Frédéric Despagne (ABB, Bordeaux, France) & Troy Francisco (Chemours, Wilmington, USA)– GCC 2015

Real-Time Detection of Toxic Chemicals in Ambient Air Using FT-IR Analyzers

www.abb.com/analytical
For more information contact ftir@ca.abb.com

Chemours™

Power and productivity
for a better world™

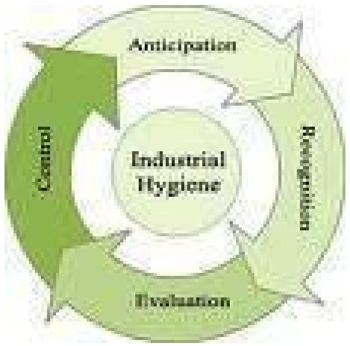
ABB

Outline

- Toxic Chemicals Detection - Background
- FT-IR Spectroscopy
  - Principle
  - Analyzer Components
  - Example Setup for Multi-Stream Gas Application
  - Key User Benefits for Toxic Leak Detection
- Example 1: Toxic Leak Detection in Chemical Plant
- Example 2: Toxic Leak Detection in Nickel Plant
- Example 3: PFIB Fugitive Leak Detection
- Conclusions

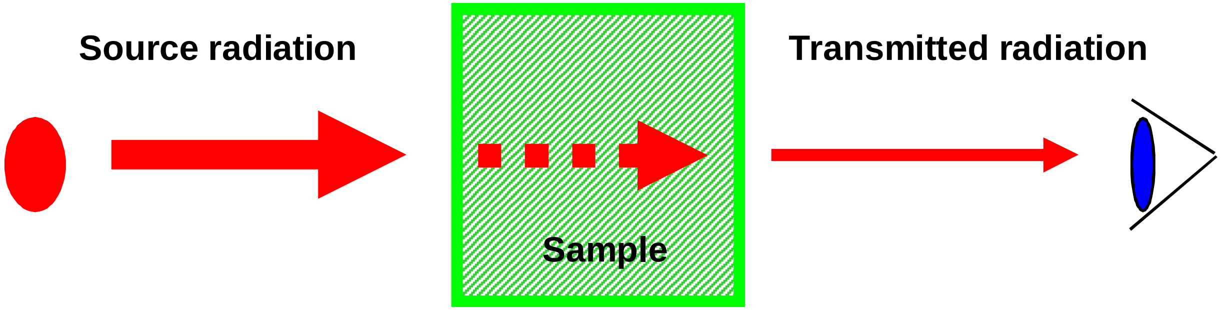
Toxic Chemicals Detection - Background

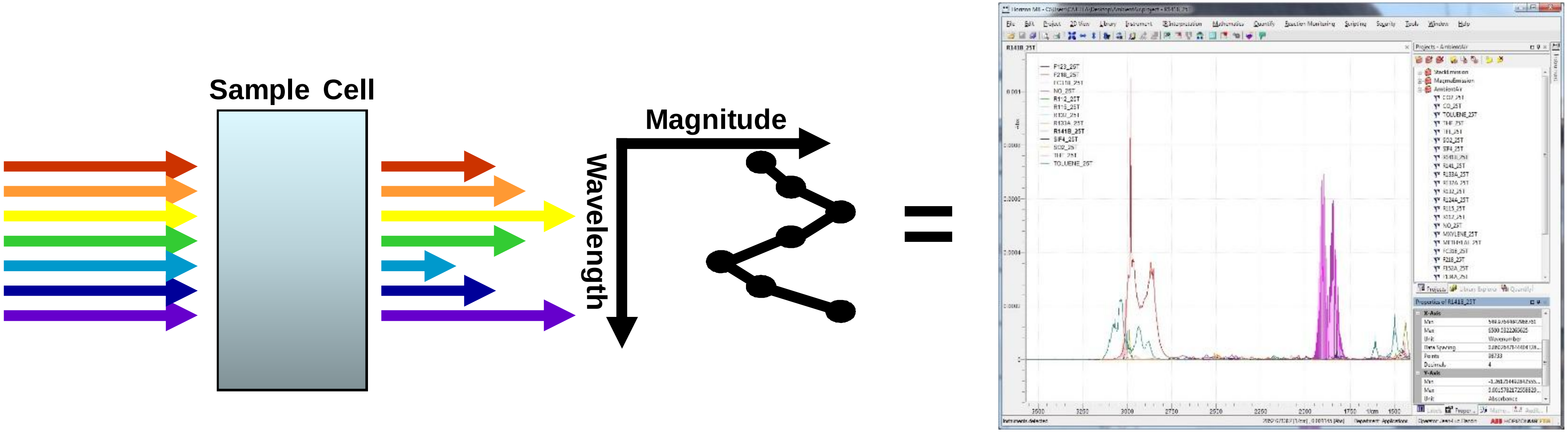
- Real-time detection of potentially harmful vapors in chemical plants is a key aspect of site personnel protection and plant safety.
- Throughout process industries, the evolution of ambient air monitoring technology is gradually shifting from photometric and chemiluminescent technologies to more advanced optical techniques such as Fourier-Transform InfraRed (FT-IR) instrumentation.
- FT-IR proves to be an attractive solution for multi-stream ambient air monitoring as it combines the key features of an efficient sensor for process safety and compliance:
  - Sensitivity (down to sub-ppb levels in some cases).
  - High up-time (no maintenance required for > 3 years).
  - No false positives.
  - Robustness with respect to interferences, chemical deactivation or poisoning.
  - Cost effectiveness (possibility to do multi-point measurement with single instrument).



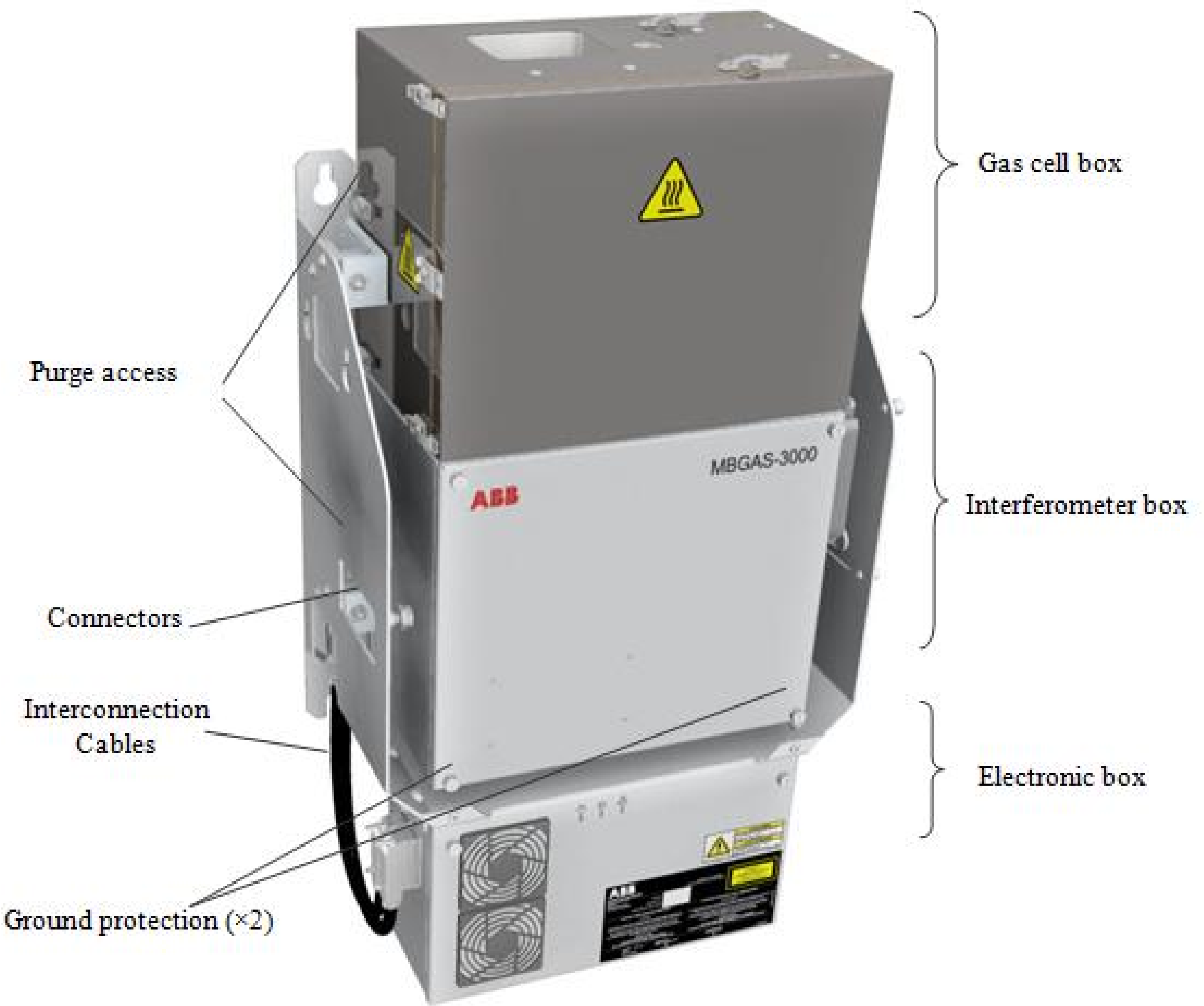
FT-IR Spectroscopy - Principle

- FT-IR technique is based on the absorption/reflection at different wavelengths of an infrared beam by a gas sample.
- The resulting signal pattern collected on the analyzer (spectrometer) constitutes the typical fingerprint of the gas sample.
- The analysis of the absorption peaks specific to the different analytes contained in the sample enables qualitative and quantitative analysis.

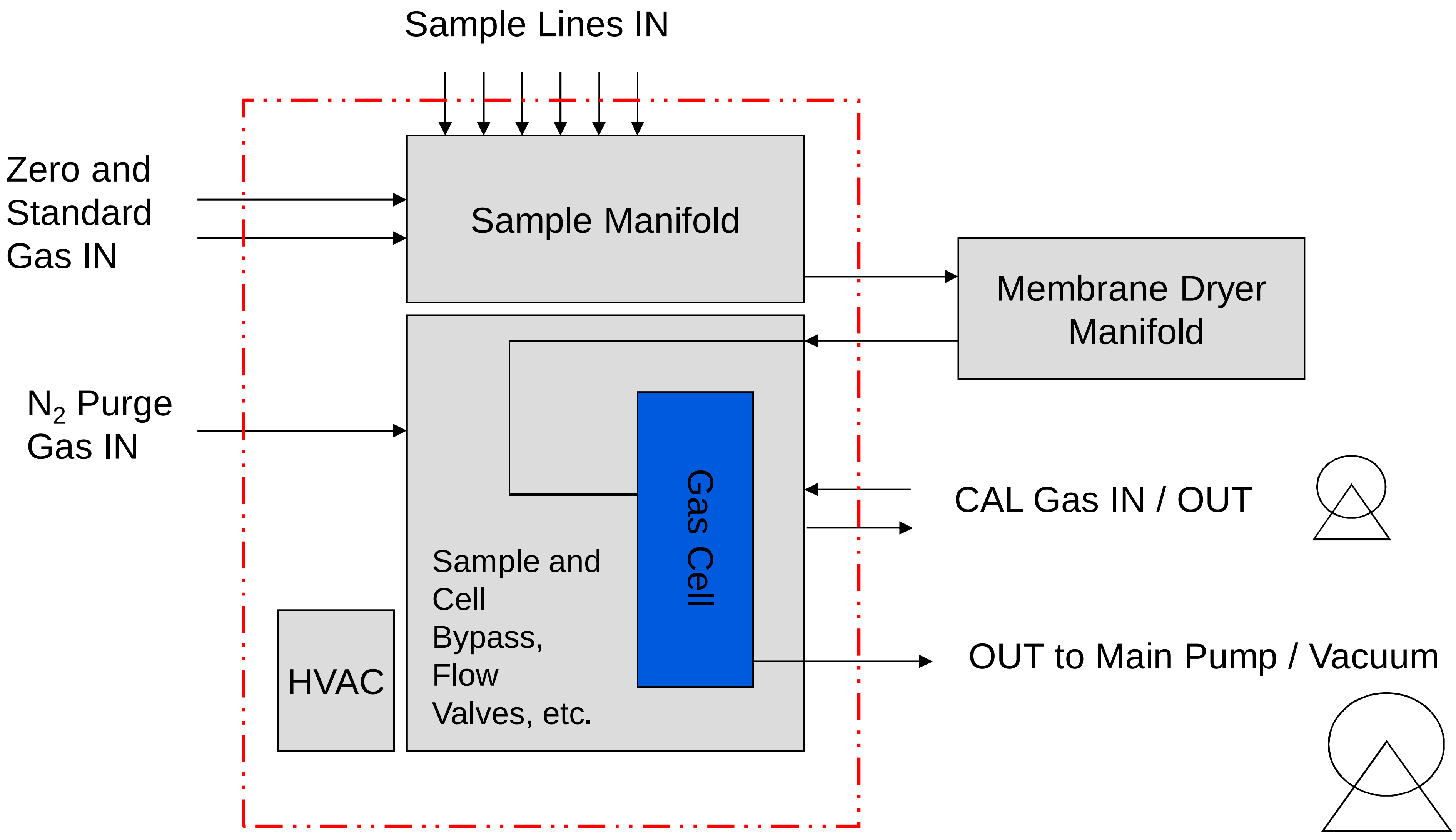




FT-IR Spectroscopy - Analyzer Components

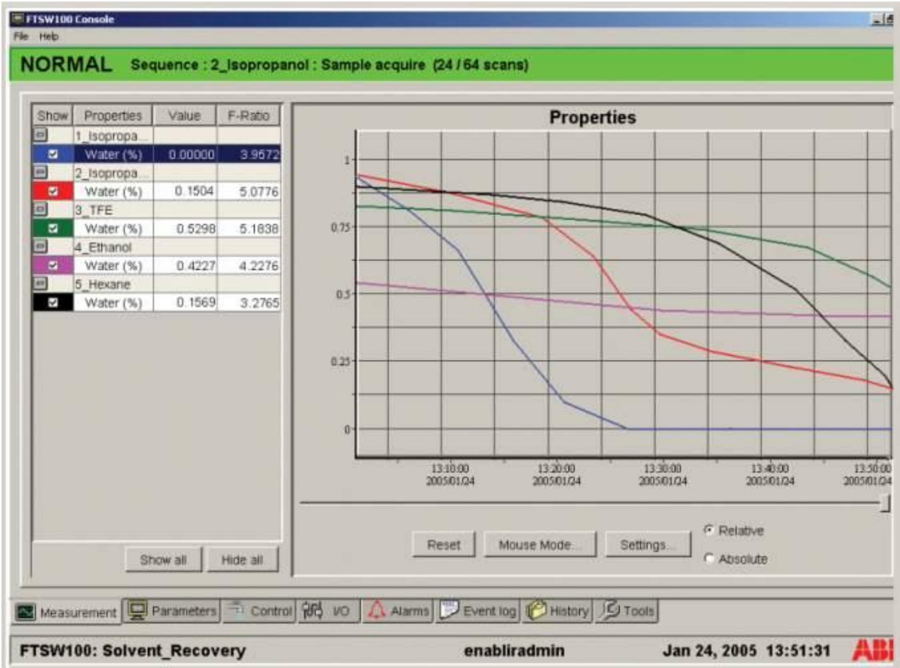


FT-IR Spectroscopy – Example Setup for Multi-Stream Gas Application



FT-IR Spectroscopy - Key User Benefits for Toxic Leak Detection

- Possibility to perform fast multi-point detection.
- Confidence that changes on control chart are real.
- Effective diagnostic capability for early alert.
- Minimal maintenance costs.



www.abb.com/analytical
ftir@ca.abb.com

Example 1: Toxic Leak Detection in Chemical Plant

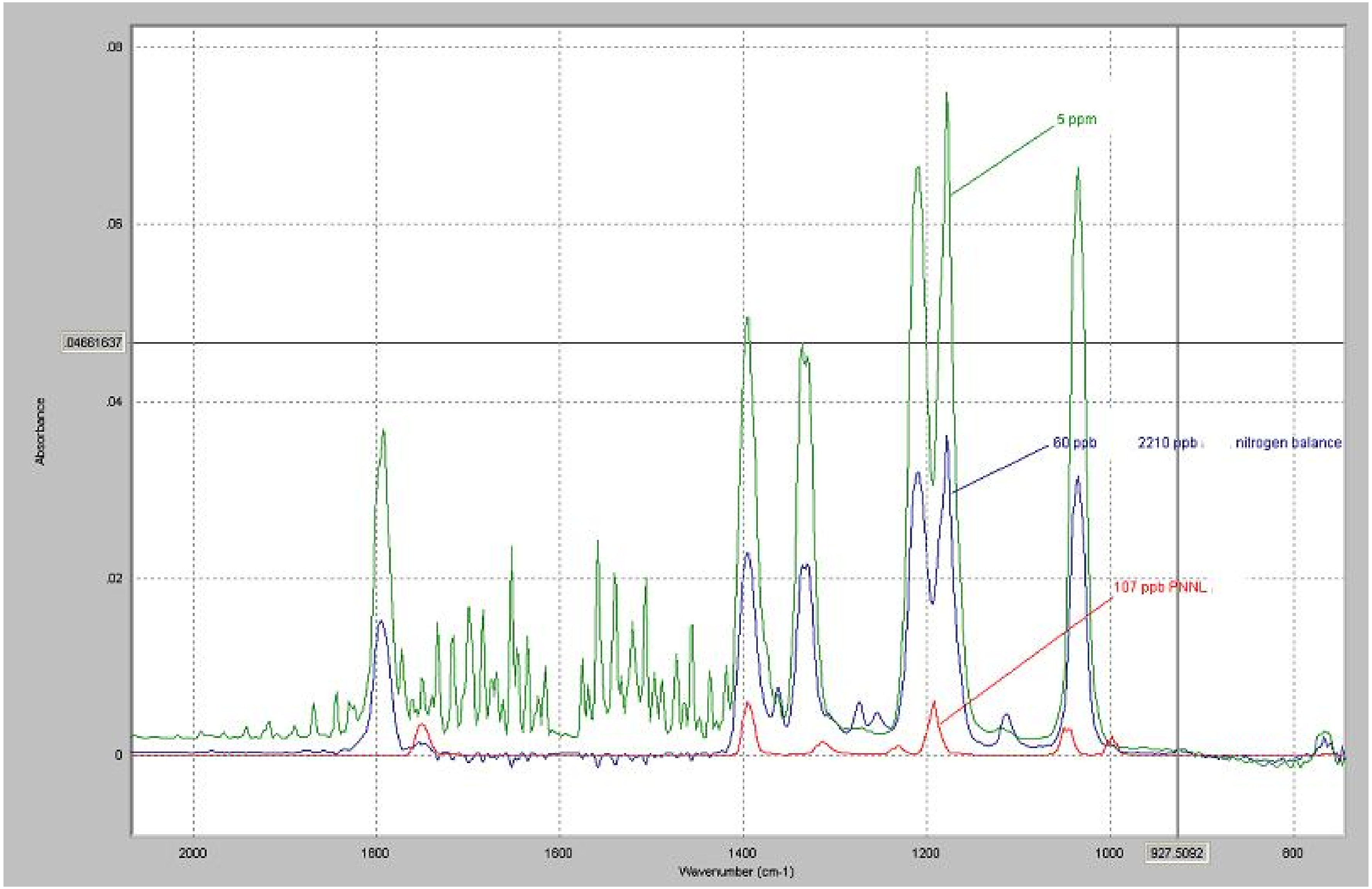
BACKGROUND

- Implementation of 40-stream ambient air ABB FT-IR analyzers with full redundancy in US specialty chemicals plant, as alternative to more costly and maintenance-intensive filter spectrometers.
- Objective: ppb-level detection of 2 toxic compounds (“P” and “H”) in the presence of interfering hydrofluorocarbons.
- All 40 points must be measured each hour → maximum acquisition time per channel is 90s.
- The two compounds have very different levels:
  - Compound P: 0-150 ppb.
  - Compound H: 0-5 ppm.
- Some streams contain only Compound P, some streams contain only Compound H, some streams contain both Compound P and Compound H.
  - The analyzers must be able to discriminate between Compound P and Compound H.
  - Further, the analyzers must be able to detect Compound P at low levels in the presence of significant amounts of Compound H.
- Limits of detection must be at least 5 levels of discrimination below ERPG-2*:
  - ERPG-2 for Compound P: 100 ppbv → LOD must be < 20 ppbv.
  - ERPG-2 for Compound H: 50 ppmv → LOD must be < 10 ppmv.

*** ERPG: Emergency Response Planning Guidelines, established by the American Industrial Hygiene Association (AIHA). The ERPG-2 defines the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual’s ability to take protective action.**

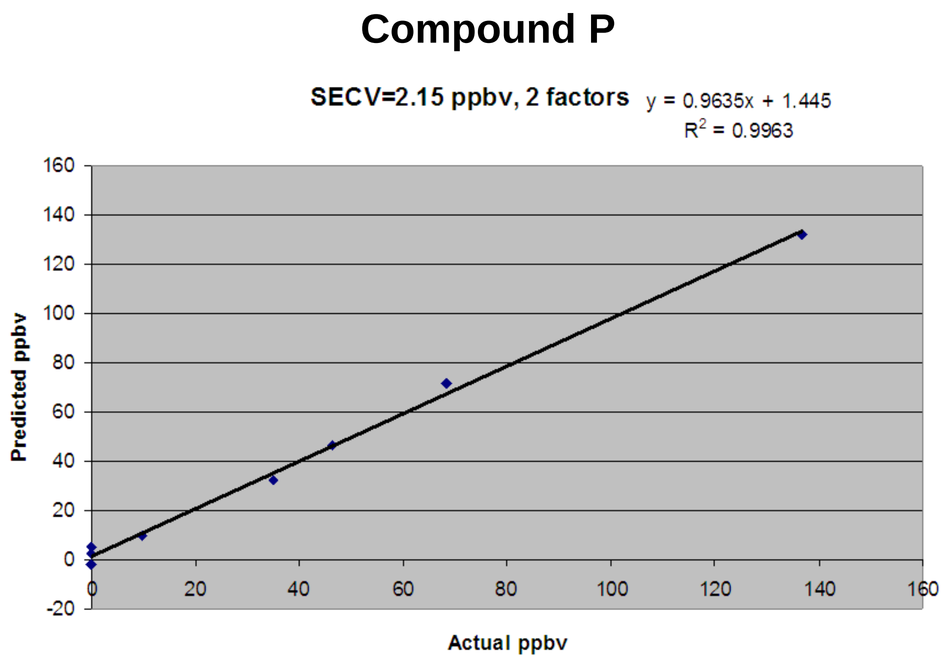
Example 1: Toxic Leak Detection in Chemical Plant

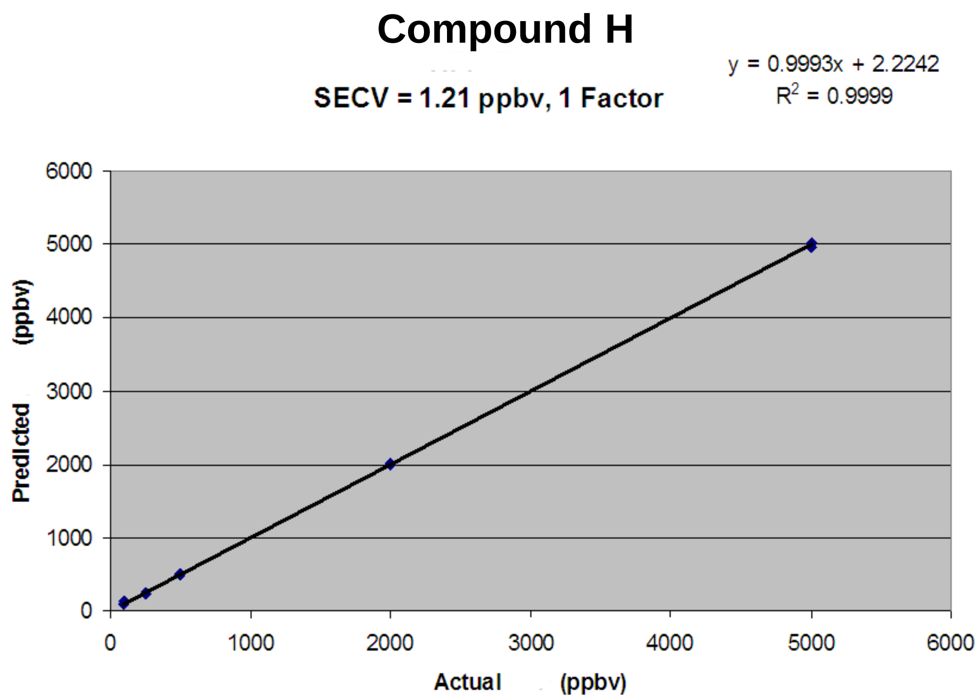
FT-IR SPECTRA OF MIXTURE OF COMPOUNDS P AND H



Example 1: Toxic Leak Detection in Chemical Plant

FT-IR CALIBRATION PERFORMANCE





- Lower detection limit (3 x SECV) for P: 6.5 ppbv
- Lower detection limit (3 x SECV) for H: 3.6 ppbv

Example 1: Toxic Leak Detection in Chemical Plant

CONCLUSIONS

- Analytical performance
  - The FT-IR process gas analyzer with a 6.4 meter long path gas cell and a room temperature DTGS detector can detect Compound P well below the ERPG-2 level of 100 ppbv, with an analysis time of approximately 90 seconds.
  - The lower detection limit of P in nitrogen is 7 ppbv (14 discrimination levels below ERPG-2).
  - Compound P can be detected in the presence of compound H when compound H is at or below its ERPG-2 level of 50 ppm.
- Economics
  - End-user cost: $13k/ sampling point (installed).
  - Annual operating cost: < $2k/system.
  - Fully installed FT-IR cost with full redundancy: $26k/point.
  - Cost for alternative technique (filter photometers) with partial redundancy: $34k/point.
- Summary
  - Lower cost/point, higher reliability, enhanced diagnostics, ultimately drove this application towards FT-IR analysis.

Example 2: Toxic Leak Detection in Nickel Plant

BACKGROUND

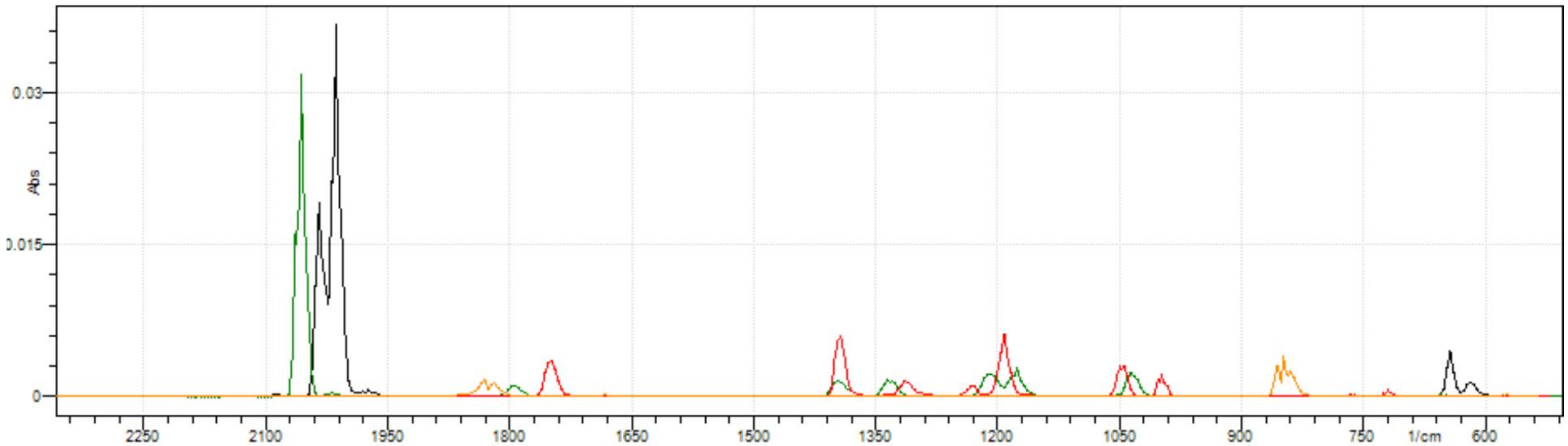
- Nickel carbonyl $Ni(CO)_4$ is one of the most toxic substances encountered in industrial processes:
  - $Ni(CO)_4$ OSHA PEL / NIOSH REL: 1 ppb (0.007 mg/m^3) TWA*
- A nickel plant located in Ontario (Canada) must perform leak detection at ppb levels of nickel carbonyl ($Ni(CO)_4$), an intermediate in the Mond process for the purification of nickel.
- Initially, the preferred ambient air monitoring technique for traces of $Ni(CO)_4$ and $Fe(CO)_5$ was chemiluminescence that provides good sensitivity (between 10 and 100 ppt).
- However, because of the chemical nature of the sensor chemical poisoning can occur, leading to serious loss of sensitivity.
- Chemiluminescense requires consumables, thus demanding regular attention, and it has a significant annual operating cost.
- In addition, $Ni(CO)_4$ and $Fe(CO)_5$ are often accompanied by high levels of CO and other vapors that can lead to false positive readings.

*** OSHA: Occupational Safety and Health Administration**
PEL: Permissible Exposure Limit
NIOSH: National Institute for Occupational Safety and Health
REL: Recommended Exposure Limits
TWA: 8h Time-Weighted Average

Example 2: Toxic Leak Detection in Nickel Plant

BACKGROUND

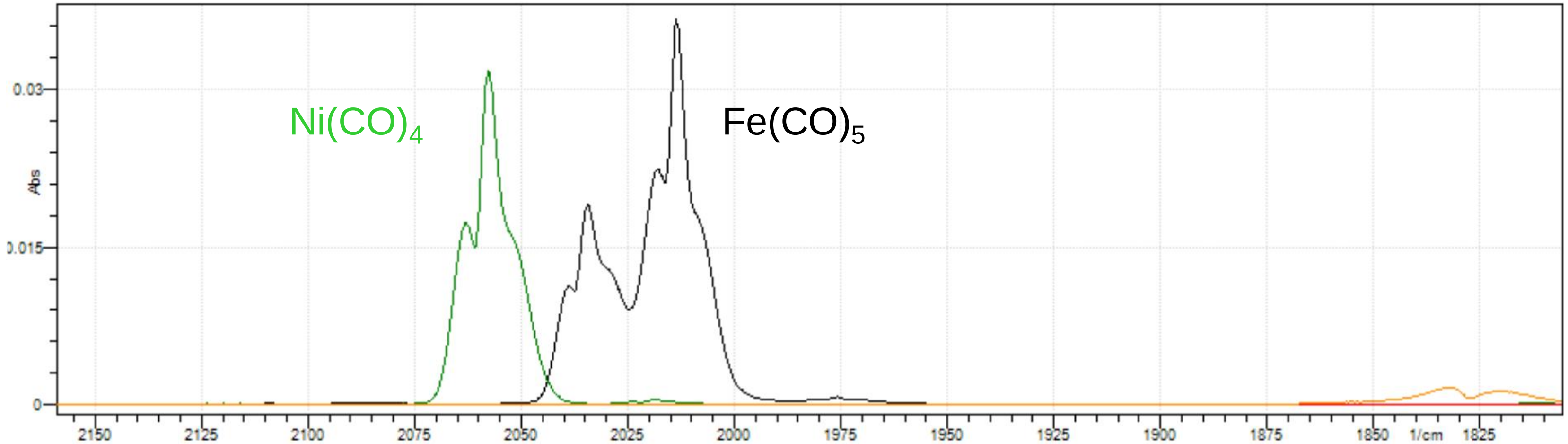
- Other analytical options: tunable diode laser spectroscopy (TDLA) → Powerful technique and high sensitivy when applied with cavity enhancement.
- However toxic vapors of complex molecules without hydrogen such as metal carbonyls or fluorinated organics present a challenge to TDLA:
  - IR spectral features occur only below 2100 cm^{-1} → Requires costly quantum cascade lasers
  - Spectral features lack sharp structure → No intensity enhancement using high resolution laser spectroscopy.
  - For those molecules, low resolution FT-IR can achieve absorbance sensitivity similar to laser spectroscopy (< 25 µA at 2 cm^{-1} resolution)
- Therefore, the plant management decided to switch measurement method based on the increased reliability, higher performance and lower maintenance costs of FT-IR technology.



Example 2: Toxic Leak Detection in Nickel Plant

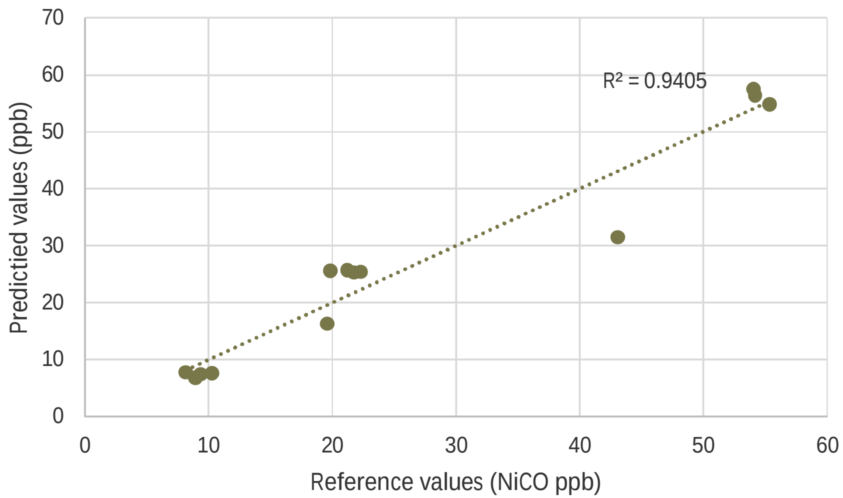
SETUP

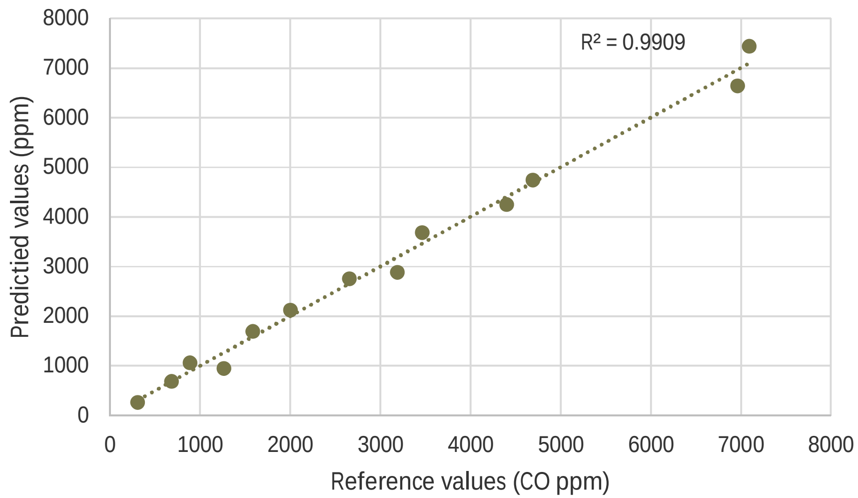
- ABB MBGAS-3000 process gas FT-IR analyzer
- Detector: DTGS
- Sampling technique: 3.24 meters pathlength gas cell
- Analysis temperature: 65-70°C
- Resolution: 2 cm^{-1}
- Number of scans: 20 (~2 mn /sample)
- Multivariate calibration models to simultaneously predict $Ni(CO)_4$ and $Fe(CO)_5$ as well as interferents (CO, CO_2, H_2O).



Example 2: Toxic Leak Detection in Nickel Plant

FT-IR CALIBRATION PERFORMANCE





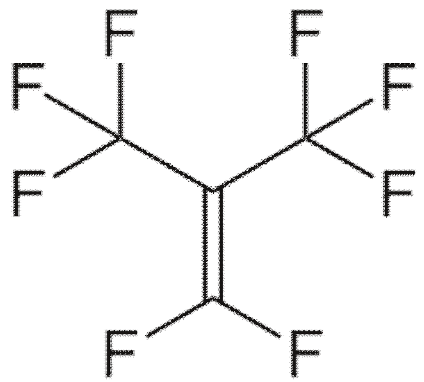
Property	Range	LOD
$Ni(CO)_4$ ppb	0 – 100	0.55
CO ppm	0 – 10 000	0.14

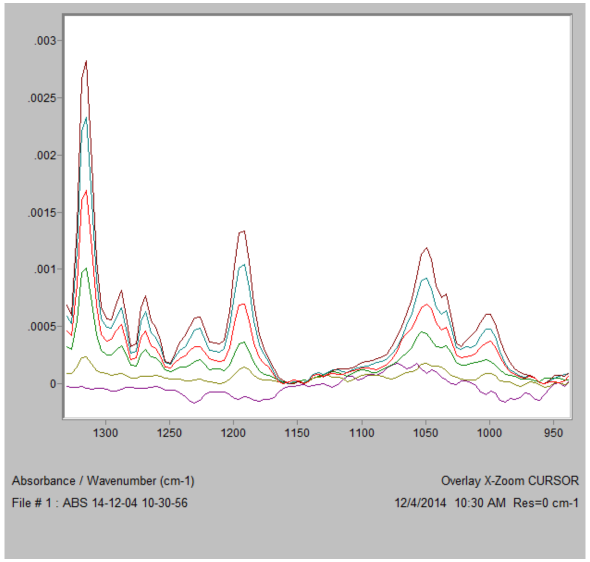
- For the most toxic compound (nickel carbonyl), the ABB MBGAS-3000 has a limit of detection of ~600 ppt.

Example 3: PFIB Fugitive Leak Detection

BACKGROUND

- Laboratory development of an FT-IR method for ambient air monitoring in specialty chemical plants, as a faster alternative to process gas chromatography.
- Objective: fugitive leak detection of perfluoroisobutylene (PFIB), a colorless gas about 10 times as toxic as phosgene. Inhalation of PFIB can lead to fatal pulmonary edema.
- A quantitative method is developed to monitor PFIB concentration over the range 4-32 ppbv.

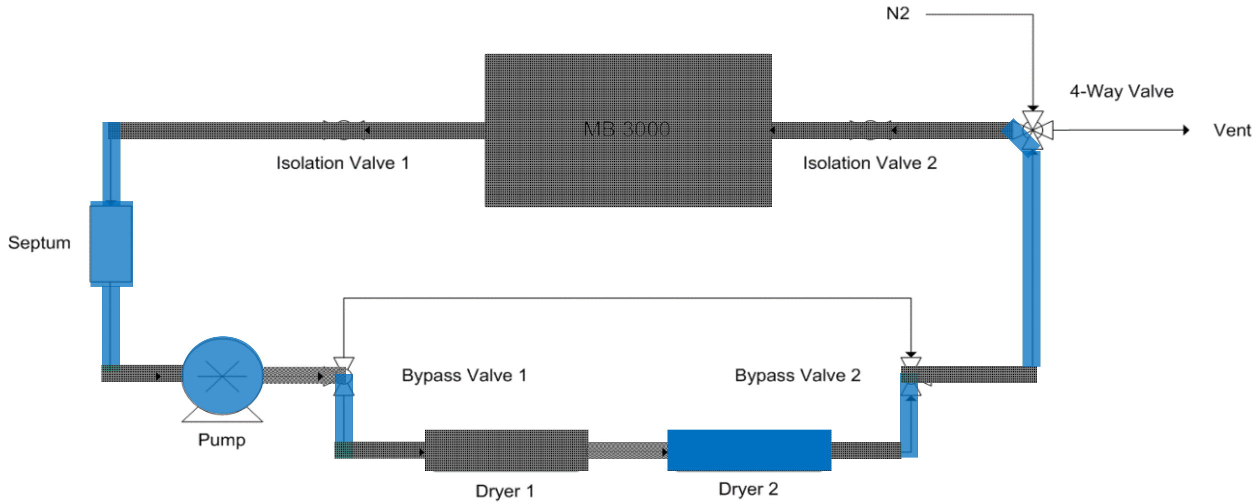




Example 3: PFIB Fugitive Leak Detection

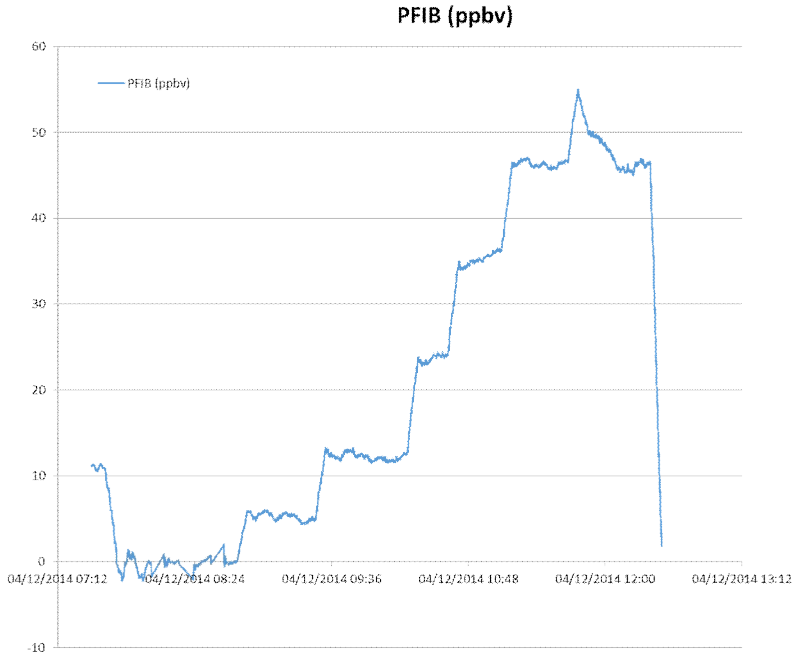
EQUIPMENT

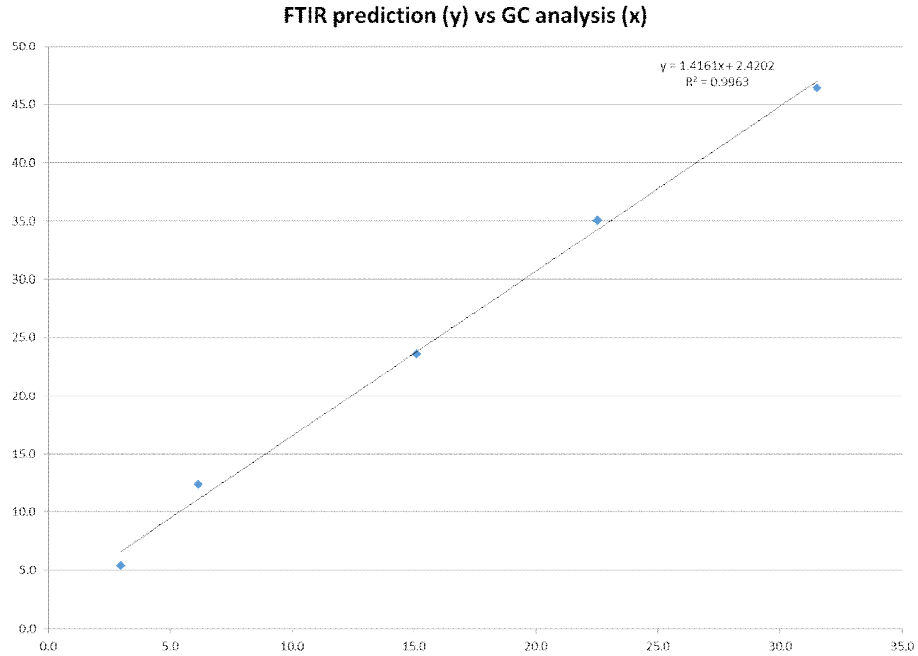
- ABB MB3000 FT-IR laboratory analyzer with enhanced case sealing procedure.
- DTGS detector (room temperature).
- CIC-Photonics 4Runner gas cell (6 meters pathlength).
- Sample loop with closed recirculation, diaphragm pump and septum port.
- Dryers: PermaPure PD-100T-12 and PD-200T-12 dryers in series.
- Reference method for calibration and comparison: R&D laboratory Agilent 6890 gas chromatograph with electron capture detector (ECD) set up for low level PFIB analysis.



Example 3: PFIB Fugitive Leak Detection

FT-IR CALIBRATION PERFORMANCE





- Comparative statistical results against GC data demonstrate the FT-IR excellent performance for PFIB detection:
  - Limit of Detection (LOD): 0.36 ppbv
  - Limit of Quantification (LOQ): 0.89 ppbv

Conclusions

- The need for gas phase measurements spans many industries and includes characterisation and identification of gas streams, regulatory emission compliance for health and human safety, and for process or quality control.
- There is a wide variety of choices for gas sensors and analyzers, however FT-IR is a dependable safety technique for ambient air monitoring and real-time detection of harmful vapors in chemical plants. It offers a unique combination of measurement speed, sensitivity, robustness against poisoning and low maintenance needs.
- Interfacing an FT-IR analyser with a PLC-controlled sample stream manifold permits the monitoring of multiple sampling points by a single instrument. This approach provides a cost-effective solution for applications such as vent monitoring, gas scrubber inlet and outlet monitoring, leak detection, confined space air quality, indoor/outdoor air monitoring and compliance to local safety and environmental requirements.

Troy W. Francisco
Research Associate
Chemours Analyzer Group
Chemicals and Fluoroproducts
The Chemours Company
ESL - E357/207
200 Powder Mill Rd
P O Box 8352
Wilmington, DE 19803
U.S.A.
Tel: +1 302.695.3158
troy.w.francisco@chemours.com
http://www.chemours.com

Frédéric Despagne
Industry Manager
ABB Measurement & Analytics
Les Bureaux du Lac 1 – Bât. 1
4 rue Théodore Blanc
33049 Bordeaux cedex
France
Tel: +33 556 112 025
frederic.despagne@fr.abb.com
http://www.abb.com
Gulf Coast Conference: booth #830

Chemours™

Power and productivity for a better world™ ABB