Measurement of trace HF in clean rooms and ambient air

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Why Hydrogen Fluoride (HF)?

- Precursor to many important compounds e.g. in pharmaceutical and polymer industry
- HF serves as a catalyst in the petrochemical industry
- One of the key chemicals in modern microfabrication
- Aluminum manufacturing process

Why Hydrogen Fluoride (HF)?

- Hydrogen fluoride is a highly dangerous gas which forms corrosive and toxic hydrofluoric acid upon contact with moisture

NFPA RATINGS (SCALE 0-4):
HEALTH=4 FIRE=0 REACTIVITY=1

- Symptoms may be delayed for <u>several days</u> especially in the case of exposure
- Breathing in hydrogen fluoride at high levels or in combination with skin contact can cause death from an irregular heartbeat or from fluid buildup in the lungs
- Sensitive and fast detection is required to avoid costly breakdown and for human safety

Measurement challenges?

- Device needs to be **sensitive** to detect substances in very low concentrations (trace level). In order to monitor changes in the background level substantially lower detection limit than the background level is required -> i.e. preferably in the **sub-ppb level**

- Hydrogen fluoride gas monitor must be very **selective** in order to distinguish HF from other chemical species present in a multi-component gas mixture, such as the **ambient air**

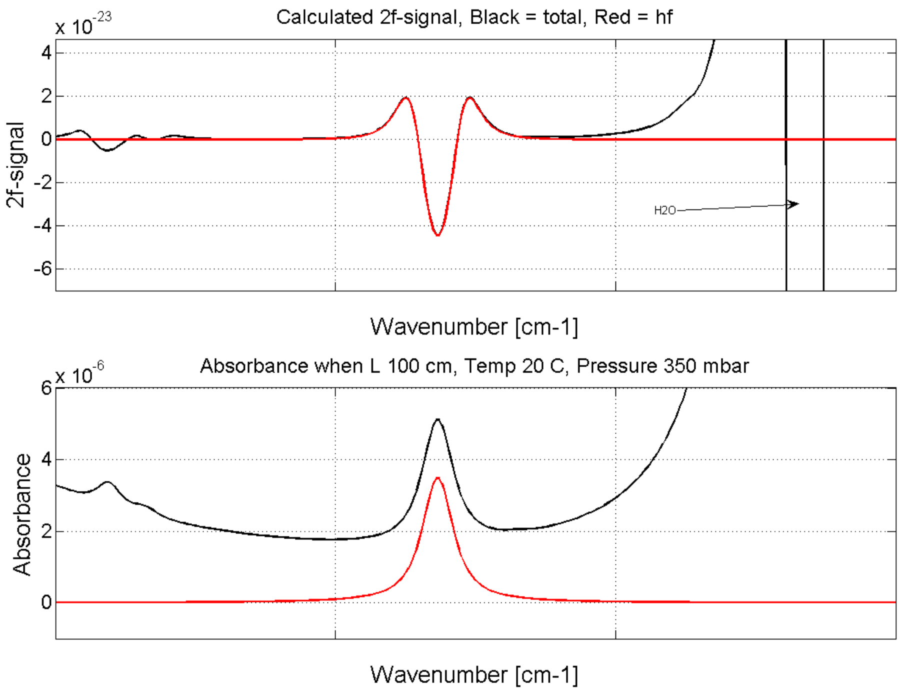
- Hydrogen fluoride is known as a very reactive chemical, which can cause severe system level problems if **suitable materials** for sample wetted parts are not chosen

- In addition, a **fast response time** ensures the possibility of real-time monitoring to avoid costly and possibly life threatening spills

Infrared laser spectroscopy

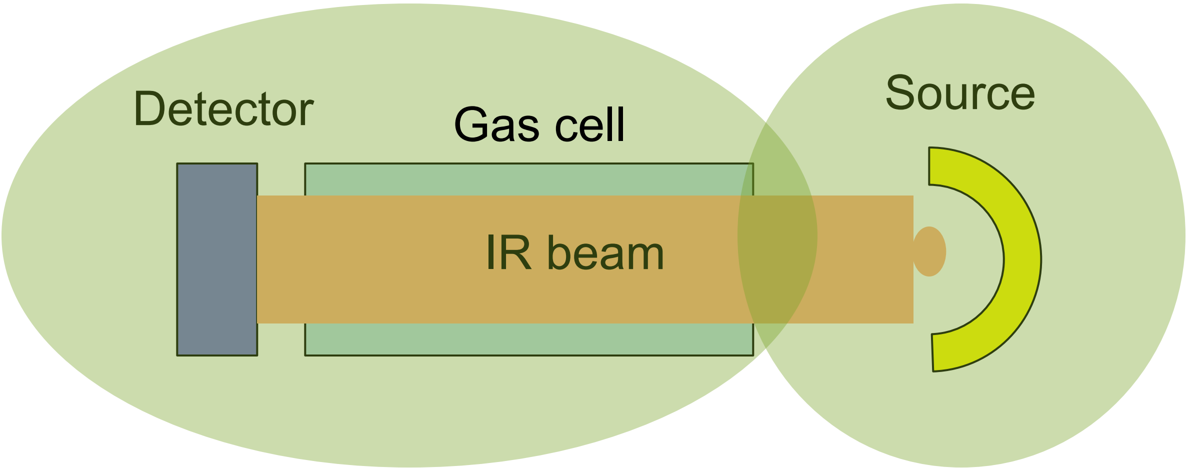
- Hydrogen fluoride is infrared active gas molecule and thus infrared spectroscopy provides a good basis for detection

- Fortunately HF has both **strong** and **isolated** molecular transitions ("peaks") in the telecom region enabling sub-ppb measurement using robust telecom hardware



10 ppb of HF in Ambient air

Infrared spectroscopy platform

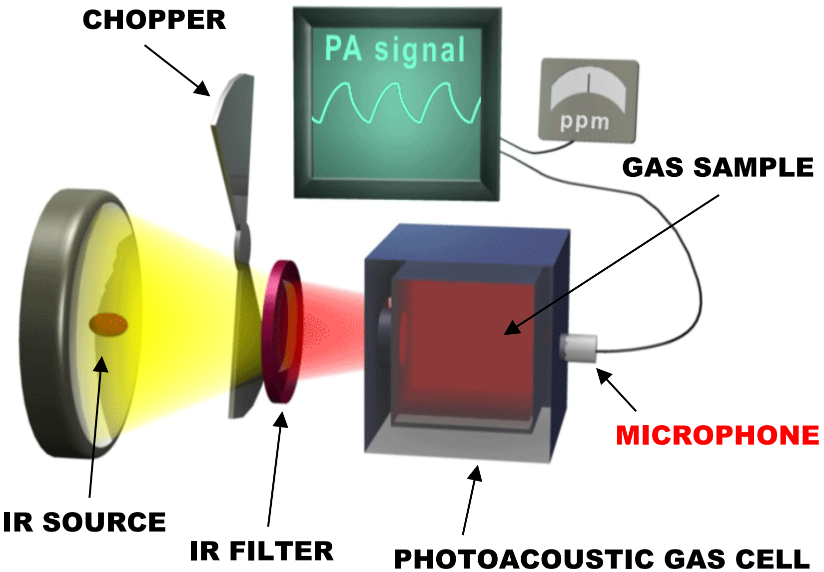


- Photoacoustic (PA) detector combines the gas cell and the detector in same functional package.
- Sensitivity is not dependent on the absorption path length which enables wide linear dynamic range and compact footprint
- High sensitivity is possible with sensitive pressure sensing technology

- Mid-IR source should be used
- Modern IR lasers (QCL or OPO) provide high output power
- Wavelength tuning allows scanning over spectral peaks and the use of chemometric analysis tools

Photoacoustic spectroscopy (PAS)

- Photoacoustic effect was discovered in 1880 by Alexander Graham Bell
- This **theoretical potential has not been reached**, **since conventional microphones have been used** for sensing the pressure pulses
- Gasera's novel cantilever sensor technology allows the use of the full potential of the photoacoustic phenomena

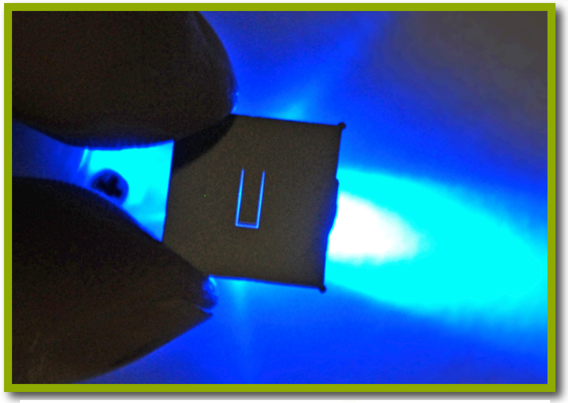


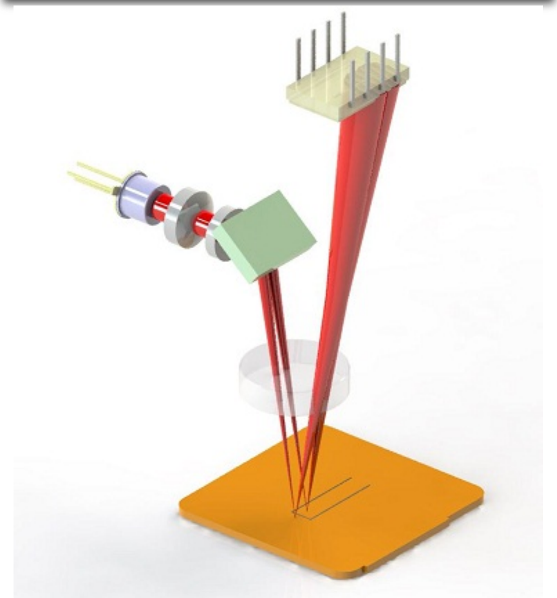
A typical setup of a conventional PAS system

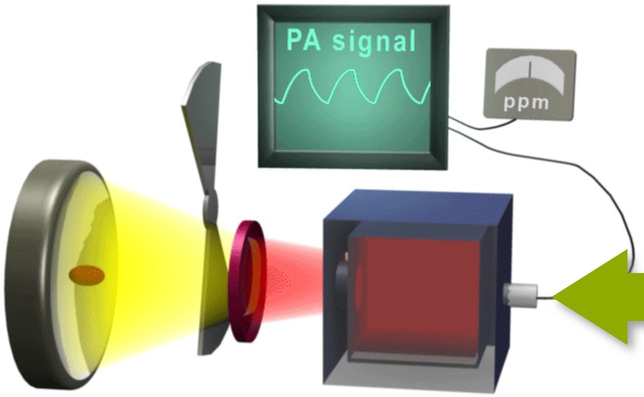
Photoacoustic spectroscopy is based on the **absorption of light** leading to the **local warming** of the absorbing volume element. The subsequent expansion of the volume element generates a **pressure wave** proportional to the absorbed energy, which can be detected via a pressure detector.

Key inventions

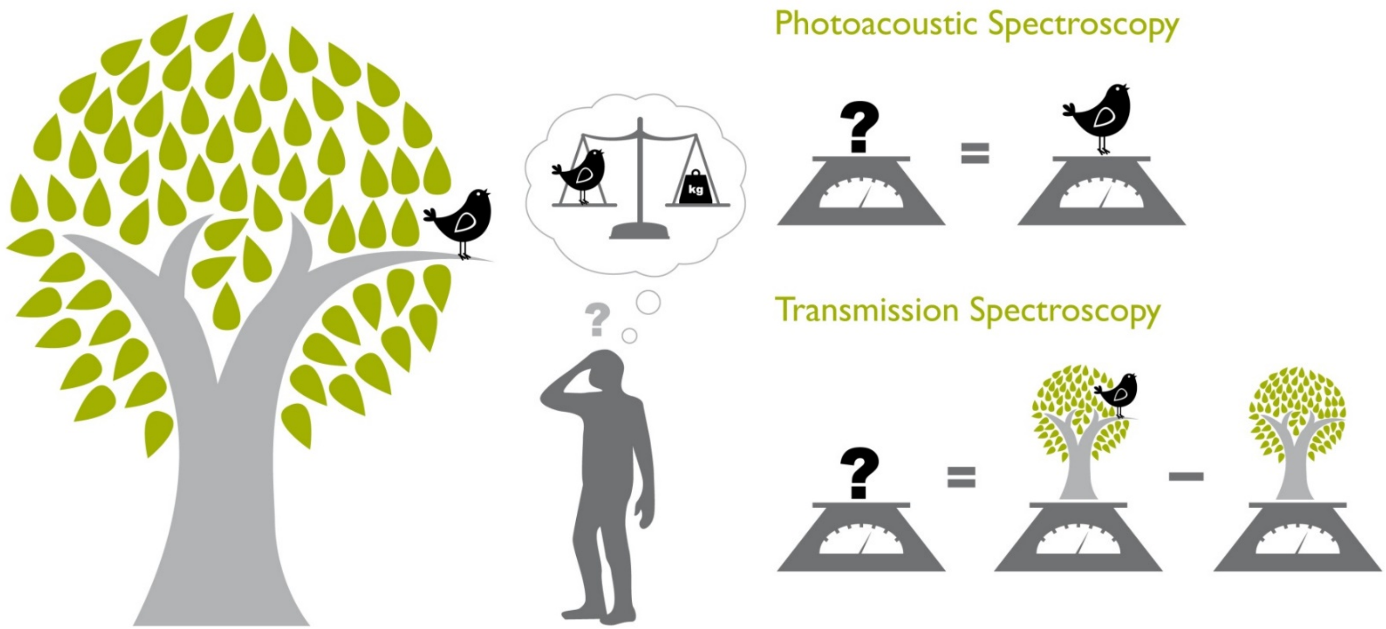
- **Cantilever sensor**
  - Over 100 times greater physical movement can be achieved compared to conventional microphone membrane – cantilever has very low string constant 1 N/m
  - Highly linear response
- **Optical readout system**
  - Contactless optical measurement based on laser interferometry
  - Measures cantilever displacements smaller than picometer (10^{-12} m)
  - Extremely wide dynamic measurement range





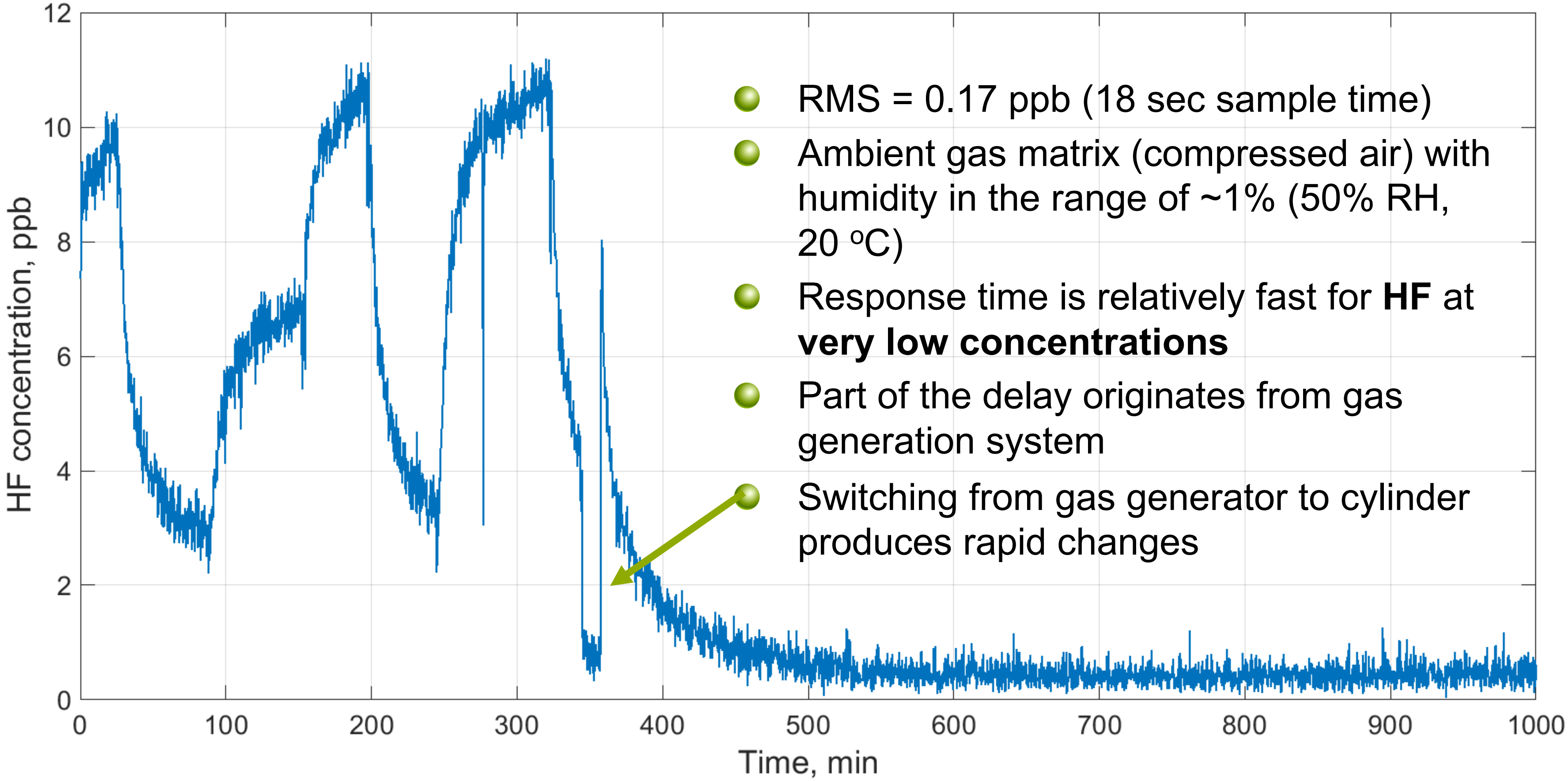


Benefits of cantilever enhanced PAS



- Absorption is measured directly in PAS which makes the measurement very accurate and free of drift -> **stability and reliability, easy to use**
- Cantilever sensor provides high sensitivity –> **below ppb detection limits**
- Sensitivity is not dependent on the optical path length -> **wide linear dynamic range, miniaturization, low sample volume**
- Many different sources can be connected to one cell -> **multi-gas capability**
- Possibility to heat the sample cell -> suitable to **wide range of process applications**

Hydrogen fluoride measurements in laboratory

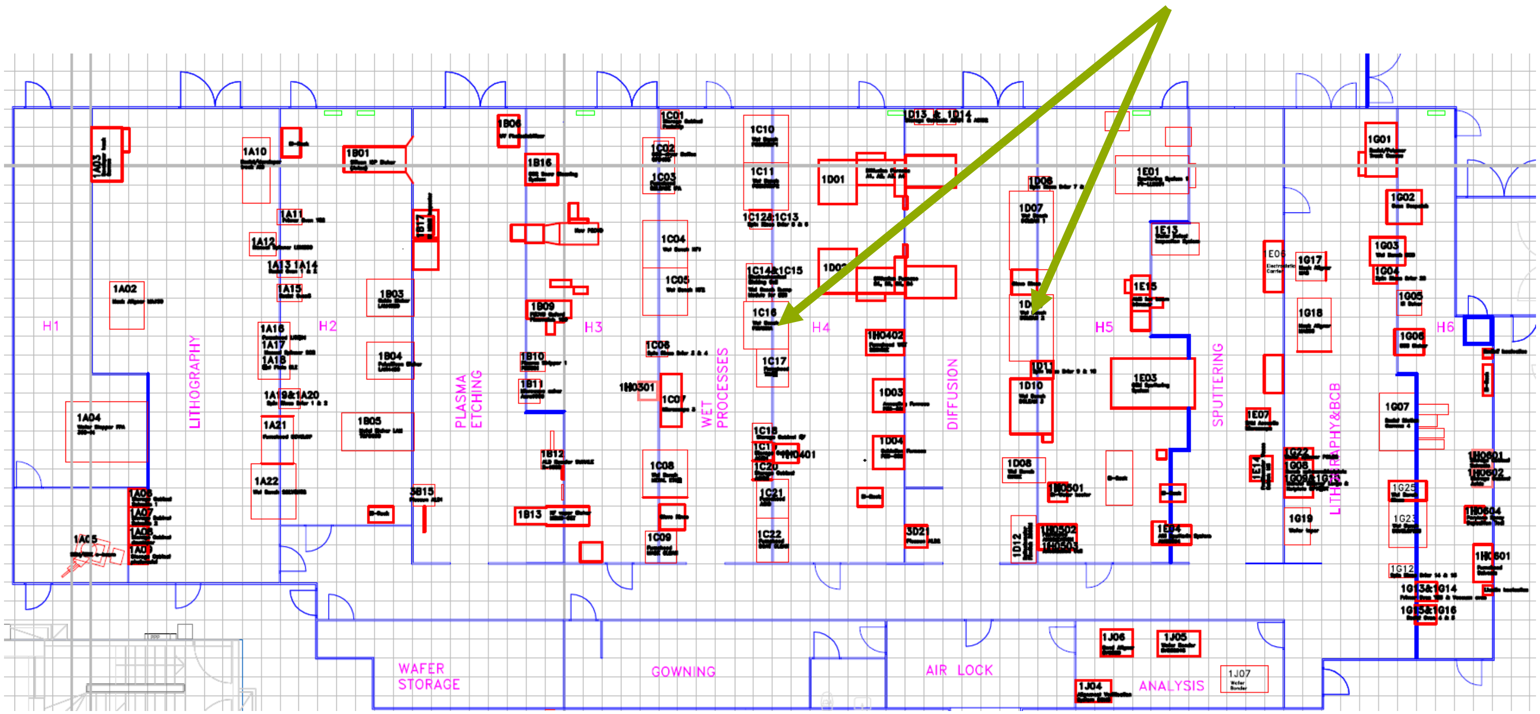


- RMS = 0.17 ppb (18 sec sample time)
- Ambient gas matrix (compressed air) with humidity in the range of ~1% (50% RH, 20 ^{o}C)
- Response time is relatively fast for **HF** at **very low concentrations**
- Part of the delay originates from gas generation system
- Switching from gas generator to cylinder produces rapid changes

Hydrogen fluoride measurements in clean rooms

- Common source of HF contamination in clean rooms is caused by human error and it can lead to costly shutdowns

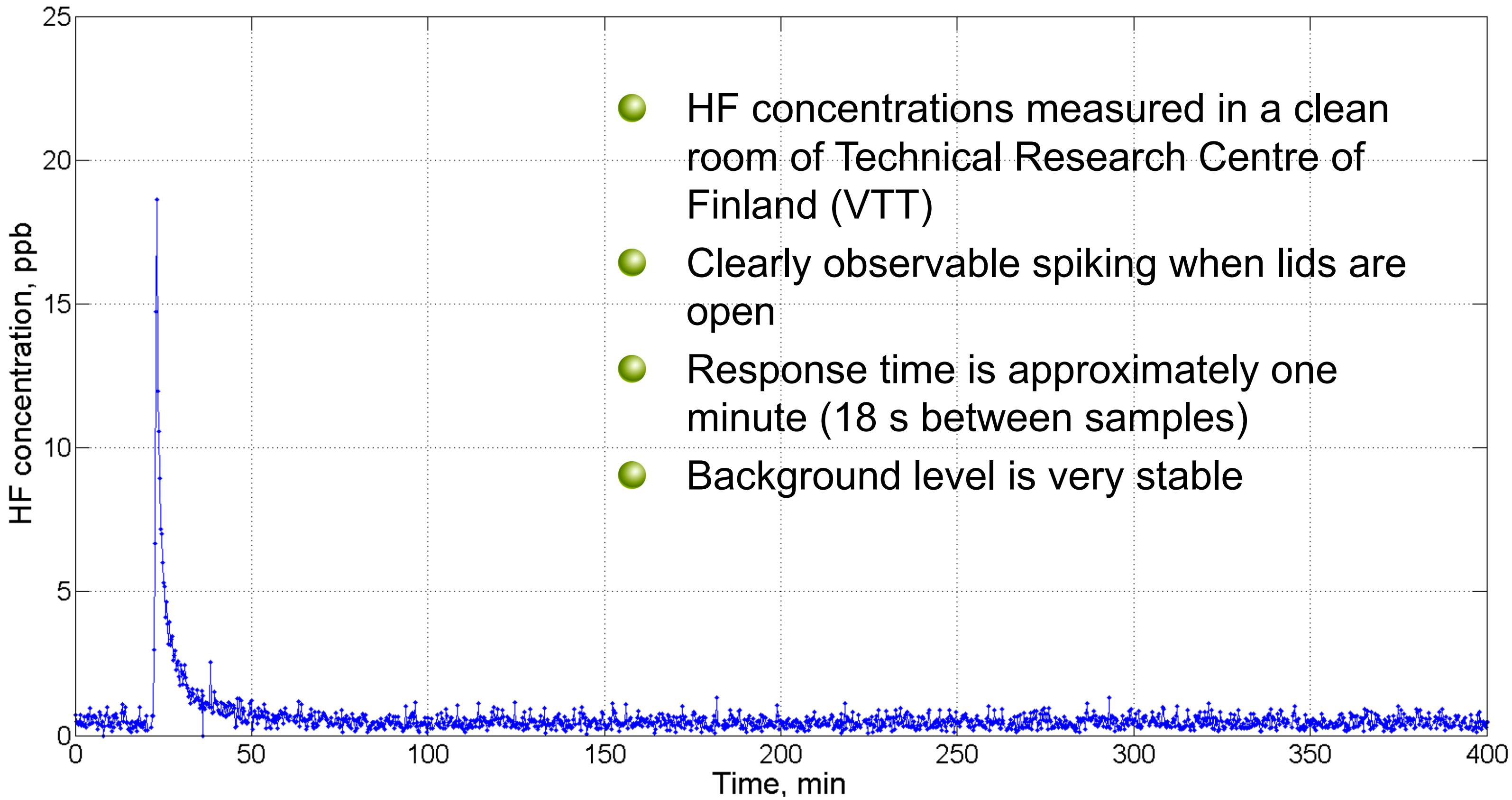
- Realtime monitoring of HF is crucial near obvious HF sources (wet benches, containers,…)



Hydrogen fluoride measurements in clean rooms

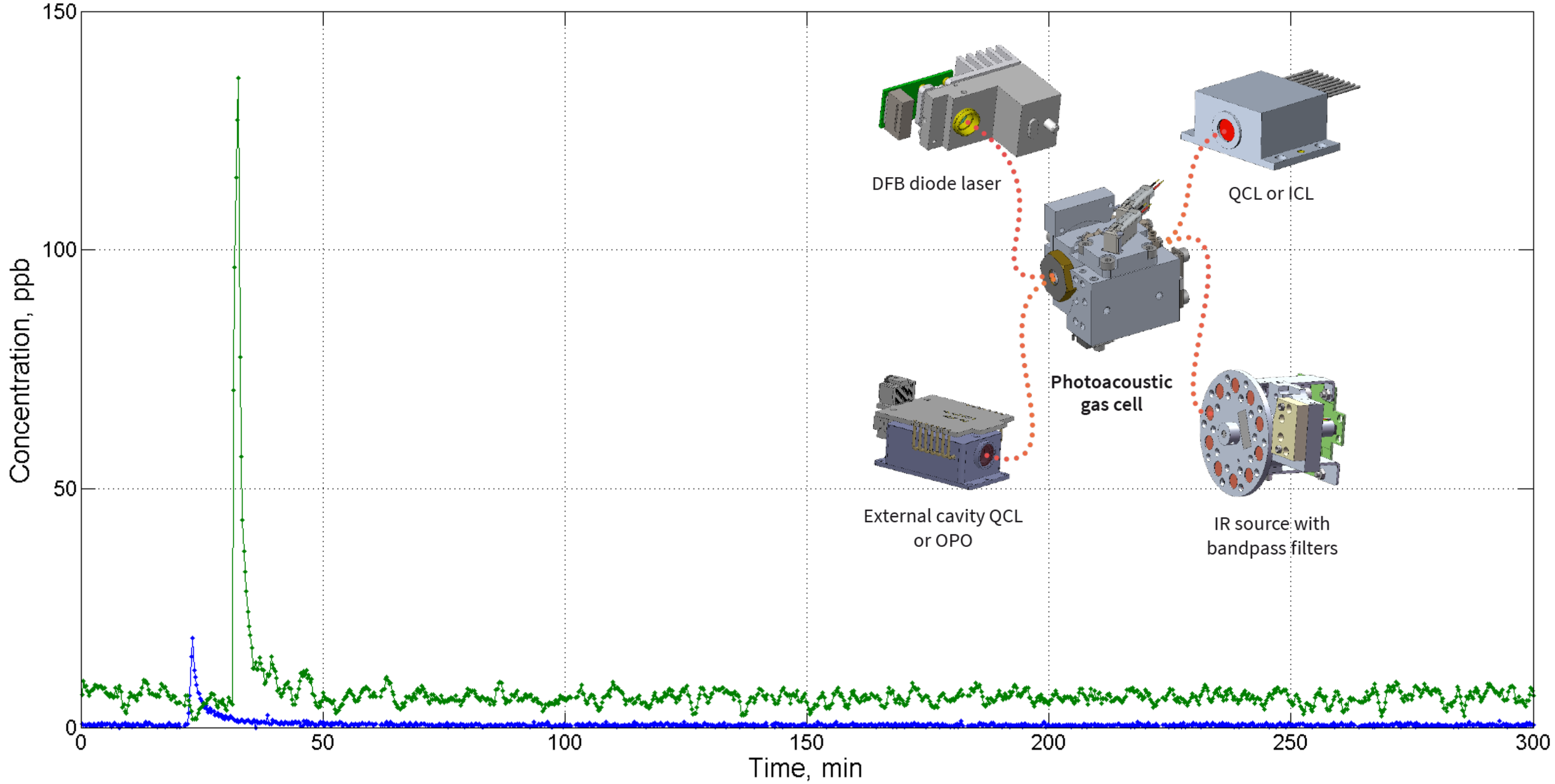
- Wet benches are primary sources of HF in many clean rooms
- Baths with about 50 % solution at elevated temperatures (up to 60 ^{o}C)
- Spiking of HF upon opening the lids
- Effective air circulation dilutes/spreads HF concentration rapidly

Hydrogen fluoride measurements in clean rooms



- HF concentrations measured in a clean room of Technical Research Centre of Finland (VTT)
- Clearly observable spiking when lids are open
- Response time is approximately one minute (18 s between samples)
- Background level is very stable

Hydrogen fluoride and ammonia measurements in clean rooms



- Clearly observable spiking of HF and NH3 when lids are open

Conclusions

- Hydrogen fluoride (HF) is a key compound in many industrial processes
- Photoacoustic detection combined with tunable laser source provides an attractive platform for selective HF monitoring
- Very low volume measurement cell enable practically realtime detection of a very reactive and difficult analyte
- Also another compounds (e.g. NH3) can be included in analysis

Thank you !

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