Traditional vs Quantum Cascade Laser Spectroscopy for CEMS Measurements

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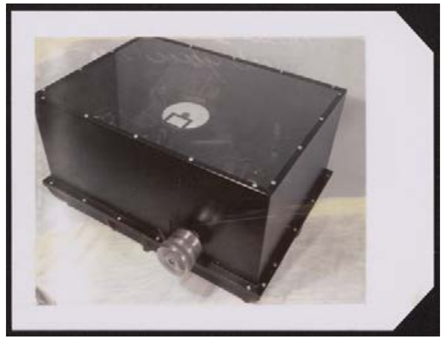
Sarah Calhoun

- Ph.D. Analytical Chemist
- 10+ years Cross-industry experience: Eastman and ExxonMobil
- Former roles as Technician, Analyzer Engineer, Chemist
- Current: North American Continuous Gas Business Development Manager at Emerson

Agenda for today

- History of Emerson’s Gas Technologies
- Traditional Technologies
- Why QCL? Capabilities and Theory
- QX1000

X-STREAM Process Gas Analysis History



Beckman IR-1

1942

1976

Binos 1

LEYBOLD-HERAEUS

1987

LEYBOLD

1988

Binos 100 & 1000

1990

ROSEMOUNT® Analytical

1993

NGA

NGA MLT

1994

2005

EMERSON™

X-STREAM

2008

2026

QX1000

History of Quantum Cascade Laser Analyzers at Rosemount

2003
- Cascade Technologies Limited established in Glasgow, Scotland

2005
- Begins first marine emission monitoring trials and demonstrates explosive detection capabilities

2007
- Develops first industrial QCL industrial gas analyser the CT2000 and secures Type Approval Certification

2010
- Signs worldwide exclusive supply agreement with Asian partner for the automotive test market
- Starts shipment of its aerosol leak detection system to Unilever plants worldwide

2012
- Signs development agreement with GSK for leak detection in the pharmaceutical market
- Successful field trial of the world's first process analytics QCL analyser, the CT3200, at an Ethylene production plant in the UK

2014
- Launches the CT5000 a hybrid QCL/TDL analyser platform capable of measuring up to 20 gases
- Ships first production leak detection system for the pMDI pharmaceutical market

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Acquired by EMERSON

2016

Launches CT5000 QCL Series Analyzers:
- CT5100
- CT5400
- CT5800

Intensive R&D, Patents and QCL IP Development

Launches 1st Process Gas Analyzer

2006
- Secures key component exclusivity and Lucent license

2004
- Releases its first QCL system

2009
- Receives ISO 9001 accreditation and moves to new, extended development and manufacturing facilities
- Signs agreement with Bosch for the supply of flue gas setting analysers for domestic boiler production
- Signs global supply agreement with WR Systems for the marine emissions monitoring market

2011
- Starts production of the CT3000 QCL OEM platform the world first modular multicomponent QCL gas analyser
- Signs development agreement with ExxonMobil for the petrochemical market

2013
- Ships its 200th CT3000 OEM platform 24 months after product launch
- Signs development agreement with Asian partner for leak detection in the food and beverage market
- Partners with European partner for the moisture in natural gas market

2014

Becomes a part of Rosemount

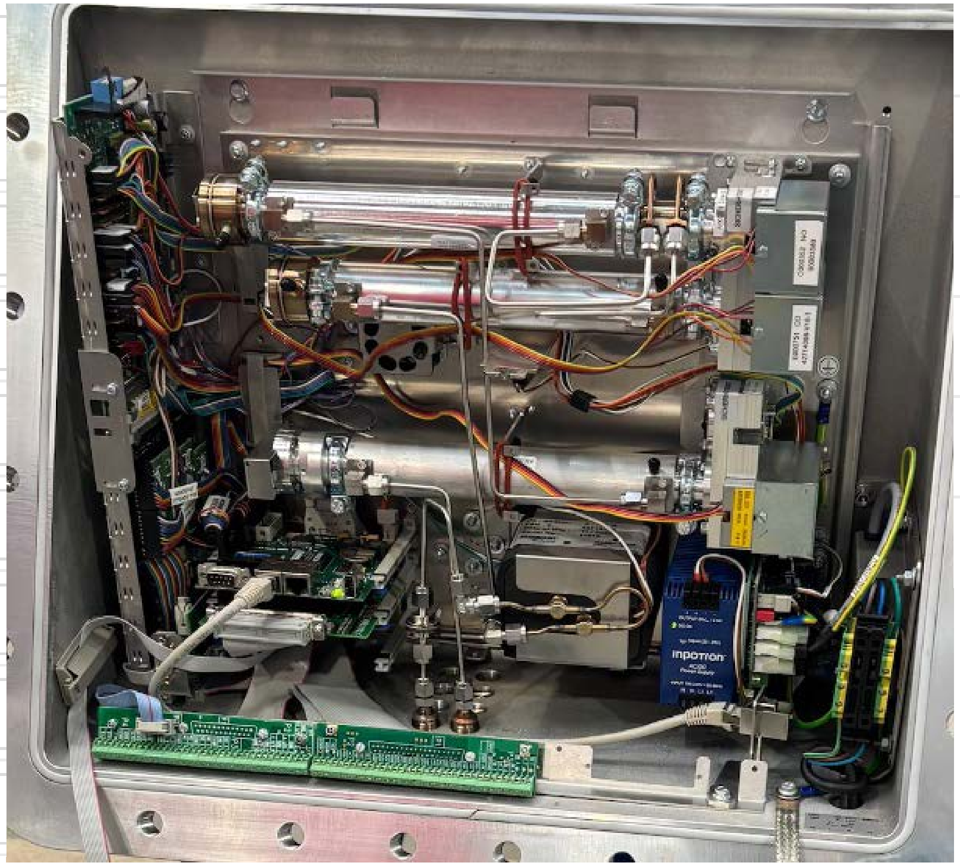
ROSEMOUNT

Emerson’s X-STREAM or Traditional Gas Analyzers

XEGP General Purpose

- Rack mount or Tabletop 19”, up to 5 channels
- 32 to 122°F ambient temperature
- CLD version: 5 to 40°C (41 to 104°F) ambient temperature

- 1 Channel - IR/UV
- 1 Channel - O2/TC/Sensor
- 2 Channel - IR/UV · IR/UV
- 2 Channel - O2/TC/Sensor · O2/TC/Sensor
- 2 Channel - IR/UV · O2/TC/Sensor
- 3 Channel - IR/UV · IR/UV · IR/UV
- 3 Channel - O2/TC/Sensor · O2/TC/Sensor · O2
- 3 Channel - IR/UV · IR/UV · O2/TC/Sensor
- 3 Channel - IR/UV · O2/TC/Sensor · O2



- 4 Channel - IR/UV · IR/UV · IR/UV · IR/UV
- 4 Channel - O2/TC/Sensor · O2/TC/Sensor · O2 · O2
- 4 Channel - IR/UV · IR/UV · IR/UV · O2/TC/Sensor
- 4 Channel - IR/UV · IR/UV · O2/TC/Sensor · O2
- 4 Channel - IR/UV · O2/TC/Sensor · O2 · O2
- 5 Channel - IR/UV · IR/UV · IR/UV · IR/UV · O2

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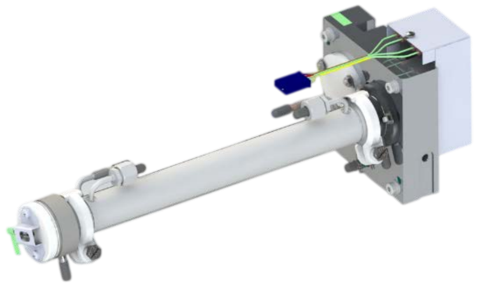
X-STREAM Measurement Ranges for Most Common Gases

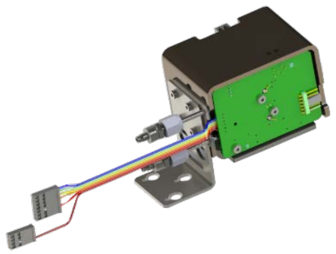
Component		Technology	Detection Limit	Lowest Range	Highest range
Carbon Monoxide	CO	NDIR	0.2 ppm	0-10 ppm	0-100%
Carbon Dioxide	CO_2	NDIR	0.1 ppm	0-5 ppm	0-100%
Nitrogen Monoxide	NO	NDIR	1.0 ppm	0-100 ppm	0-100%
Nitrogen Dioxide	NO_2	NDUV	0.25 ppm	0-25 ppm	0-10%
Nitrous Oxide	N_2O	NDIR	1.0 ppm	0-100 ppm	0-100%
Sulfur Dioxide	SO_2	NDUV	0.25 ppm	0-25 ppm	0-100%
Methane	CH_4	NDIR	1.0 ppm	0-100 ppm	0-100%
Ethane	C_2H_6	NDIR	10 ppm	0-1000 ppm	0-20%
Ethylene	C_2H_4	NDIR	4.0 ppm	0-400 ppm	0-100%
Ammonia	NH_3	NDIR	1.0 ppm	0-100 ppm	0-100%
Hydrogen	H_2	TCD	40 ppm	0-2000 ppm	0-100%
Oxygen	O_2	PMD	100 ppm	0-1 %	0-100%
Oxygen	O_2	traceO2	0.1 ppm	0-10 ppm	0-1%

For higher ranges, better detection limits may apply: 1% or 0.5% of range

Multi-component, multi-method gas analysis for selective measurement of more than 60 gases from ppm to % range

Rosemount X-STREAM *Enhanced* Measurement Technologies





NDIR or NDUV

(non-dispersive infrared of non-dispersive ultraviolet)

CO, CO_2, SO_2, NO_2,
NO, N_2O, NH_3

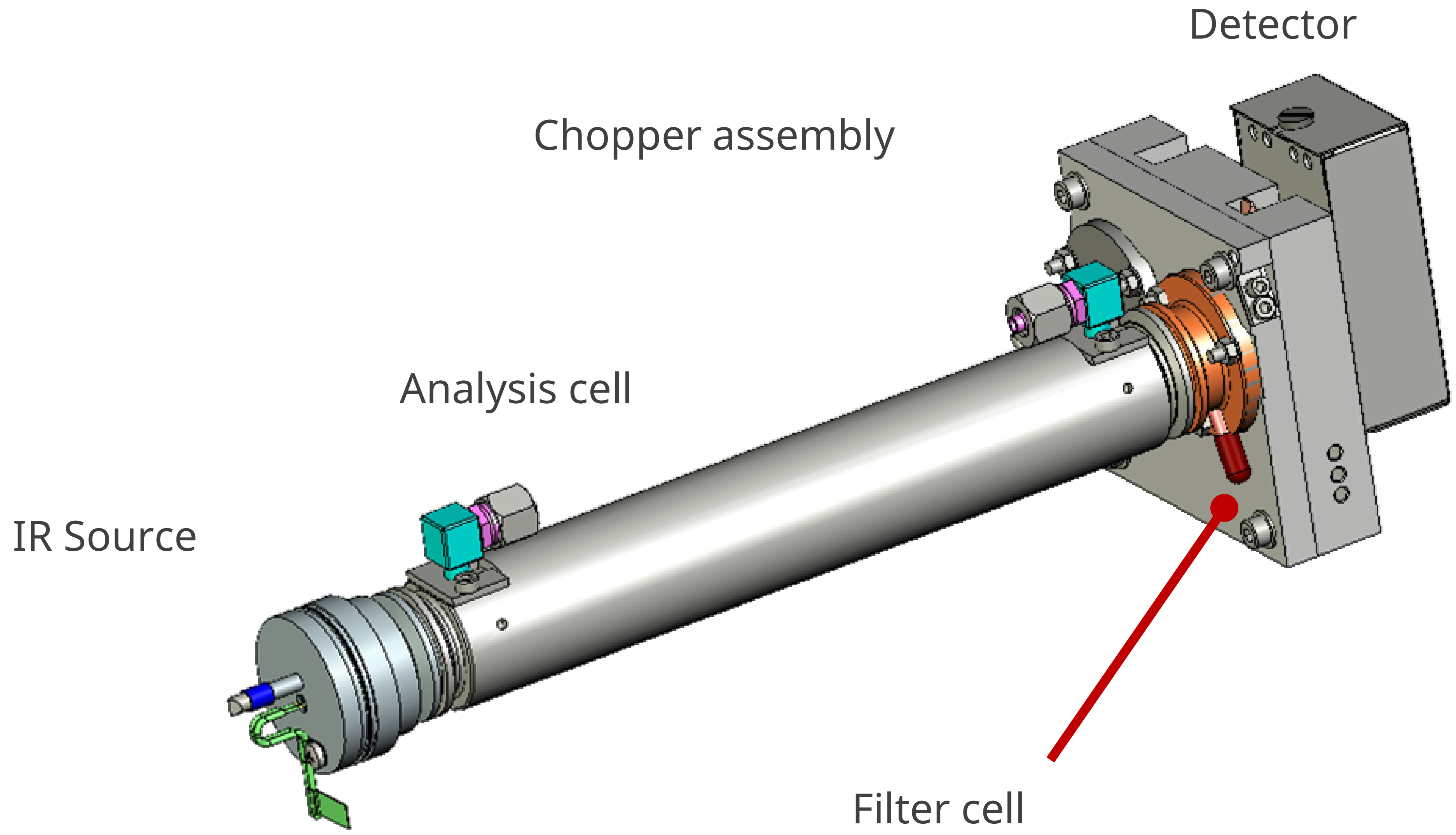
and many more…

PMD

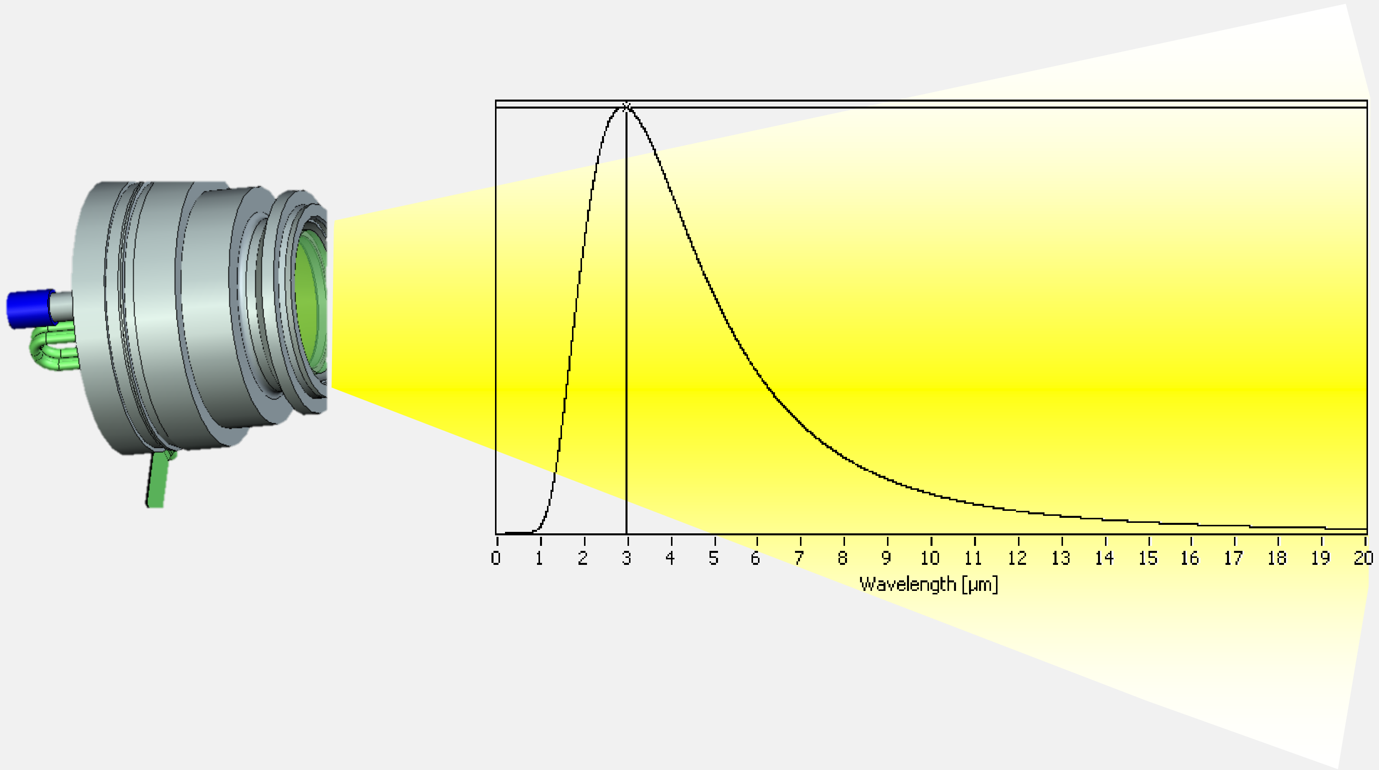
(Paramagnetic)

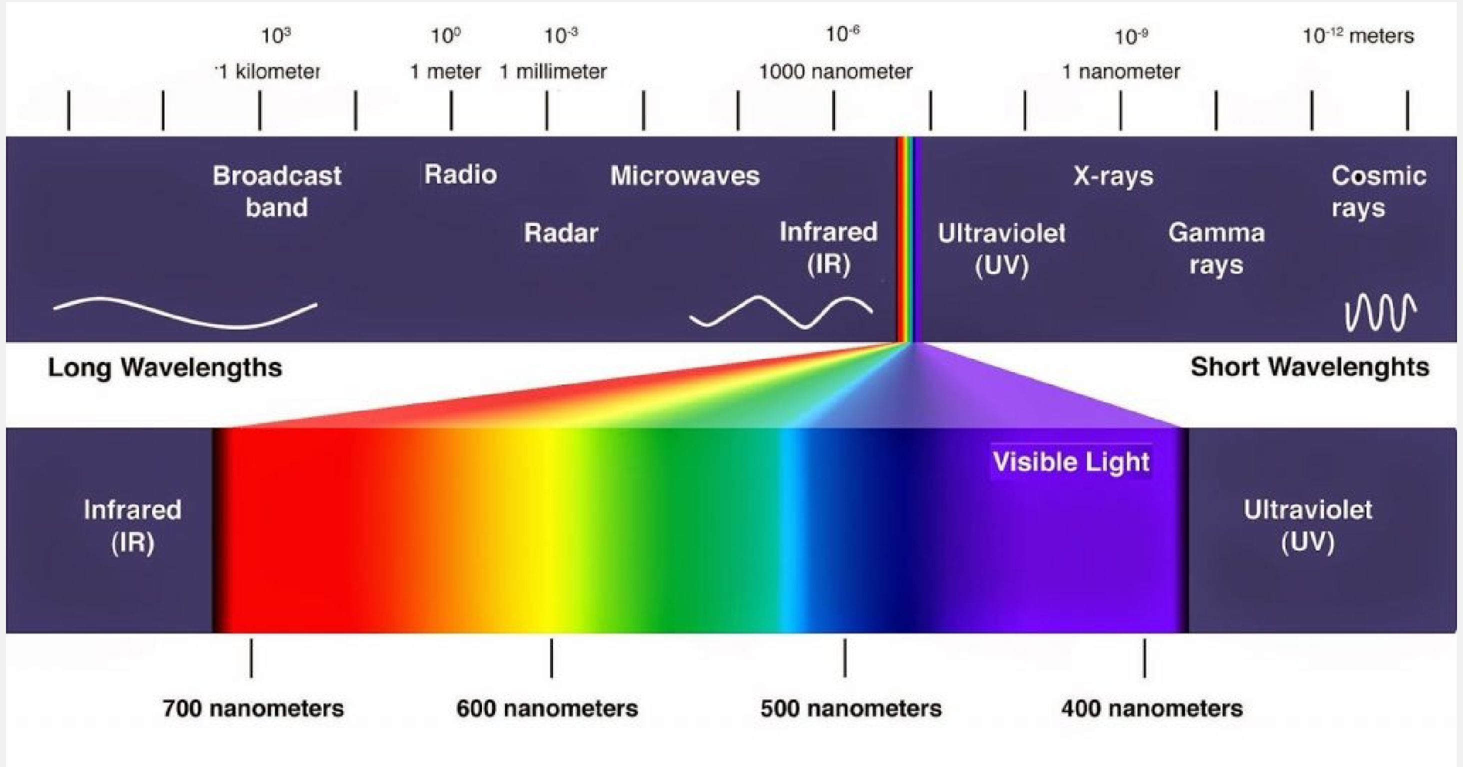
O_2

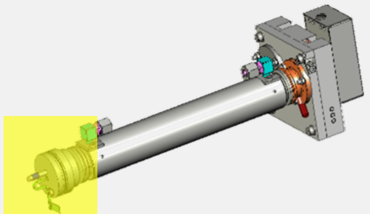
NDIR Module


Detector
Chopper assembly
Analysis cell
IR Source
Filter cell

IR Source-Variable based on Application-Full Infrared Spectrum

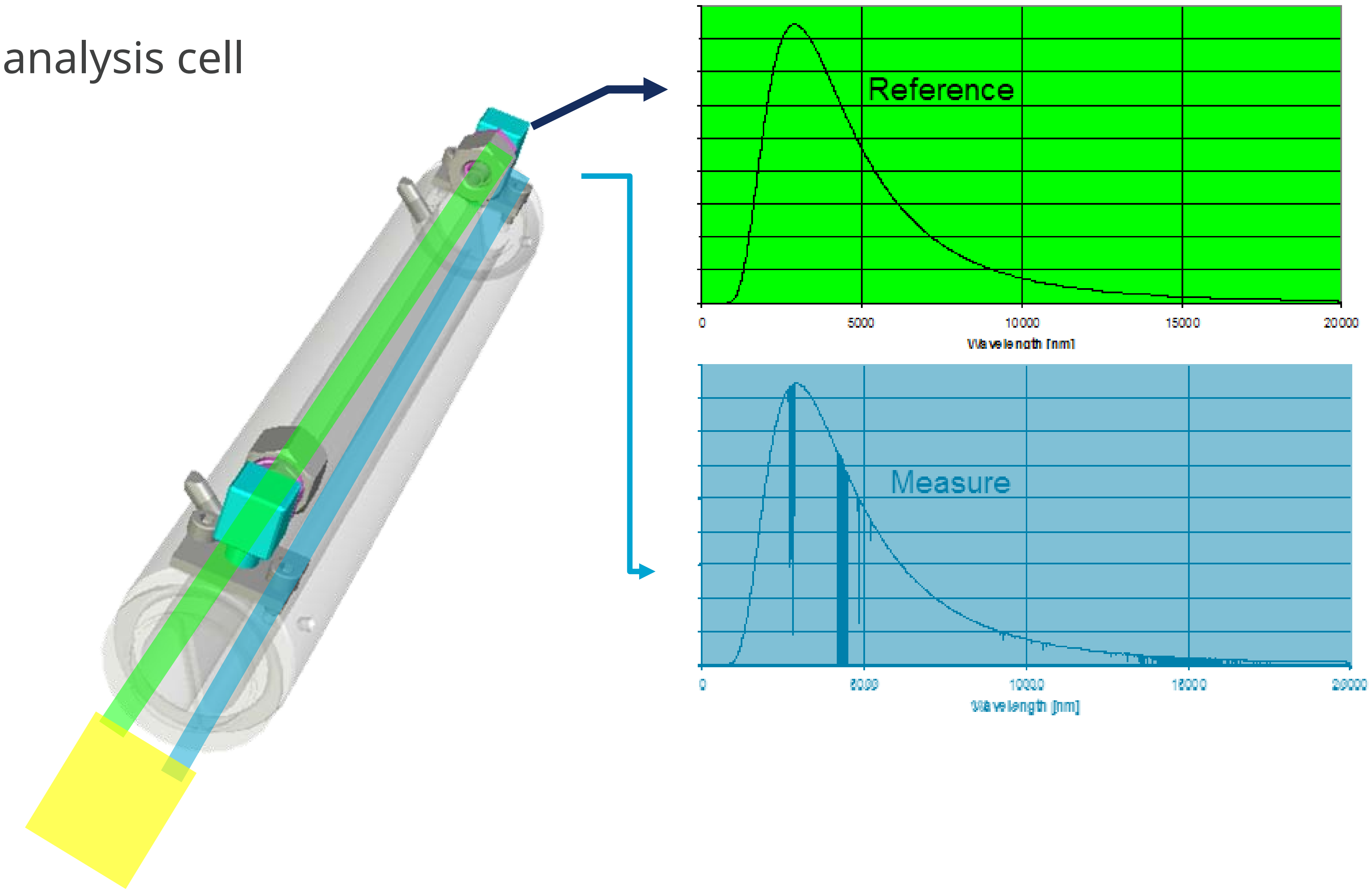


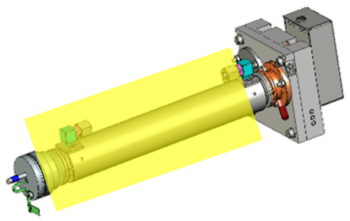




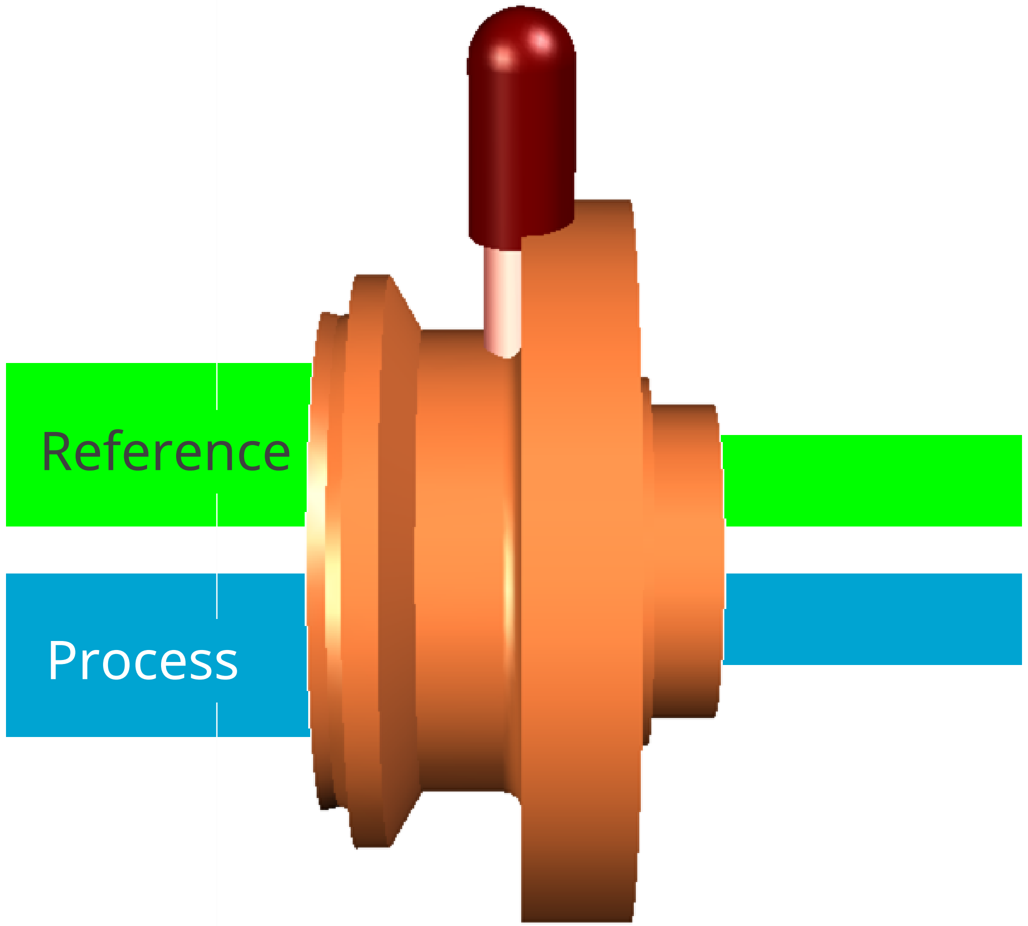
Analysis cell-Specific to Application- Length, and Reference Gas

- Absorption in analysis cell

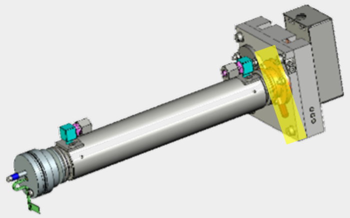




Optical Filter Cell- Variable to Application

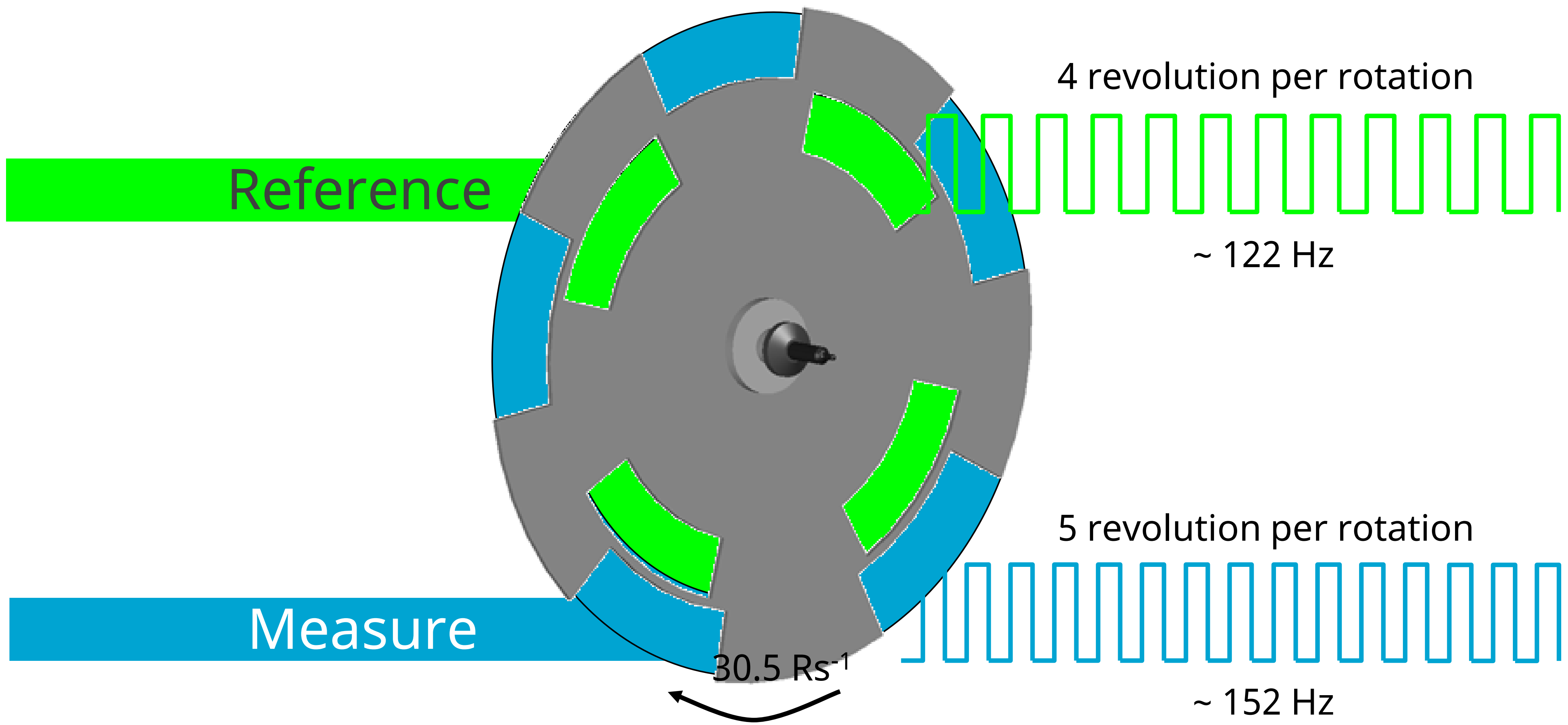


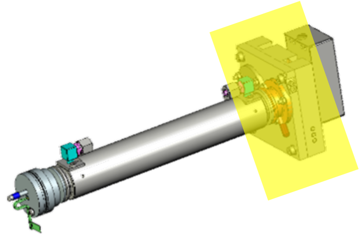
Concentrates light to increase sensitivity and makes the measurement more selective. When the absorption wavelength of measuring component and filling gas overlap, then cross interferences are eliminated. The most common example is to eliminate CO_2 during CO measurement.



Chopper Window Generic

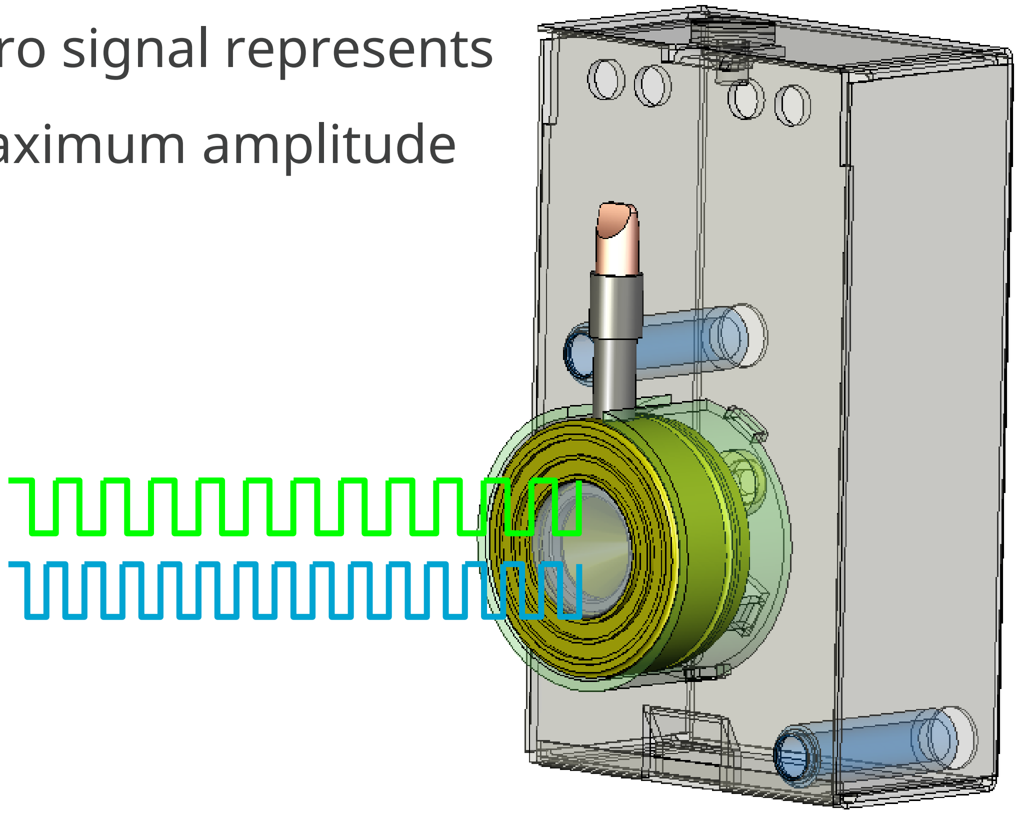
- 4/5 Method Chopper wheel ensure frequencies of Ref vs Measurement are different
- Most competitors have 1-3 measurement windows in their chopper window

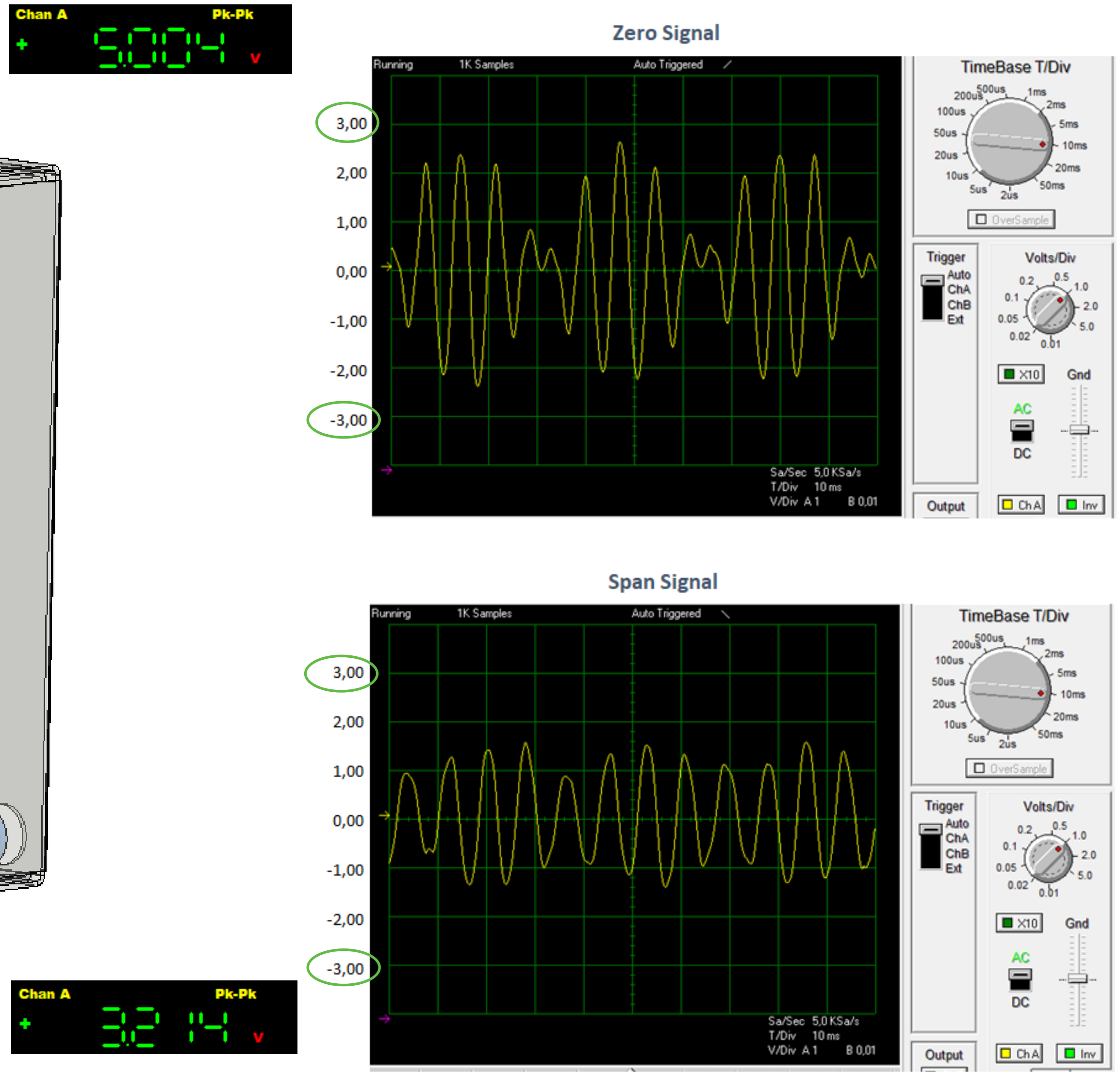


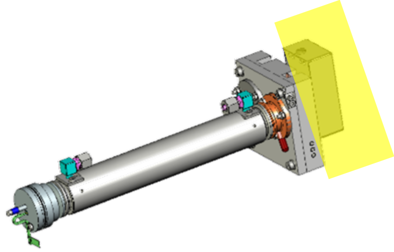


NDUV Detector- Variable based on Analyte

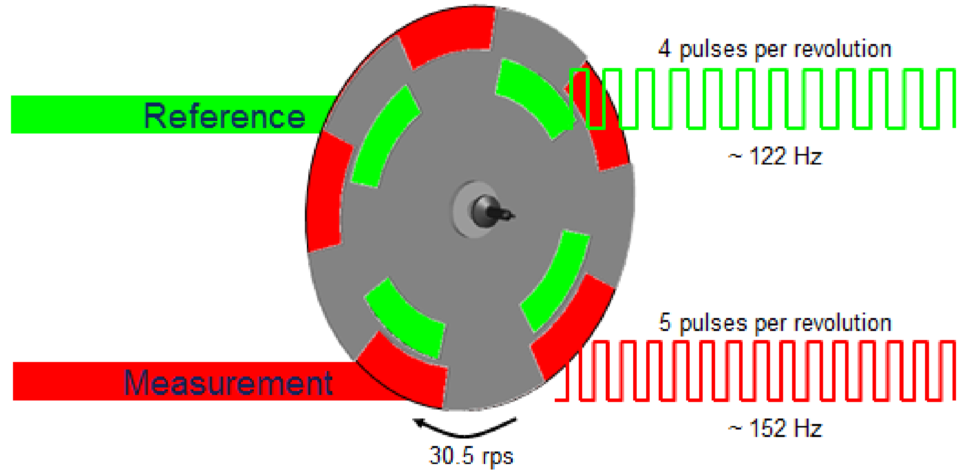
Zero signal represents maximum amplitude

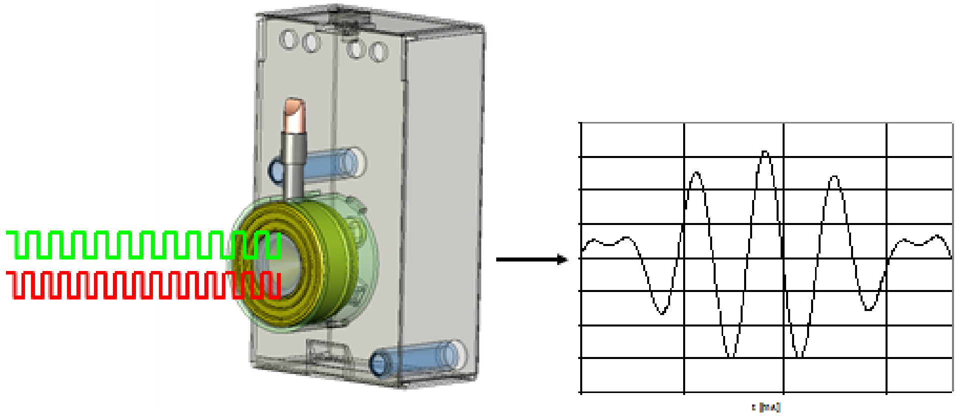


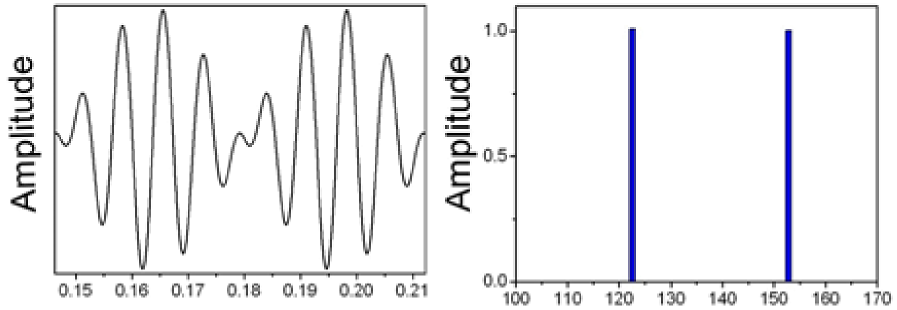




Patented INTRINZX™ Photometer Technology







- Chopper with a special 4/5-wheel imprints frequencies on the continuous IR und UV sources-**self checking mechanism to ensure functionality**
- Detector measures sum signal of the reference side with 122 Hz and the measurement side with 152 Hz
- Frequency filtering separates 122 Hz from 152 signal
- **Ratio of both signals is used for concentration calculation**
- INTRINZX™ features high dynamic ranges and signal stability as variations cancel out
- Proprietary **glass soldering** technology to seal the gas inside the photometer components resulting in enhanced NDIR detector lifetimes

How the XECLD Works

Chemiluminescent NOx Analysis History from Beckman Instruments

Beckman Model 951 NO/NOX Analyzer

1970s

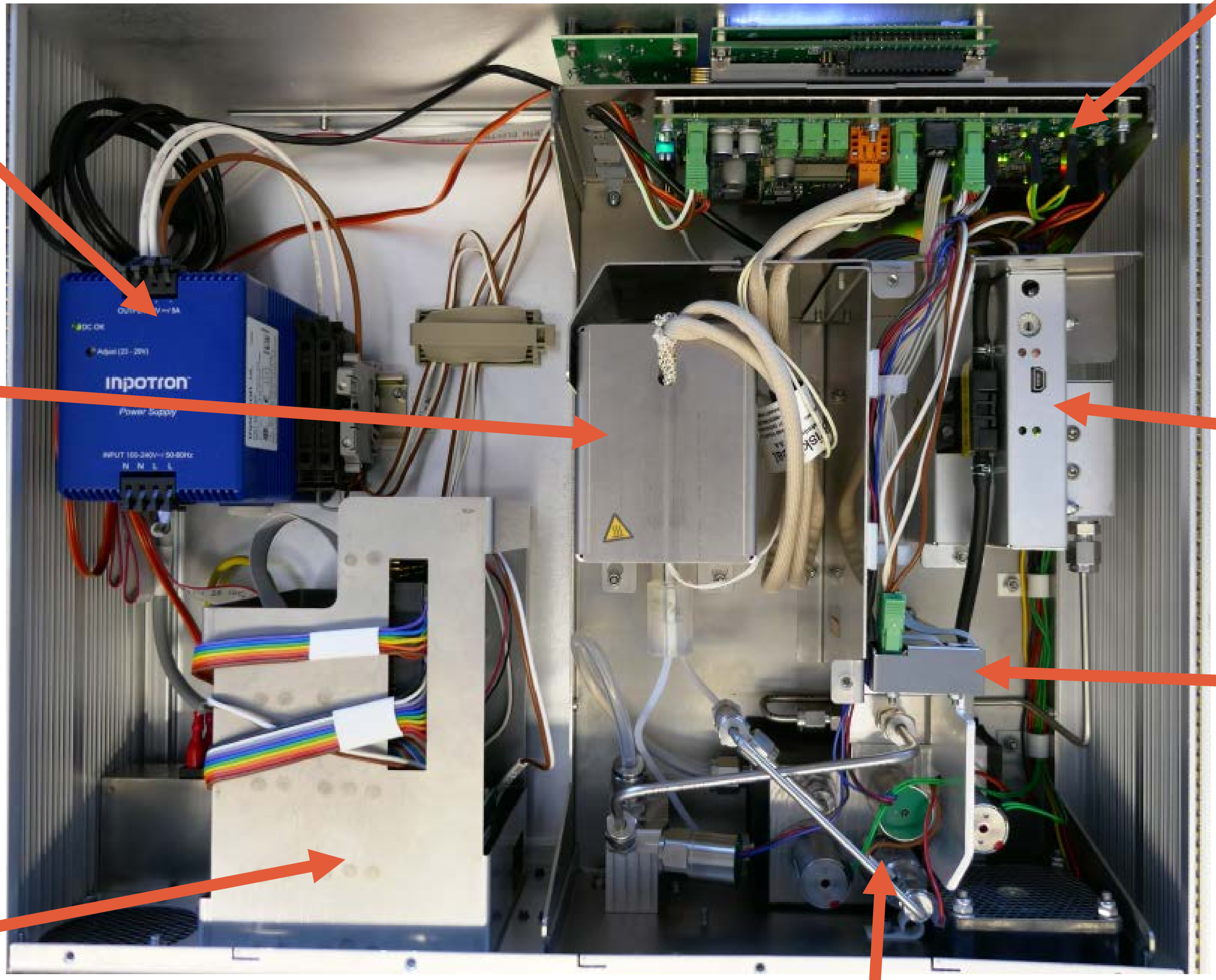
This instrument was used for a wide range of applications, including measuring nitrogen oxides in the atmosphere and in automobile emissions.

Beckman Instruments, Inc. became interested in measuring, controlling, and fighting air pollution in the late 1940s and early 1950s, when company president Arnold O. Beckman became the scientific adviser to the Los Angeles Chamber of Commerce's Air Pollution Control Officer. Many of the instruments that were developed by Beckman Instruments in the 1940s and 1950s as standalone items became incorporated into or re-purposed as smog-fighting systems.

"Beckman Model 951 NO/NOX Analyzer," 1970–1979. Beckman Historical Collection, Box 84. Science History Institute. Philadelphia. https://digital.sciencehistory.org/works/fb494872c.

Rosemount 951C
*Retired in 2020

XECLD – Inside View



Nitrogen Oxides

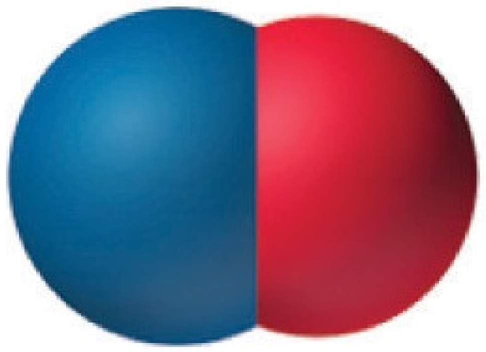
<u>C</u>hemi**<u>L</u>**uminescence **<u>D</u>**etectors (CLD) are specific for the measurement of Nitrogen Oxides (NOx)

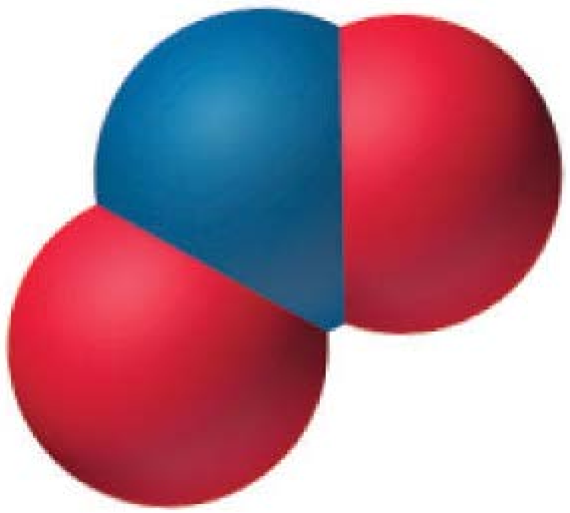
Nitrogen Oxides are different oxidation states of Nitrogen

NO = Nitric Oxide

NO_2 = Nitrogen Dioxide

$$NO + NO_2 = NO_X$$





Theoretical Background – Chemiluminescence

- Chemiluminescence is light emission from a chemical reaction

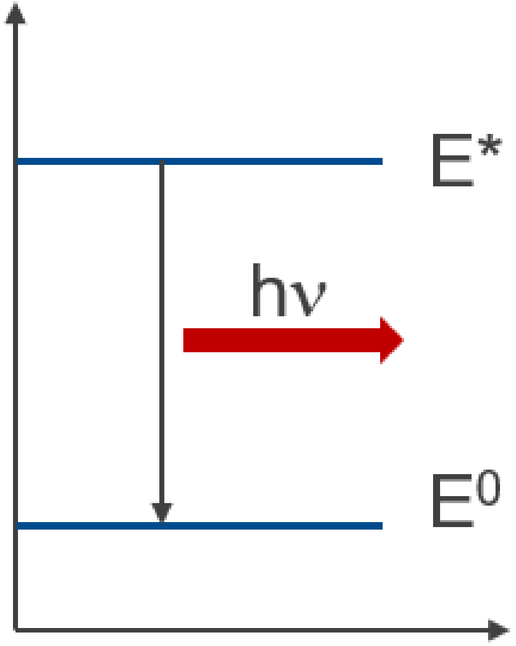
- Process steps
  - Chemical reaction results in formation of intermediates with excited electronical states (E*)

    $A + B \rightarrow C^* + D$

  - The intermediate returns to ground state (E^0) by emission of light photon $h\nu$

    $C^* \rightarrow C + h\nu$

The emitted light is proportional to the concentration of the excited molecule.



NO_x Measurements – Three Process Steps

1. NO_2 must be reduced to NO

$$NO_2 + C \rightarrow NO + CO$$

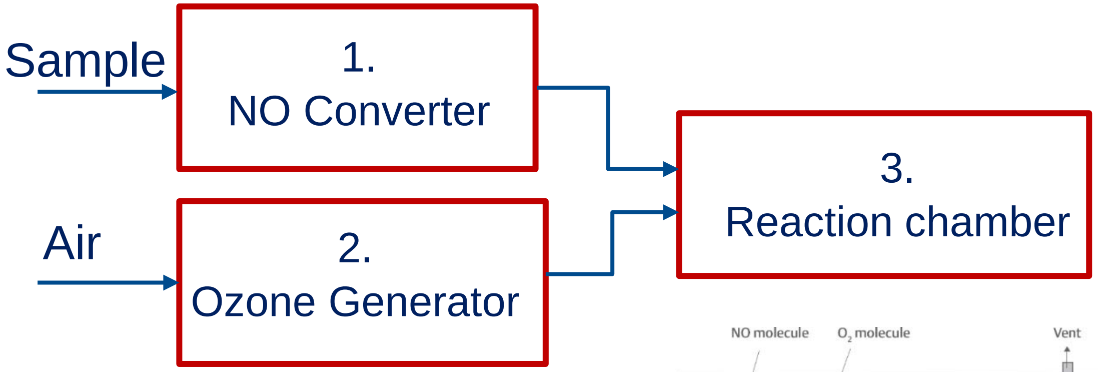
2. Ozone (O_3) must be generated from Oxygen (O_2)

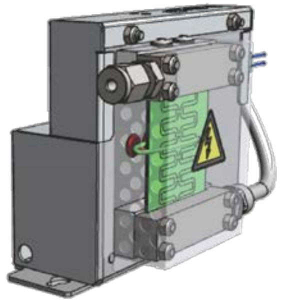
$$3\ O_2 \rightarrow 2\ O_3$$

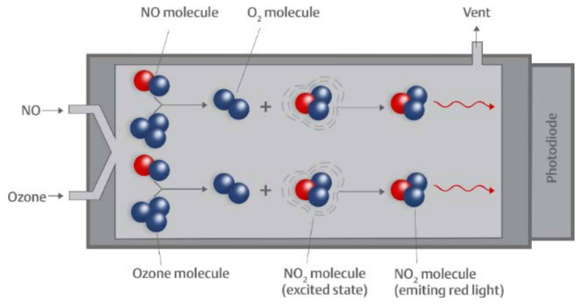
3. NO reacted with O_3 producing NO_2 in an excited energy state, where it can release a photon to be detected by the detector

$$NO + O_3 \rightarrow NO_2^* + O_2$$

$$NO_2^* \rightarrow NO_2 + h\nu$$

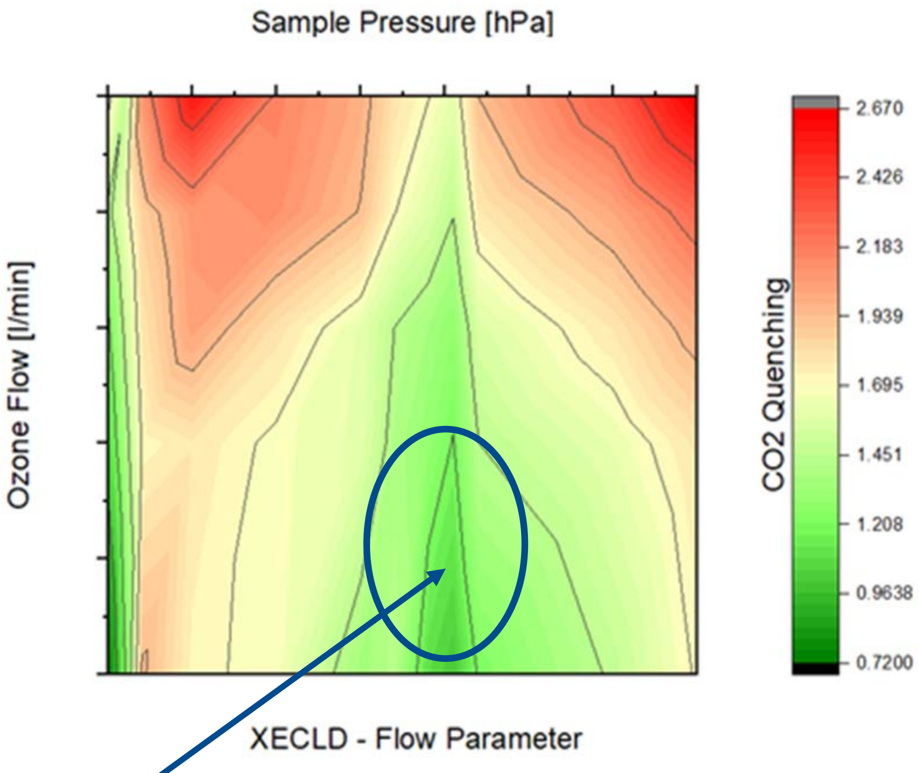






Chemiluminescent NOx Advancements/ Old technol

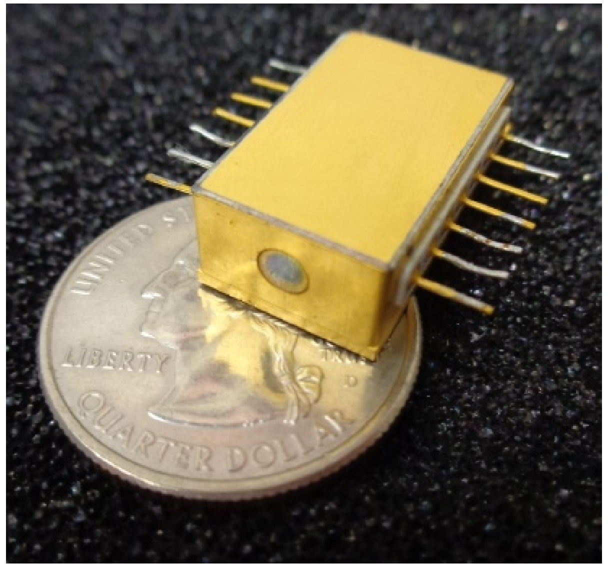
- NO2 Converter using Vitreous Carbon
  - 98% conversion rate
  - No conversion of Ammonia
- Ozone Generation via High Voltage Discharge Source
  - Works with air instead of needing O2 cylinders
  - High conversion rate and lower energy/longer life than UV lamps
- CLD Reaction Chamber design eliminates quenching errors
  - Tight control of O3 flow, Sample Pressure
  - Operates at Atmospheric Pressure – No vacuum pump needed



Optimal operation Zone

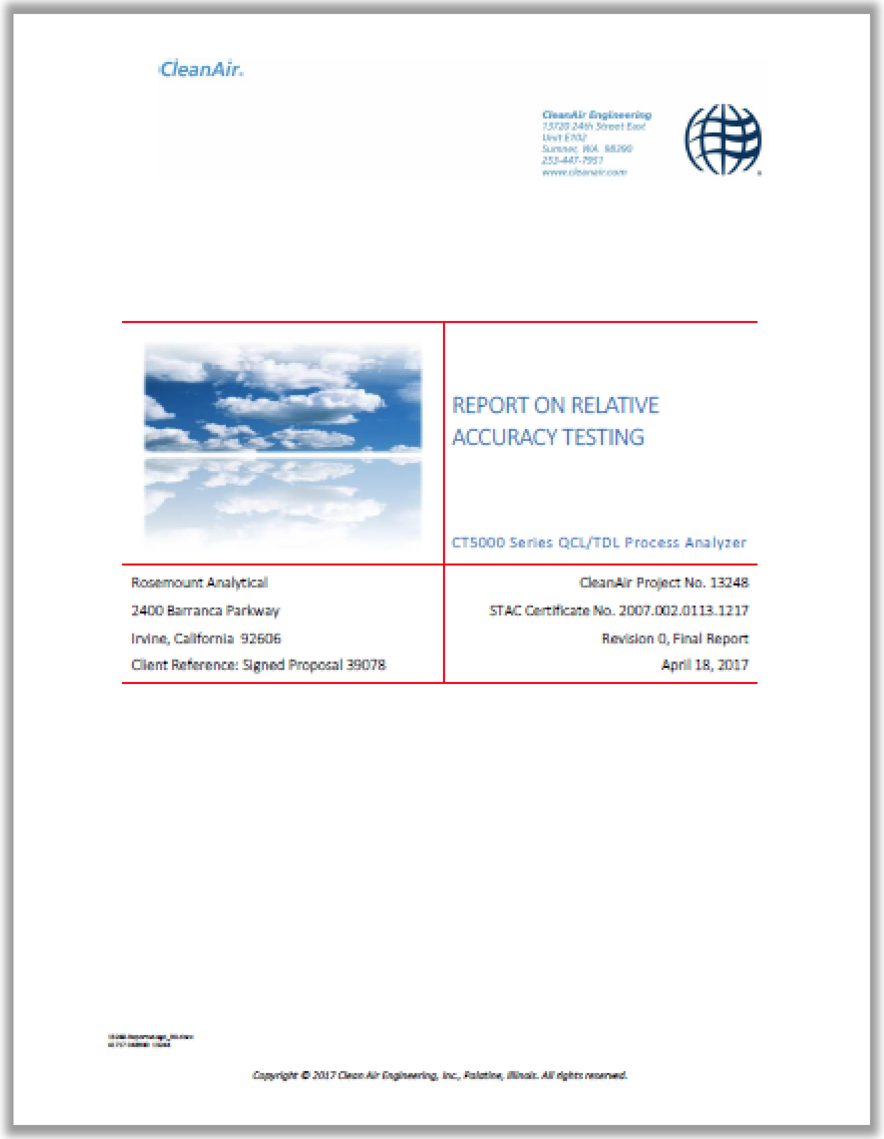
Quantum Cascade Laser Capabilities and Theory

Semiconductor Lasers are Proven Technology



First Certified Laser CEMS in 2017

- QCL: Mid IR source
  - More than 20 years since first development
  - QCL is an established technology
  - QCL: one of the best sources of mid-IR emission
  - MTTF values greater than 10 years
  - 10,000 laser modules operating in the field
- RATA performed with CT5000 series analyzer
- Gas fired heater at BP Cherry Point
- Performance met or exceeded conventional analyzers



CleanAir.

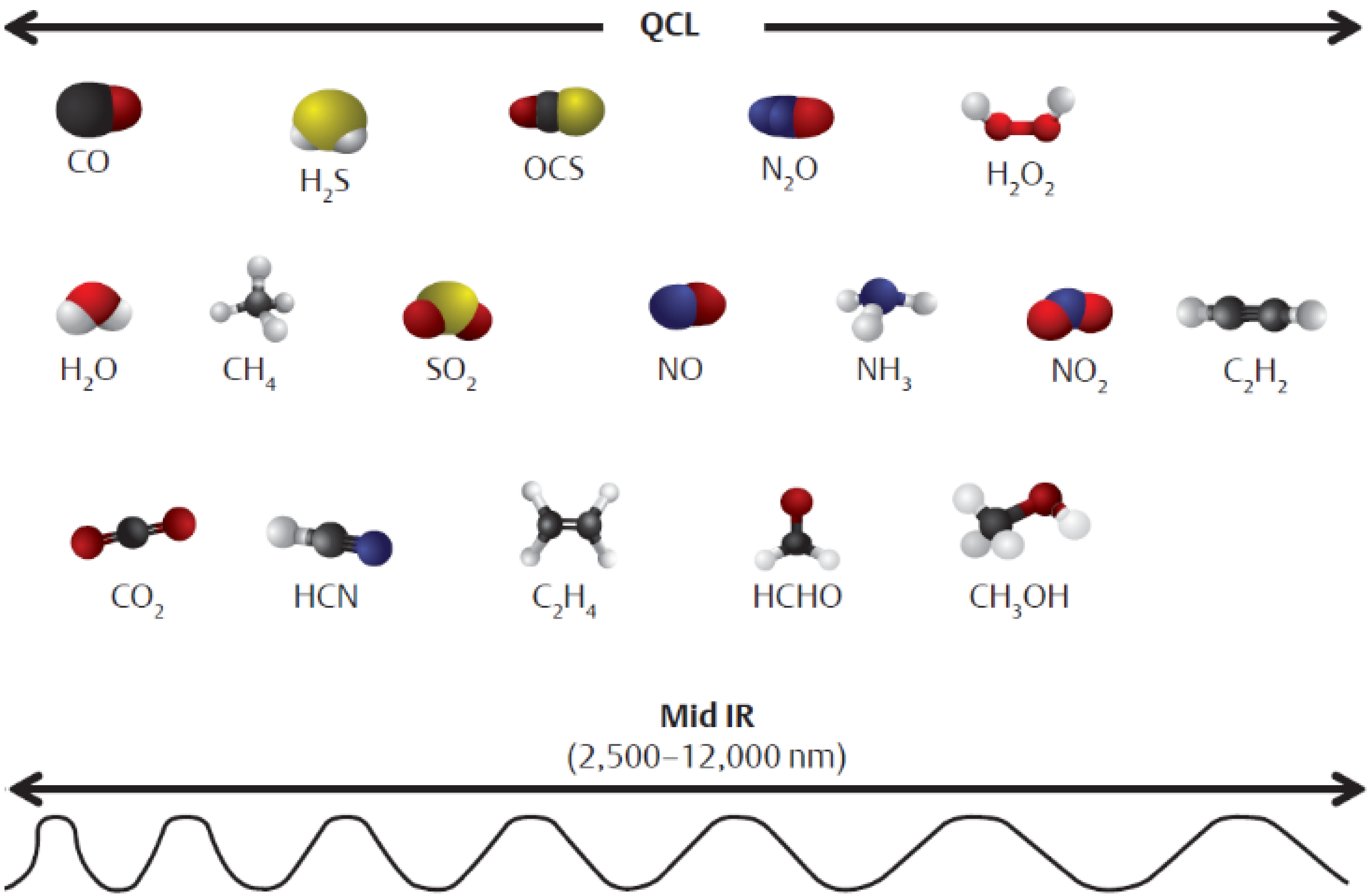
CleanAir Engineering
13720 24th Street East
Unit E102
Sumner, WA 98390
253-447-7957
www.cleanair.com

REPORT ON RELATIVE ACCURACY TESTING

CT5000 Series QCL/TDL Process Analyzer

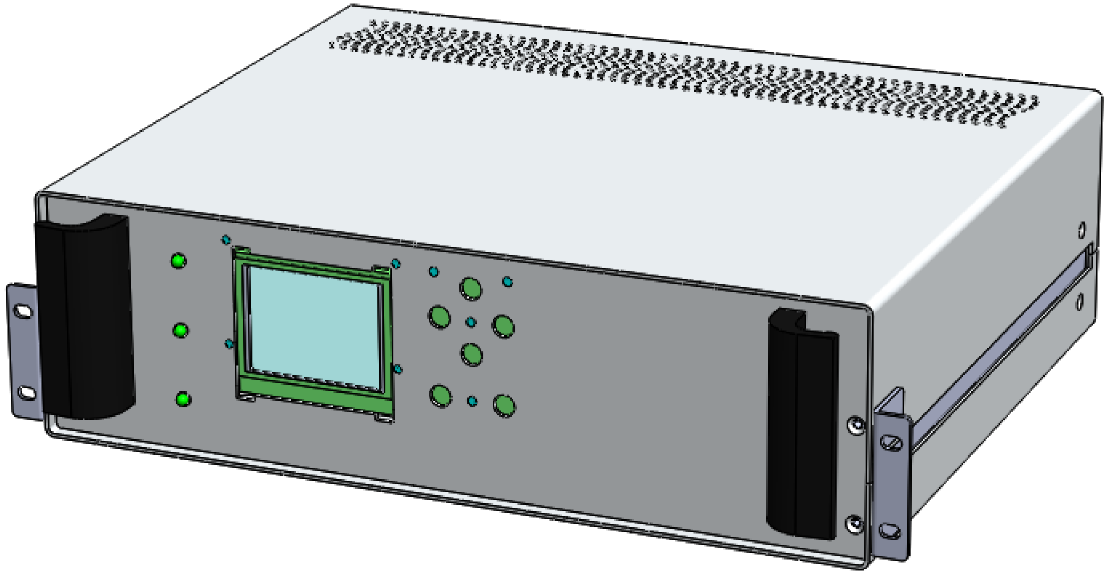
Rosemount Analytical	CleanAir Project No. 13248
2400 Barranca Parkway	STAC Certificate No. 2007.002.0113.1217
Irvine, California 92606	Revision 0, Final Report
Client Reference: Signed Proposal 39078	April 18, 2017

Common Analytes of Interest

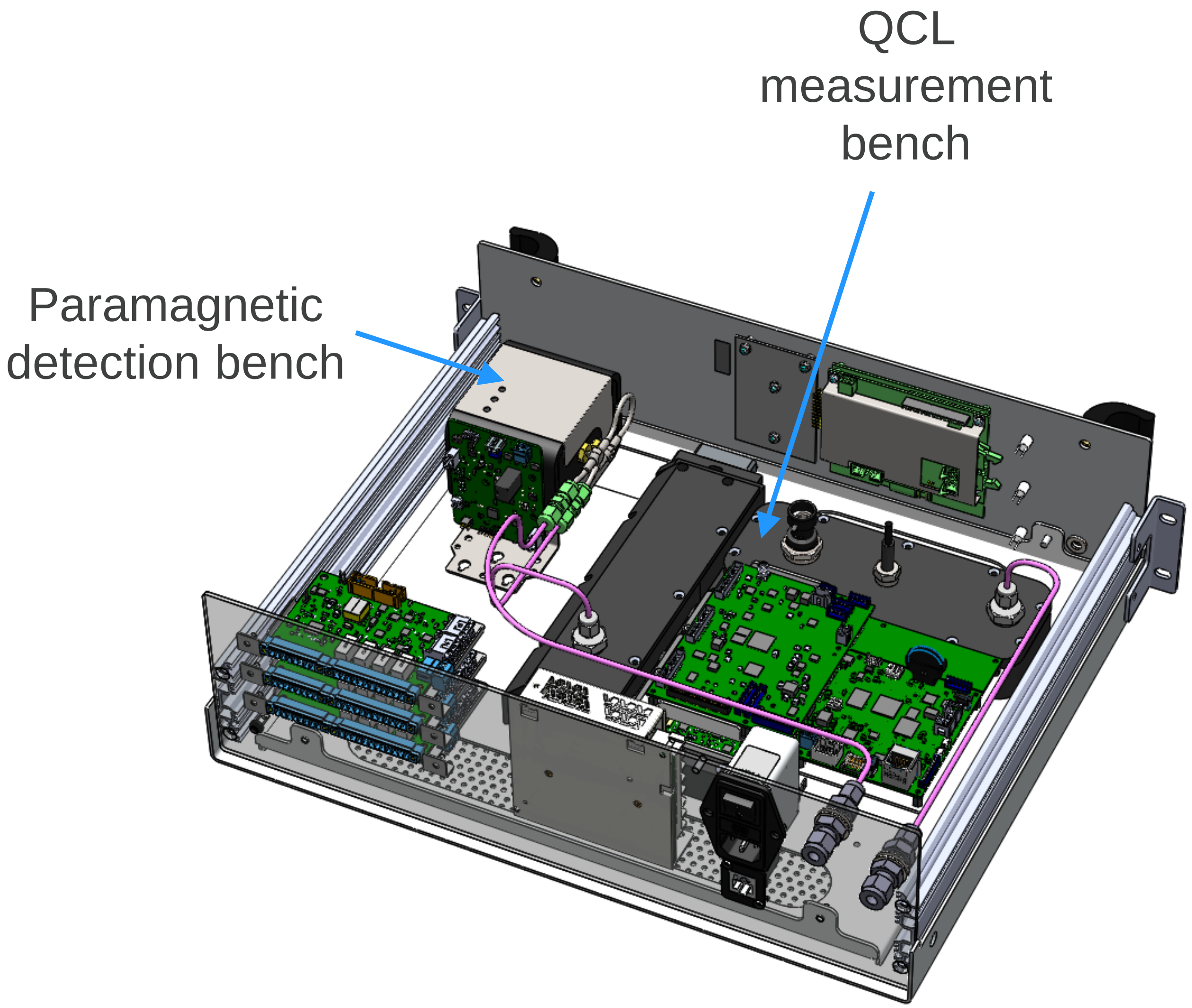


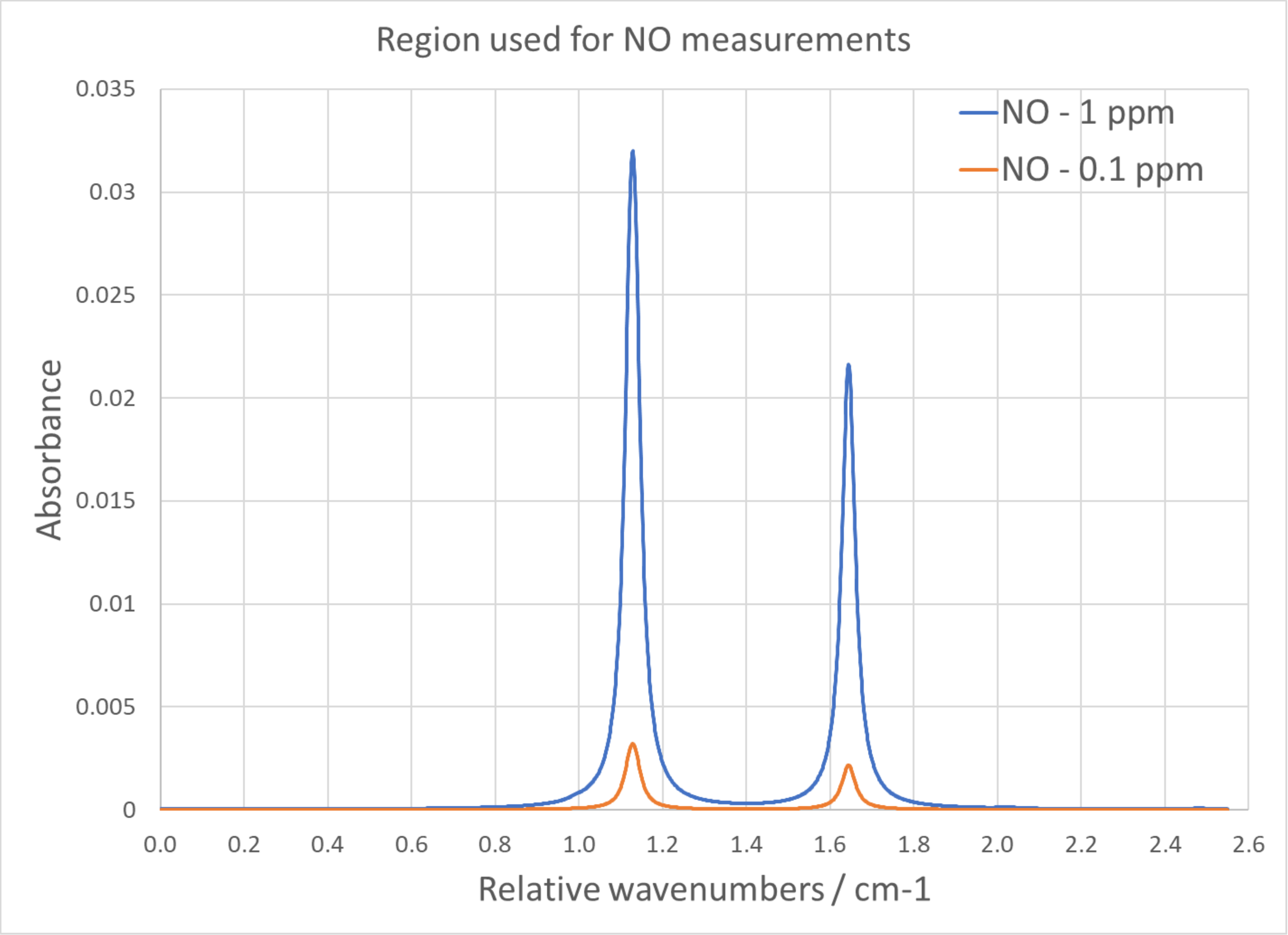
QX1000 Analyzer Technology Difference

- Modular repairable
- Intuitive interface
- No moving parts, no consumables
- Direct absorption spectroscopy for reliability
- Laser modules provide specific wavelengths
- Multiple Lasers-Up to 3
- Laser stability with 10 – 15 year lifespan
- Little or no drift
- Real time data for all measurements



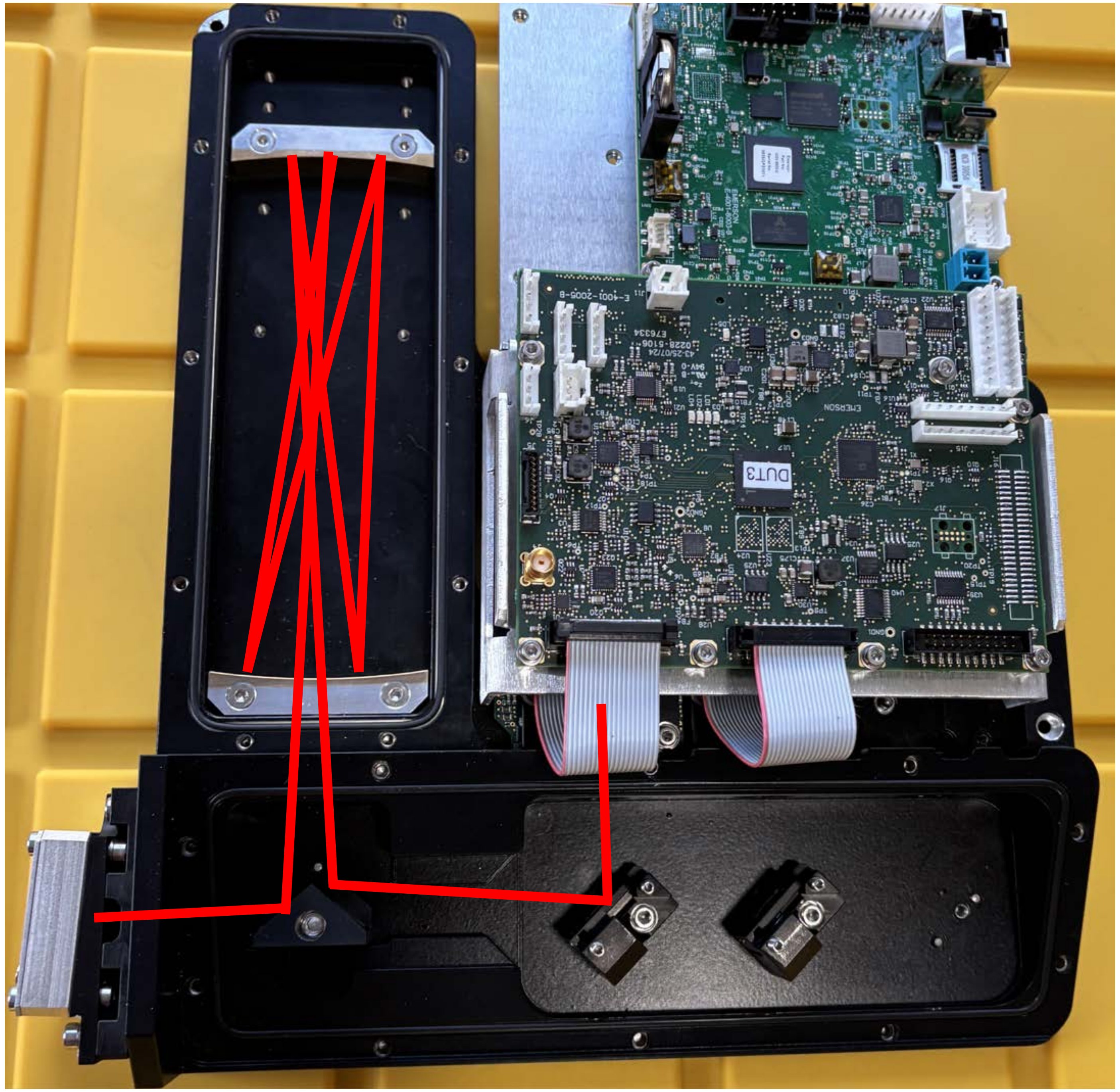
Absorption Peak



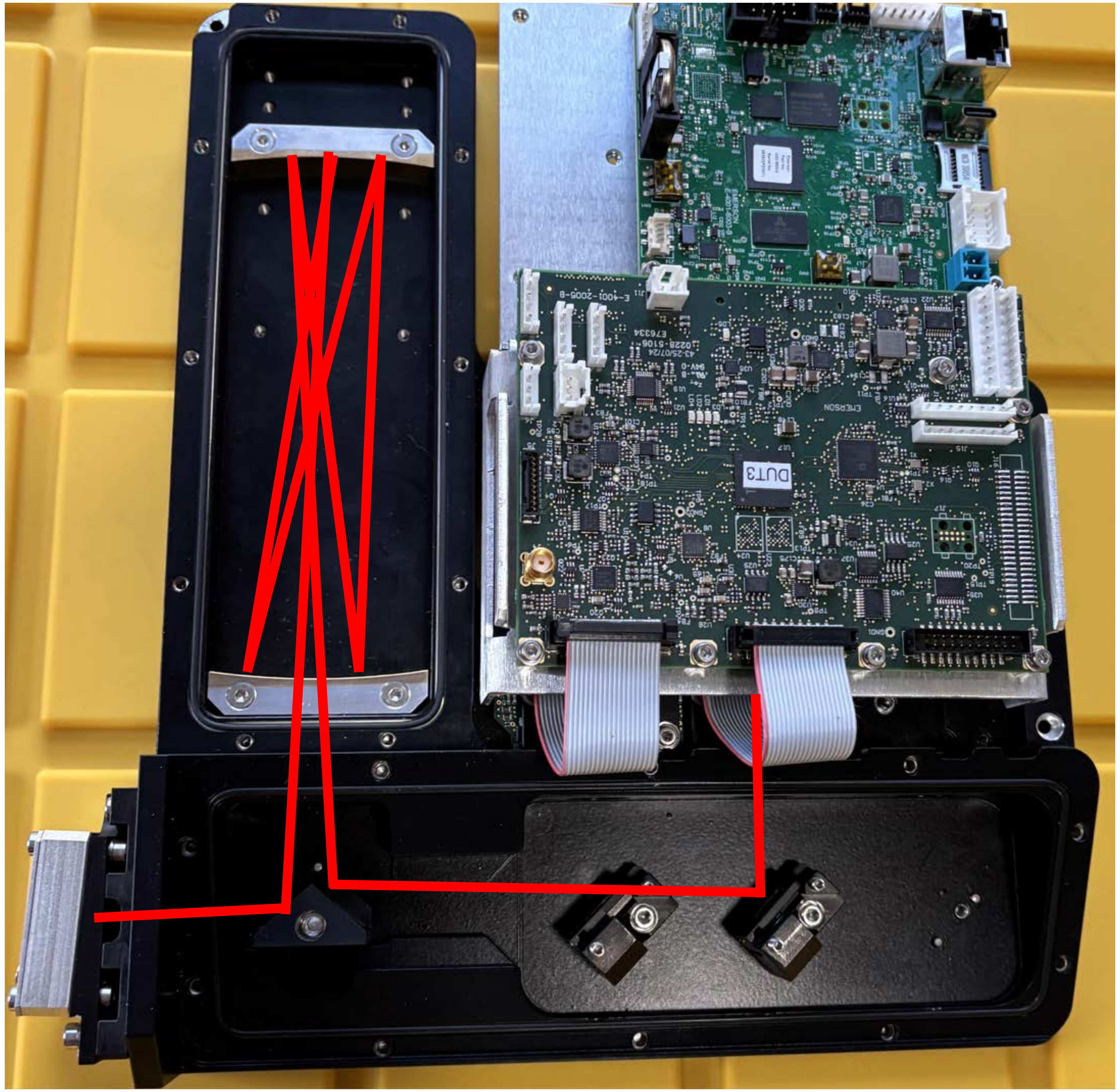


QX1000 Laser Module

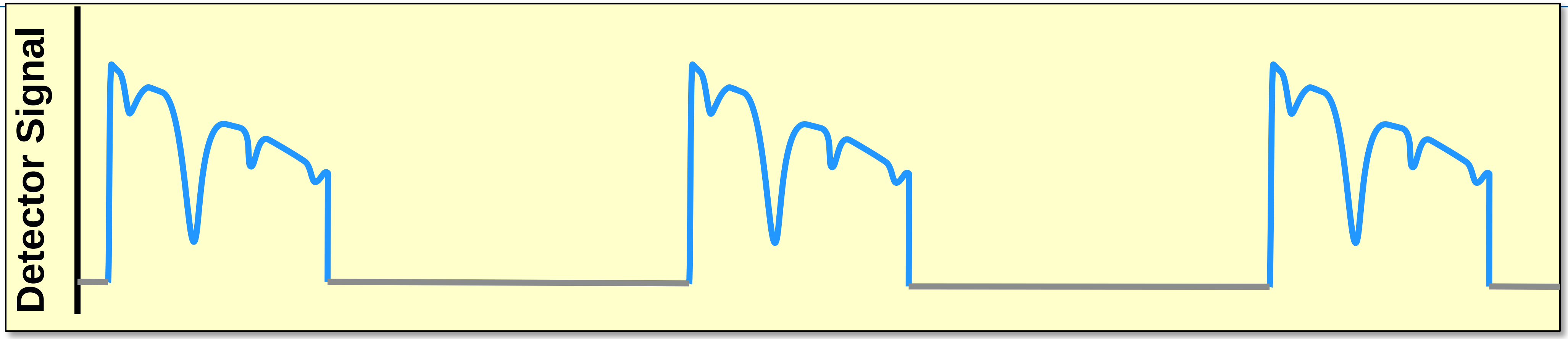
QX1000 Bench Laser 1



QX1000 Bench Laser 2



Patented "Chirp" Technique



- When power is applied, QCL heats up
- As temperature increases, laser wavelength increases
- Laser "sweeps" the frequencies where components of interest absorb
- Thermo electric cooler built into laser package cools the laser back down to starting temperature
- Each "chirp" is under 1 millisecond enabling thousands of spectra collected per second

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Cascade-Excellent Long-Term Stability

- Concentration derived from first principles using the Beer Labert Law

    - Adsorption, A= α x concentration x path length

- The path length does not change with time
- The adsorption properties of the gas (α) do not change with time
- This give stable measurements that do not drift with time
- The analyzers can be field validated and calibrated against a gas cylinder to provide confidence in the measurement and comply with customer requirements

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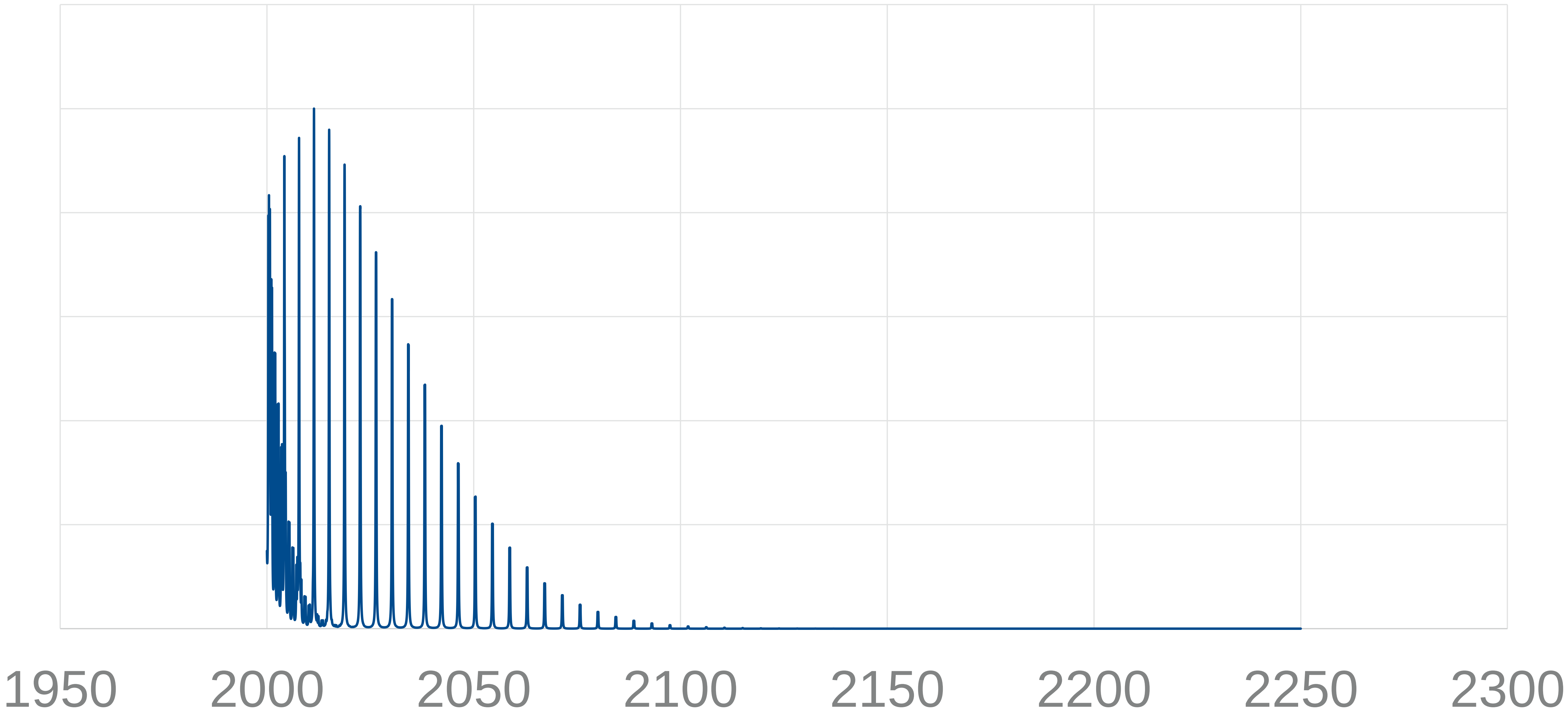
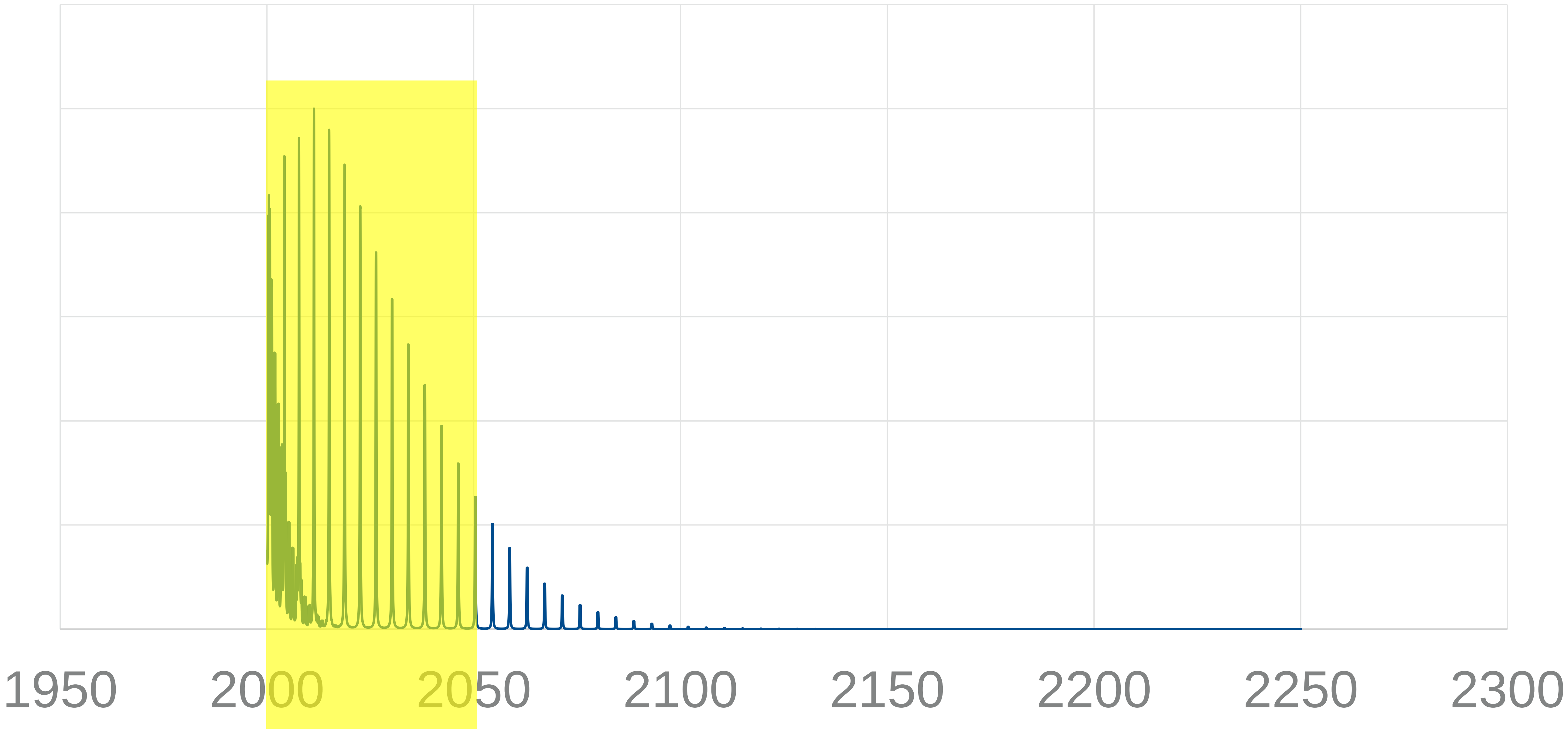
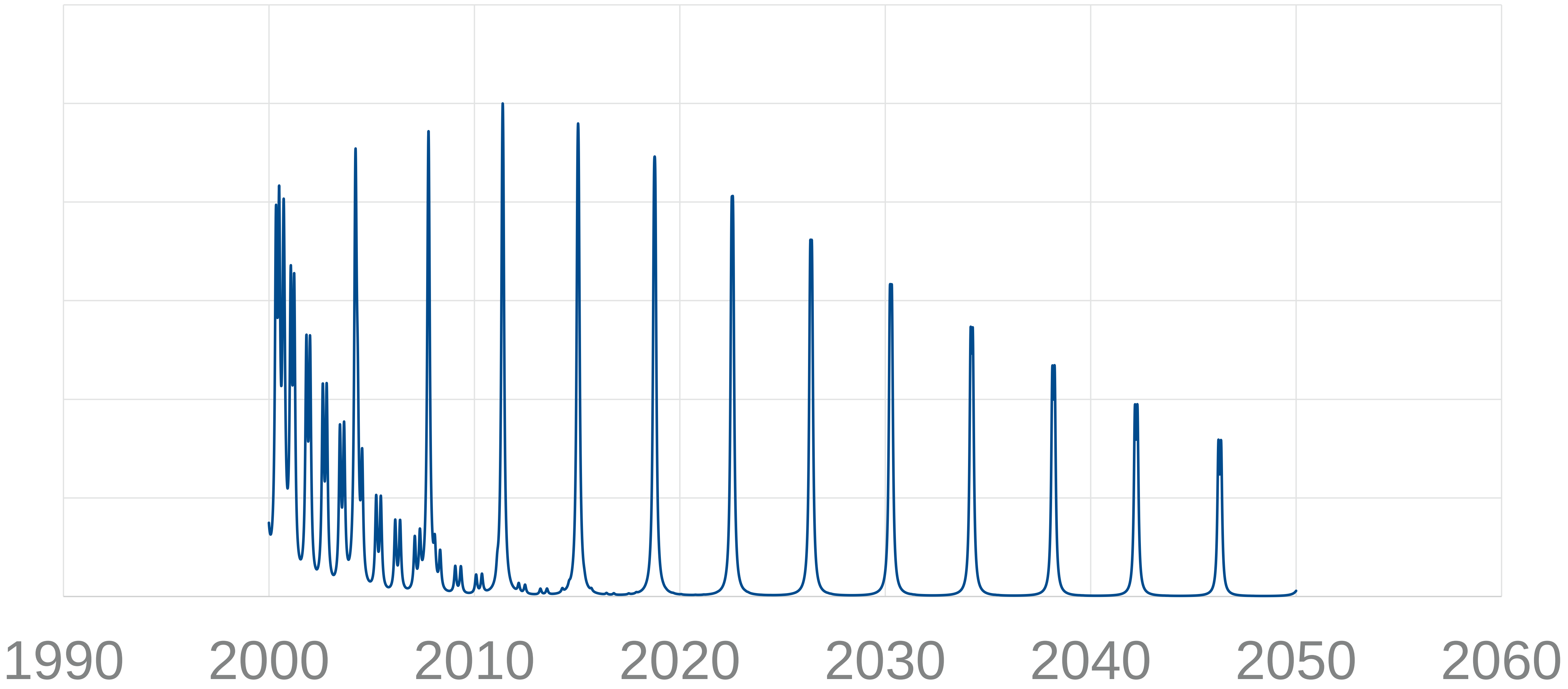
NO Full Spectrum



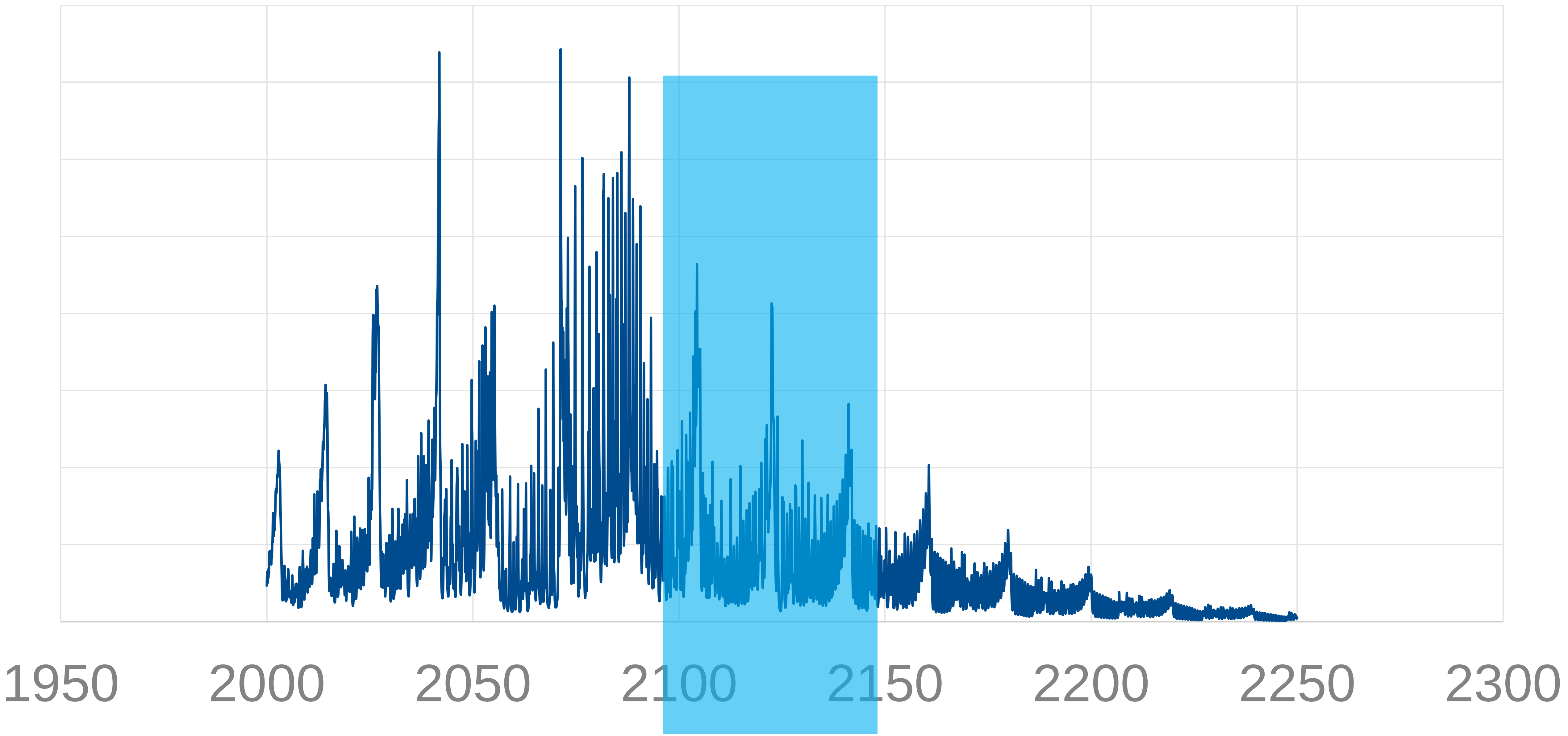
NO Full Spectrum



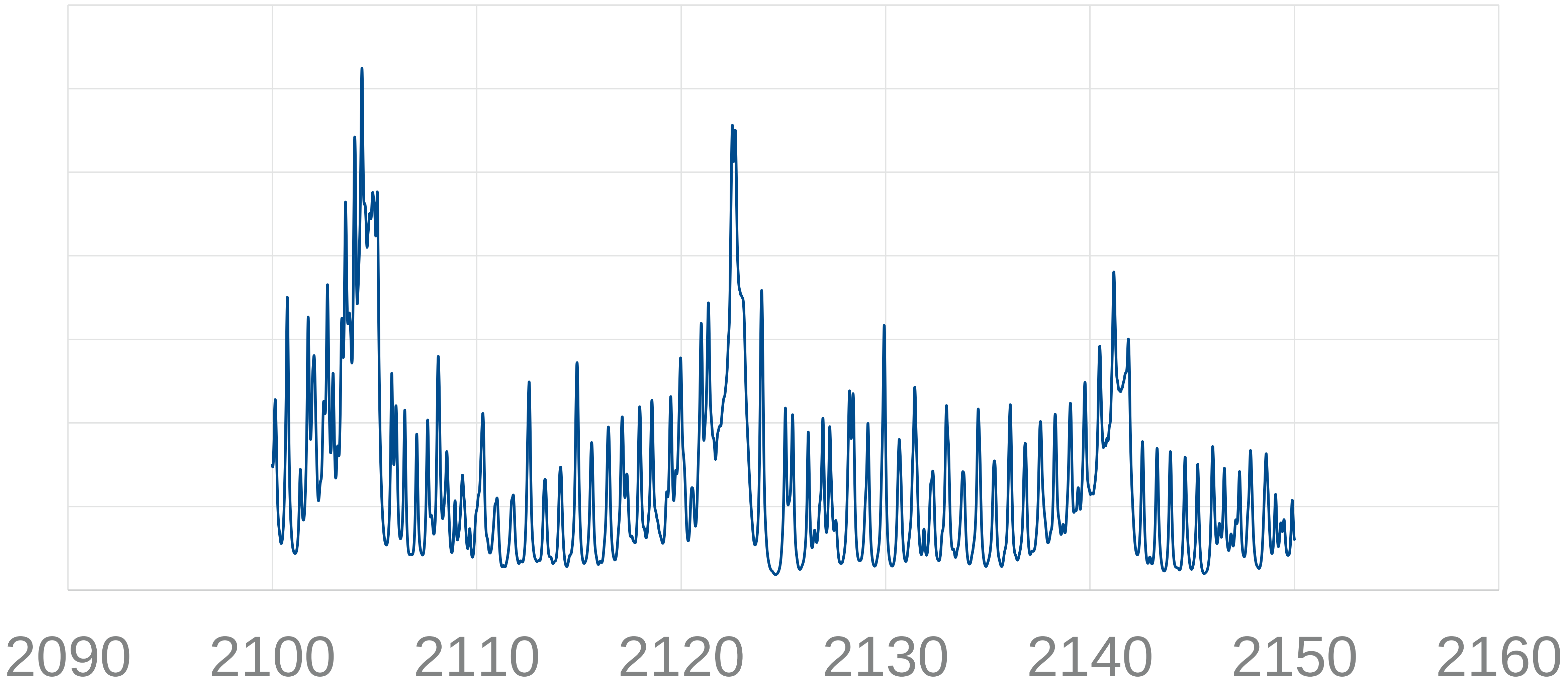
NO Snip



NO2 Full Spectrum



NO2 Snip



QX1000 Gas Specification Ranges

Gas*	Min. LOD	Min. Range	Max. Range
NO	0.3 ppm	0 – 45 ppm	0 – 2200 ppm (LOD 2.5ppm)
NO_2	0.15 ppm	0 – 20 ppm	0 – 500 ppm (LOD 0.5 ppm)
CO	0.1 ppm	0 – 15 ppm	0 – 4500 ppm (LOD 5 ppm)
CO_2	0.01%	0 – 1.5 %	0 – 100 % (LOD 0.1%)
SO_2	0.3 ppm	0 – 45 ppm	0 – 1100 ppm (LOD 1.5 ppm)
O_2	0.05 %	0 – 25 %	0 – 25 % (LOD 0.05%)

Sample System Suggestions for QX1000 Conversion

- Heat sample line from takeoff to the chiller inlet above dewpoint.
- Install a pressure gauge right after the sample chiller and maintain pressure 7-10 PSIG.
- Atmospheric vent nearby, analyzer has internal pressure sensor in the cell that should be 760 Torr or less, if no significant back pressure is present.
- User rotameter to ensure flow rate max 2.1 SCFH.
- Sample chiller at 4C with moisture indicator (ensures moisture is less than 9000 ppm).
- Swagelok SST 7-micron filter or equivalent.
- Scrubber needed if acid gas or ammonia are present.

Contacts

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Thank You!