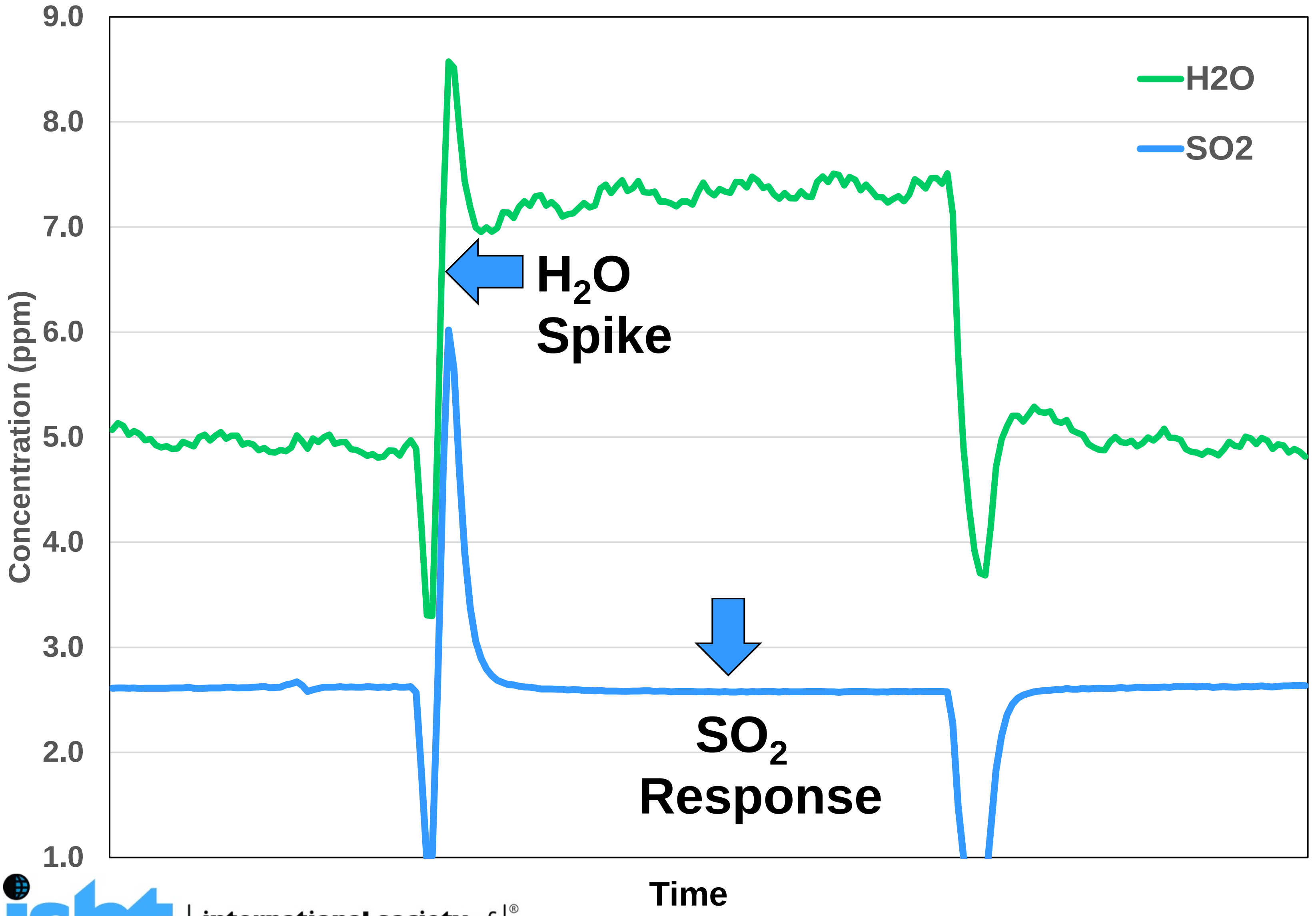
SO_2 IR Bands (No CO_2 or H_2O bands shown)



SO_2

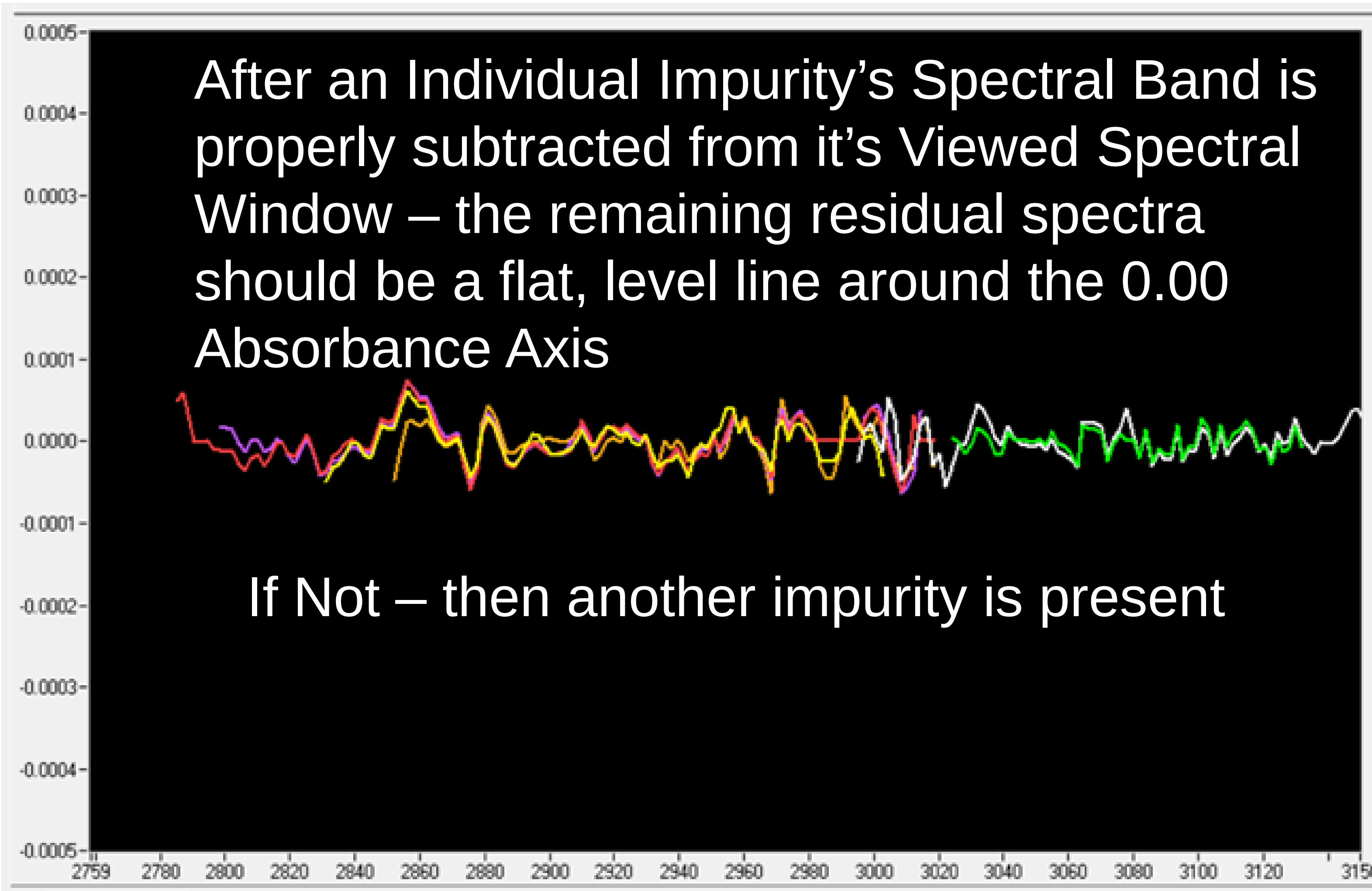
international society *of* beverage technologists

Effect of H_2O on SO_2 FTIR Measurement

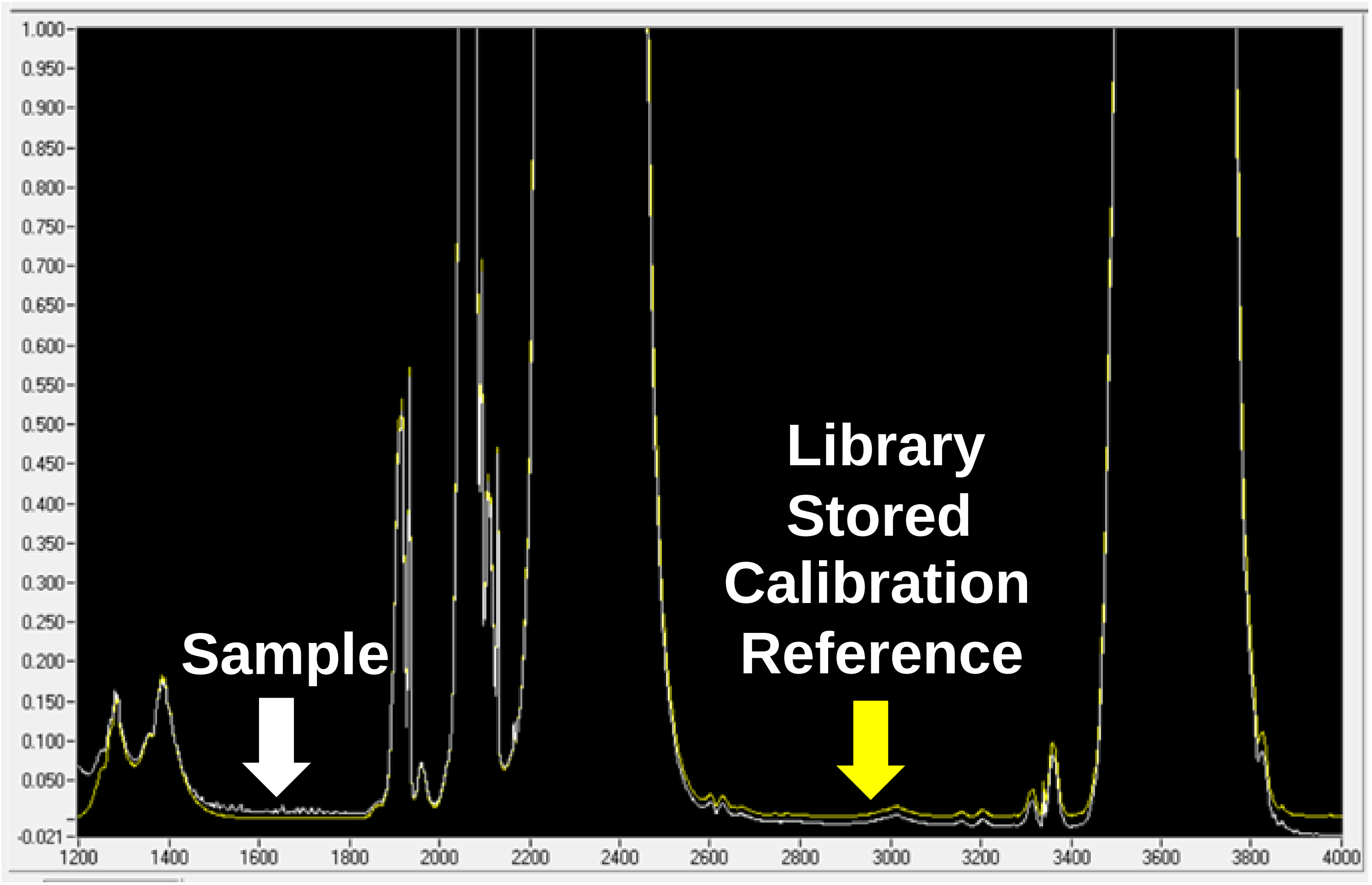


international society of beverage technologists

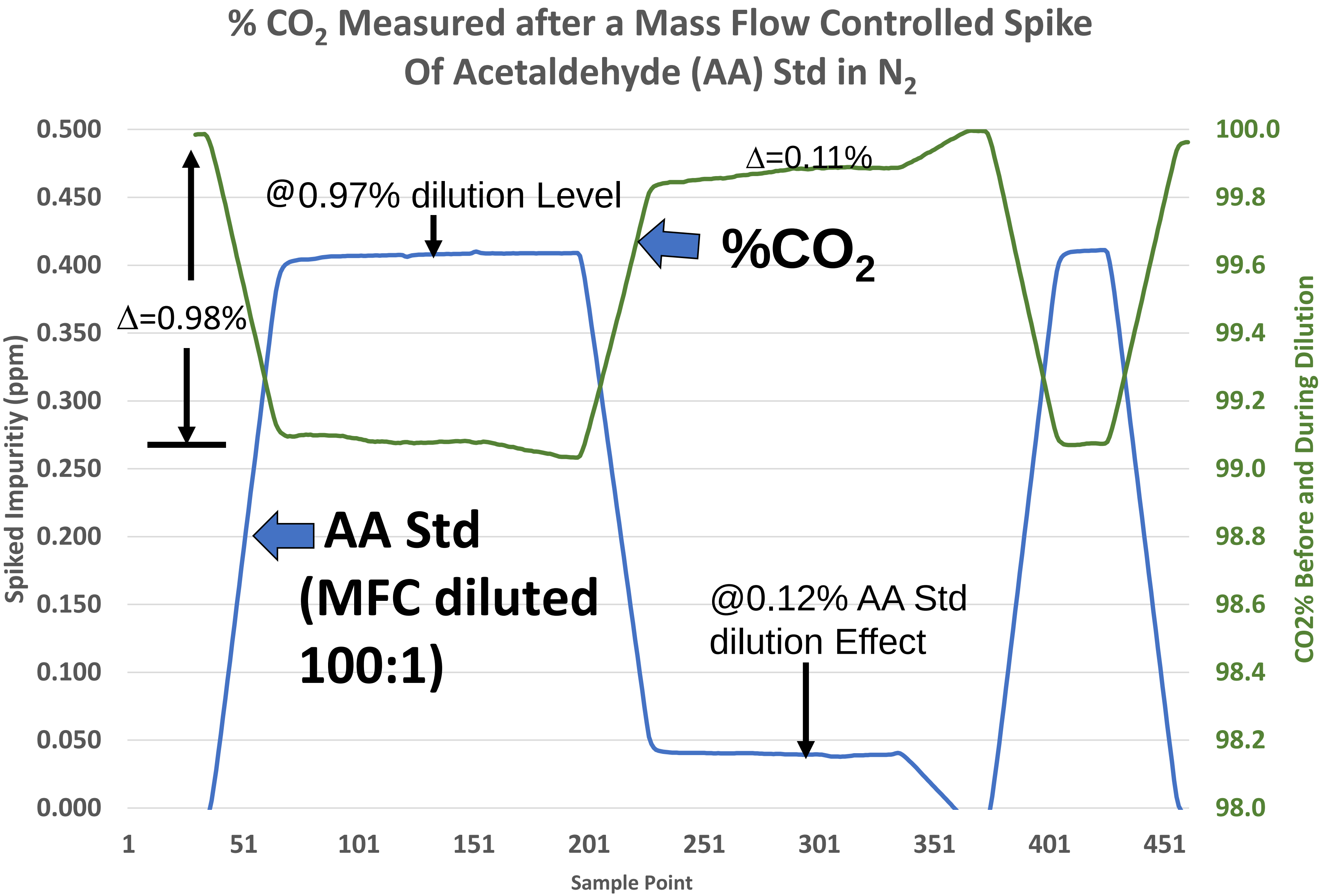
How do we know we have good "Interference Corrected" results for an impurity?



99.99% CO_2 IR Absorbance Spectrum
(Highly Stabile Response for %CO_2 Purity Monitoring)

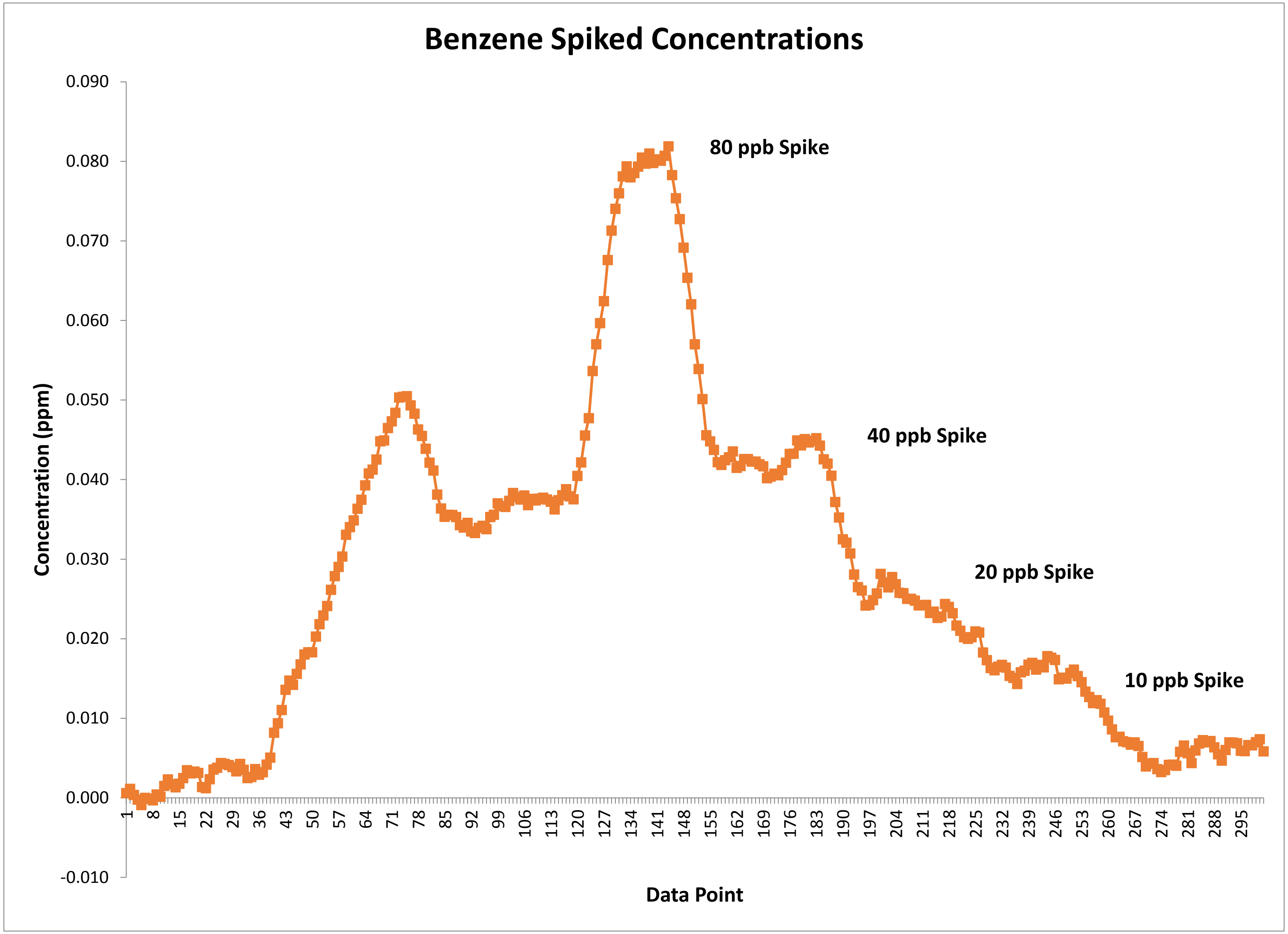


isbt international society of beverage technologists®



This Response Stability should allow for CO_2 %Purity by FTIR vs Zahm Nagel

Benzene (AHC) Std MFC Spiking Response



isbt | international society of beverage technologists®

UV-Fluorescence Detection of Sulfur Species as TSC

Step One: Totally Convert all sulfur impurity species in the sample into 1 oxidized (SO_2) form by a catalytic reactor oven (ex. ISBT Method 13.0)

$$C_nH_{2x}S_y + O_2 \rightarrow n\ CO_2 + x\ H_2O + y\ SO_2$$

For CO_2 Samples, Reactor Oxygen is provided by precisely flow-metered Clean Dry Air (CDA)

UV Fluorescence TSC Detection

Step Two: Detect the total created SO_2 with UVF

$$SO_2 \xrightarrow[\text{UV Excitation Source Lamp} = I_o]{h\nu\ (214\ nm)} SO_2^{*} \rightarrow SO_2 + h\nu\ (350\ nm)$$

UV Excitation

Source Lamp = I_o

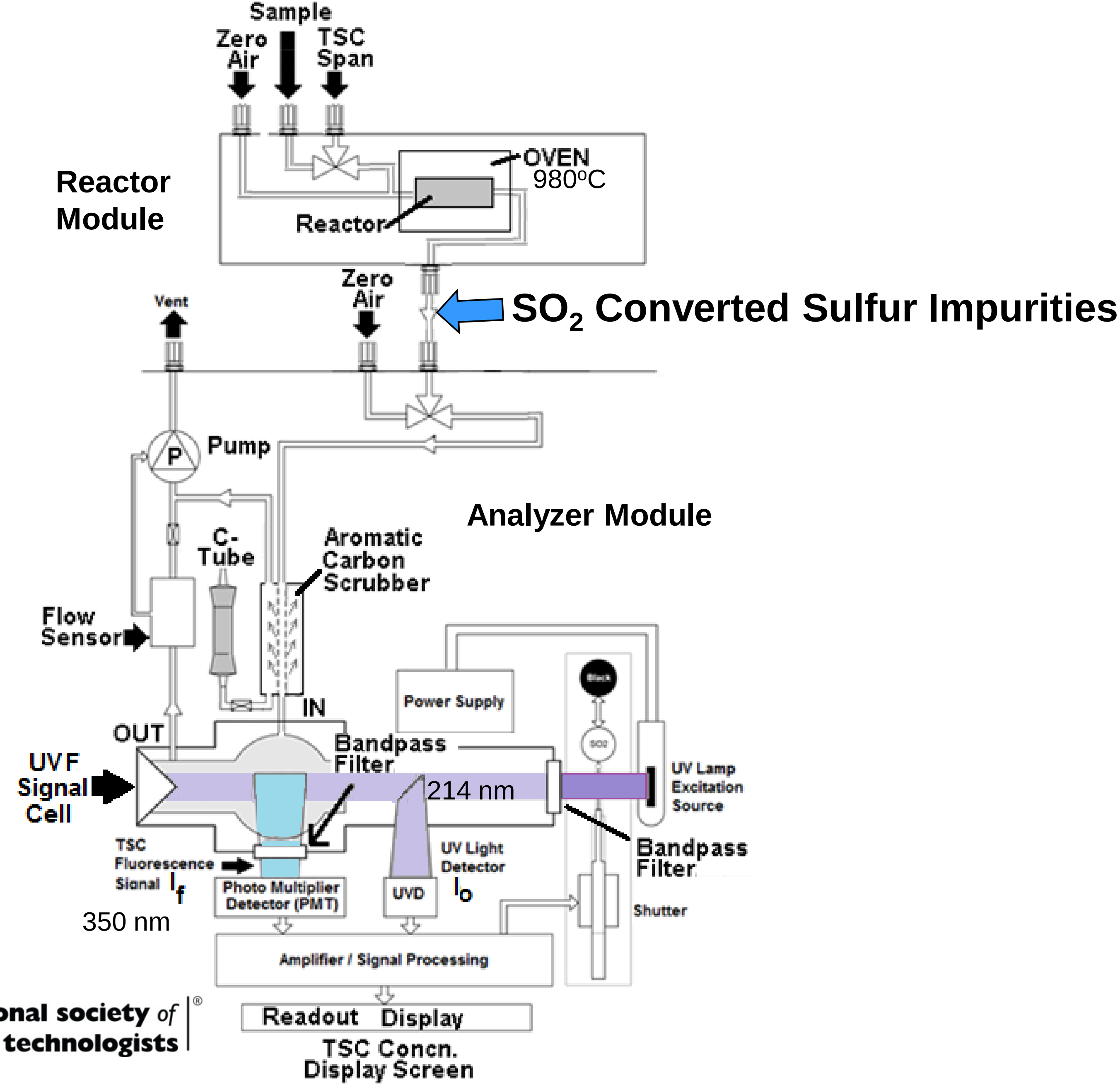
Emitted UV Fluorescence

TSC Signal $=I_f$

- **Detection with bandpass filter centered around 350nm to minimize any background interference**
- **Permeation Scrubber to remove trace of aromatics which can interfere with UVF sulfur measurement**
- **Photomultiplier detection (very sensitive)**
- **Result: MDL of <2 ppb TSC**

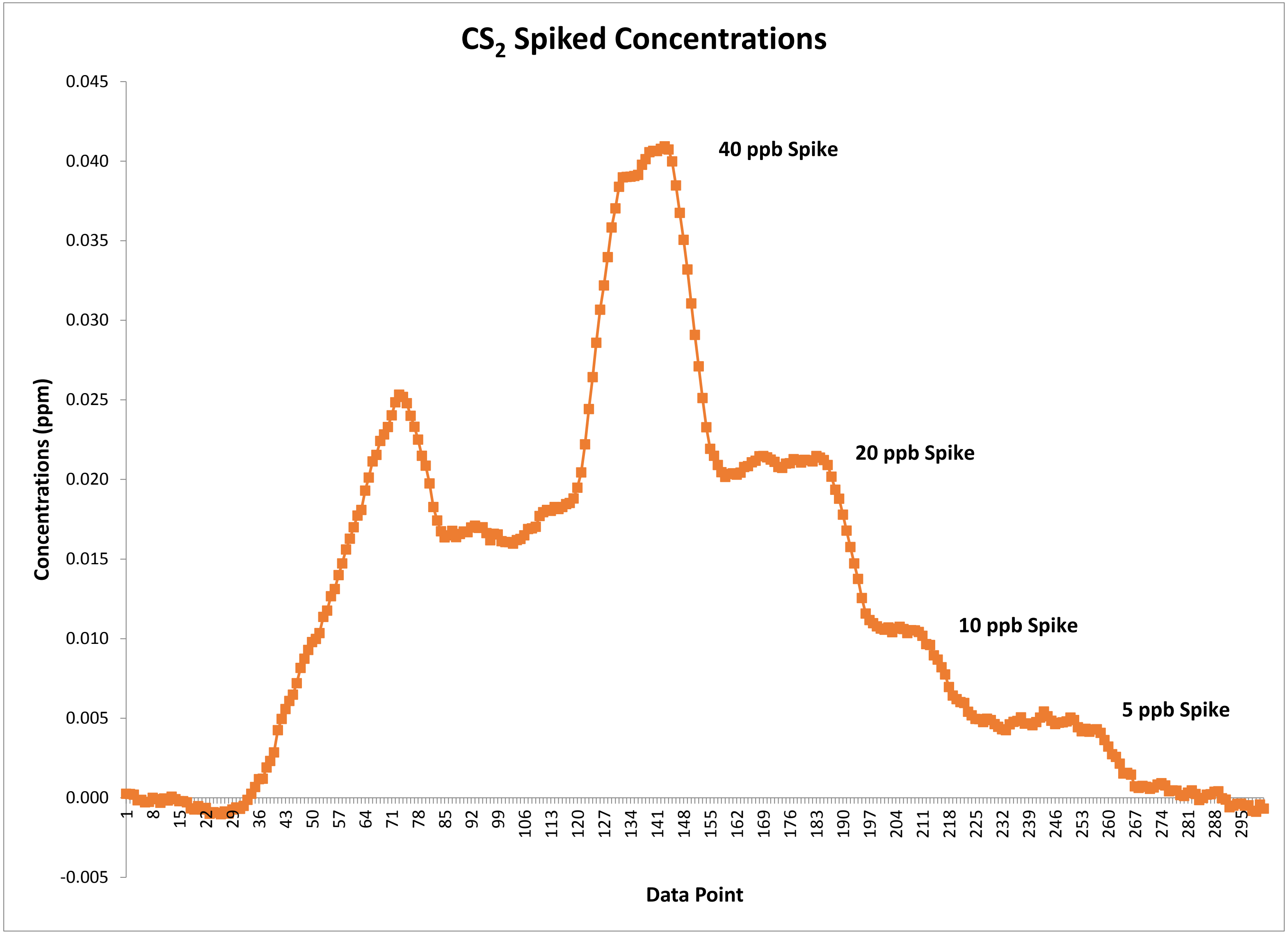
isbt international society of beverage technologists®

UV-Fluorescence TSC Detection (as SO_2)



isbt international society of beverage technologists

UVF MFC Spiking Results – TSC Gas Std (CS_2)



Summary: FTIR-UVF Detection Limits vs ISBT Guideline Recommended

MDL = Minimum Detection Limit

IMPURITY	IR-UVF MDL	ISBT MDL
Benzene (AHC)	2 ppb	**2-5 ppb**
Total Sulfur (TSC)	2 ppb	**30 ppb**
SO_2	2 ppb	**30 ppb**
TNMHC	20 ppb	**500 ppb**
THC	20 ppb	**500 ppb**
CH_4	6 ppb	**500 ppb**
H_2O	40 ppb	**5,000 ppb**
Acetaldehyde	3 ppb	**100 ppb**
Acetone	3 ppb	**NA**
CO	20 ppb	**1,000 ppb**
NH_3	20 ppb	**250 ppb**
HCN	40 ppb	**200 ppb**
NO	**20 ppb**	**250 ppb**
NO_2	**6 ppb**	**250 ppb**
Ethane	5 ppb	**NA**
Propane	5 ppb	**NA**
Pentane	5 ppb	**NA**
Methanol	10 ppb	**2,000 ppb**
CO_2 % Purity	**+/- 0.1%**	**+/-0.1%**

isbt | international society *of* beverage technologists®

MAX Analytical Technologies

Airborne Labs International

Real-time ppb CO_2 Impurity Detection by an Advanced FTIR-UVF System

Thank you for your time & attention

Questions?

BevTech 2018

isbt international society of beverage technologists®