Avancées technologiques dans la surveillance en continue de substances toxiques à l’état de traces dans l'air par FTIR

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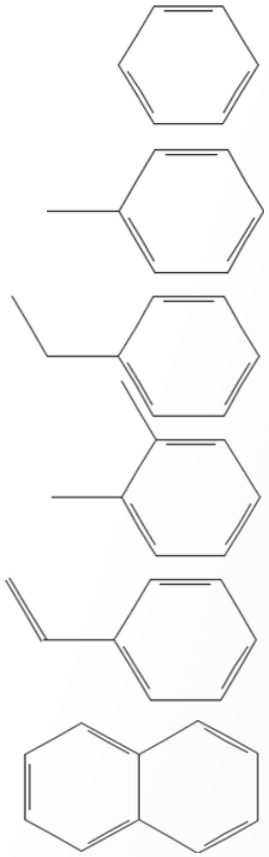
Cas d'application:

Monitoring BTEXSN en air ambiant



Benzene

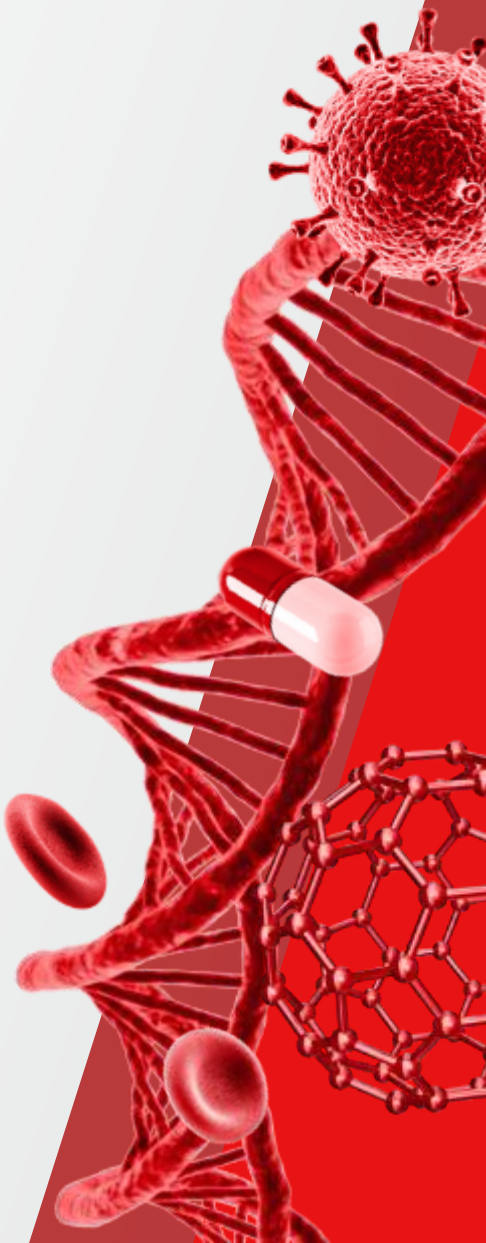
Toluene

Ethylbenzene

Xylenes

Styrene

Naphthalene



MAX-iR FTIR Gas Analyzer

June 27th 2023

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CONTEXT

Environmental application

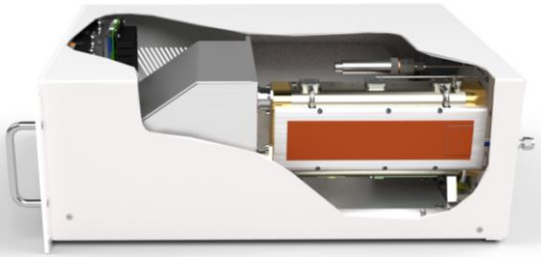
- Petroleum refineries and chemical processing companies can have hundreds of compounds present on their site and a release of any of these compounds at levels exceeding OSHA's exposure limits could harm plant personnel and residents downwind of the facility
- Only few technologies can simultaneously measure and speciate hundreds of gases in real-time at the levels required to protect the health
- Continuous monitoring approach is necessary to immediately respond to a chemical release and prevent community exposure.
- Recent innovations in data analysis algorithms and a novel approach to zeroing spectral interferences, brings FTIR at the sensitivity and specificity to measure air toxics simultaneously at trace levels (ppb) -> **ambient air monitoring and fire effluents determination applications**

Solution

MAX-iR™

FTIR GAS ANALYZER

Max Analytical Technologies, USA

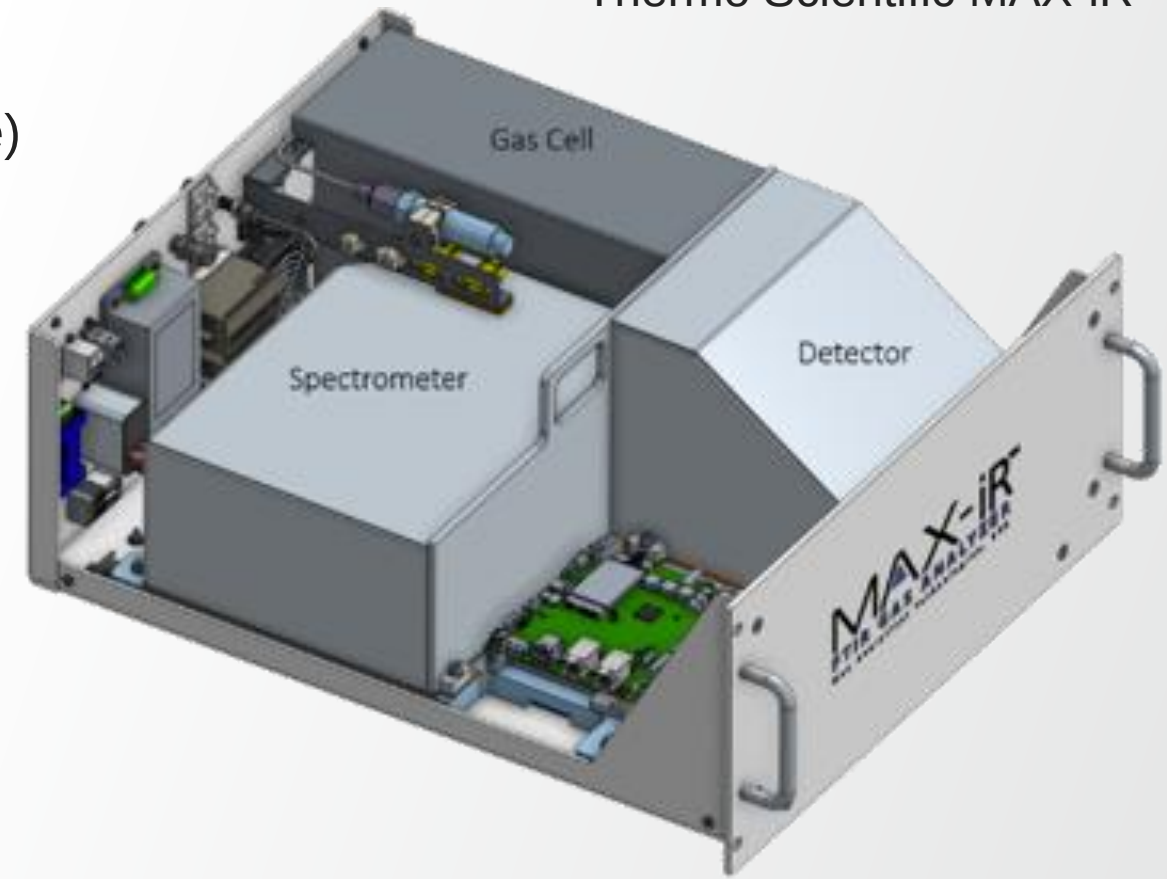


MAX-iR™ FTIR Gas Analyzer

Features and Benefits

- Quantitative spectral library — never calibrate!
- Real time gas analysis (1Hz)
- 1-32cm^{-1} resolution spectrometer (20+ year lifetime)
- 10m high throughput multi-pass gas cell (0,5l)
- VCSEL diode (10-year lifetime)
- SiC IR source (10-year lifetime)
- Single crystal ZnSe beamsplitter
  - Thermal stability
  - Non-hydroscopic (no purge required)
- DTGS detector
  - No LN_2 required
  - Full mid-IR spectral range (500-5000cm^{-1})
- Precision temperature and pressure sensors
- 5U - 19-inch standard rack

Thermo Scientific MAX-iR



Designed for field use

Feasibility Study N°01:

BTEXSN

- **Measurement in Humid, Ambient air**

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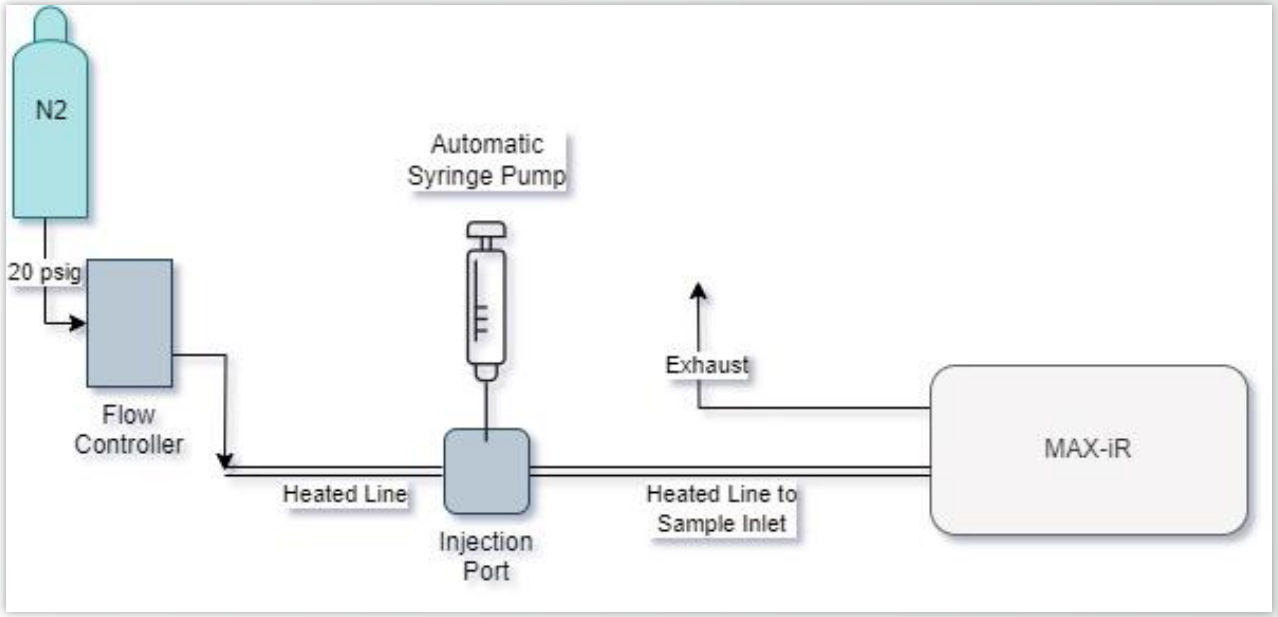
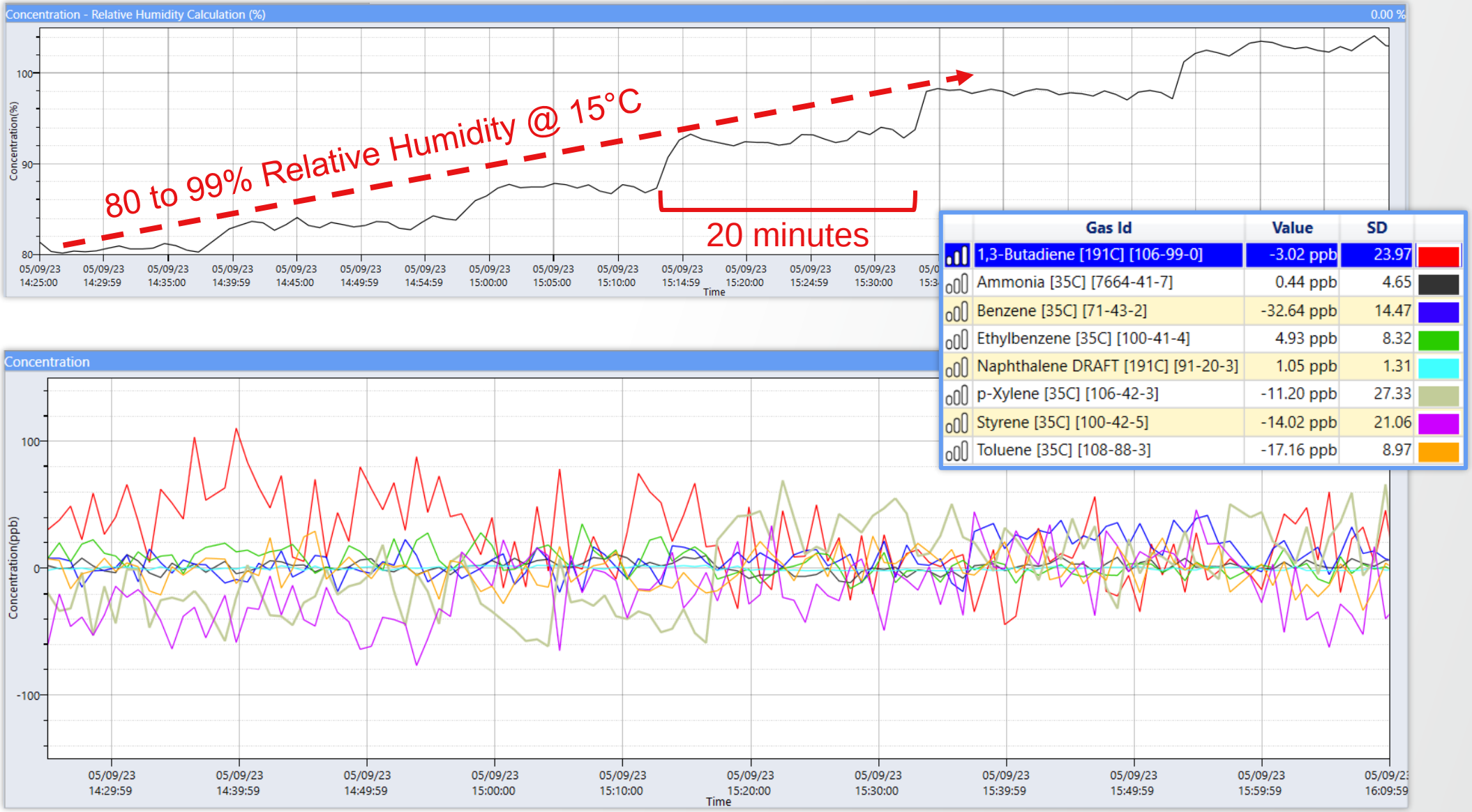
BTEXSN Measurement in Humid, Ambient Air

Feasibility Study (East Windsor, CT / USA)

- Lab testing of the MAX-iR's BTEXSN measurement in a controlled environment
- Sample gas: humidified nitrogen, **80-99% Relative Humidity (RH)**
  - Injected and vaporized distilled water into a heated line
  - Diluted the vapors in UHP nitrogen to control the RH% levels
- Test conditions: analyzed the sample at 5 different levels ranging from 80-99% RH
  - Measured each level in 20-minute intervals
  - Collected one data point every 60 sec
- FTIR analysis: quantifying the requested VOCs
  - Water calibration in the quant method
  - Sample interference spectra are collected to reduce biases due to water, CH4, and CO2
- Goal: estimate the detection limits (DL) and measurement bias of the target chemicals



80-99% RH vs. Measurement Bias on a MAX-iR

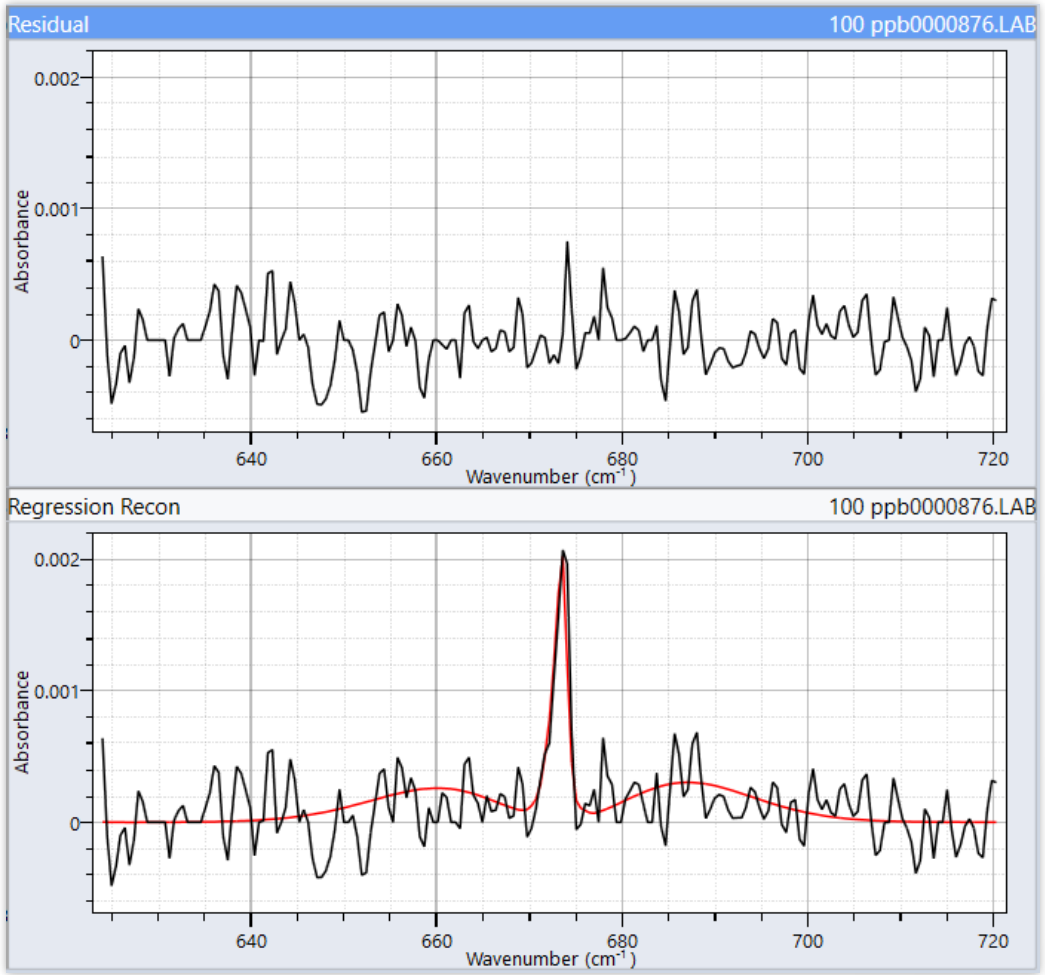


Feasibility Study N°02:

- **100ppb of Benzene diluted in UHP Nitrogen**

100ppb of Benzene Diluted in UHP Nitrogen (Video)

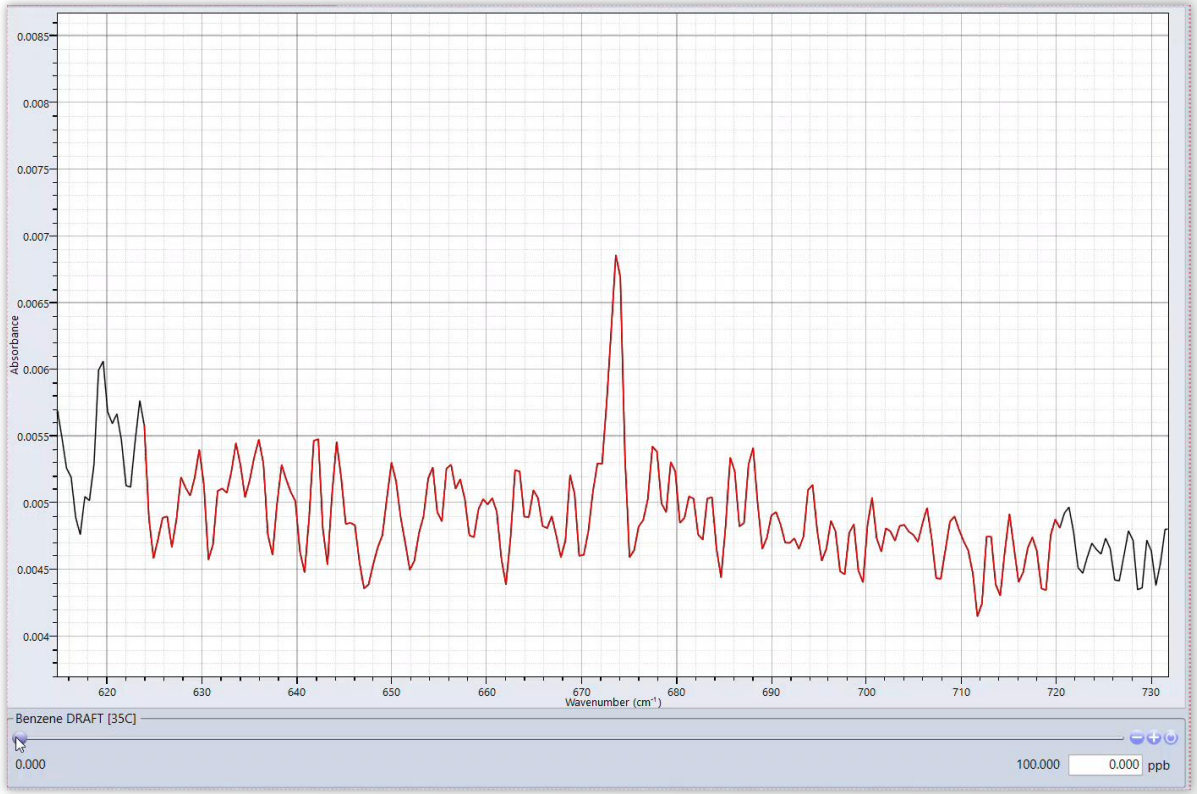
Residual vs. Regression Reconstruction



Ref spectrum (calib curve)

Measured spectrum

Video: 100ppb down to 60ppb (DL) of Benzene



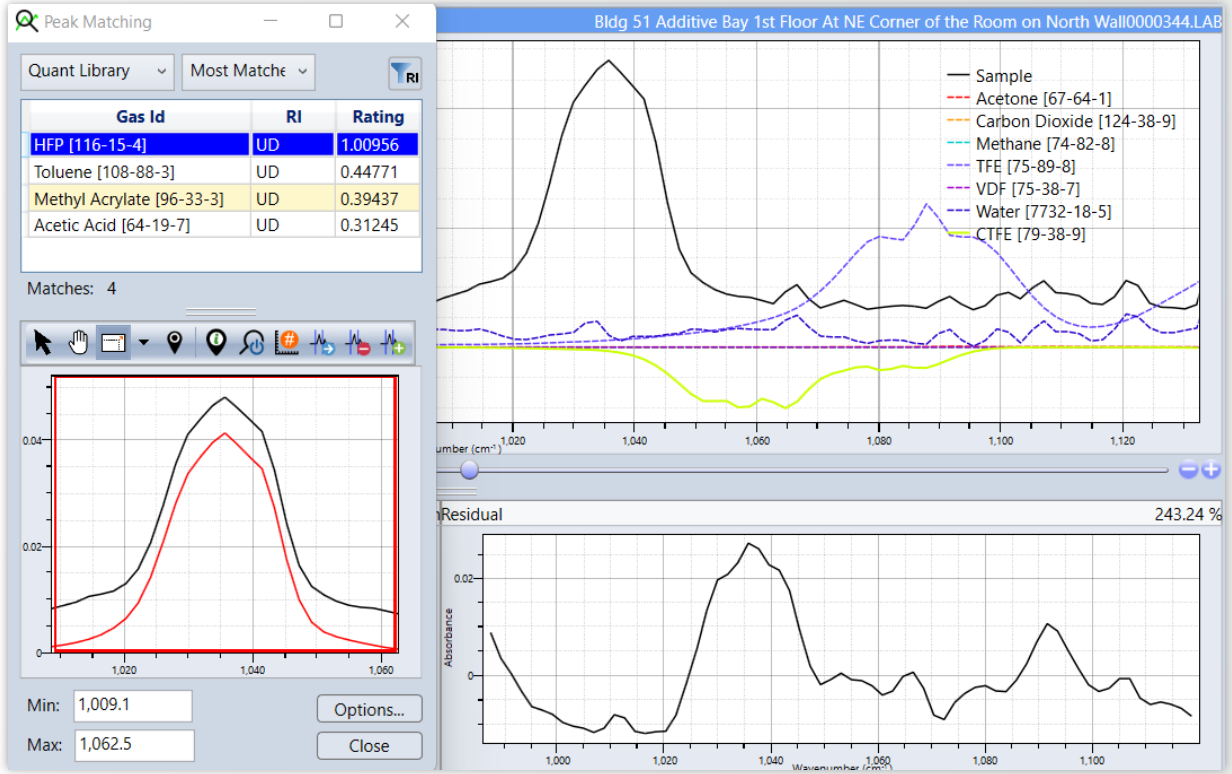
60ppb is detectable above the detector noise!

MAX Analytical Peak Matching Tool

Identify unknown compounds on the fly

- **When to use**? An unknown absorbance appears in the sample spectrum
- Search from the compounds in the quant library or the NIST and EPA database
- Ranked based on fit of the calibration spectrum to the sample

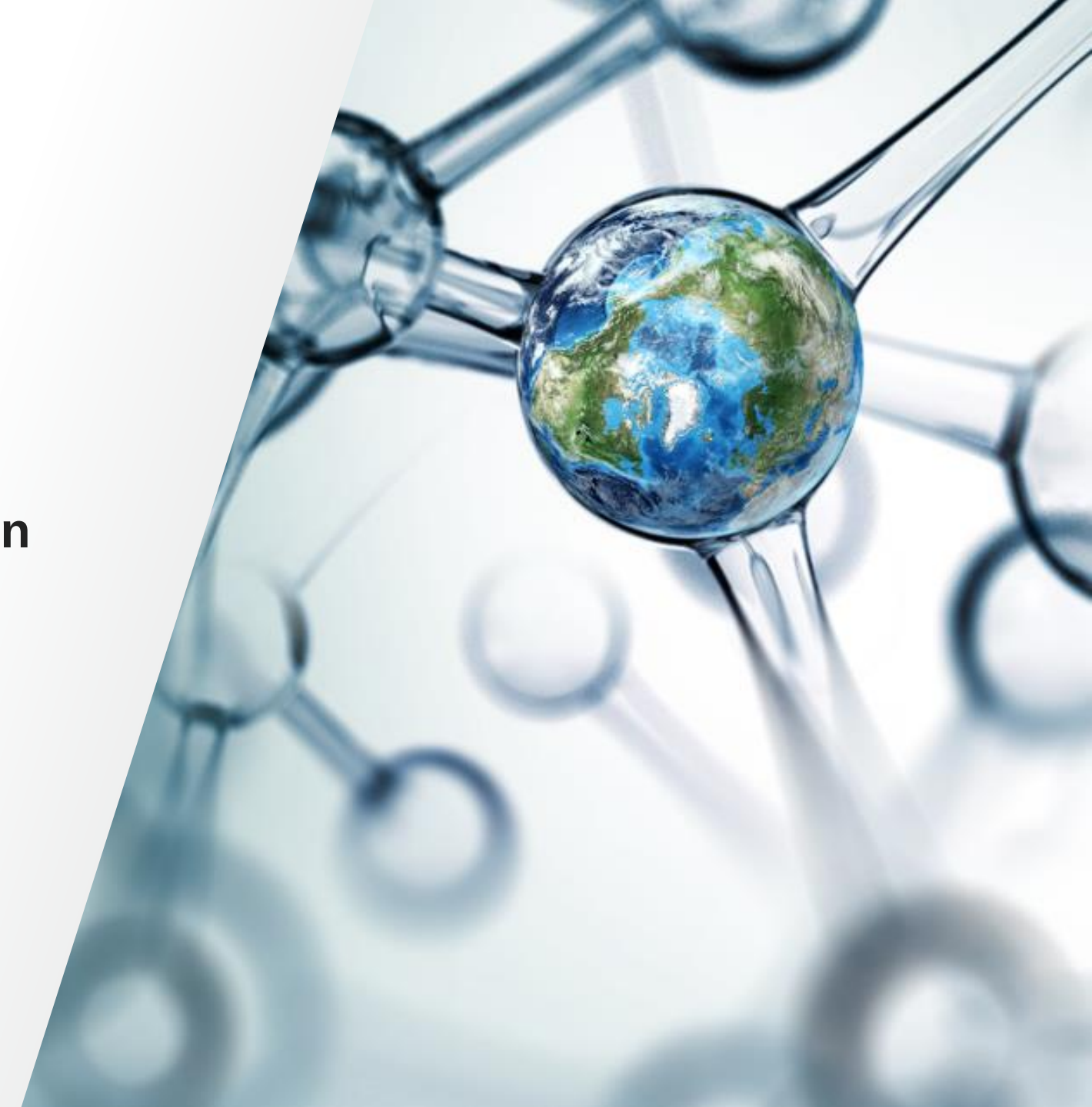
- FTIR spectra can be reprocessed to identify unknown compounds because each chemical as a unique molecular structure
  - **Perfect for the industrial accident application**



Users can rapidly optimize their methods if the sample matrix changes.

Feasibility Study N°03:

- **Spiked Benzene and impacts on other compounds?**



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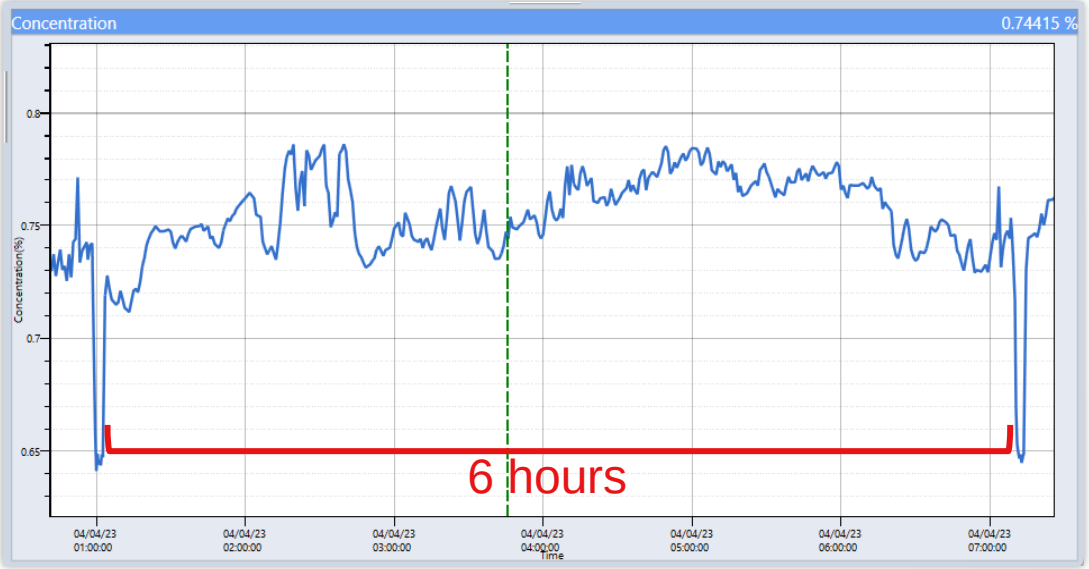
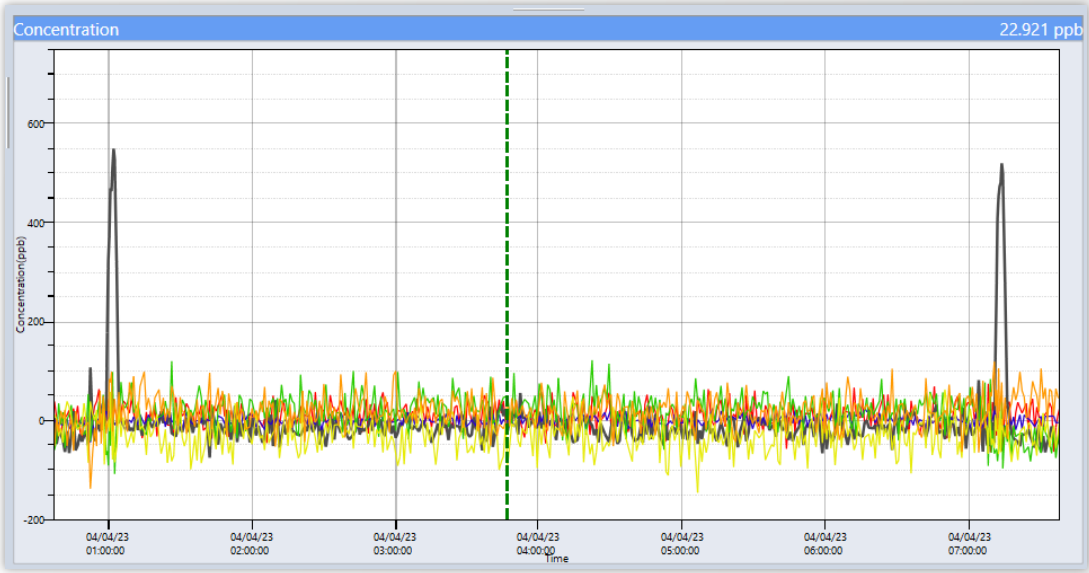
MAX-iR Ambient VOC Monitoring

Outdoor BTEX Monitoring

- Sampling outdoor, ambient air
  - Water content ranges from **11-82% Relative Humidity (RH)**
  - Unheated sampling line
- Analyzed at 1.0 cm-1 resolution with a DTGS detector at 35°C
- 500 ppb of benzene were spiked into the native stream every 6 hours

Gas Id	Value	SD
1,3-Butadiene [191C] [106-99-0]	-0.66 ppb	21.00
Benzene [35C] [71-43-2]	23.41 ppb	23.12
Ethylbenzene [35C] [100-41-4]	-4.03 ppb	8.22
p-Xylene [191C] [106-42-3]	45.25 ppb	29.24
Styrene [35C] [100-42-5]	-12.02 ppb	30.70
Toluene [35C] [108-88-3]	-3.69 ppb	32.96
Water % [35C] [7732-18-5]	0.74415 %	0.00669



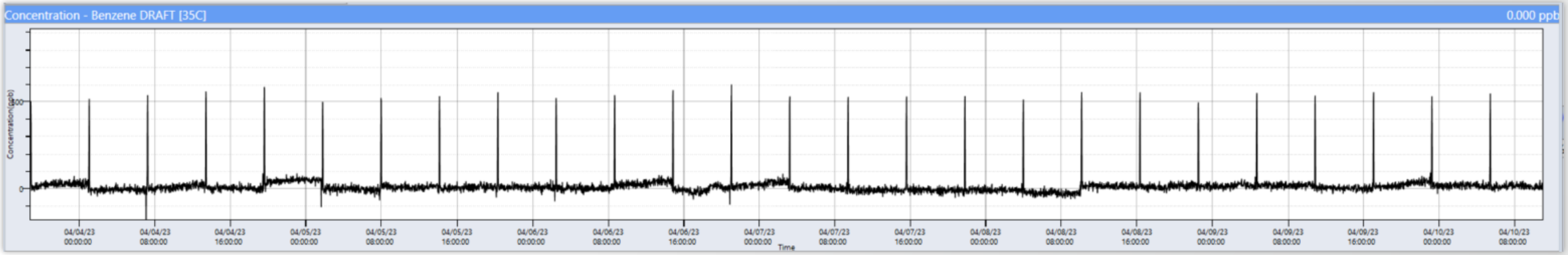


MAX-iR Ambient VOC Monitoring

7-Day Benzene Calibration Drift and Spike Recovery Study

Spike #	Benzene Native (ppb)	Benzene Spike (ppb)	Dilution Factor (As CO2)	% Recovery
1	4	498	0.12	86%
2	-11	517	0.15	77%
3	14	517	0.15	70%
4	17	544	0.14	81%
5	23	577	0.15	78%
6	-9	491	0.13	86%
7	6	498	0.13	84%
8	-12	509	0.15	77%
9	-12	547	0.11	109%
10	-5	496	0.12	89%
11	17	521	0.13	81%
12	-11	560	0.14	89%
13	8	565	0.14	86%
14	-10	524	0.12	95%

Spike #	Benzene Native (ppb)	Benzene Spike (ppb)	Dilution Factor (As CO2)	% Recovery
15	-14	524	0.13	93%
16	16	525	0.13	84%
17	-22	520	0.13	96%
18	-12	499	0.12	96%
19	11	528	0.12	92%
20	11	523	0.12	88%
21	21	496	0.14	72%
22	0	538	0.12	100%
23	-1	535	0.12	99%
24	-1	549	0.12	98%
25	0	517	0.12	93%
26	21	519	0.13	82%
Average	**2**	**524**	**0.13**	**88%**
Spike RSD	**4.65%**			



Detection Limit (DL) Assessments on a MAX-iR (*)

All DL's estimated with a 60 sec scan rate in outdoor, ambient air

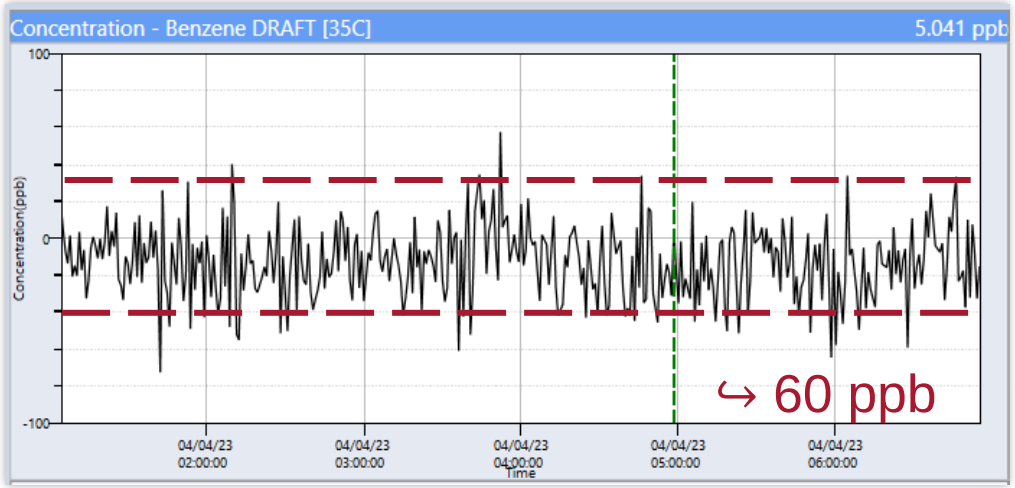
Gas	CAS #	Minimum Detection Limit (ppb)
1,3-Butadiene	106-99-0	73
Acetic acid	64-19-7	18
Ammonia	7664-41-7	25
Benzene	71-43-2	63
Butane	106-97-8	31
Carbon dioxide	124-38-9	12
Carbon monoxide	630-08-0	70
Ethylbenzene	100-41-4	36
Ethylene oxide	75-21-8	26

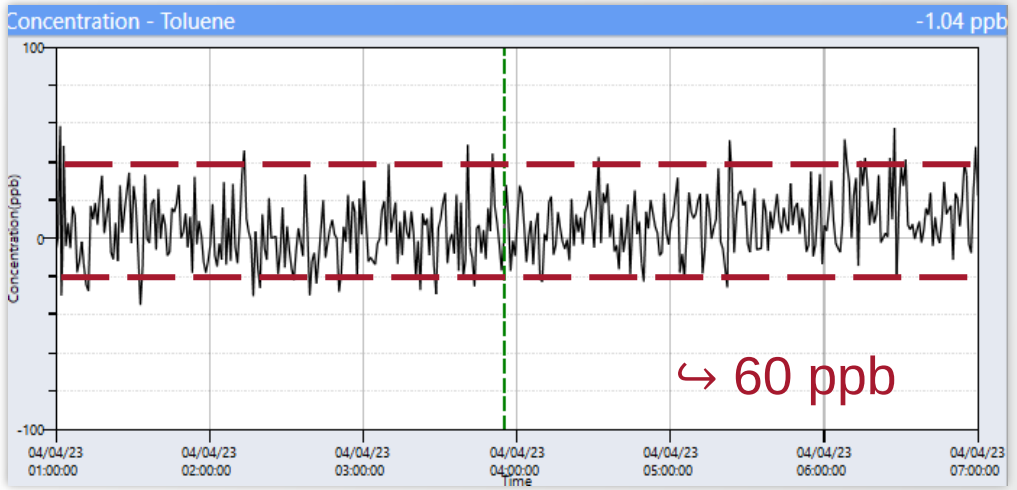
Gas	CAS #	Minimum Detection Limit (ppb)
Hydrogen bromide	10035-10-6	111
Hydrogen chloride	7647-01-0	28
Methanethiol	74-93-1	185
Methyl acrylate	96-33-3	15
Naphthalene	91-20-3	6
Nitric oxide	10102-43-9	80
Nitrogen dioxide	10102-44-0	132
Styrene	100-42-5	89
Toluene	108-88-3	71

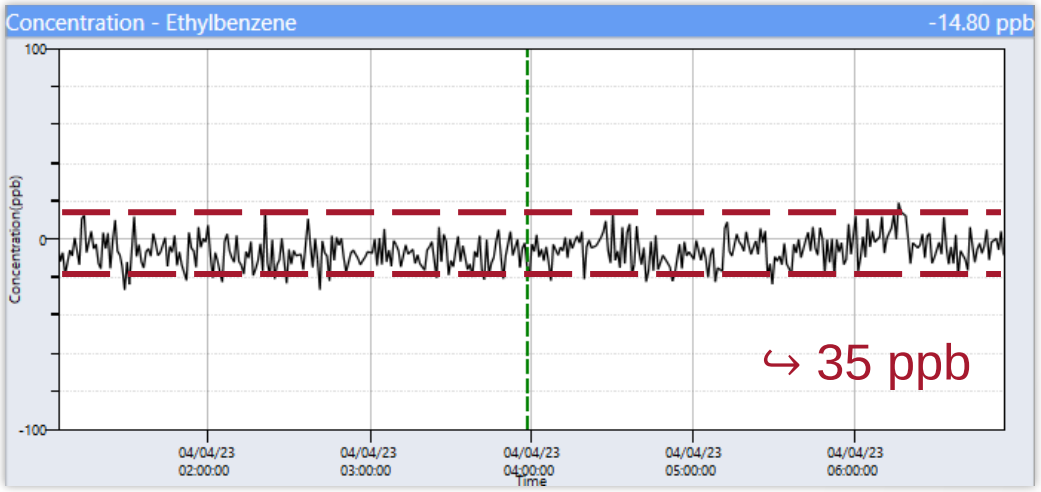
(*) **Detection Limit (DL)** is defined as 3 times the Standard Deviation (σ) for 12 consecutive measurements in high purity N2 (zero gas)

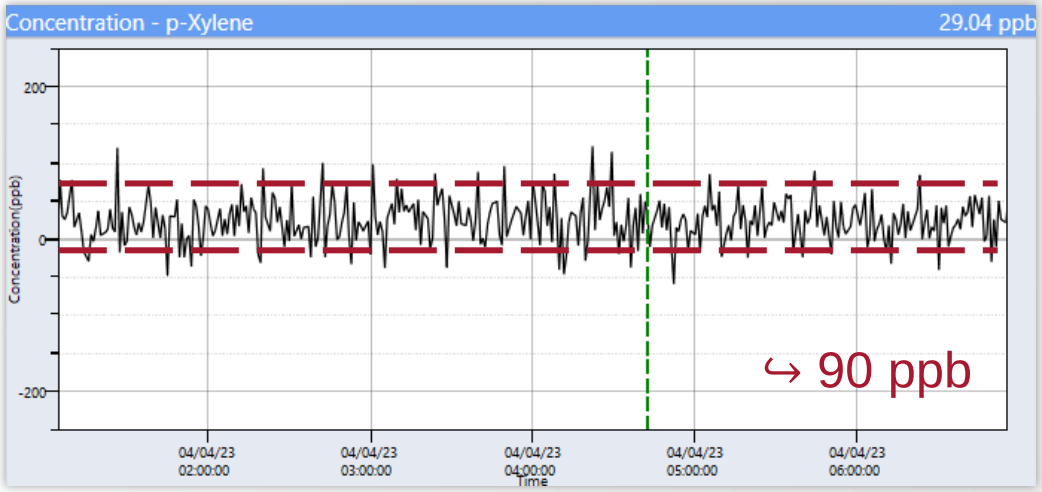
MAX-iR Ambient VOC Monitoring

BTEX Detection Limits: **Benzene** / **Toluene** / **Ethylbenzene** and **p-Xylene**





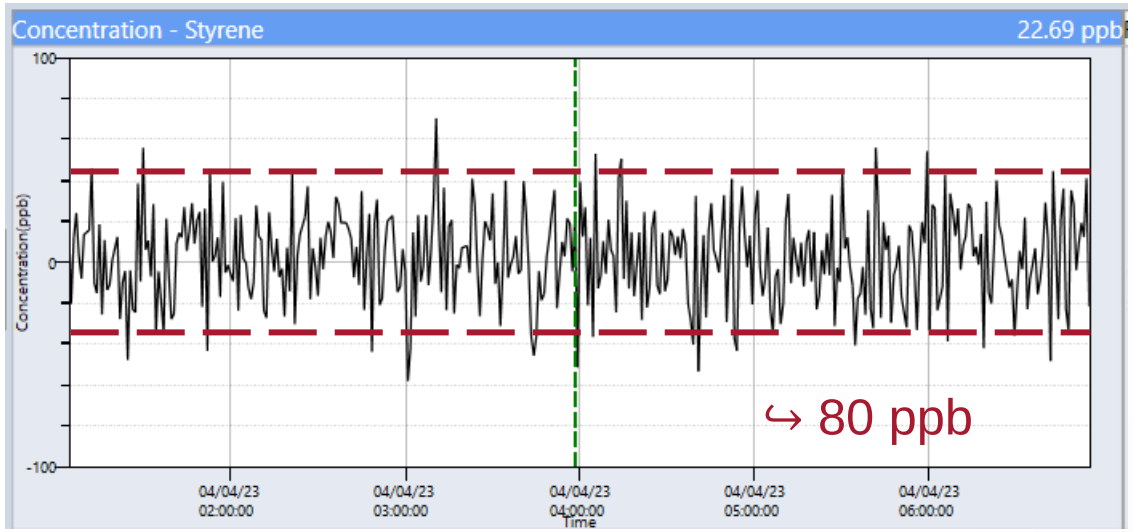


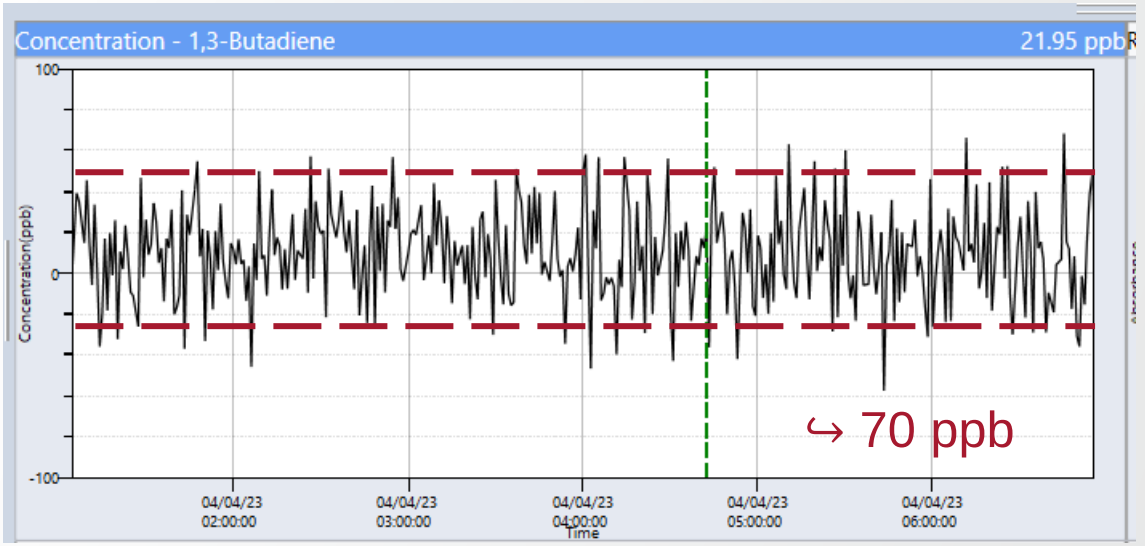


Actual MAX-iR Minimum DL (Scaled to Fit) =

MAX-iR Ambient VOC Monitoring

Detection Limits: **Styrene** and **1,3 - Butadiene**





Actual MAX-iR Minimum DL (Scaled to Fit) =

Conclusions of the feasibility studies:

Feasibility study N°01

- Ambient level humidity has no impact on gaseous species measurement with MAX-iR

Feasibility study N°02

- Benzene: perfect match between quant library Vs 100ppb in the sample stream

Feasibility study N°03

- Spiked Benzene (500 ppb) has shown no impacts on other gaseous compounds

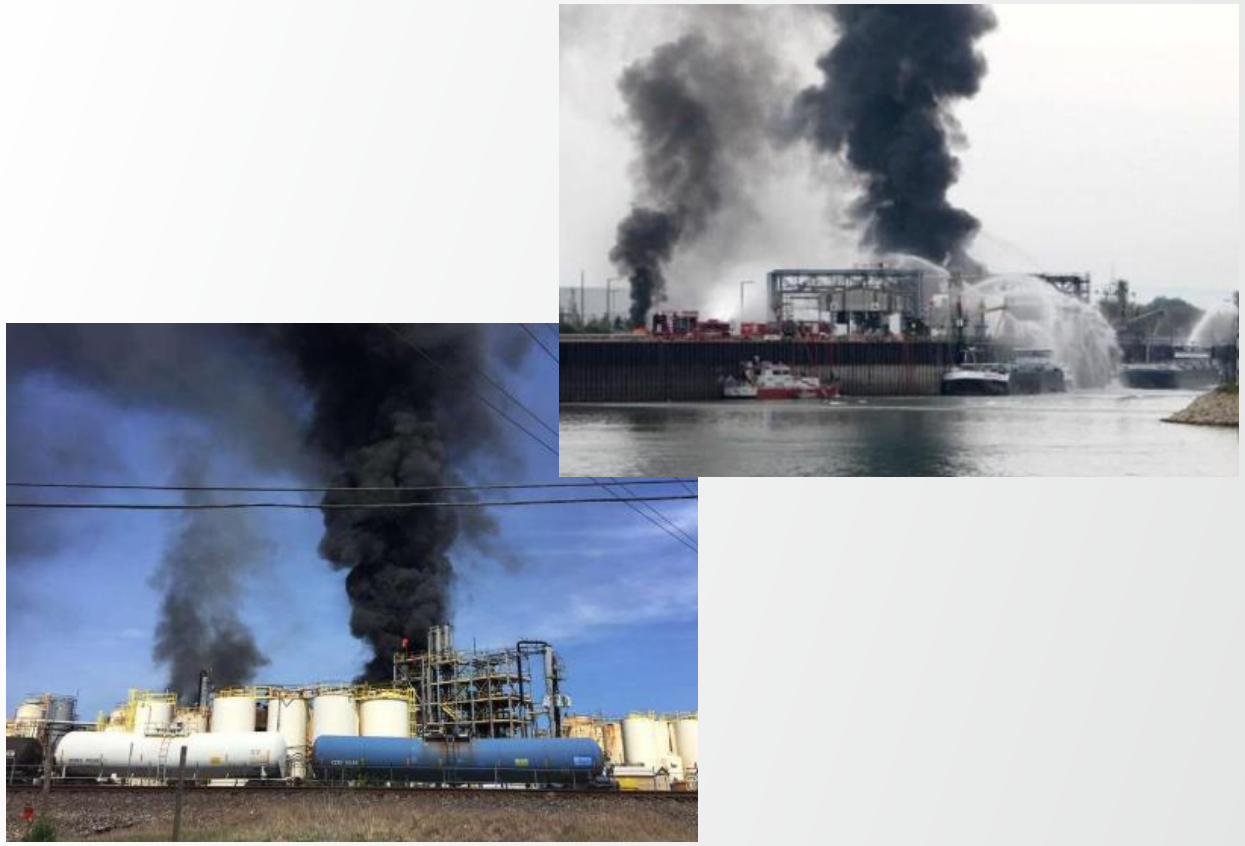
Test	Measure	Criteria	Result
7-Day Spike Recovery	% Recovery	80-120%	88%
7-Day Repeatability	RSD	< 5%	4.65%
Limit of Detection (Benzene)	3σ	-	63ppb

Main advantages of OE-FTIR on Industrial accidents:

- **Ability to measure and speciate many compounds simultaneously and in real-time!**

- **Ability to validate + reprocess the data**
  1. Visually with the reconstruction
  2. Statistically with R2

- **No cross-interference to moisture**



Market Experience and Applications

Industrial Gas / Semiconductor

ASU bulk gas certification (N_2, Ar, He, O_2)
Beverage grade CO_2 Certification
Hydrogen purity
Semiconductor specialty gas analysis
Semiconductor abatement efficiency

Environmental

Ambient air monitoring – HAPs / VOCs / GHG
Ethylene oxide continuous emissions monitoring
Source testing (US EPA Method 320)
Other CEM Applications (NO_x, NH_3)
Formaldehyde emissions testing (YYYY)

Industrial Hygiene and Safety

HAPs, fluorinated VOCs air monitoring
Ethylene oxide air monitoring (Sterilization)
Phosgene air monitoring

Industrial Process

Acid fluoride process monitoring
Acetylene impurity in bulk ethylene
Propyne impurity in bulk propylene
Methane, ethylene, CO impurities in bulk ethane

Informations related to MAX-iR

Application notes & Webinars:

FTIR Gas Analysis | MAX-iR FTIR Gas Analyzer | Thermo Fisher Scientific - FR

GAS System Products Line Offerings

MAX-IR	MAX-iAQ	MAX-EMS-10	MAX-Bev	MAX-ATS
Multiple use e.g. Bulk/purity gas	20 Channel Ambient Air	Source/Emission Monitoring	CO2 Monitoring	MAX-ATS Special Request

Questions?

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We take pride in our Mission

We enable our customers to make the world healthier, cleaner and safer

Merci

MAX-iR Application notes & Webinars:

FTIR Gas Analysis | MAX-iR FTIR Gas Analyzer | Thermo Fisher Scientific - FR

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