EPA/TUV Certified FTIR CEM and Ultra Low Level HCl CEM for Combustion Facilities

CEMTEK 2014

Oct 1-3, 2014

Peter G. Zemek

mks Technology for Productivity

MultiGas™ FT-IR
Automated HCl CEM Systems

MKS Instruments

On-Line Product Group

2 Tech Drive, Suite 201
Andover, MA 01810
Tel: 978-482-5364

Conventional Analyzers

- CO and CO_2
  - Infrared Absorption using filters – single wavelength band
  - FTIR measures multiple wavelengths including background
    - No baseline monitoring – Zero Drift
    - Signal & temperature variation – Calibration Drift
    - FTIR has minimal zero and calibration drift
- NO and NO_2
  - Chemiluminescence – Emission measurement from reaction
    - NO_2 first converted to NO – conversion efficiency affected by NH_3
    - Chemiluminescent reaction affected by NH_3 also
  - FTIR is a direct measurement of NO and NO_2
    - Can measure other nitrogen gases like N_2O and NH_3
- Hydrocarbons
  - Flame Ionization Detector – FID
    - Burns all hydrocarbons
    - Generate a proportional signal to level of Carbon
    - Each type of hydrocarbon have different responses
  - FTIR measures each VOC individually
    - VOC is calculated by multiplying FID response factor and adding

Advantages of FTIR Analyzers

- Multiple components <u>Simultaneously</u>
  - <u>Canned pre-validated method</u> – Load and GO!
  - HCl, HF, VOCs, NO_x, SO_2, CO_2, CO, H_2O,
  - CH_2O, CH_4, HCN, SO_3, THC, etc.
  - Additional components
    - No hardware change
    - Can be added in the field
- Measurements done Hot-Wet
  - Hot-wet required for polar components HCl
  - Works with High CO_2 and H_2O (40%)
  - No Chemical Conversions
- Simple Operation
  - No daily maintenance
  - No daily calibration
  - High sensitivity gas cell
    - Small volume (200mL)
    - Long path length (5.11m)
- Low Maintenance
  - Laser replacement (3-4 years)
  - Cell cleaning (at maintenance interval if needed)

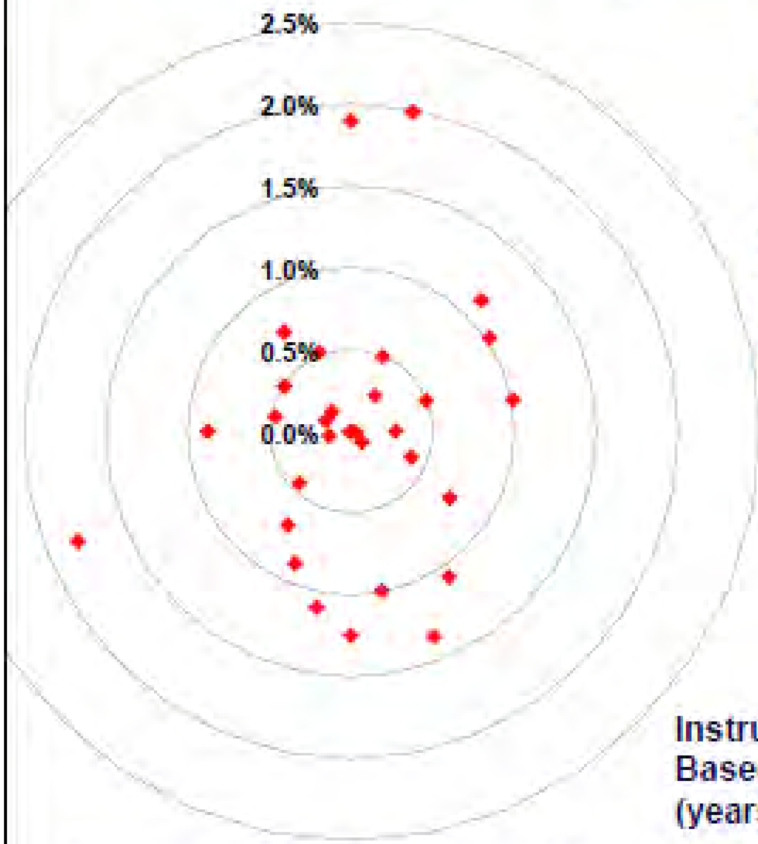
MKS 2030 Analyzer Technology

- **MultiGas™ 2030 CEM-Cert - core analyzer technology**
- **High resolution FTIR (0.5 cm^{-1}):**
  - minimal cross-interference from water (up to 40%) or other gas components
- **All units maintain the same calibration & can reference a standard library of calibration spectra due to:**
  - Patented, linearized MCT (Hg/Cd/Te) detector response
  - Heated gas cell (191°C) with automatic temperature & pressure compensation
  - Peak analysis routines which keep resolution & frequency tolerances exceedingly tight
  - Fixed pathlength gas cell & securely aligned optics
- **Eliminates the need for calibration gases during routine operation**

MultiGas™ 2030 CEM-Cert

FTIR Do not Drift or Change Response

MKS Machine Independent Calibrations



Out of Box

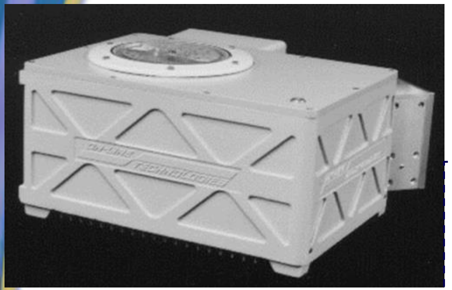
Easily able to transfer calibrations from one instrument to another

Instrument to Instrument Variation
Based on Ethylene Measurements
(years 2000 - 2002)

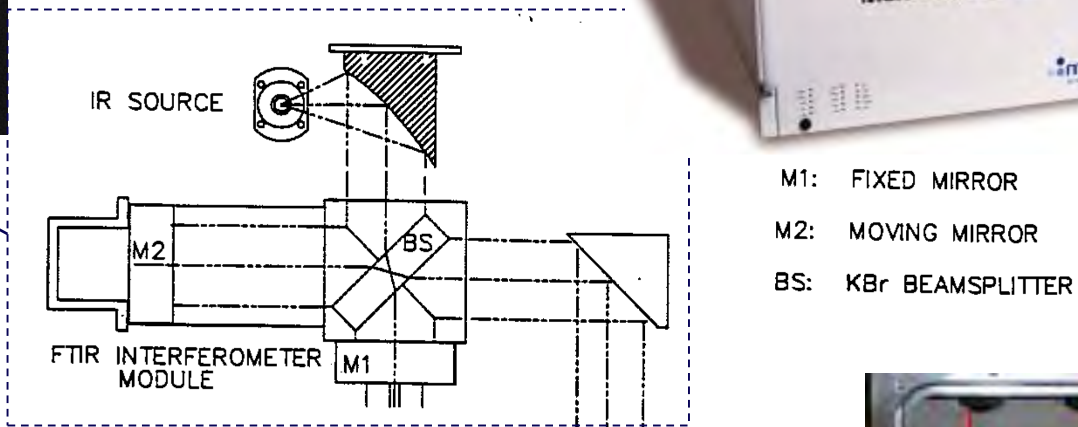
Demonstration of instrument to instrument variability
none of these instruments calibrated for Ethylene

MKS Instruments 10

FTIR Instrumental Parts



Interferometer



Integrated Rack Mount System

20/20™ Long Path (5.11m) Gas Cell Ni-SS-Inconel, 200 ml Volume, ZnSe, Kalrez, MgF2 optics

Detector TE-MCT

Continuous Emissions Monitoring Systems (CEMS)

- **Typical users:**
  - Waste incinerators – Industrial & municipal
  - Power plants
  - Cement kilns
  - Industrial combustion plants
  - Turbines
- **FTIR-based CEMS advantages:**
  - Ability to monitor a large range of combustion species simultaneously
  - Direct measurements of hot, wet samples without sample conditioning
- **CEMS market strictly regulated EU:**
  - **TÜV & MCERTS** certification essential for market participation in Europe & UK

Incinerator plant – Leverkusen
MGS300 field test site used by TÜV Rheinland

TÜVRheinland® CERTIFIED
Suitability Tested
EN 15267
QAL1 Certified
Regular Surveillance
www.tuv.com
ID 0000039319

mCERTS
THE ENVIRONMENT AGENCY'S MONITORING CERTIFICATION SCHEME

MKS sampling components

- **MGS300-SP sample probe: Removes particulates while maintaining "hot, wet" sample integrity:**
  - Heated sample path 180°C - 220°C
  - Stainless steel construction with PTFE filters
  - Includes gas calibration port

- **MGS300-EP eductor pump: Provides consistent sample flow to the MultiGas™ gas cell:**
  - Air flow driven eductor pump with no moving parts for high reliability & low maintenance
  - Heated sample path 180°C - 220°C
  - Stainless steel construction with sintered metal dust filter

- **MGS300-HL heated line: Transports sample from the probe to the MultiGas™ gas cell:**
  - Rugged construction with excellent thermal insulation – low heat loss
  - Stainless steel inner core

MKS TÜV Certification

- **MGS300 CEMS is TÜV & MCERTS certified having met the requirements of the DIN EN 15267-3 standard:**
  - Monitoring of emissions from stationary sources
- **A full 12-months of field testing was completed at a working incinerator plant, qualifying the MGS300 for a <u>6-month</u> maintenance interval**
- **The MKS 2030 achieved best overall "uncertainty" performance for the emission components tested**
- **MKS 2030 meets US EPA 40 CFR part 60/75 requirements**


Umwelt Bundes Amt

TÜVRheinland® Precisely Right.

CERTIFICATE

of Product Conformity (QAL1)

Certificate No.: 0000039319

Certified AMS:	MGS300 for CO, SO_2, NO, NO_2, HCl, HF, CH_4, CO_2, H_2O, N_2O and NH_3
Manufacturer:	MKS Instruments Inc. 651 Lowell Street, Methuen, MA 01844 USA
Test Institute:	TÜV Rheinland Energie und Umwelt GmbH

This is to certify that the AMS has been tested and found to comply with:

EN 15267-1: 2009, EN 15267-2: 2009, EN 15267-3: 2007 and EN 14181: 2004

Certification is awarded in respect of the conditions stated in this certificate (see also the following pages).

TÜVRheinland CERTIFIED — Suitability Tested EN 15267 QAL1 Certified Regular Surveillance

Publication in the German Federal Gazette (BAnz.) of 23 July 2013

German Federal Environment Agency
Dessau, 20 August 2013

i. A. Dr. Marcel Langner

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qal1.de info@qal1.de


sira CERTIFICATION — CSA Group — MCERTS — Environment Agency

PRODUCT CONFORMITY CERTIFICATE

This is to certify that the

MGS300
Continuous Emissions Monitoring System

Manufactured by:
MKS Instruments Inc.
651 Lowell Street,
Methuen,
Massachusetts,
01810,
USA

Has been assessed by Sira Certification Service
And for the conditions stated on this certificate complies with:

MCERTS Performance Standards for Continuous Emission Monitoring Systems, Version 3.4 dated July 2012
EN15267-3:2007,
& QAL 1 as defined in EN 14181: 2004

Certification Ranges:

CO	0 to 75 mg/m^3	0 to 300 mg/m^3	0 to 1500 mg/m^3
CH_4	0 to 15 mg/m^3	0 to 50 mg/m^3	0 to 500 mg/m^3
HCL	0 to 15 mg/m^3	0 to 90 mg/m^3	0 to 200 mg/m^3
N_2O	0 to 50 mg/m^3	0 to 100 mg/m^3	0 to 500 mg/m^3
NO	0 to 200 mg/m^3	0 to 400 mg/m^3	0 to 1500 mg/m^3
NO_2	0 to 50 mg/m^3	0 to 100 mg/m^3	0 to 1000 mg/m^3
SO_2	0 to 75 mg/m^3	0 to 300 mg/m^3	0 to 2000 mg/m^3
HF	0 to 3 mg/m^3	0 to 10 mg/m^3	
NH_3	0 to 10 mg/m^3	0 to 75 mg/m^3	
CO_2	0 to 75 mg/m^3		
H_2O	0 to 75 mg/m^3		

Project No	: 16A30952
Certificate No	: Sira MC130234/00
Initial Certification	: 08 October 2013
This Certificate issued	: 08 October 2013
Renewal Date	: 07 October 2018

R Cooper I Eng MInst MC
Technical Director

MCERTS is operated on behalf of the Environment Agency by

Sira Certification Service
12 Acorn Industrial Park, Crayford Road, Crayford
Dartford, Kent, UK DA1 4AL
Tel: +44 (0)1322 520500 Fax: +44 (0)1322 520501

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TÜV vs US-EPA for FTIR

- If CEM passes all Installation Validation Specifications, Lab tests and proven itself in field for 6 months, only daily QA/QC for ALL compounds is
  - zero
  - quarterly gas offerings test
- In US, PS15 require daily
  - zero, mid, and high gas level (CO, CO_2, H_2O, SO_2, NOx)
  - No on-going QA/QC
- In US, PS18 (draft) requires daily
  - zero
  - dynamic spike or
  - wet/dry cal gas challenge (zero or low and high) (HCl only),
  - Option to use PS15 (dry cal gas offerings at 3 levels)

EPA Test Facility – PS18 RTP, NC
MKS Reference Method -Anchor

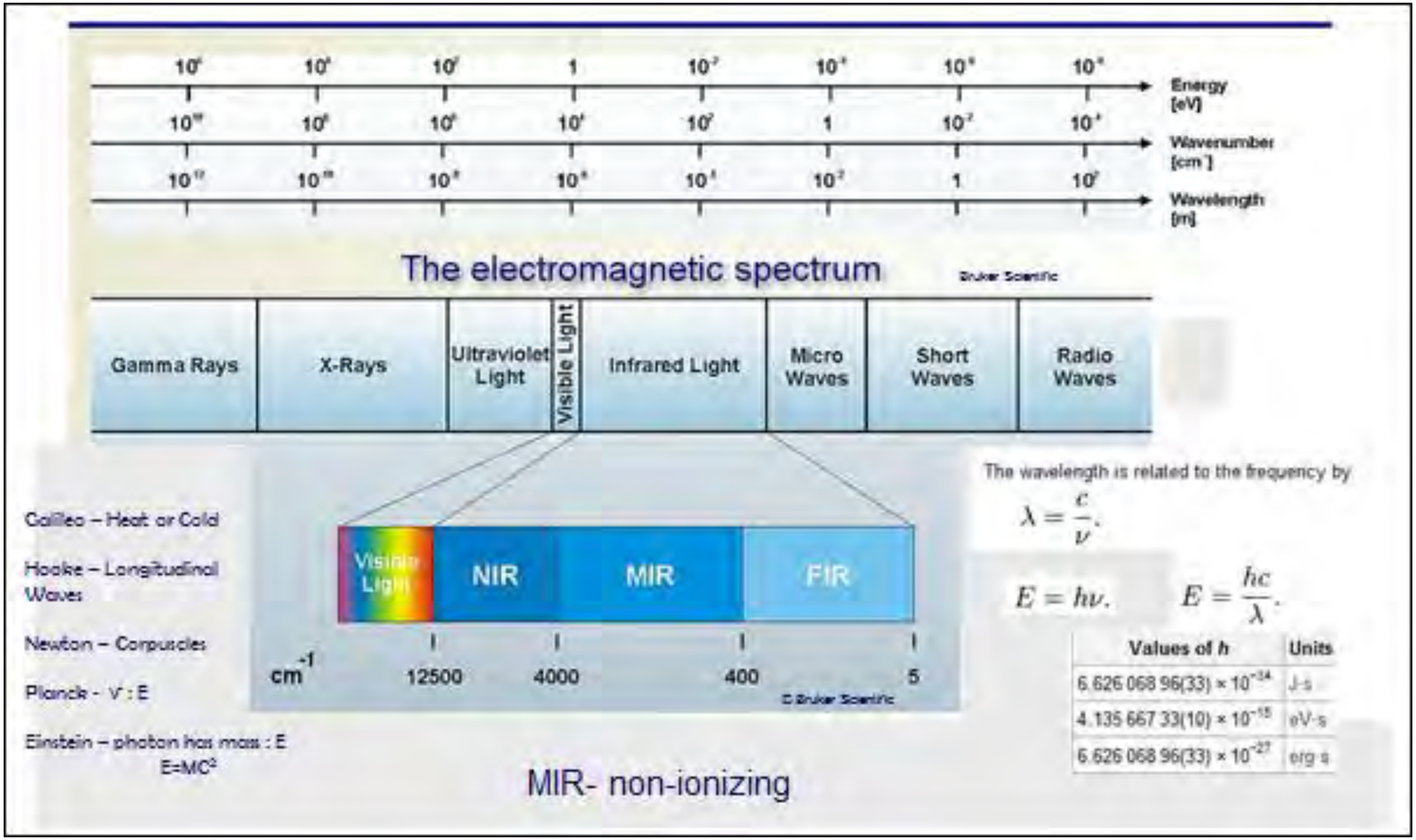
- ORD's Multi-Pollutant Combustion Research Facility
  - 4M Btu/h down-fired combustor firing coal and/or NG
  - Multiple pollution control configurations possible
    - SCR, ESP, FF, Wet Scrubber
  - Duct injection of gases to control emission profiles and combinations
    - HCl, SO_2, NO_x, CH_4, CO, NH_3, H_2O, CH_2O
  - All CEMS and RM measurements from same basic location

EPA REFERENCE METHODS – MKS FTIRs - Anchors for Testing (EPA and Industry)

- Looking at 3 different high resolution FTIR analyzers
- Focus on DLs, measurement quality and RM performance at very low HCl levels LN2, TE9, HS
- Point of reference for HCl Gas Standards

Crash Course FTIR

The Electromagnetic Spectrum

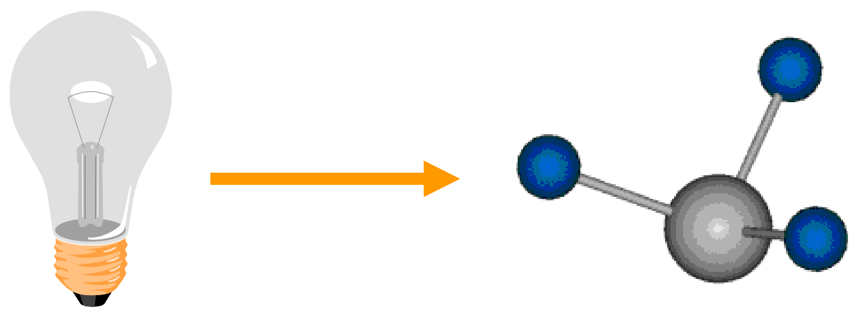


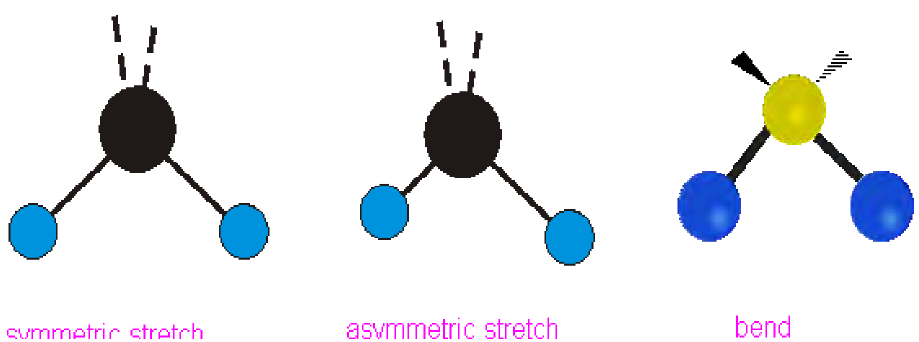
Infrared Spectroscopy

- Infrared light (IR) waves at discreet frequencies to molecular bond motions
  Vibrational and pure rotational motions
- When the frequencies match, energy is absorbed by that bond and resulting excitation increases molecular bond energy state (non-ionizing)
- The energy absorbed by the bond at discreet frequencies is proportional to the # of molecules
- FTIR spectrum is a plot of decreased energy at discreet frequencies corresponding to the absorption bands of the compounds in the sample. High resolution 0.5 cm^{-1}

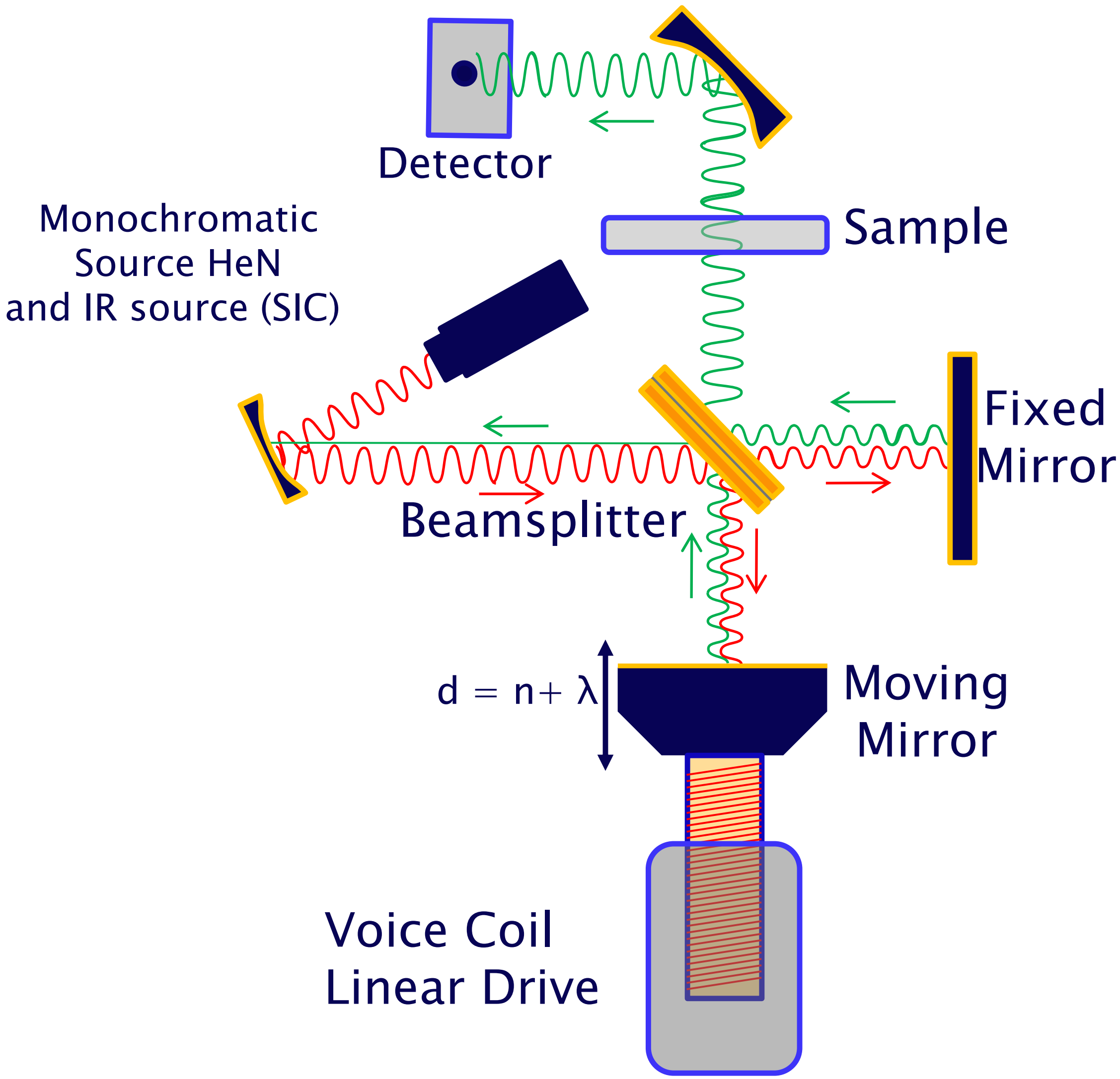
Infrared (IR) Spectroscopy

- Based on IR light absorption
  - Energy (IR radiation) heats molecule - vibrations and rotations
  - The pattern and intensity of the spectrum provides all the information about gas (type and concentration)

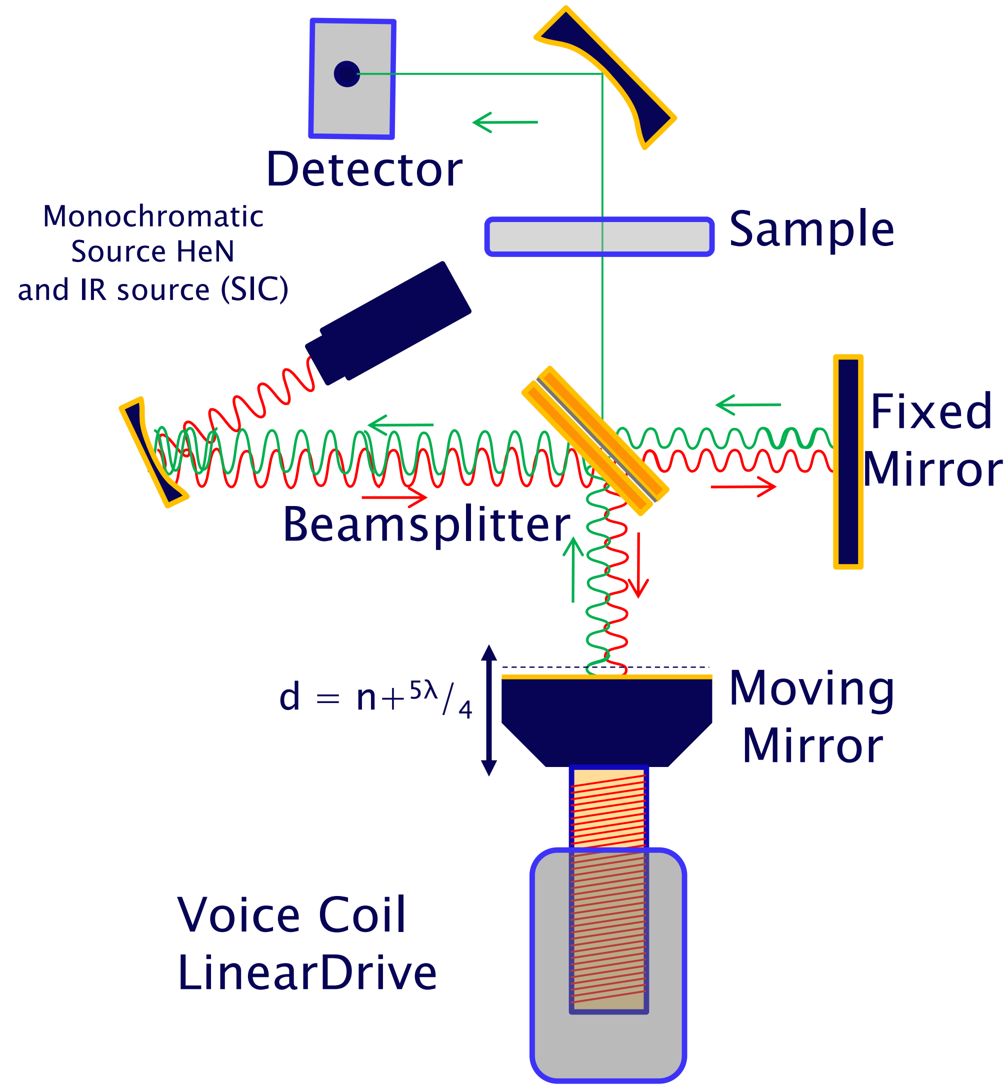




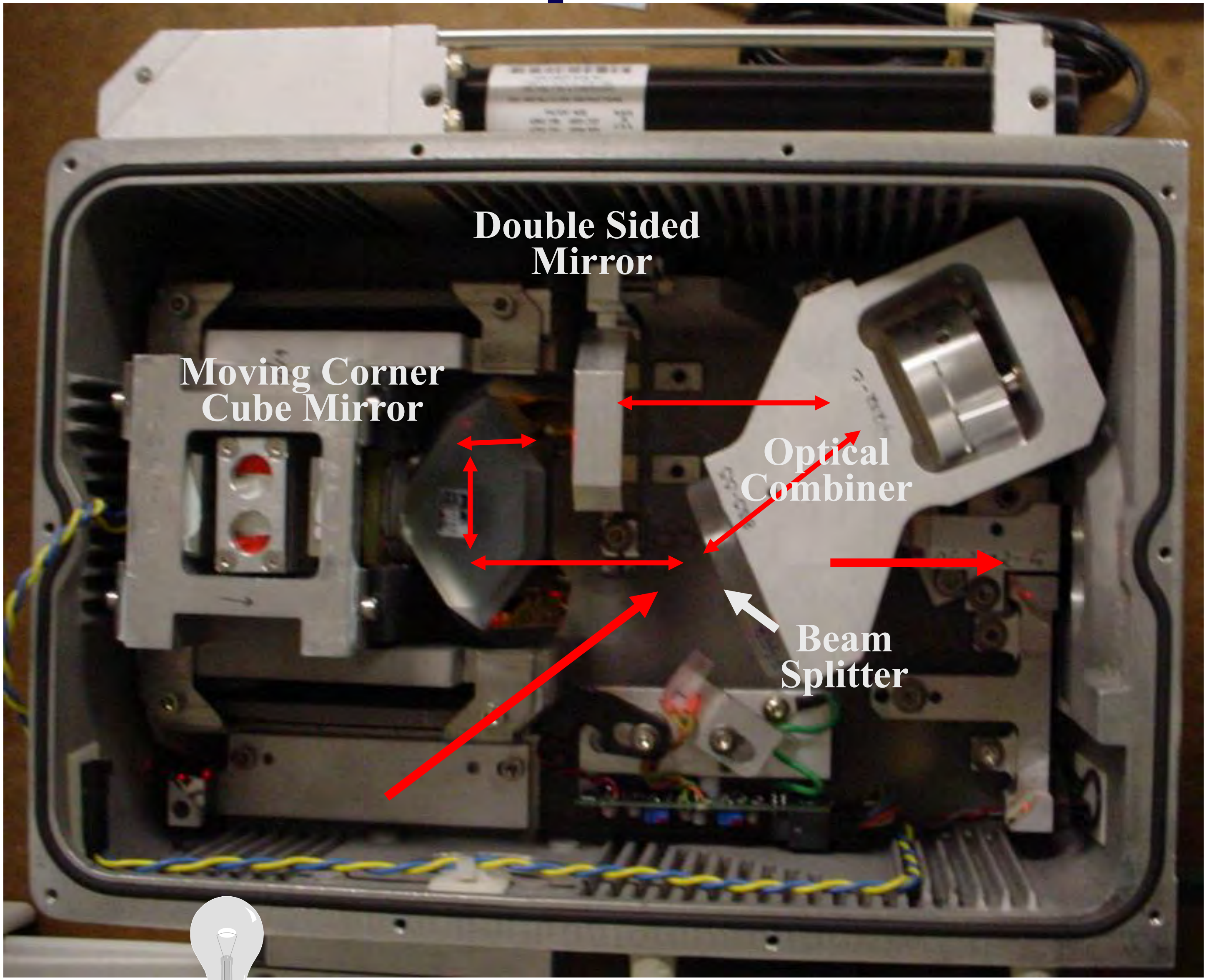
Interferometer: Retardation = 0



Interferometer: Retardation=$^{1}/_{2}\ \lambda$

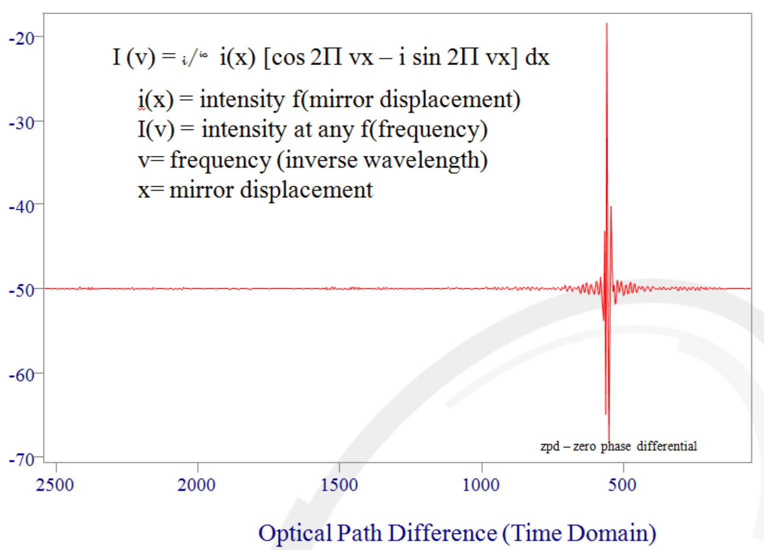


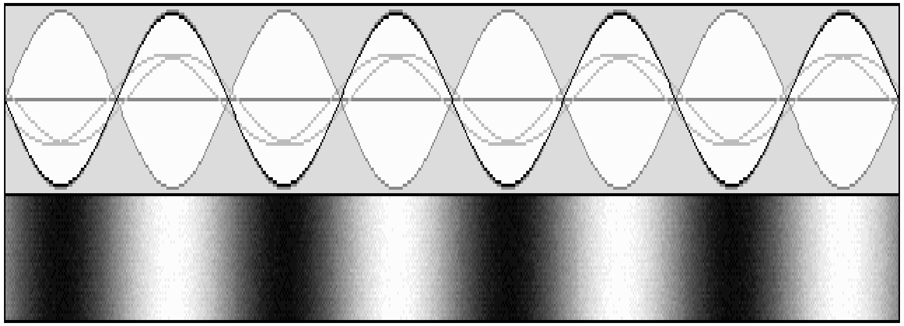
MKS FTIR Top View



To Optics Box

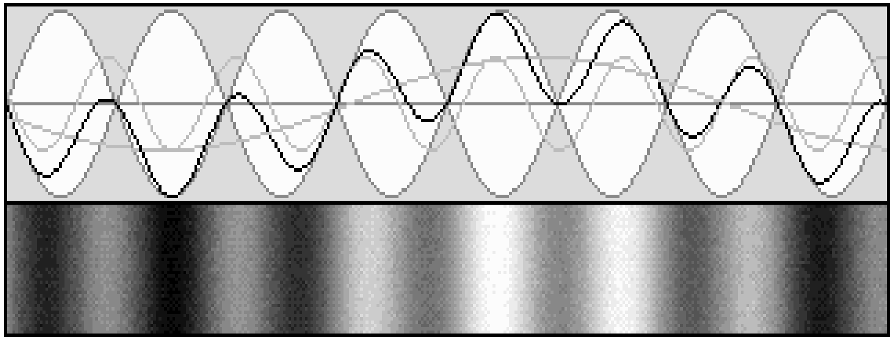
The interferogram





$$I(\delta) = B(\nu)\cos(2\pi\nu\delta)$$

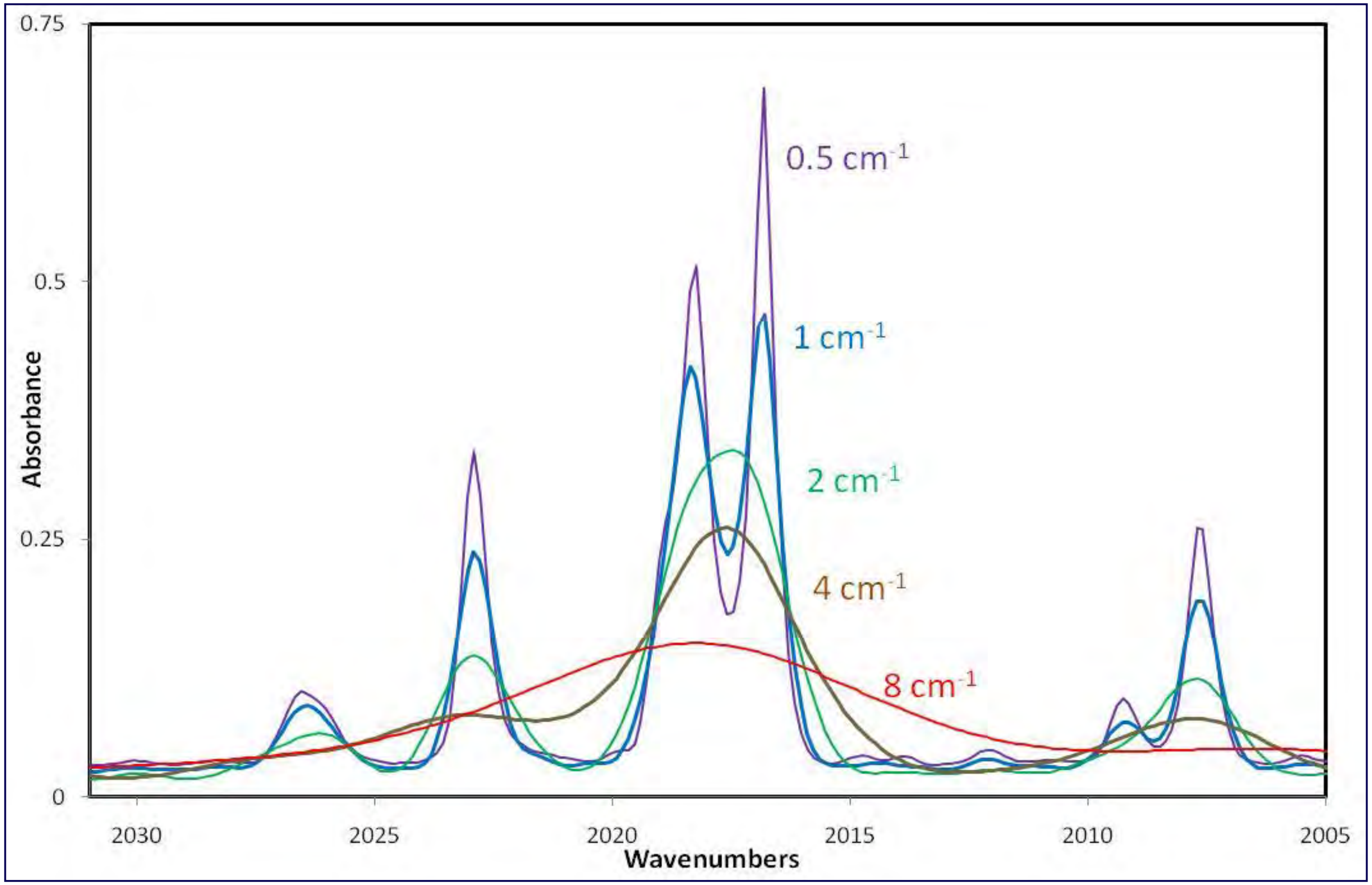
$$B(\tilde{\nu}) = A\int_0^{\infty} I(\delta)\cos(2\pi\tilde{\nu}\delta)d\delta$$



where B(ν) = Intensity at wavenumber ν (ν=1/λ in cm)
and I(δ) = the corresponding interferogram
A is a constant of the integration.

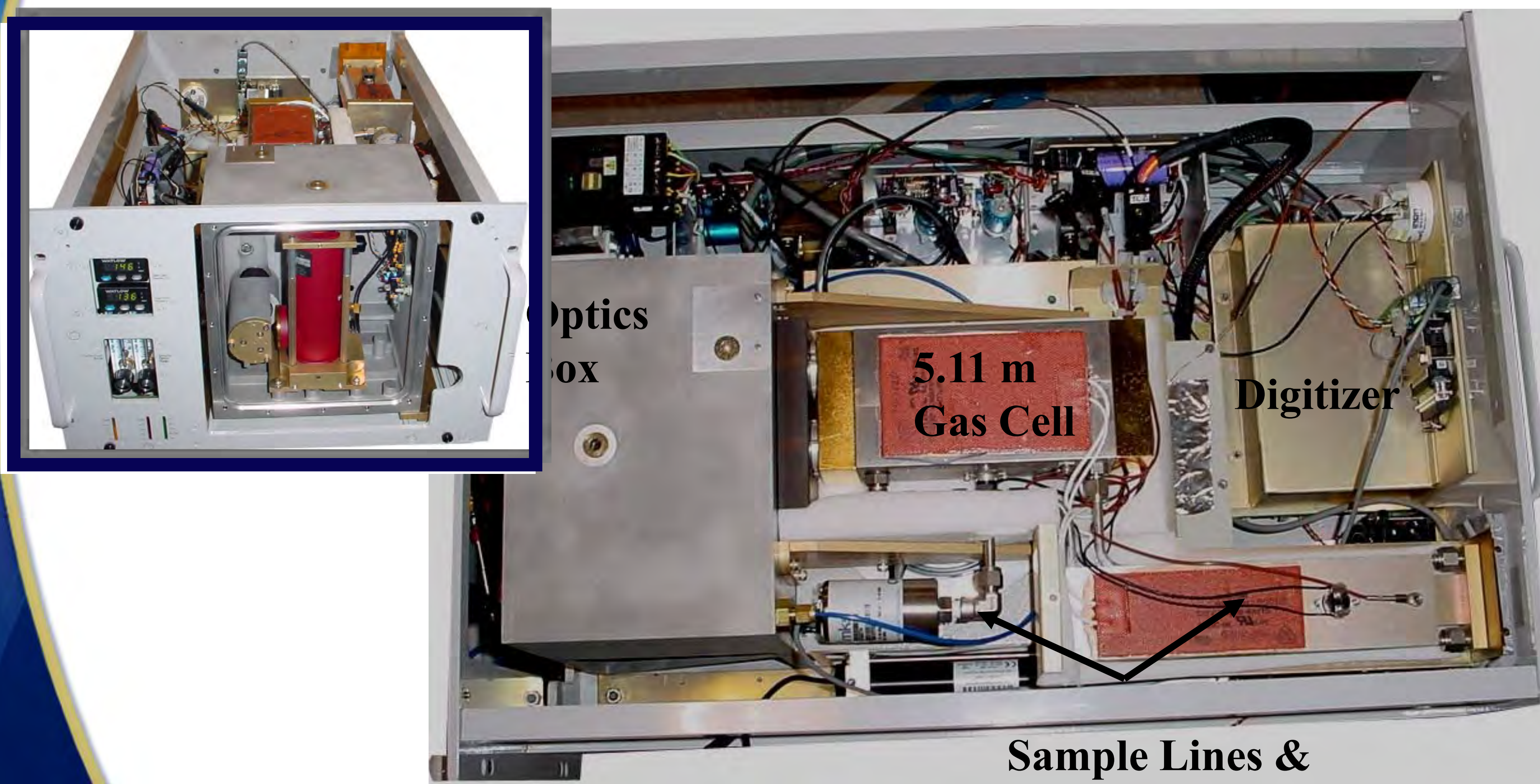
Resolution

- Resolution – distance of moving mirror path
  - Lower number = better resolution; slower

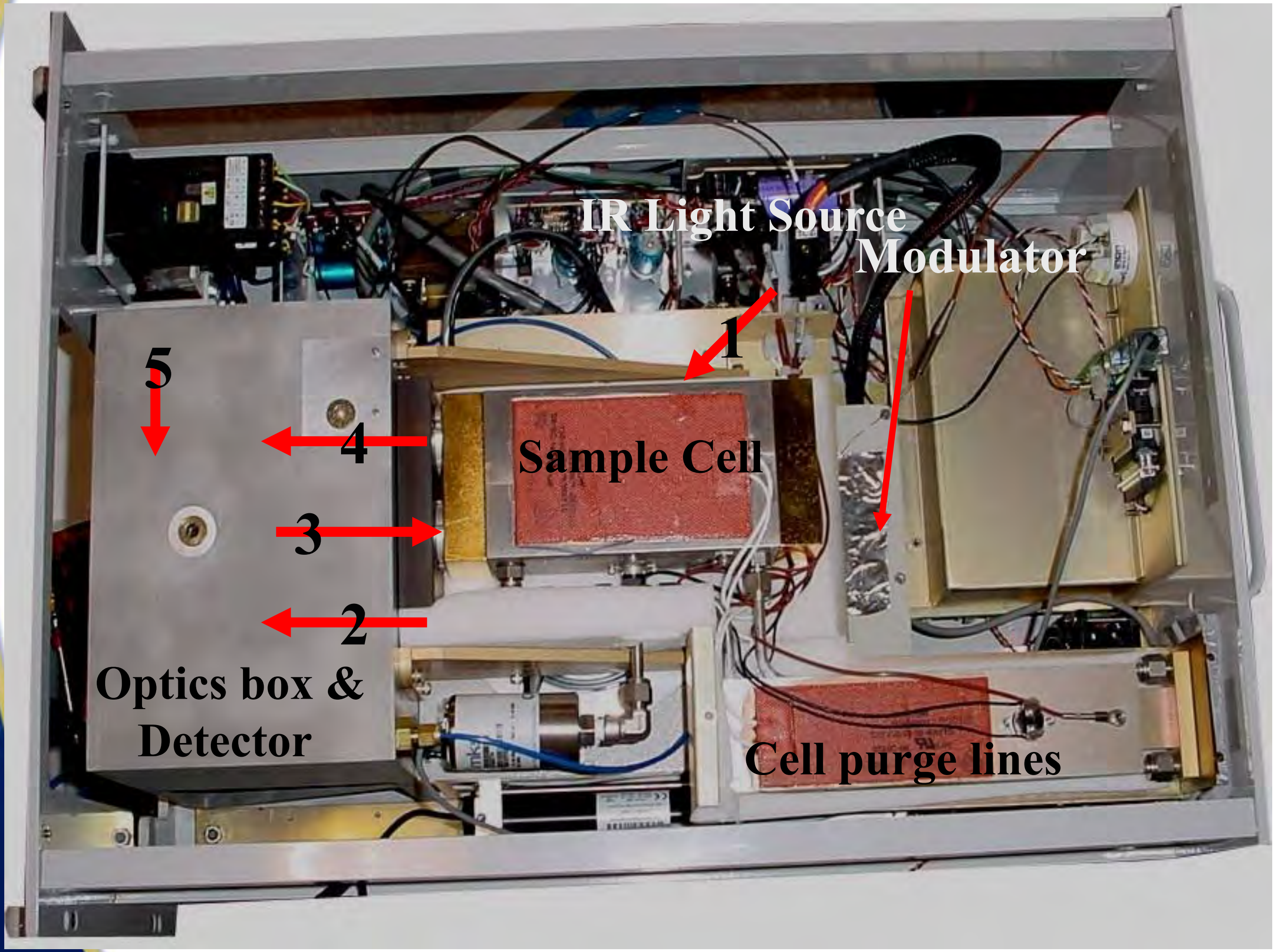


Water vapor at different resolutions

MultiGas 2030 FT-IR Gas Analyzer

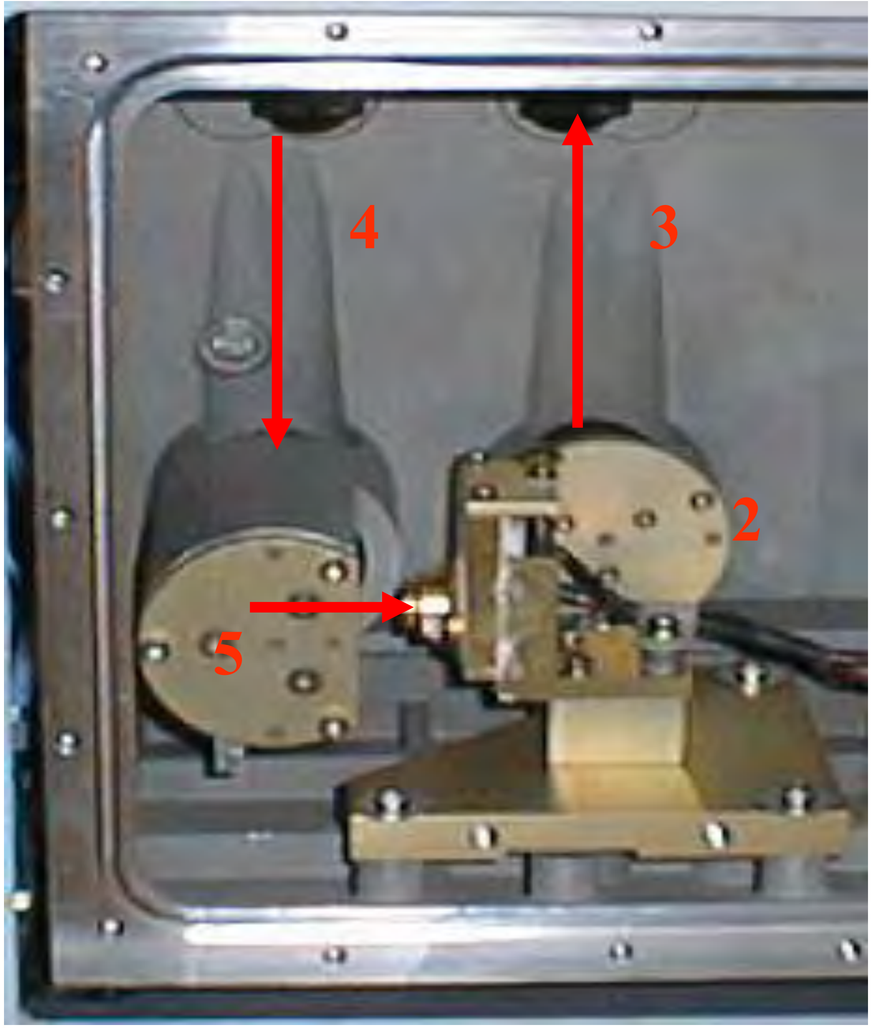


IR Light through MultiGas Analyzer



1. IR Light goes into FTIR
2. Modulated light from FTIR to Optics box
3. Light enters gas cell
4. Light exits gas cell
5. Light directed onto detector

IR Light Through Optics Box

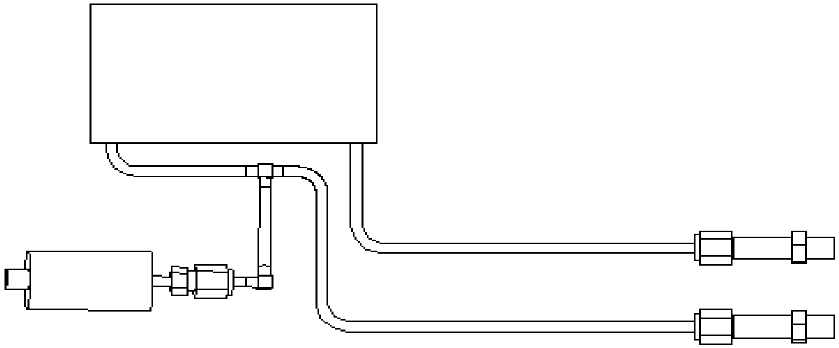


2. Modulated light enters Optics box (OB) from FTIR
3. Light leaves OB and enters gas cell
4. Light enters OB from gas cell
5. Light directed onto detector

Note: Detector Shown is TE-cooled MCT normally
Combustion Detector is LN_2-cooled MCT (shown later)

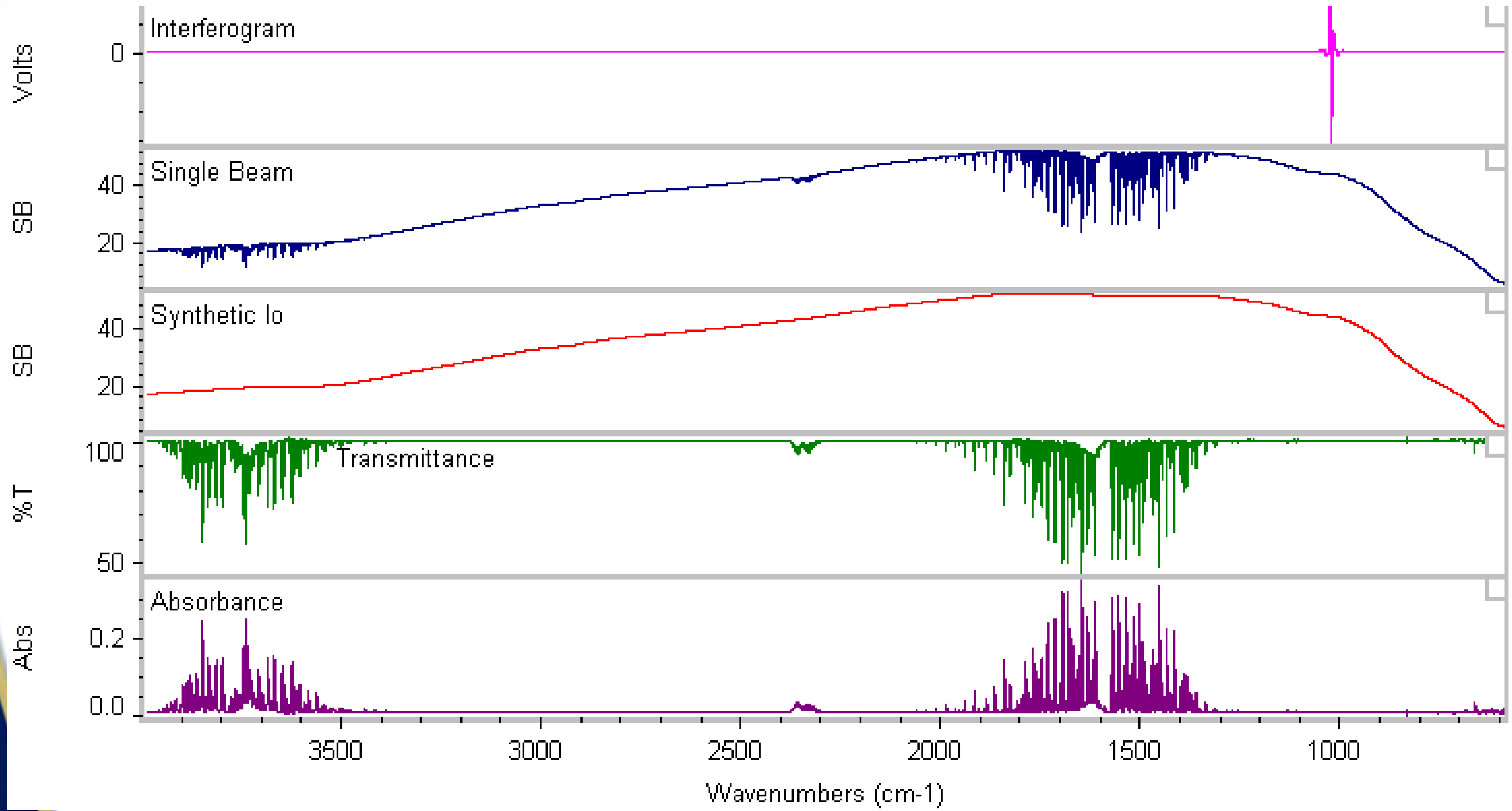
MultiGas Cell Advantage

20/20™ Long Path (5.11m) Gas Cell



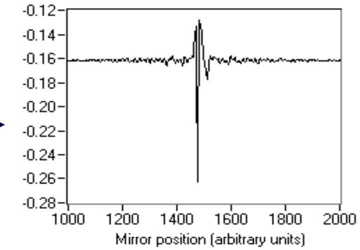
- Gas Cell
  - 5.11 m, 200 mL volume
  - 32 passes through cell
  - Long path - small volume -->provides fast response
  - Ni-coated Al, SS, Dursan cell
  - Alignment indexing pads
- Mirrors
  - O-ring “face” seal
  - Corrosive resistant coating
  - High light throughput
- Windows
  - ZnSe, KBr
  - Others Available

FTIR Processing Sequence

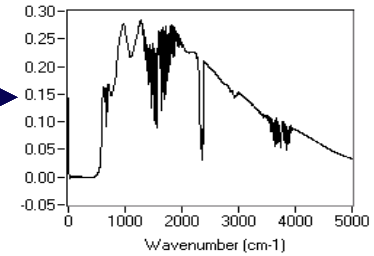


Summary Spectral Data

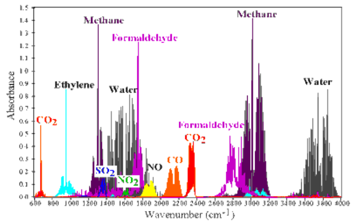
1) Acquire interferogram (detector signal as a function of time or mirror movement)



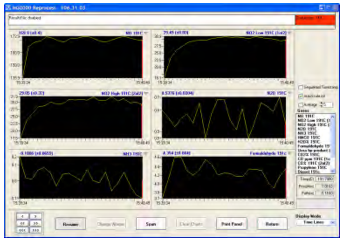
2) Apply Fourier Transform to get the single beam (signal as a function of wavenumber in cm^{-1})



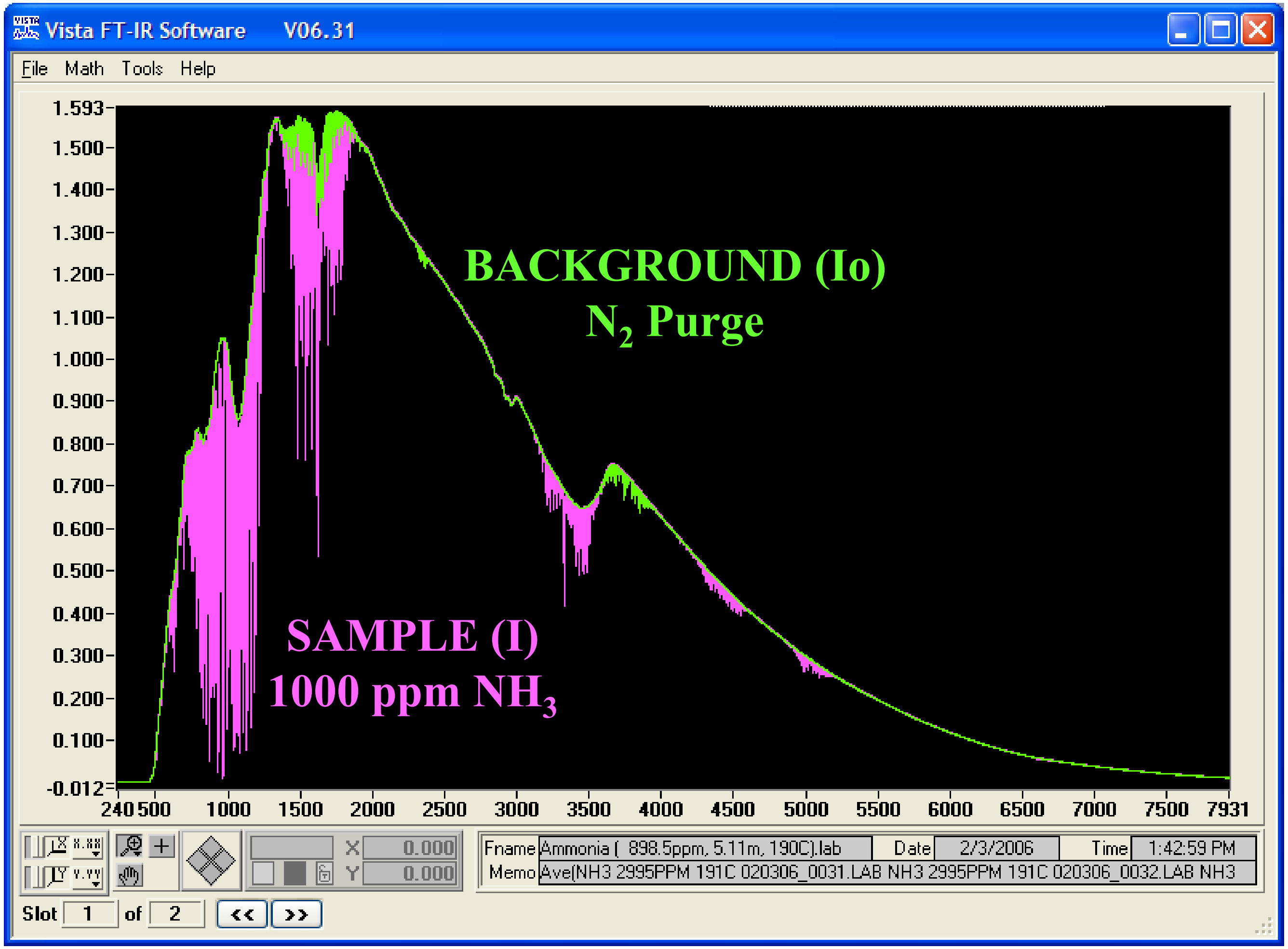
3) Normalize with N_2 background spectrum to get absorbance spectrum (absorbance vs wavenumber)



4) Apply CLS algorithm to extract multiple gas concentrations, plot as a function of time, or transfer values through communication protocol

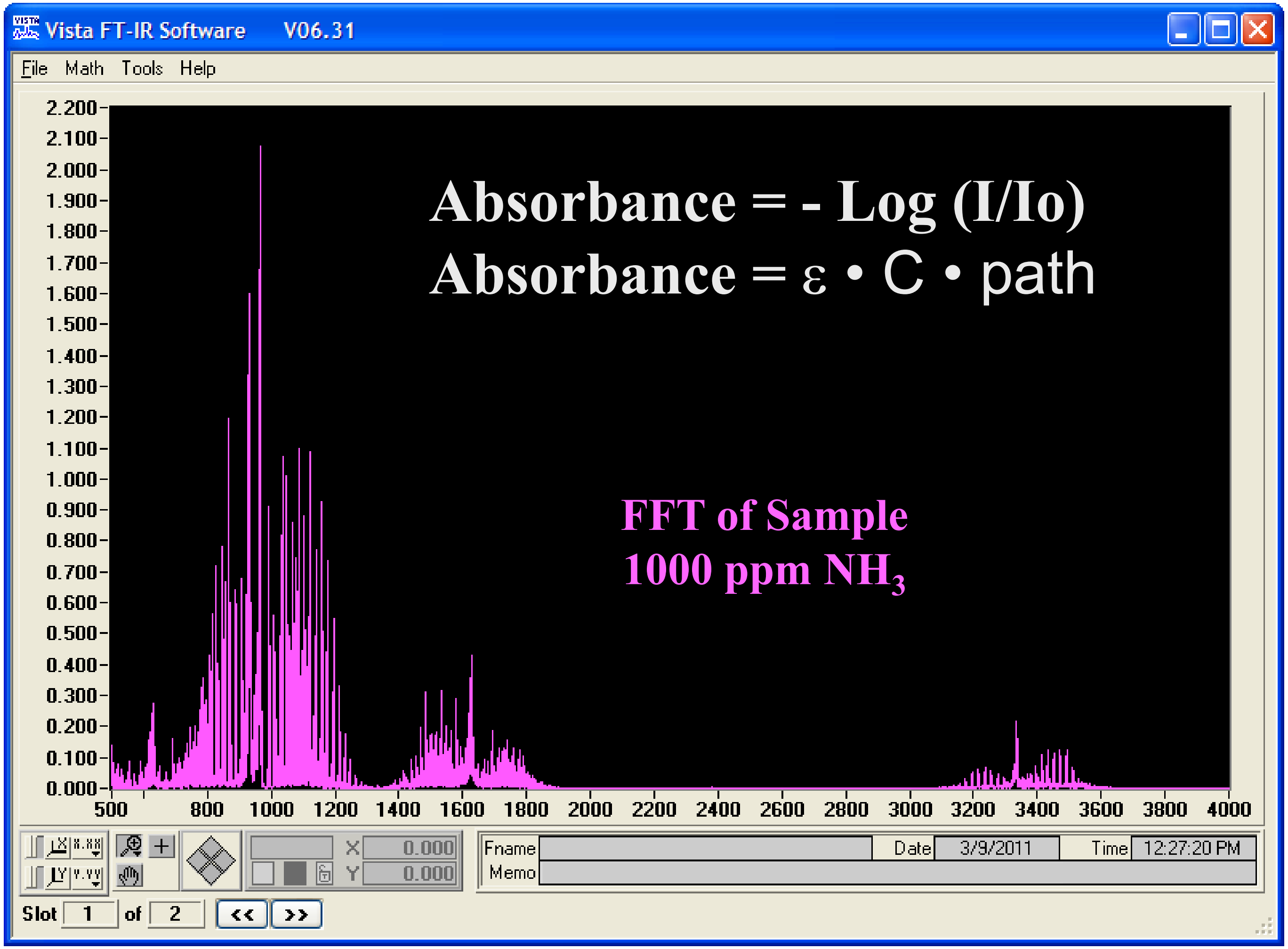


Background and Sample

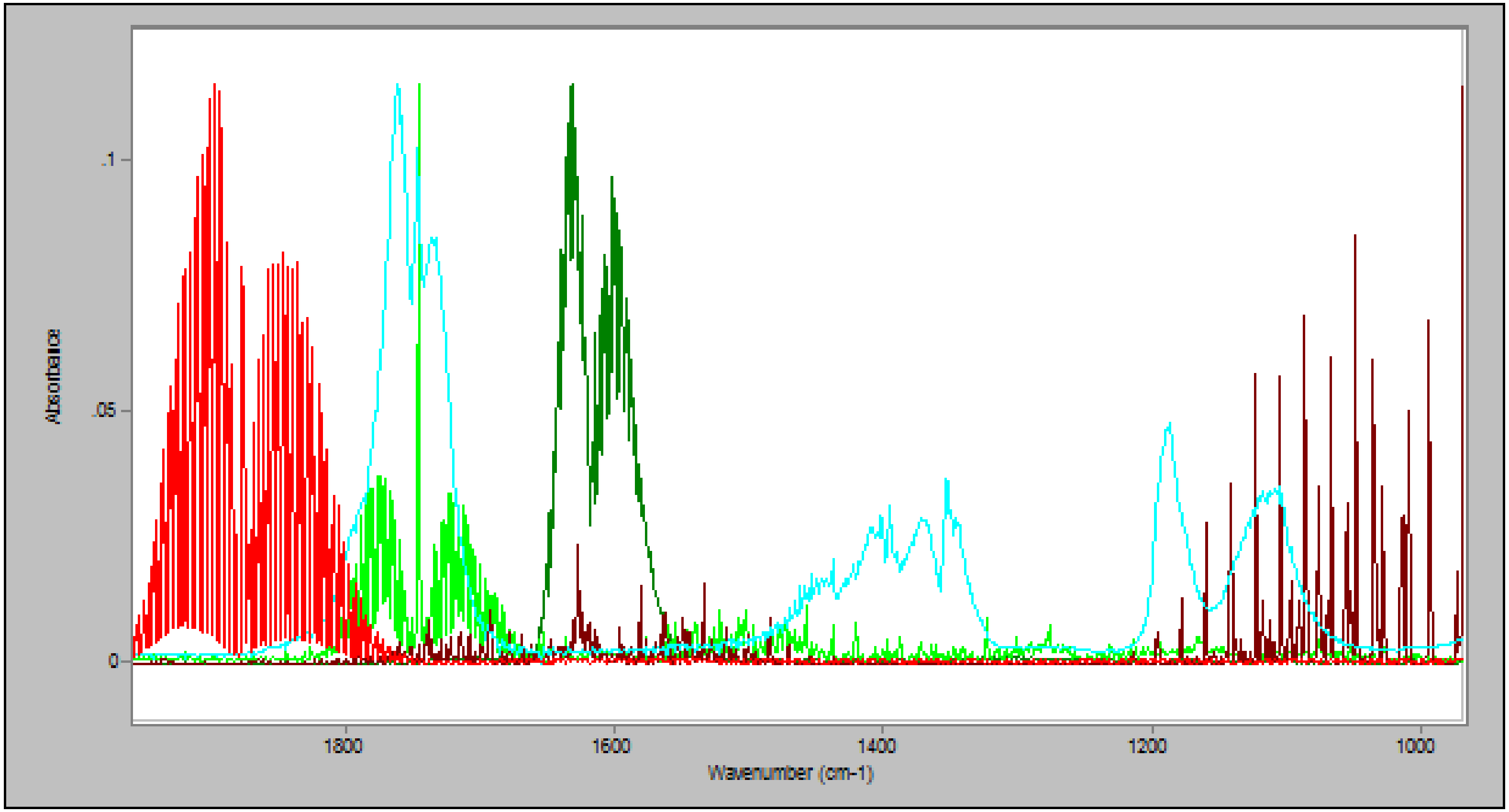


Absorbance = - Log (I/Io)

Absorbance is Proportional to Concentration



Multi-Component Absorbance Spectrum



FTIR Analysis Method

- Analytical Method
  - Classical Least Squares (CLS) then

    Beers Law, Abs = a b c ← **measured spectrum**

    a absorptivity coefficient or ε ← **from calibration**

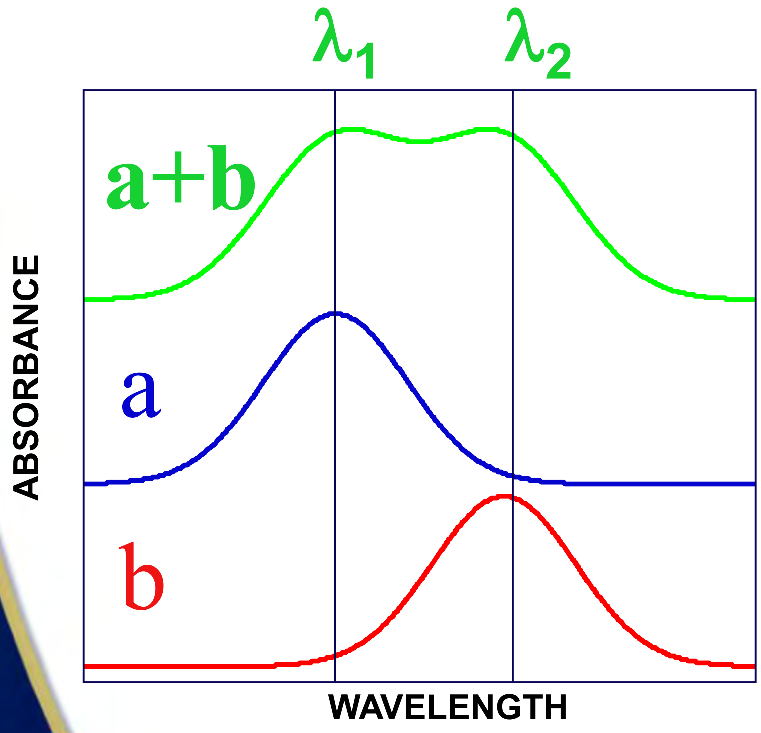
    b path length ← **fixed (5.11 meter)**

    c sample concentration (calculated) ← **what we want**
  - **Canned Method - No user input necessary**
  - **Hot and Wet, No sample change – No ionization**
  - **No pressure drop across sample cell**
  - 1 scan/second - 1 data point every 30 seconds
  - **Self -validating sample method EPA M320 or ASTM D6348-12**

Classical Least Squares

$$A_{\lambda_1} = K_{a_{\lambda_1}} C_a + K_{b_{\lambda_1}} C_b$$

$$A_{\lambda_2} = K_{a_{\lambda_2}} C_a + K_{b_{\lambda_2}} C_b$$



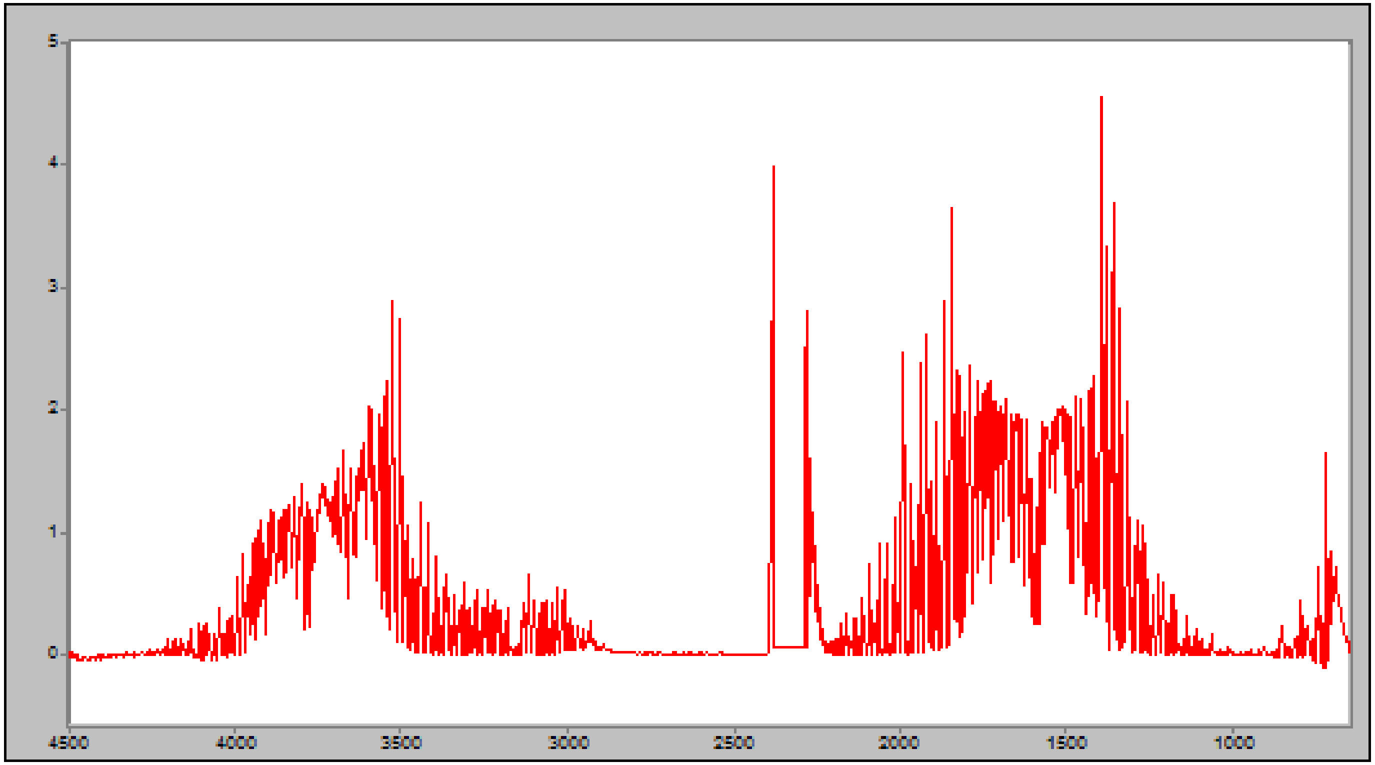
Model

- Based on Beer's Law
- Relatively fast computationally
- More complex mixtures
- Wavelengths used need to be greater than #components
- Noise reduced as #λs increase

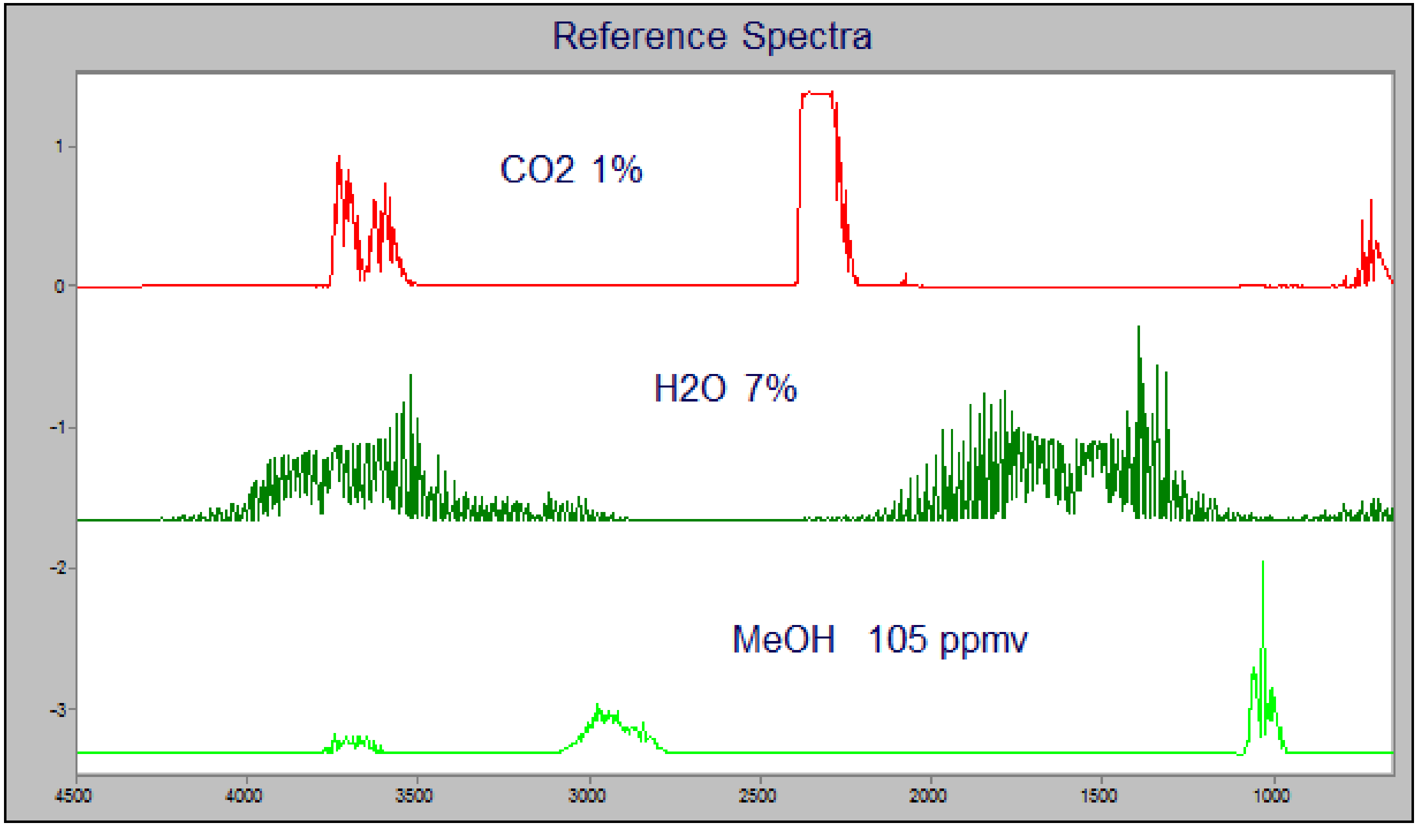
CLS Spectral Analysis → Finds factors for all reference spectra in method/recipe to recreate the sample spectrum

Example of CLS Subtraction

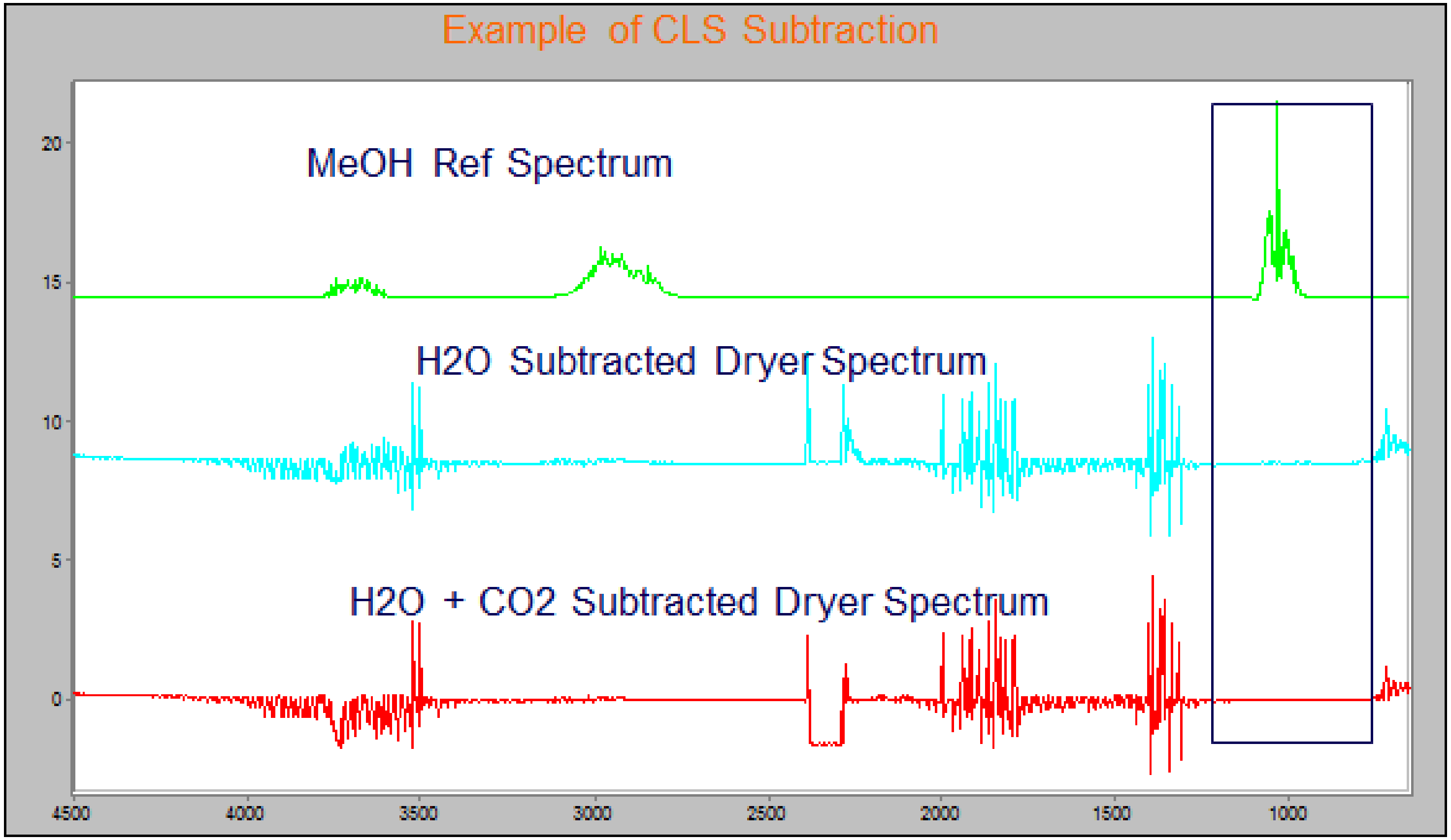
Raw Dryer Sample



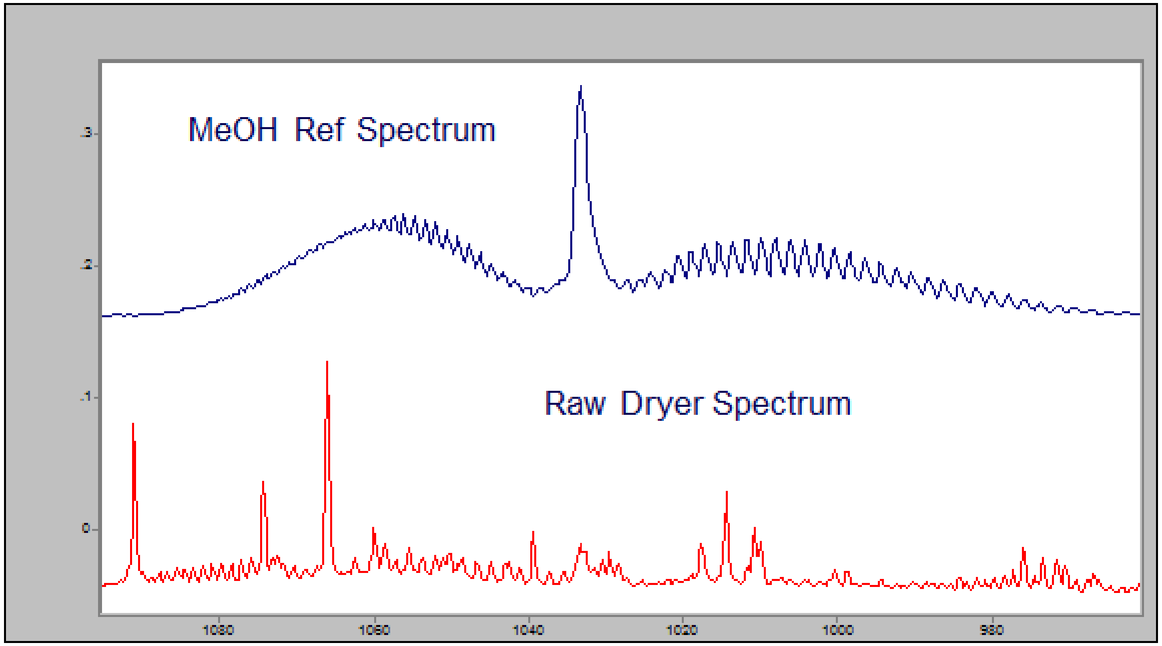
Example of CLS Subtraction

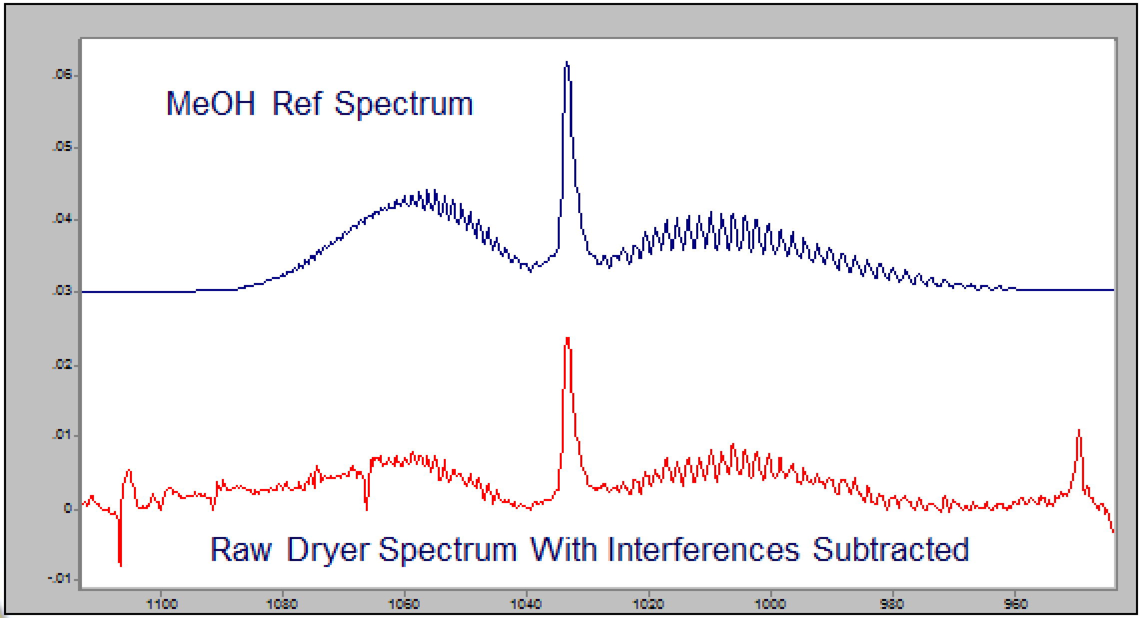


Example of CLS Subtraction

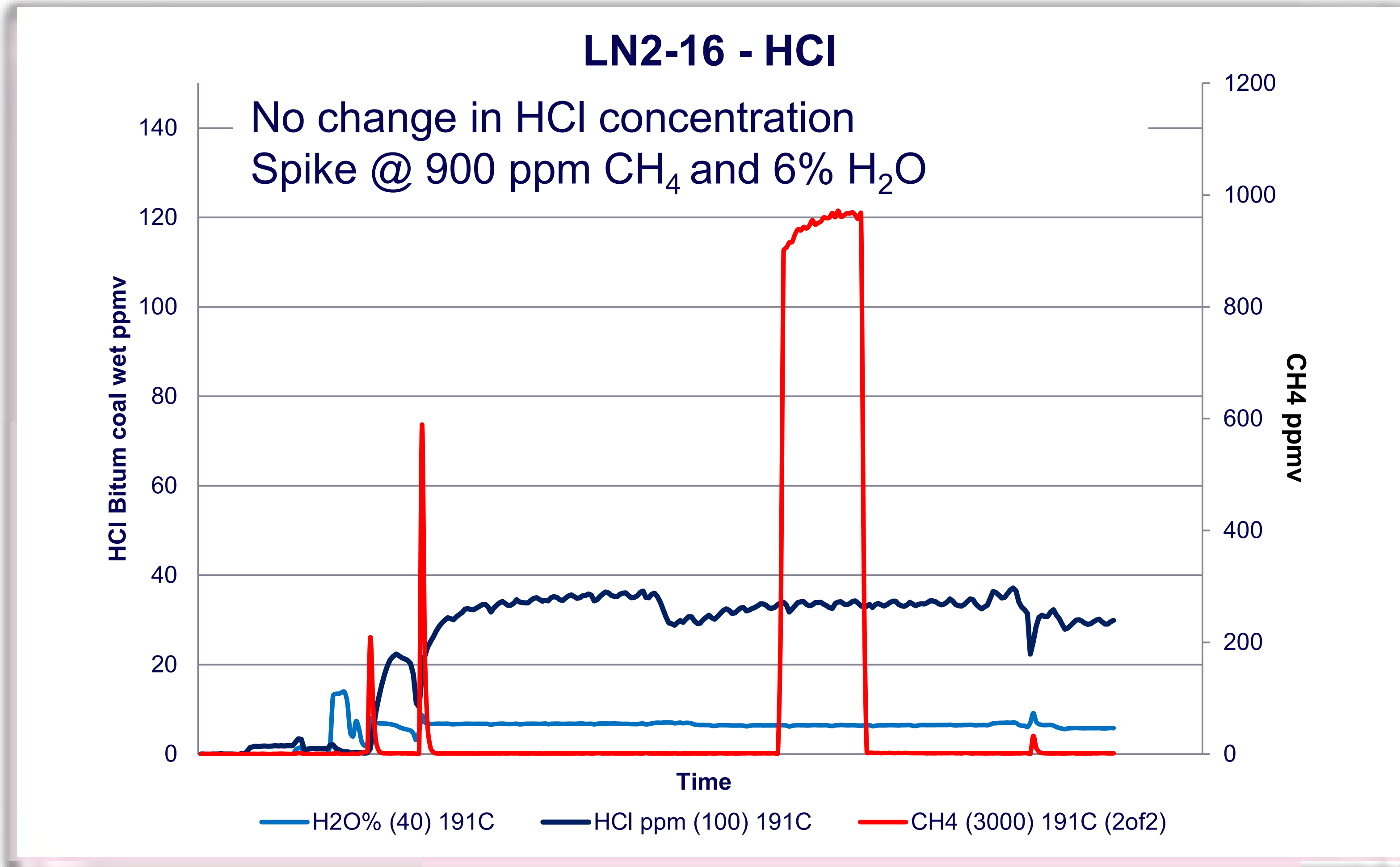


Example of CLS Subtraction

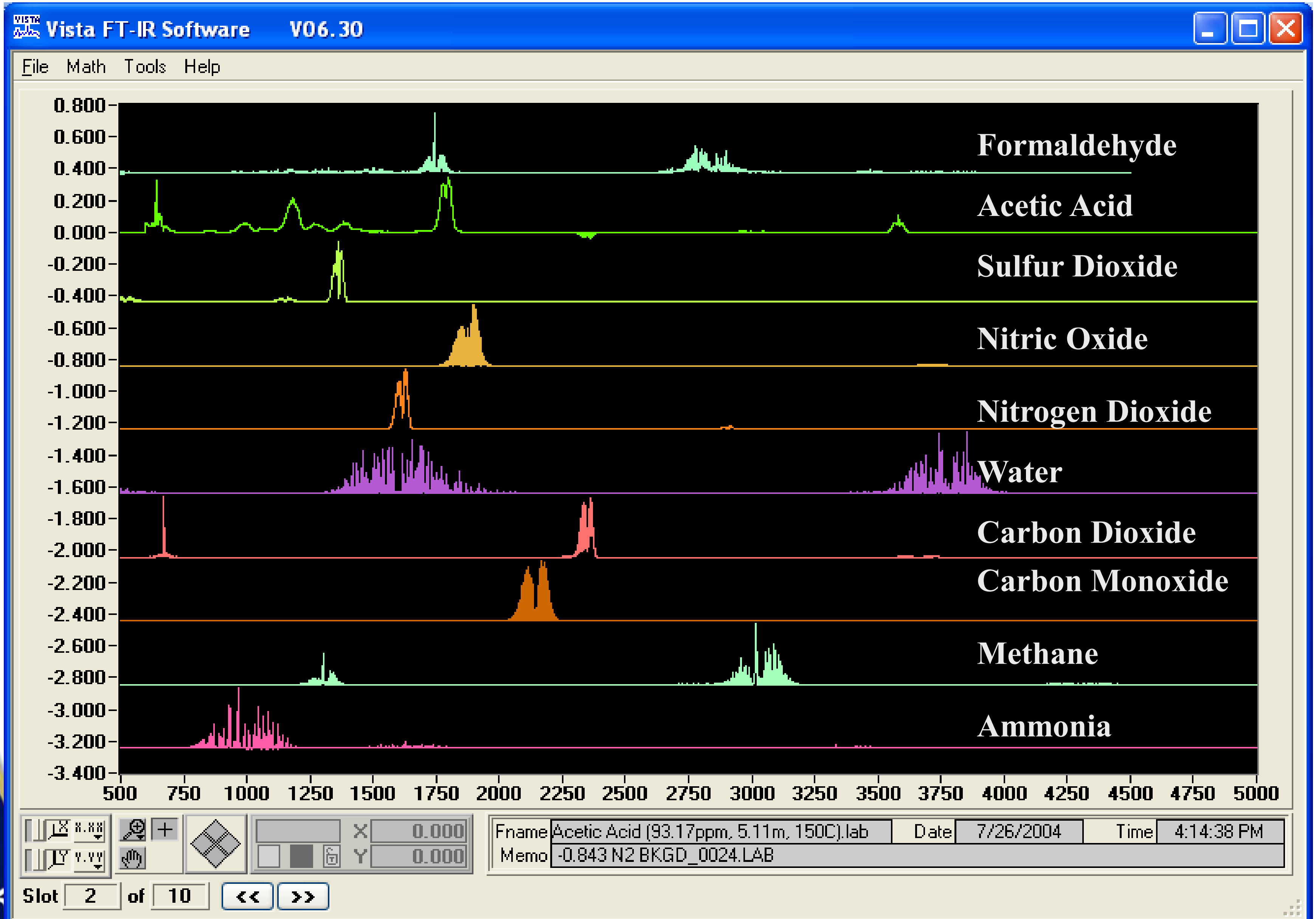




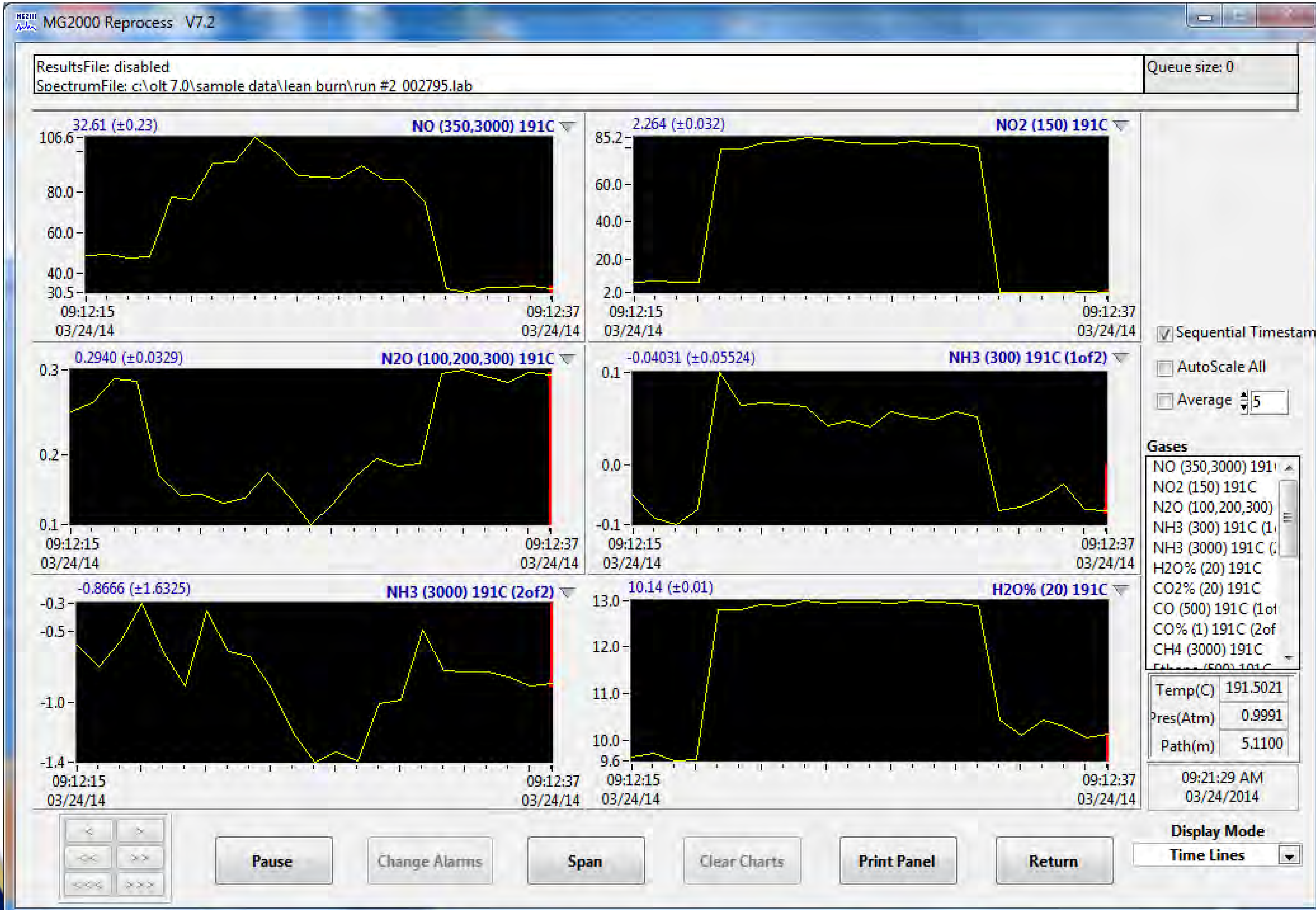
EXAMPLE of No Cross Sensitivity



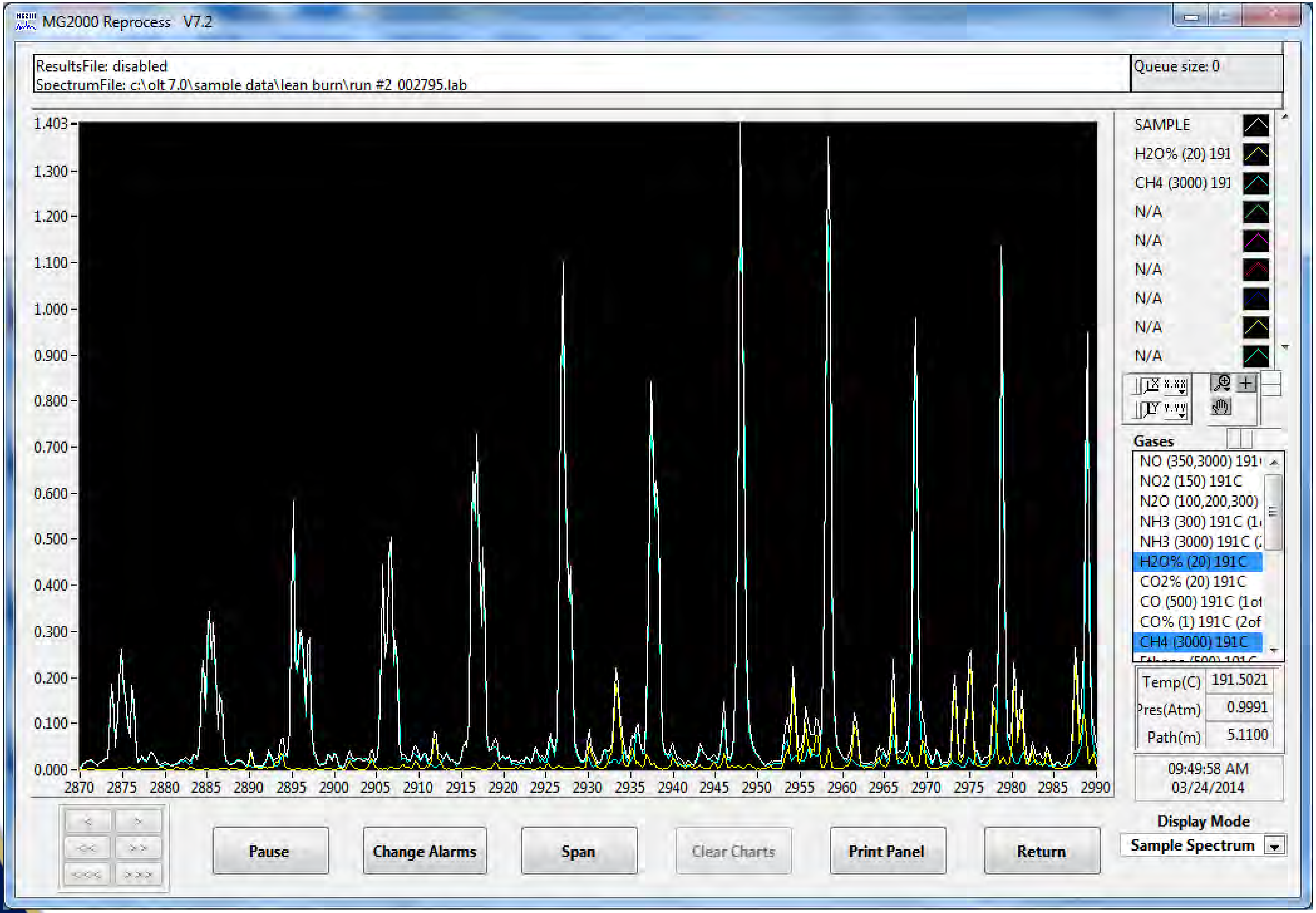
Ten Typical Components



Run Screen (Timelines)

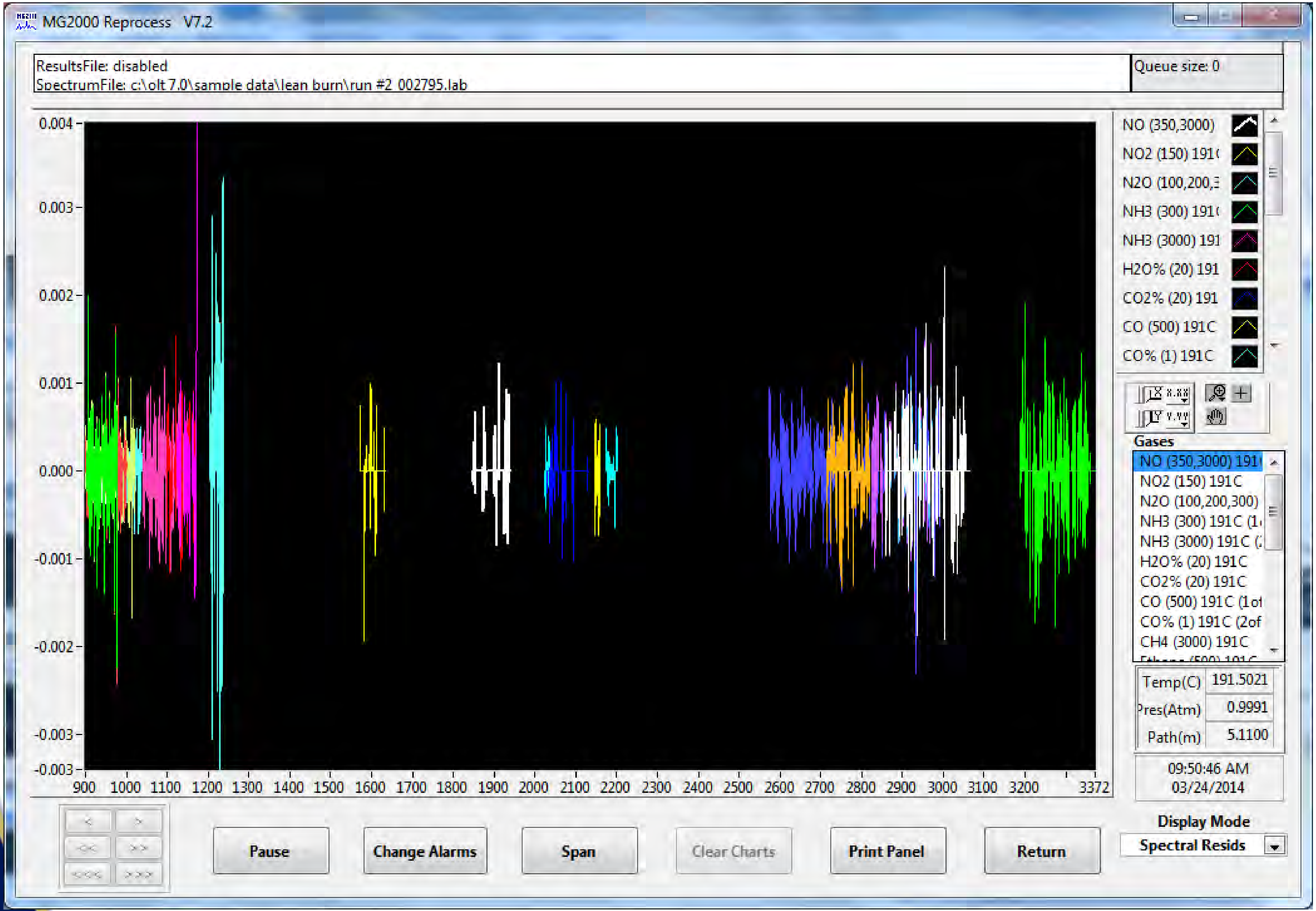


Run Screen (Expanded Spectrum)

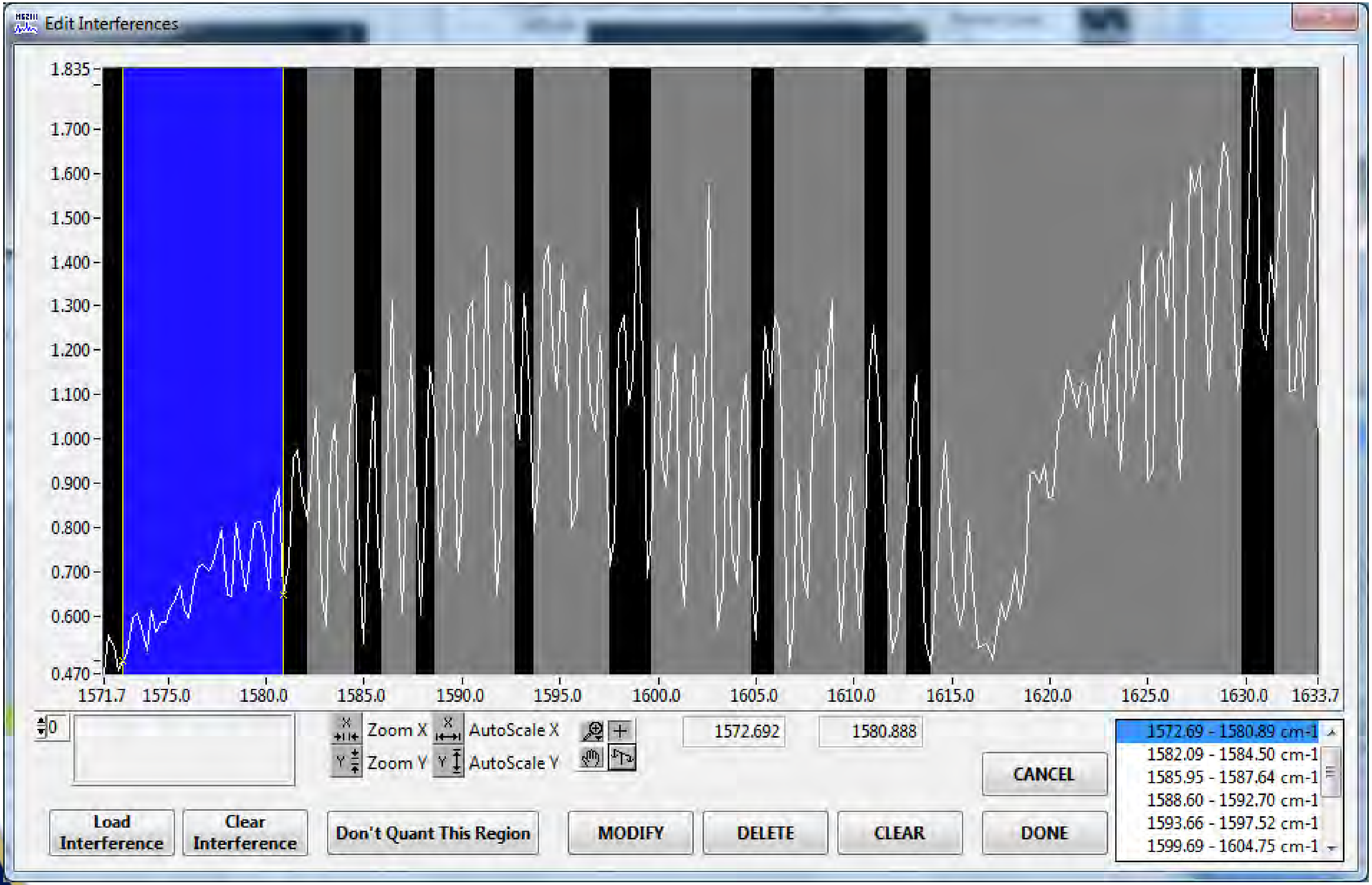


mks

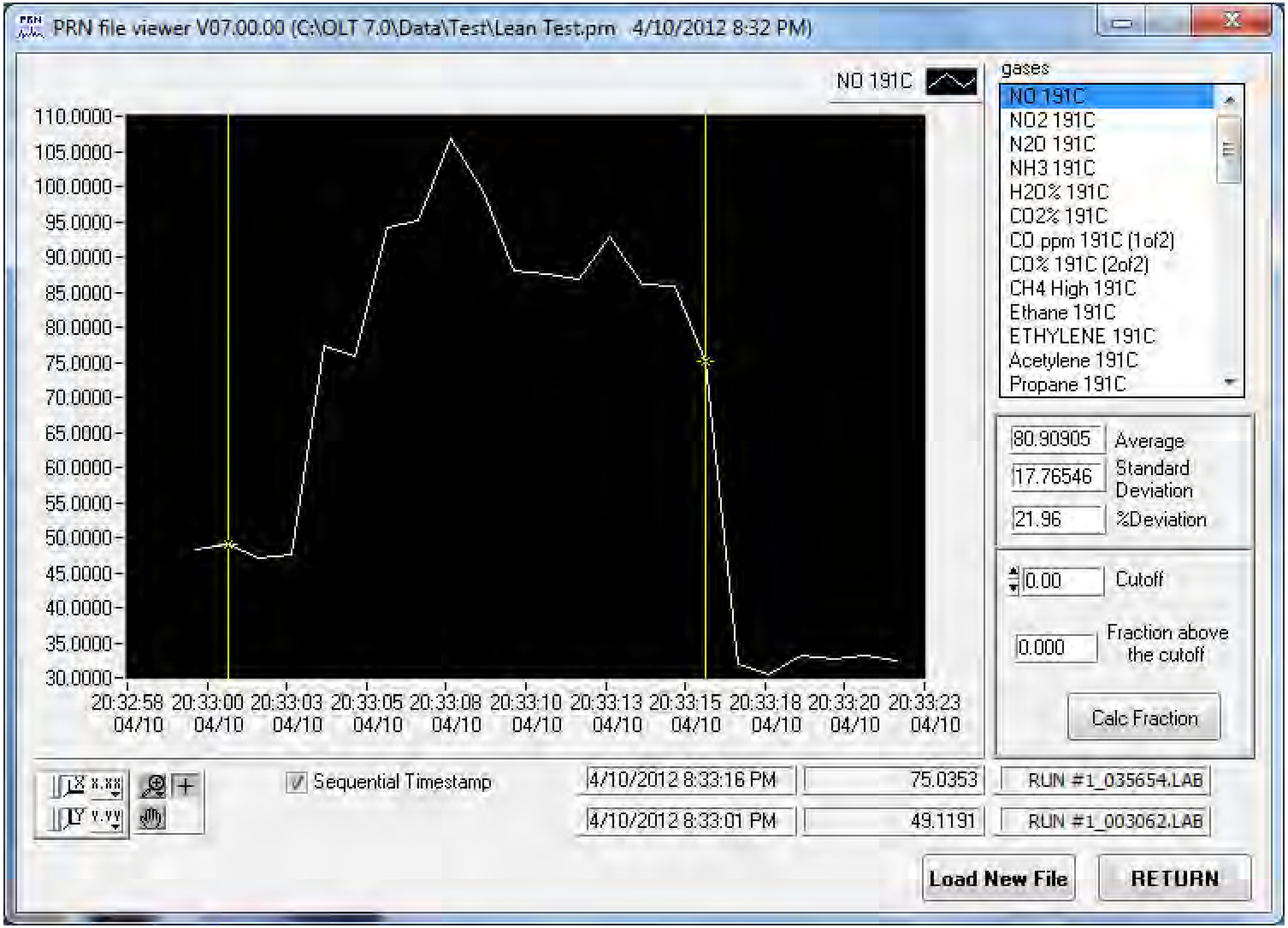
Spectral Resids Screen



Edit Analysis Band



PRN File Viewer



Place cursors to determine Average / STD and DL

Method Analyzer

Use for post data collection validation

TÜV / MCERTS certified ranges & detection limits

Gas comp.	Cert. range	Supp. range 1	Supp. range 2	ELV (WID)	Detection limit *
NH_3	0-10 mg/m^3	0-75 mg/m^3	-	10 mg/m^3	0.35ppm
CO	0-75 mg/m^3	0-300 mg/m^3	0-1500 mg/m^3	50 mg/m^3	0.50ppm
SO_2	0-75 mg/m^3	0-300 mg/m^3	0-2000 mg/m^3	50 mg/m^3	0.60ppm
NO	0-200 mg/m^3	0-400 mg/m^3	0-1500 mg/m^3	130 mg/m^3	0.50ppm
NO_2	0-50 mg/m^3	0-100 mg/m^3	0-1000 mg/m^3	50 mg/m^3	0.40ppm
HCl	0-15 mg/m^3	0-90 mg/m^3	0-200 mg/m^3	10 mg/m^3	0.20ppm
HF	0-3 mg/m^3	0-10 mg/m^3	-	1 mg/m^3	0.25ppm
CH_4	0-15 mg/m^3	0-50 mg/m^3	0-500 mg/m^3	10 mg/m^3	0.30ppm
CO_2	0-25%	-	-	0-25%	0.025%
H_2O	0-40%	-	-	0-40%	0.25%
N_2O	0-50 mg/m^3	0-100 mg/m^3	0-500 mg/m^3	50 mg/m^3	0.10ppm

* Estimated detection limits calculated as three times the standard deviation in 25% water

mks

TÜV Ranges & Uncertainties MKS 2030 CEM Analyzer

Gas Comp.	Cert. Range	Supp. Range 1	Supp. Range 2	ELV	U/C	U/C Req.
NH_3	0-10 mg/m^3	0-75 mg/m^3	-	10 mg/m^3	6.2%	30.0%
CO	0-75 mg/m^3	0-300 mg/m^3	0-1500 mg/m^3	50 mg/m^3	6.2%	7.5%
SO_2	0-75 mg/m^3	0-300 mg/m^3	0-2000 mg/m^3	50 mg/m^3	7.0%	15.0%
NO	0-200 mg/m^3	0-400 mg/m^3	0-1500 mg/m^3	130 mg/m^3	6.8%	15.0%
NO_2	0-50 mg/m^3	0-100 mg/m^3	0-1000 mg/m^3	50 mg/m^3	4.1%	15.0%
HCl	0-15 mg/m^3 0-10 ppmv	0-90 mg/m^3	0-200 mg/m^3	10 mg/m^3	8.1%	30.0%
HF	0-3 mg/m^3	0-10 mg/m^3	-	1 mg/m^3	19.3%	30.0%
CH_4	0-15 mg/m^3	0-50 mg/m^3	-	10 mg/m^3	7.0%	22.5%
CO_2	0-25%	-	-	0-25%	3.3%	7.5%
H_2O	0-40%	-	-	0-40%	3.4%	7.5%
N_2O	0-50 mg/m^3	0-100 mg/m^3	0-500 mg/m^3	50 mg/m^3	4.5%	15.0%

1 ppm HCl = 1.49 mg/m^3

TÜV Testing of MKS 2030 CEM Analyzer

TÜV Rheinland CERTIFIED

Passed TÜV certification with lowest or low relative uncertainty when compared with competitors

	SO2	HCl	NH3	HF
MKS	**7.0% of 50 mg/m^3**	**8.1% of 10 mg/m^3**	**6.2% of 10 mg/m^3**	**19.3% of 1 mg/m^3**
Comp 1	9.4% of 50 mg/m^3	12.0% of 10 mg/m^3	9.6% of 10 mg/m^3	*18.4% of 1 mg/m^3
Comp 2	10.5% of 50 mg/m^3	12.2% of 10 mg/m^3	6.4% of 10 mg/m^3	30.3% of 1 mg/m^3
Comp 3	9.4% of 50 mg/m^3	12.8% of 10 mg/m^3	8.0%	Not specified
Comp 4	11.5% of 50 mg/m^3	11.4% of 10 mg/m^3	10.6% of 10 mg/m^3	19.9% of 2 mg/m^3

	NO	NO2	N2O	CO
MKS	**6.8% of 130 mg/m^3**	**4.1% of 50 mg/m^3**	**4.5% of 50 mg/m^3**	**6.2% of 50 mg/m^3**
Comp 1	6.5% of 131 mg/m^3	5.7% of 200 mg/m^3	4.4% of 100 mg/m^3	6.0% of 50 mg/m^3
Comp 2	9.5% of 130 mg/m^3	10.6% of 70 mg/m^3	13.6% of 20 mg/m^3	8.7% of 50 mg/m^3
Comp 3	19.3% of 40 mg/m^3	N/A	N/A	9.9% of 50 mg/m^3
Comp 4	9.1% of 130.4 mg/m^3	10.6% of 60 mg/m^3	15.3% of 20 mg/m^3	9.0% of 50 mg/m^3

* Requires 2 FTIRs (1 dedicated to HF)

TÜV Testing of MKS 2030 CEM Analyzer

Passed TÜV certification with lowest or low relative uncertainty when compared with competitors

	CO_2	H_2O	CH_4
MKS	**3.3% of 25%**	**3.4% of 40%**	**7.0% of 10 mg/m^3**
Comp 1	5.0% of 25%	6.2% of 30%	N/A
Comp 2	6.7% of 25%	5.7% of 40%	15.6% of 20 mg/m^3
Comp 3	N/A	3.0% of 40%	N/A
Comp 4	4.1% of 20%	4.2% of 30%	N/A

NEW: MultiGas 2030 HiSens
High Sensitivity HCl Analyzer for CEM

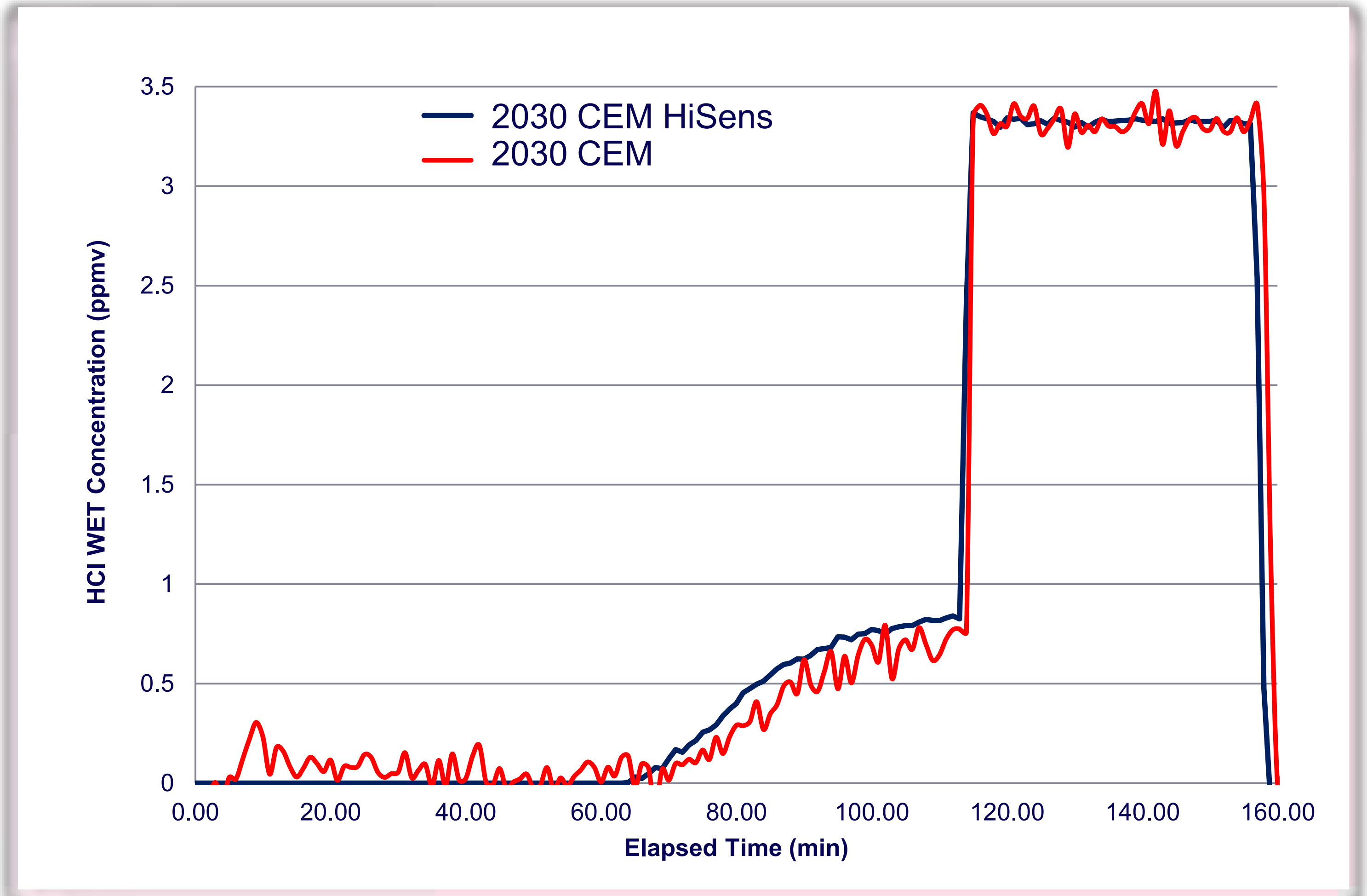
- HCl detection limit **30 ppbv (3-sigma basis)**
- Hot and Wet – 200mL Sample Volume
- **No N_2 Background** → easier integration than standard FTIR – turn on and go
- "Canned" Method
- Can measure HCl, CH_2O, HF, H_2O, N_2O, CH_4 with similar high sensitivity

MKS FTIR Analyzer Solutions for CEM

	HCl DL*	Main Components Measured	Information
2030 CEM (Broadband) TUV Certified EPA Method Compliant	0.15 ppm	HCl, SO_2, NO_x, CO, CO_2, H_2O, NH_3, HF, N_2O, CH_4, CH_2O	• No LN_2 required • Requires daily N_2 Zero • 6 mo. maintenance interval • > 95% uptime
2030 CEM HiSens (High-sensitivity) EPA Method Compliant	0.03 ppm	HCl, Formaldehyde, HF, CO, CO_2, CH_4	• No LN_2 required • No daily N_2 Zero • > 97% uptime

* DL (Detection Limit) given as ASTM D3648-12 *MDC2* (3σ in 30% H_2O and 25% CO_2 containing spectra, 1 min acquisition time)

MKS CEM Analyzers Comparison



HCl Detection Limits - 3 Options

HCl Calculated Detection Limits (ppmv)

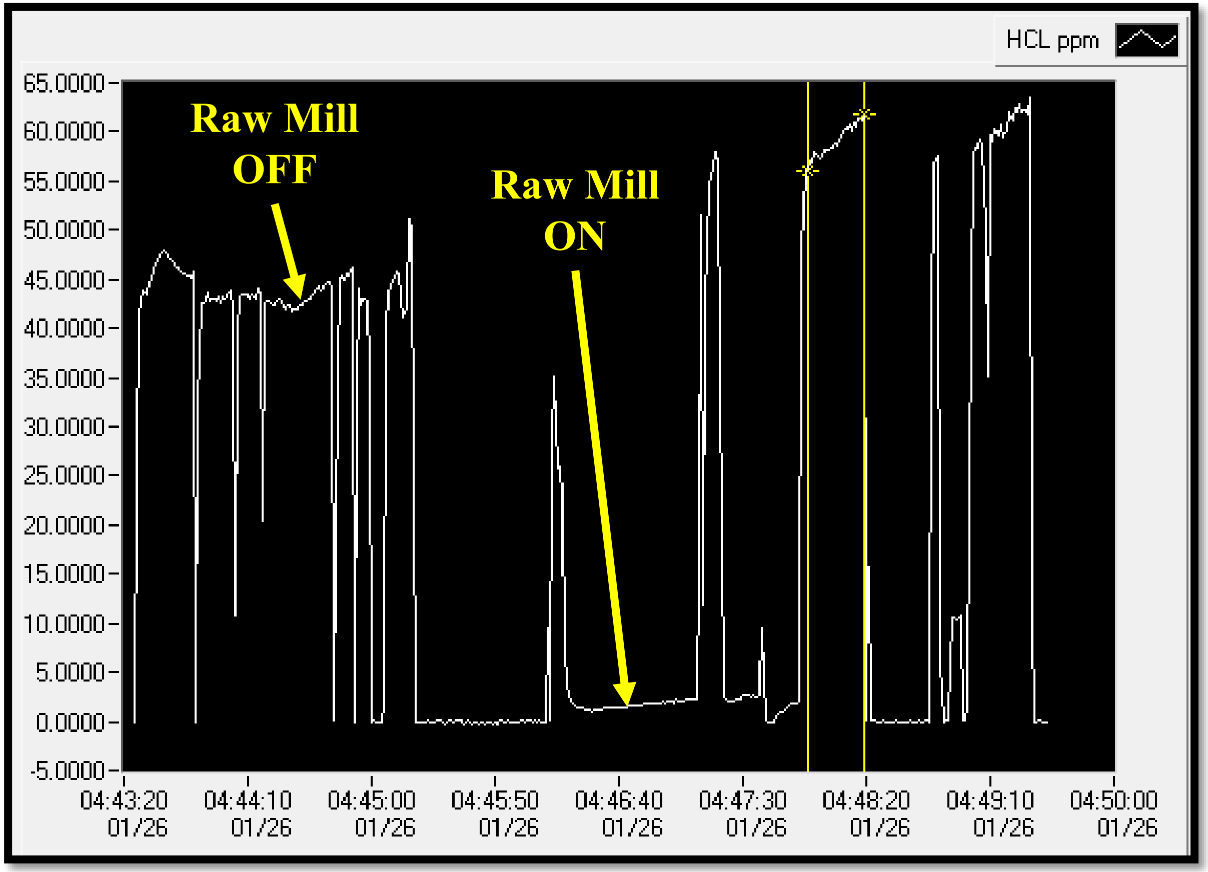
System Config	ASTM MDC 1	ASTM MDC 2	ASTM MDC 3	EPA M320 MAU[3]
LN2[1] -16	0.14	0.14	0.15	0.25
TE[2]5	0.25	0.05	0.06	0.35
TE9	0.37	0.20	0.66	0.67

1 Liquid Nitrogen

2 Thermoelectrically Cooled Mercury Cadmium Telluride (MCT) fast detector 0.5 cm^{-1} resolution

3 MAU – Maximum Analytical Uncertainty

Examples of HCl Concentration Profiles at Cement Plants

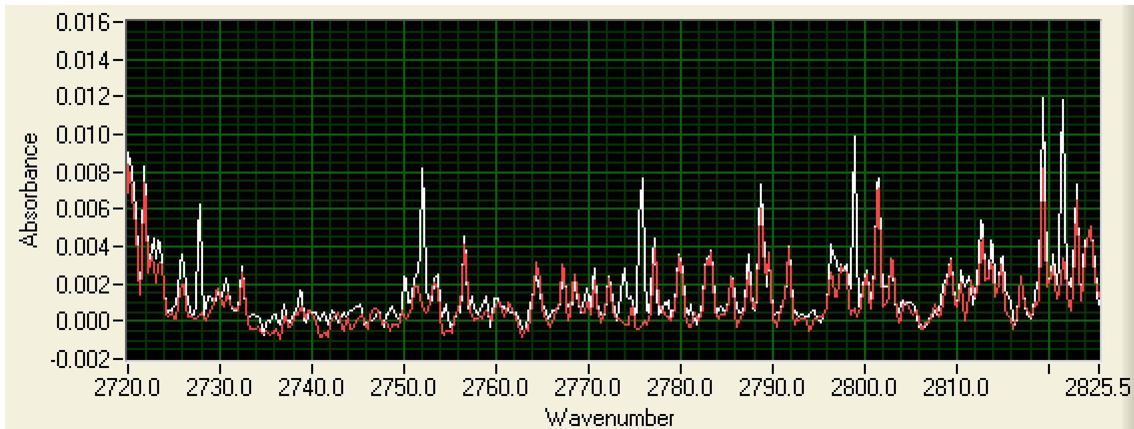


Concentration (ppm)

Time

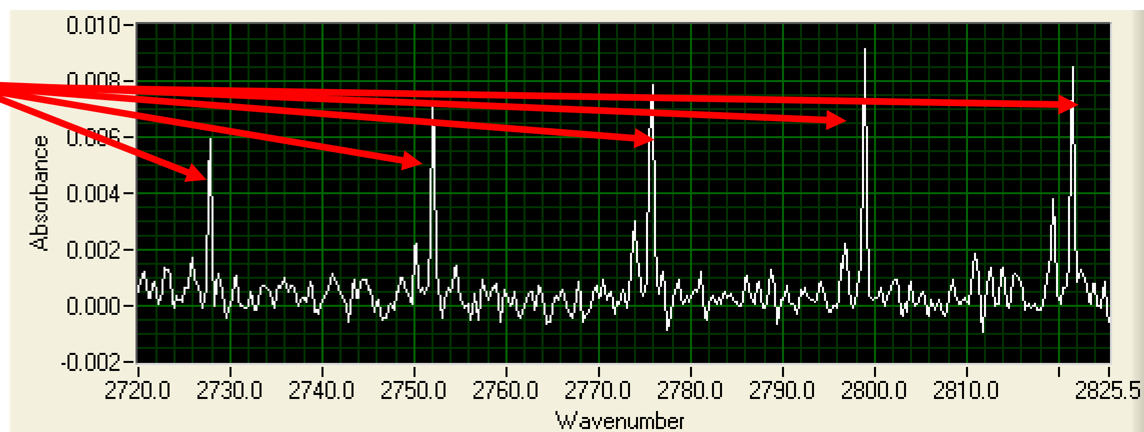
Powerful Technique - HCl Measurements with FTIR

Sample (white) with 5 ppm HCl and 12% water (red)



H2O subtraction

HCl peaks clearly visible after H_2O subtraction

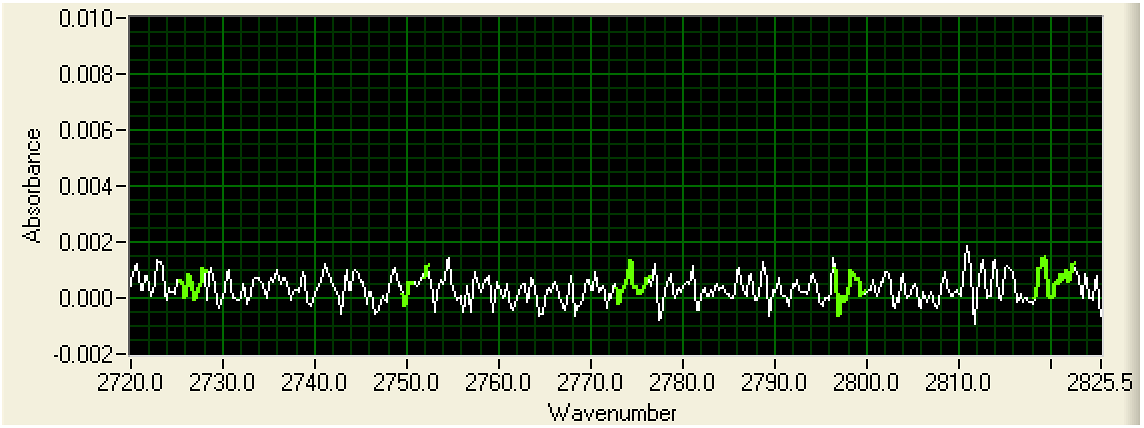


Powerful Technique - HCl Measurements with FTIR

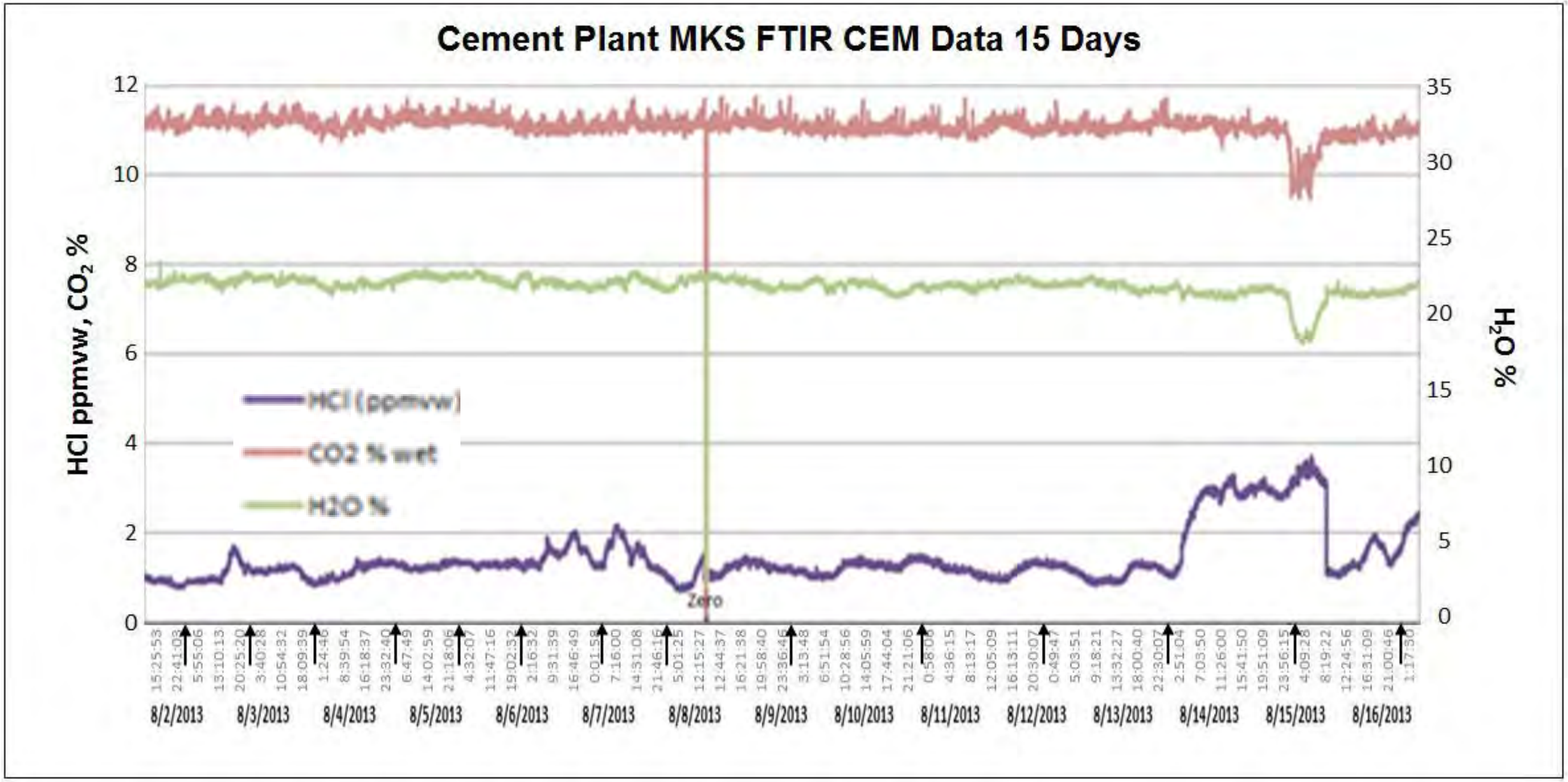
HCl calibration peaks (red and green)

HCl subtraction

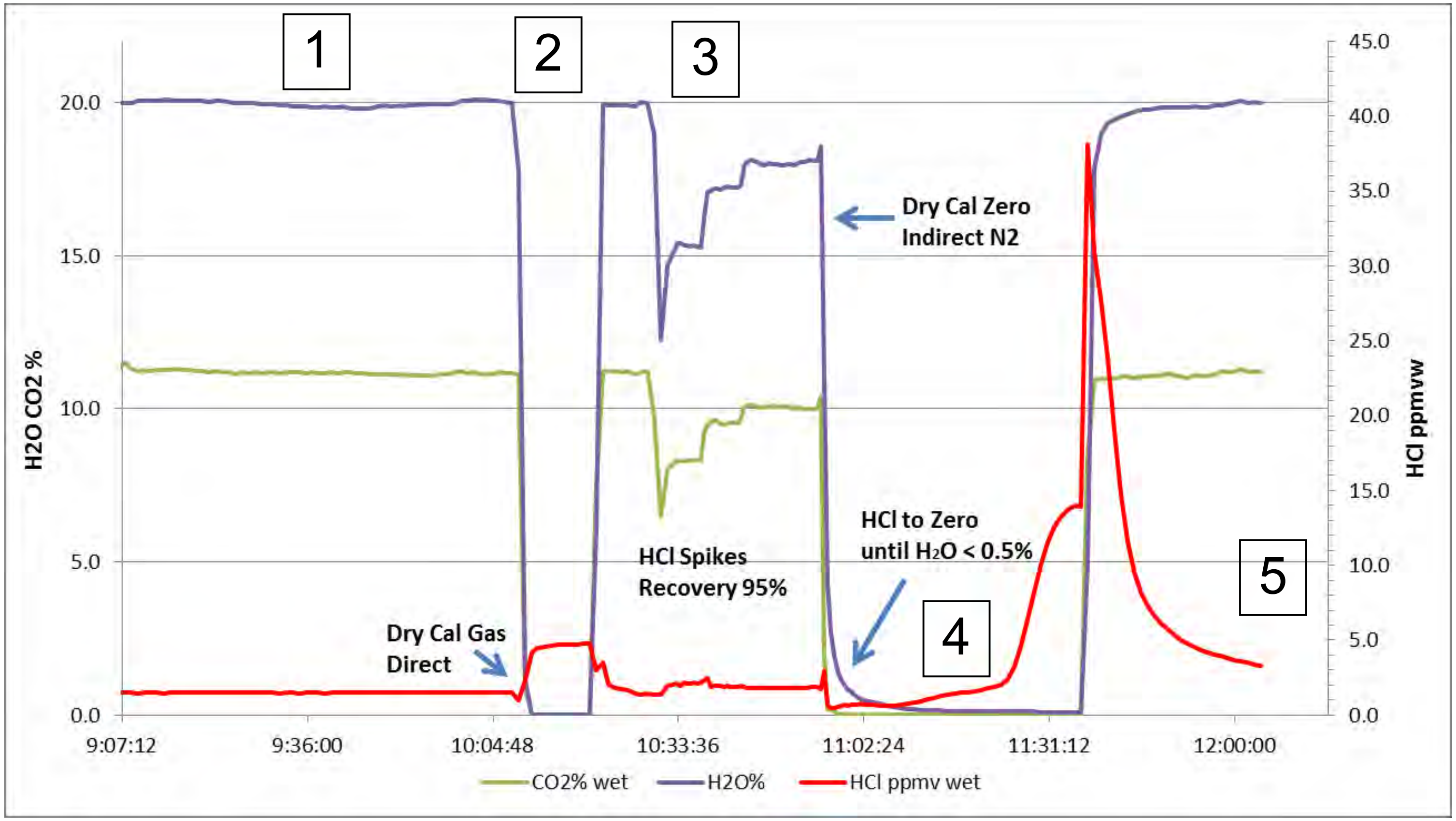
After HCl subtraction, only noise left



Example CEM Cement Field Data 15 Days



CEM Passes Dynamic Spike Tests
Even with Significant Filter Cake Present



1. Conditions as-found: no Filter Change or Blowback – 4 months
2. Introduction of HCl calibration gas
3. HCl Dynamic spikes with 95% recovery
4. Run nitrogen through filter => Filter cake dries out, sublimes to HCl gas where concentration increases rapidly
5. Return to Steady-State

FTIR Reference Methods (RM) for CEMS Validation and RATA[a]

- Method 301
  - Field Validation of Pollutant Measurement Methods From Various Waste Media
- Method 320[b]
  - Measurement of Vapor Phase Organic and Inorganic Emissions by Extractive FTIR (Includes FTIR Protocol)
- Method 321[c]
  - Measurement of Gaseous HCl Emissions at Portland Cement Kilns by FTIR Spectroscopy
- ASTM D6348-12
  - Standard Test Method for Determination of Gaseous Compounds by Extractive Direct Interface Fourier Transform Infrared (FTIR) Spectroscopy

a. Relative Accuracy Test Audits
b. 1 of 2 RM for EGU (EPA M26/26A)
c. Only acceptable RM for Portland Cement MACT

Performance Specifications for FTIR CEMS from EPA

- Switching from FTIR spectral requirements to performance-based requirements
- Performance Specification 15 (PS-15)
  - For Extractive FTIR CEM Systems in Stationary Sources, App B and Procedure 1 of Appendix F until new PS (20 yrs. old)
  - Petitioned to be changed to include dynamic spikes (self validating)
- Performance Specification 18 (PS-18) in development
  - Specific to HCl (Spring 2014)
  - Technology neutral (but FTIR included)
  - Initial Instrument Qualification and Installation
  - On-going QC promulgated separately

PS-18 Evaluation Test Procedures

- Interference tests
- Limit of Detection (LOD) determination
- Response time test
- Calibration error test
- 7-day calibration drift test
- Stratification test
- Use of Relative Accuracy Test (RATA) and/or Dynamic Spiking Test (DST)

Comparison PS/RM for FTIR

Parameter	PS-15	PS-18 Draft	EPA M320	ASTM D6348-03,12	M301
Dates Promulgated	Feb 2000	Feb 2014?	Feb 2000, Protocol 1995	Feb 2003, '10,'12	June 1991, '04, '11
Cal Gas Direct Accuracy	5%, 7% w/bias	NA	2% or 5%	5%	NA
Dynamic Spike Recovery	+-30%	+-15%	+-30%	+-30%	+-30% to 50%
# of Spike Runs	24 (M301), 3 (M320)	6?	3	1	24
Interference test	No (just mentions them)	<3% span combined	No	bias check	No
Method Relative Accuracy (DQO)	20% (RM in denom) 15% (Emiss Limit in denom) SO2 (10% Emiss Limit) PS2 < 15%	2.5%	2%	Acc 10% Prec 5%	t-test comparison
"Bias" Correction	Yes	?	">30% is not valid method", but apply a corr factor	May	Yes, above 10%
Calibration Error Test	10%	3 pt, <5%, intercept <15% of Span	No One Knows	No	depends on RM
Dry Cal check	**YES (All Compounds) Daily**	?	Yes, but select set..no HCl	Yes, but select set..no HCl	depends on RM
7-Day Drift	No	3% of span/day	No	No	No
Detector linearity	3 point, 2%/5%	yes?	3 point, 2%/5%	3 point, 2%/5%	NA
Detection Limitations	depends on RM	LOS, MDC#3, LOD	MAU, OFU	MDC#1, MDC#2*, MDC#3	PLQ*, LOD
Cell Volumes per Data Pt.	10 spiking, 5 sample	5?	5	5	NA
Conf Intervals	depends on RM	99%?	95%	95%	99% LOD, 95% t-test
				* Reviewed/Revised	
Manual Data Verification	NA (Yes RATA RM)	NA (Yes RATA RM)	YES	YES	NO
Calibration Transfer Standard (CTS)	5%	?	5%	5%	NA

*MDC #2 = PLQ (no longer used)

PS15 Data Storage Discrimination (Changed!)

For 2 Week Period Store:

- one sample interferogram per hour
- All sample absorbance spectra (about 12 per hr, 288 per day)
- All background and CTS raw data
- resolution, path length, apodization, sampling time, sampling conditions, and test conditions for all sample, CTS, calibration, and background spectra

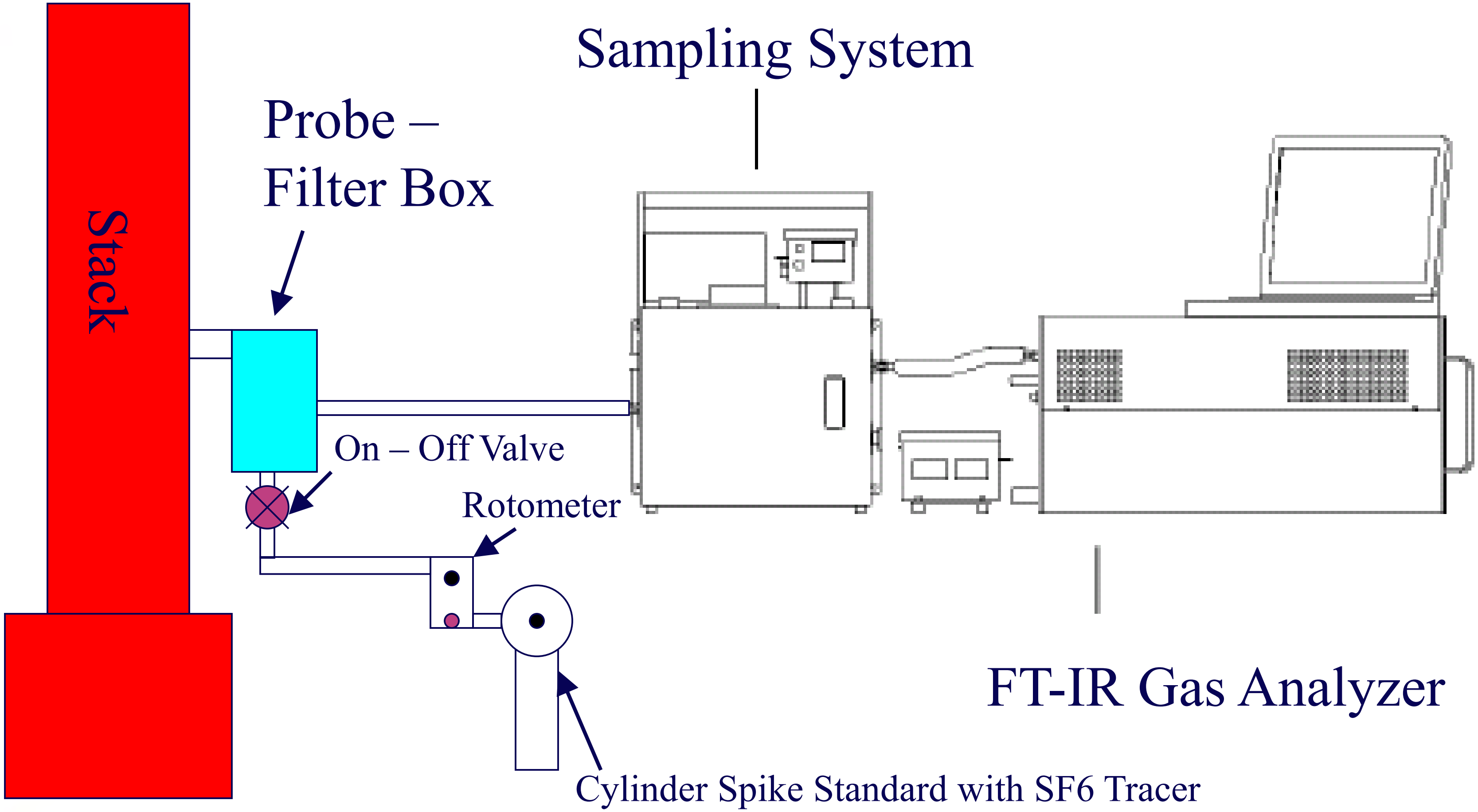
After 2 weeks…….until? Calculated Results

- Sample and calibration interferograms (raw data)!
- Period? (unspecified) PS18 = None specified; Validation data (5yrs)
- All of the other documentation

What is Dynamic Spiking?

1. A way to demonstrate that adding a cumulative amount of a target compound to a native system will result in a recovery within a specified range
2. Demonstrates the following:
    1. Sampling system bias
    2. Instrument bias
    3. Analytical Methodology (Data Retrieval Bias)
    4. Interferences bias
        1. Chemical
        2. Molecular (spectral change i.e. ILS)
3. Typically “at least one target compound” EPA M320
4. Target Compound that is the most difficult of reactive to recover
5. Typically +-30%, PS-18 +- 15%

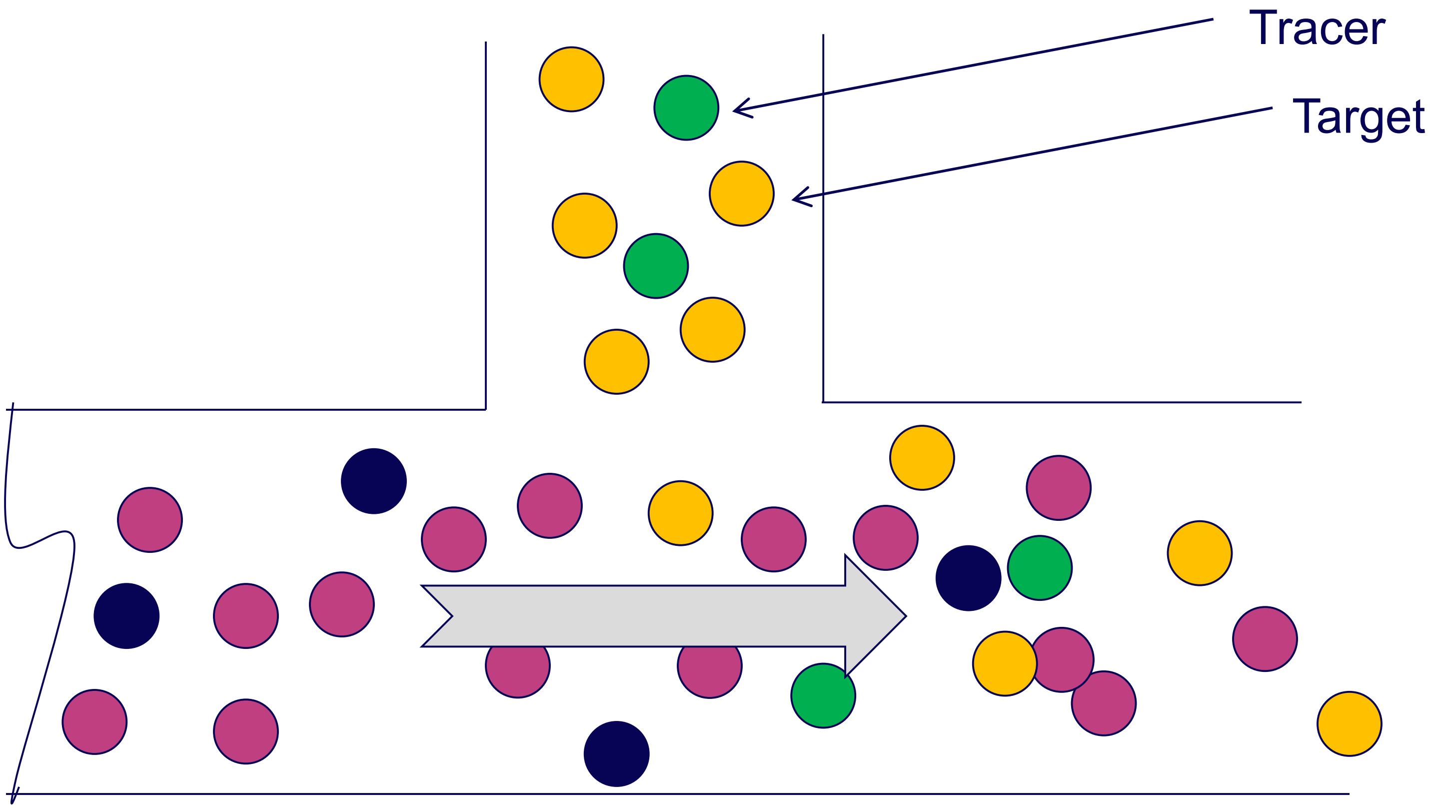
Spike Recovery Test



Calibration gas added at 10% of total flow

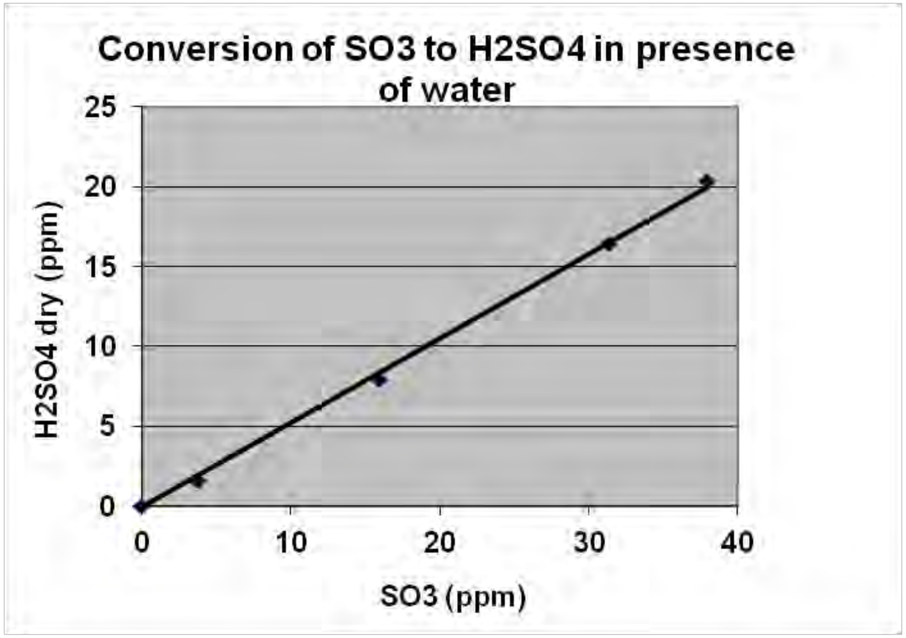
Stack effluent remains at 90% of total flow

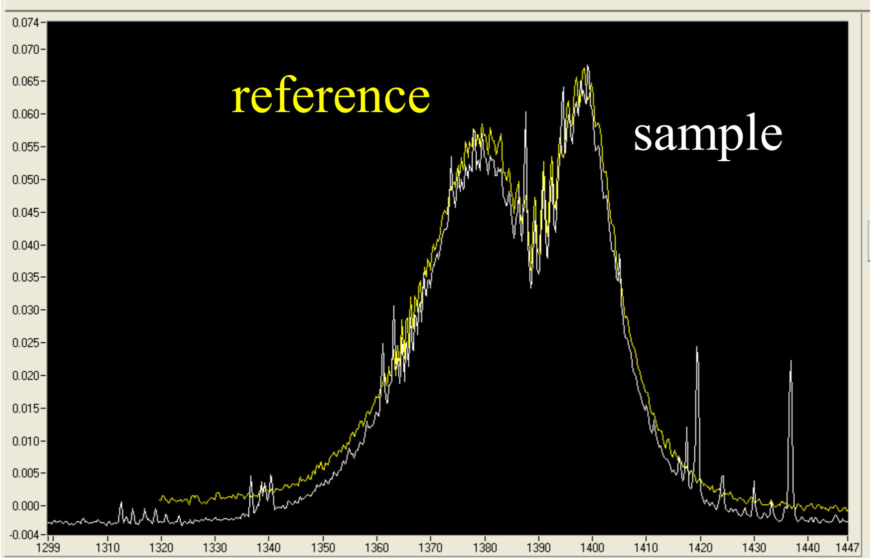
Dynamic Spiking – PS18, PS15, M320/321, ASTM D6348-12



Dry SO_3 Tests

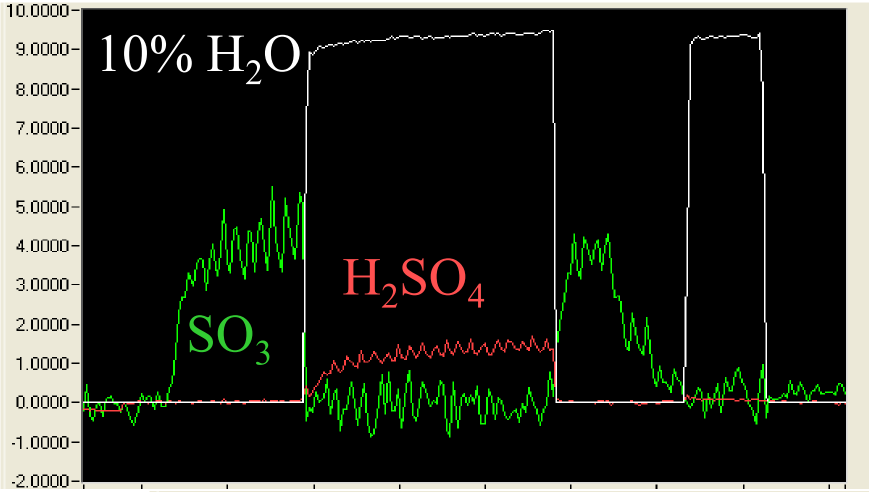
- H_2SO_4 calibration (0-140 ppm) matches data for a very reactive, difficult to transport compound (SO_3)
- There is a very good spectral match

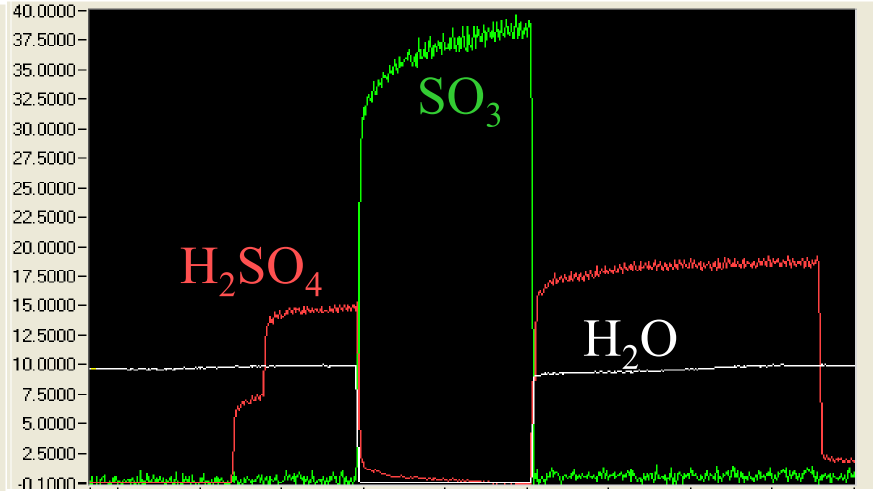


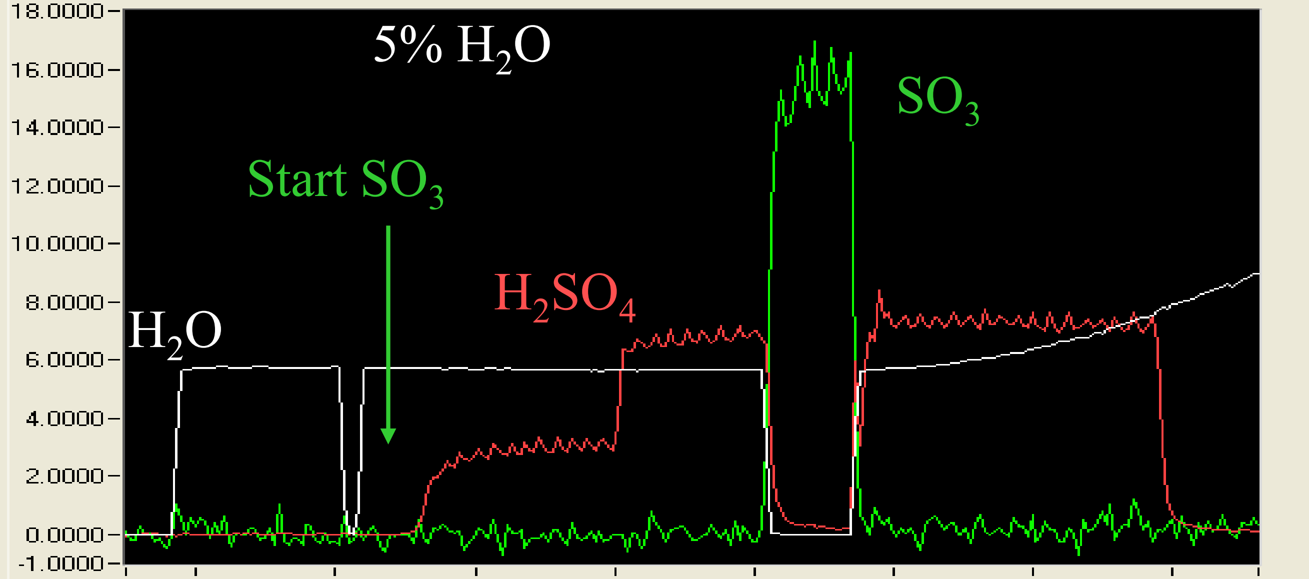


Strong linear correlation, with 1 mole H_2SO_4, 1 mole SO_3 under dry conditions

Lab Test : Add H_2O to Dry SO_3 (no SO_2)







The SO_3 immediately converts into H_2SO_4

Difficulties

1. Chemical Reactions between molecules in the sampling system
   a. Ammonia and Sulfur = Ammonium Sulfate Salts (ammonium bisulfate – ABS)
   b. Ammonia and Hydrochloric Acid = Ammonium Chloride and other Salts
2. Chemical or Surface reactions of Sampling system with molecules in the gas stream sometimes called “passivation”
   a. Teflon and Polar Compounds NH3, HCl, HF, CH2O (Use HDPE)
   b. Dry Calibration Gases - Moisture facilitates transport – Preferential binding
3. Temporal Resolution - Non Steady-State
   a. Constantly changing native concentrations
   b. Batch Reactors
   c. Constantly increasing or decreasing concentration

Conclusion

1) FTIR-based CEMS being deployed in the field to achieve low maintenance and very low MDC
2) High-Sensitivity FTIR-based Analyzer designed specifically for CEM based components HCl, HF, CH_2O, CH_4, N_2O
3) EPA, EPRI, CMA studies involving instruments from multiple manufacturers tested on gas and coal pilot plants use MKS FTIR as true reference

Conclusion

4) Because the FTIR has a broad analyzing window, industry opposed to having extraneous information generated by the FTIR provided to EPA

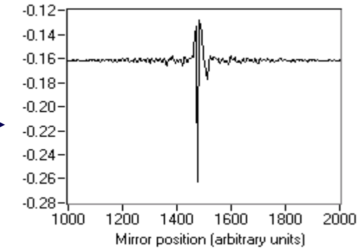
    No raw spectra savings!   Only crunched data!

5) Some portions of the PS-15 document requires dry gas spans to be used, like older traditional CEMs which were unable to analyze the data hot and wet (PS18 can choose wet or dry)
6) EPA has agreed verbally in Round Table Meetings that PS-15 and EPA M320 should be modified

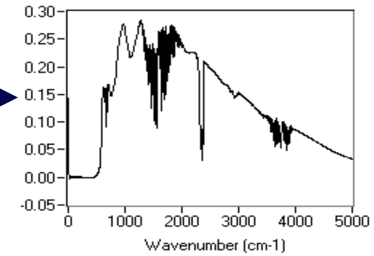
Questions?

Summary Spectral Data

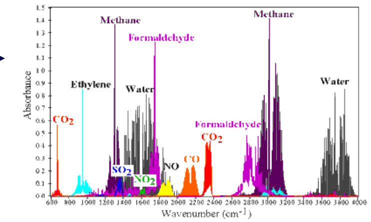
1) Acquire interferogram (detector signal as a function of time or mirror movement)



2) Apply Fourier Transform to get the single beam (signal as a function of wavenumber in cm^{-1})



3) Normalize with N_2 background spectrum to get absorbance spectrum (absorbance vs wavenumber)



4) Apply CLS algorithm to extract multiple gas concentrations, plot as a function of time, or transfer values through communication protocol