Online Analytical Solutions Experts

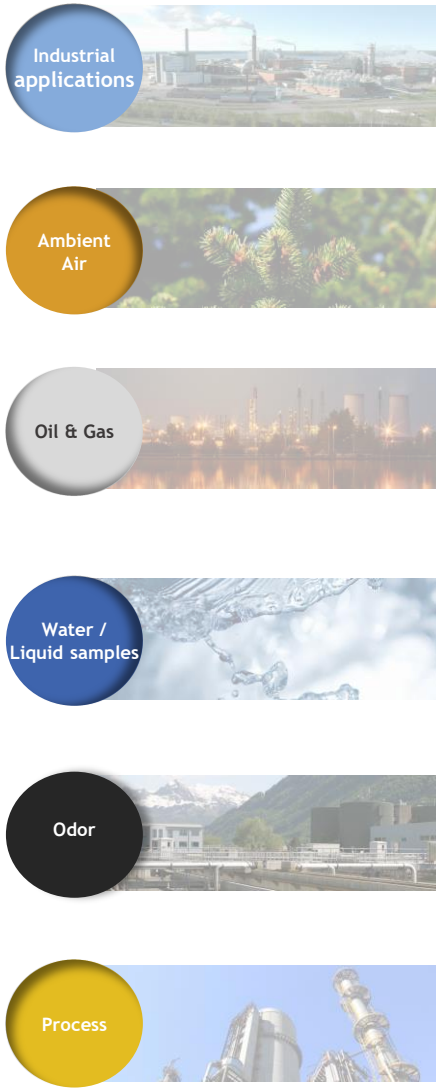
Chromatotec Sales Meeting

France, Saint-Antoine, July 5 to 7

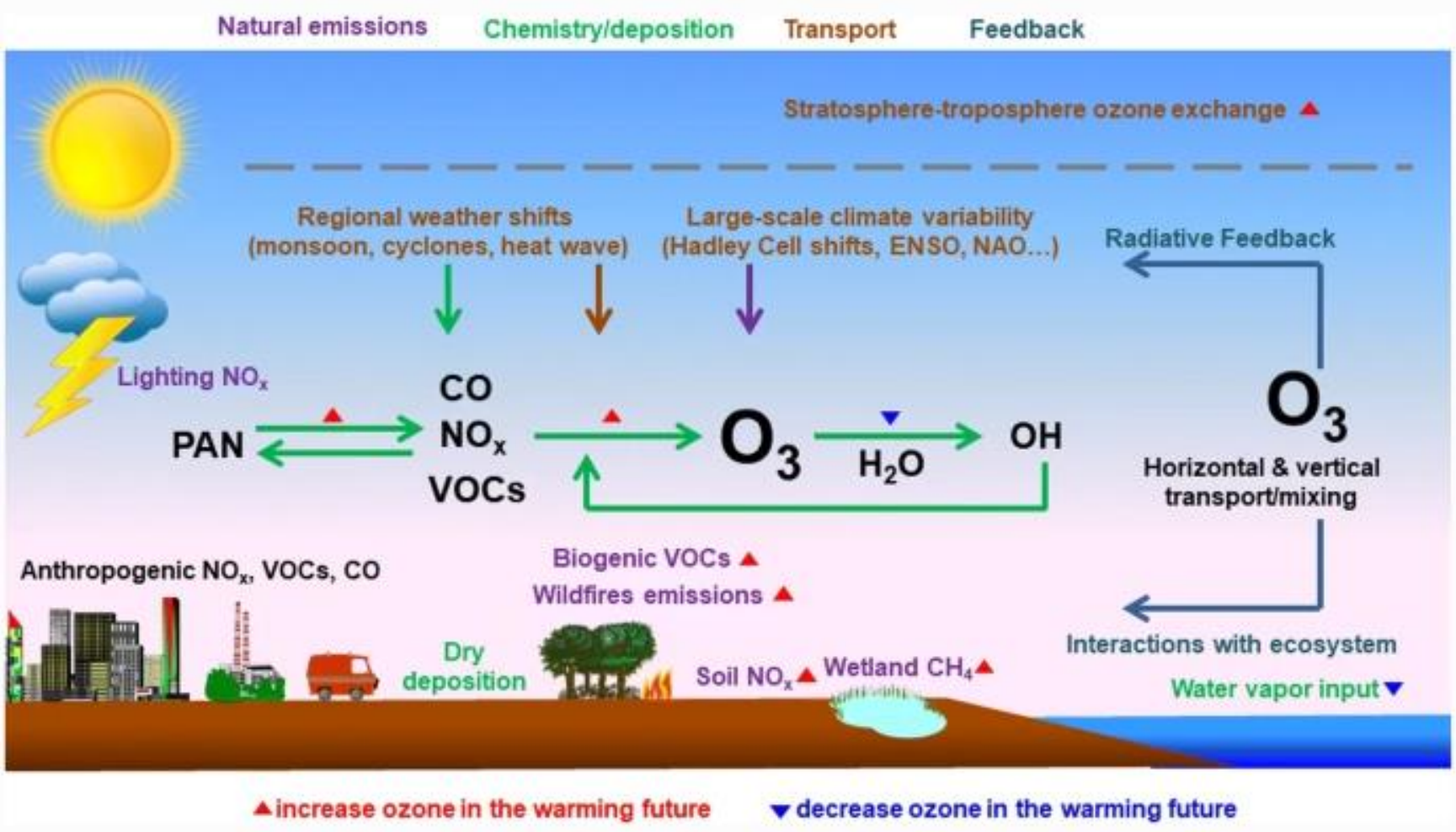
Online Analytical Solutions Experts

Micro Formaldehyde

Portable analyzer for continuous formaldehyde monitoring in ambiant air



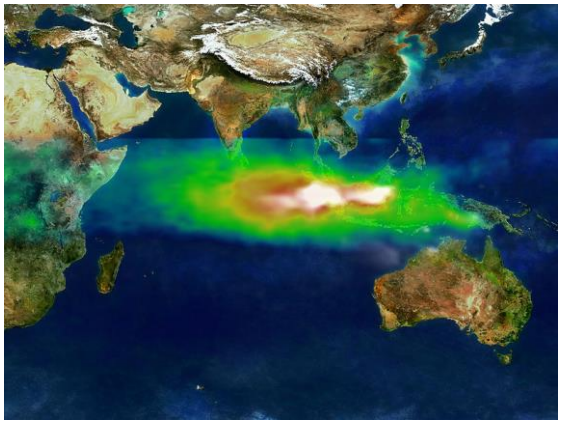
Ozone precursors



Ozone precursors

- Ozone concentration has multiplied 5 times in the last century in the middle latitudes of the northern hemisphere:
  - From 10 ppb in 1874
  - To approximately 50 ppb today (increase of 1.6% per year)
  - The trend is higher (2.4% a year) over the last decades.[1]

- In order to stop this global trend, directives have been written concerning the reduction of ozone precursors emissions (NOx, VOC like formaldehyde) to define national emission maxima.



[1]The International Geosphere-Biosphere Program - World Climate Research Program
[2]http://visibleearth.nasa.gov/view_rec.php?id=1651

VOCs

- 100+ different chemicals
- Anthropogenic sources
  - BTEX from road traffic
  - Chlorinated compounds from industries
- Biogenic sources
  - Isoprene and Monoterpenes from trees
  - Natural emissions occur predominantly in the tropics (23°S to 23°N)
- VOCs and PM 2.5 relation
  - 50% of dry mass PM 2.5 are composed by OA: Organic Aerosol
    - 60% SOA Secondary Organic Aerosol from VOCs [1,2]

[1] *Kanakidou et al. Atmos. Chem. Phys., 5 2005.*
[2] *Haddad et al. Atmos. Chem. Phys. Discuss., 2010*

VOCs

- European list 31 VOCs including **BTEX** and **formaldehyde** (WG13 work on new European list)
  - In Europe, ambient air legislation targets Benzene
    - With annual target value of 5 µg/m^3
- US EPA lists
  - PAMS 56 including **BTEX** or 58 (including alpha and beta pinenes) – **formaldehyde included**
  - New PAMS 61 including **BTEX, 1-3 Butadiene, alpha and beta pinenes – formaldehyde included**
  - TO14: including **BTEX**, Cl-VOCs
  - TO15: including **BTEX**, Cl / Br / O-VOCs

ANNEX X of European directive 2008/50/EC

Analyzed by airmoVOC C2 to C6

- **C2** Ethane = C2
- Ethene / ethylene
- **C3** Propane = C3
- Propene
- isobutane (2-méthyl propane)
- **C4** n-butane = C4
- Acetylene
- trans-2-butène
- 1-butene
- 1,3-Butadiene
- cis-2-butène
- Iso-pentane (2-methyl butane)
- **C5** n-pentane =C5
- 1-pentene
- 2-methylpentane = I Hexane
- **C6** n-hexane =C6
- isoprene

Analyzed by airmoVOC C6 to C12

- **C6** Benzene
- **C7** n-heptane = C7
- Toluene
- **C8** 2,2,4-trimethylpentane = Iso Octane
- n-octane =C8
- Ethylbenzene
- m-xylene
- p-xylene
- o-xylene
- **C9** 1,3,5 trimethylbenzene
- 1,2,4 trimethylbenzene
- 1,2,3 trimethylbenzene

Analyzed by airmoHCHO

Formaldehyde

Analyzed by ChromaTHC

Total non-methane hydrocarbon

Many other VOCs can be added to this list and monitored with the same system

Formaldehyde monitoring – Different technologies

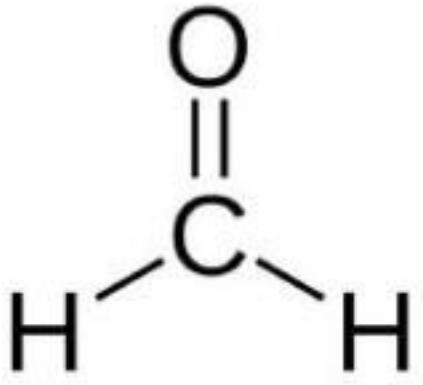
1. Official method with HPLC and DNPH cartridges
2. Online autoGC-FID with methanizer : airmoHCHO
3. Laser technology
4. Portable microfluidic technology

MicroFormaldehyde portable analyzer

Why analyze formaldehyde ?

- Formaldehyde is present in :
  - Chemical, pharmaceutical, funeral industries
  - Paper plants
  - Indoor air (paintings, coatings)

- Formaldehyde effects :
  - Irritating, breathing issues (<500 ppb)
  - Carcinogenic (>500 ppb)
  - Risk of death (> 20 ppm)



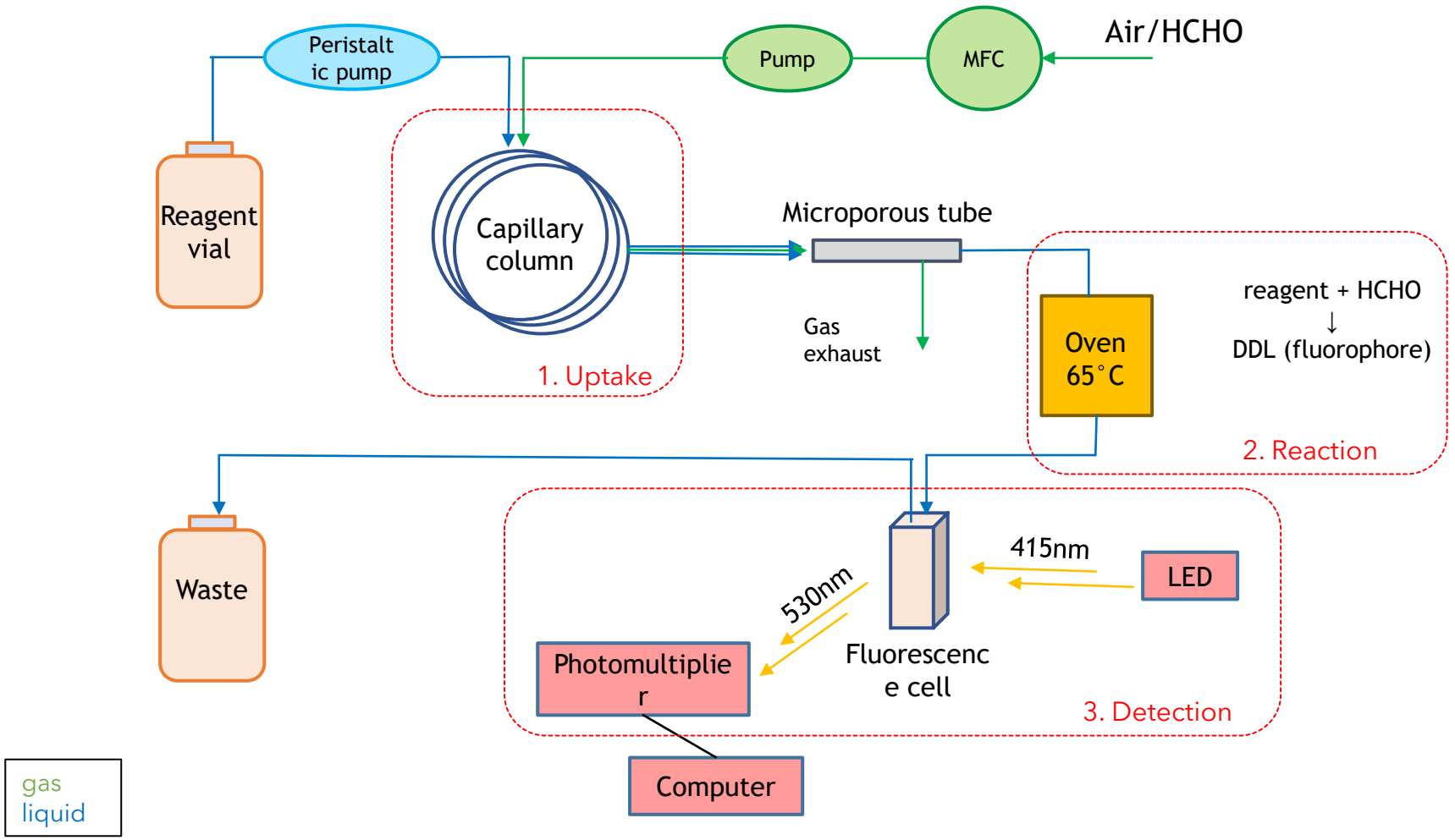
https://www.atousante.com/risques-professionnels/cmr-cancerogenes-mutagenes-toxiques-reproduction/formaldehyde/formaldehyde-effets-sante/

New portable micro Formaldehyde analyzer

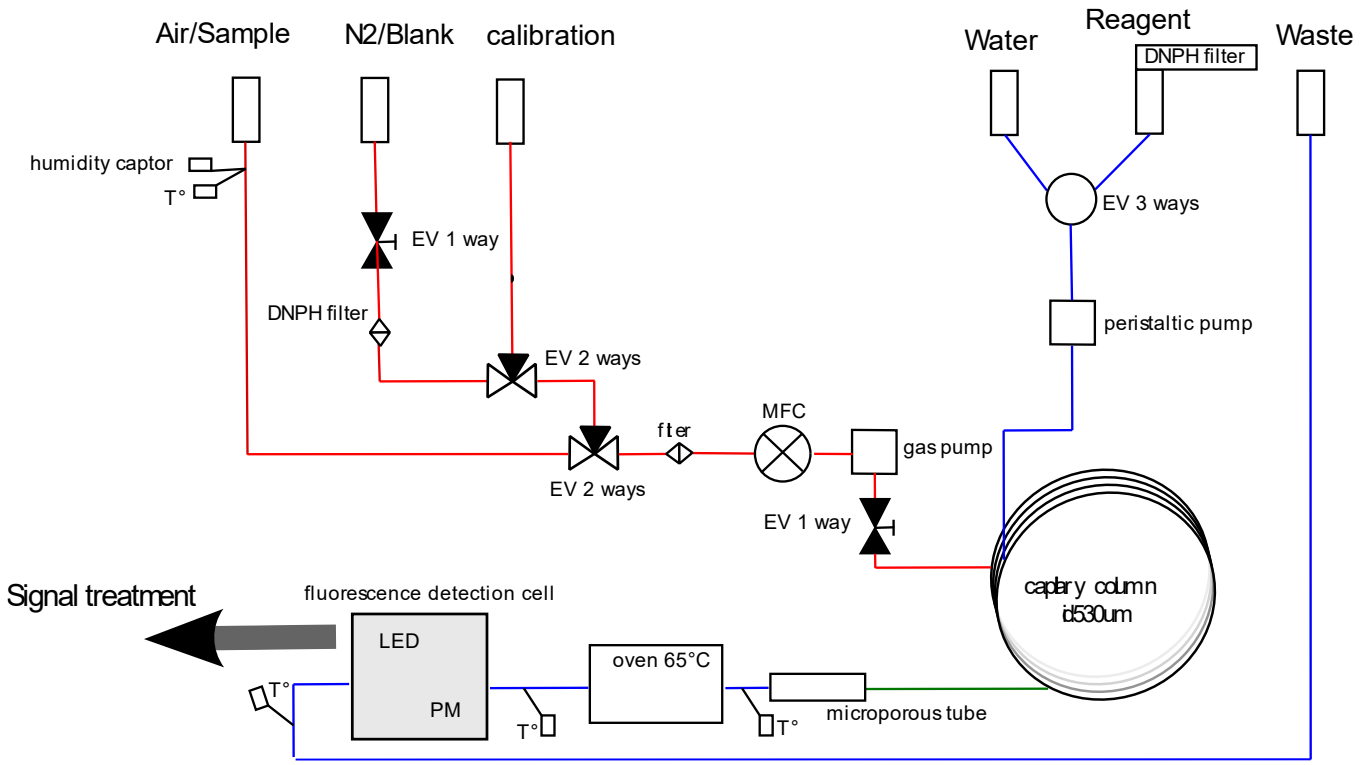
Dimension	32 cm × 28 cm × 15 cm
Weight	6,5kg
Limit of detection	1 µg/m3
Linearity range	0 – 400 µg/m3
Trapping type	Microfluidic annular flow
Derivitization reagent	Fluoral-P (acetylacetone)
Detection type	Fluorescence

Developped in collaboration with CNRS French Research Center

Wall mounted autoGC

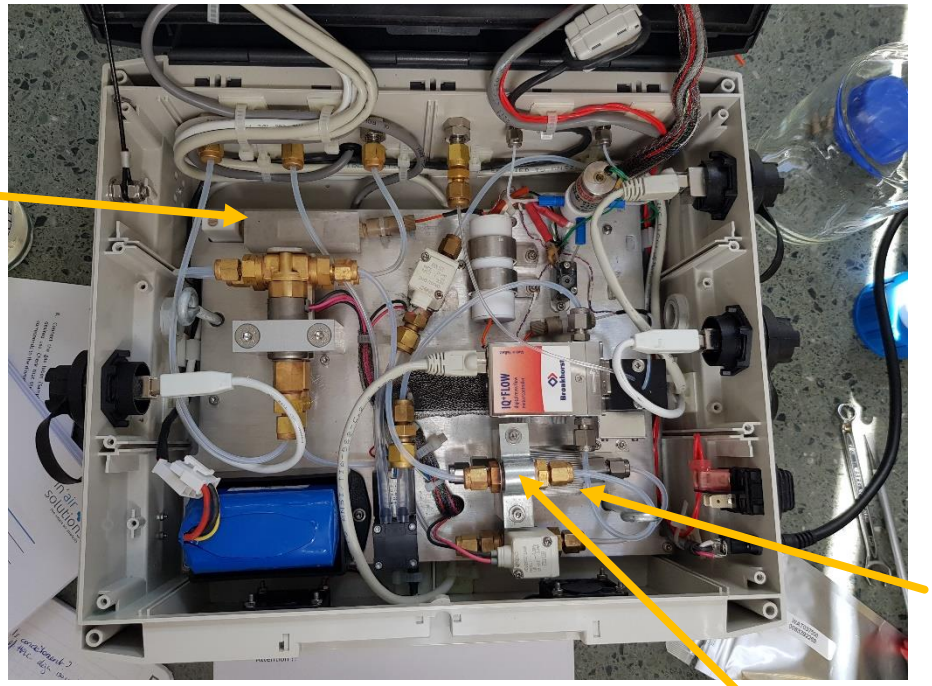


Full scheme


Air/Sample
N2/Blank
calibration
Water
Reagent
Waste
DNPH filter
humidity captor
T°
EV 1 way
DNPH filter
EV 3 ways
peristaltic pump
EV 2 ways
MFC
fter
gas pump
EV 2 ways
EV 1 way
capilary column
id530um
Signal treatment
fluorescence detection cell
LED
PM
T°
oven 65°C
T°
microporous tube

Internal view

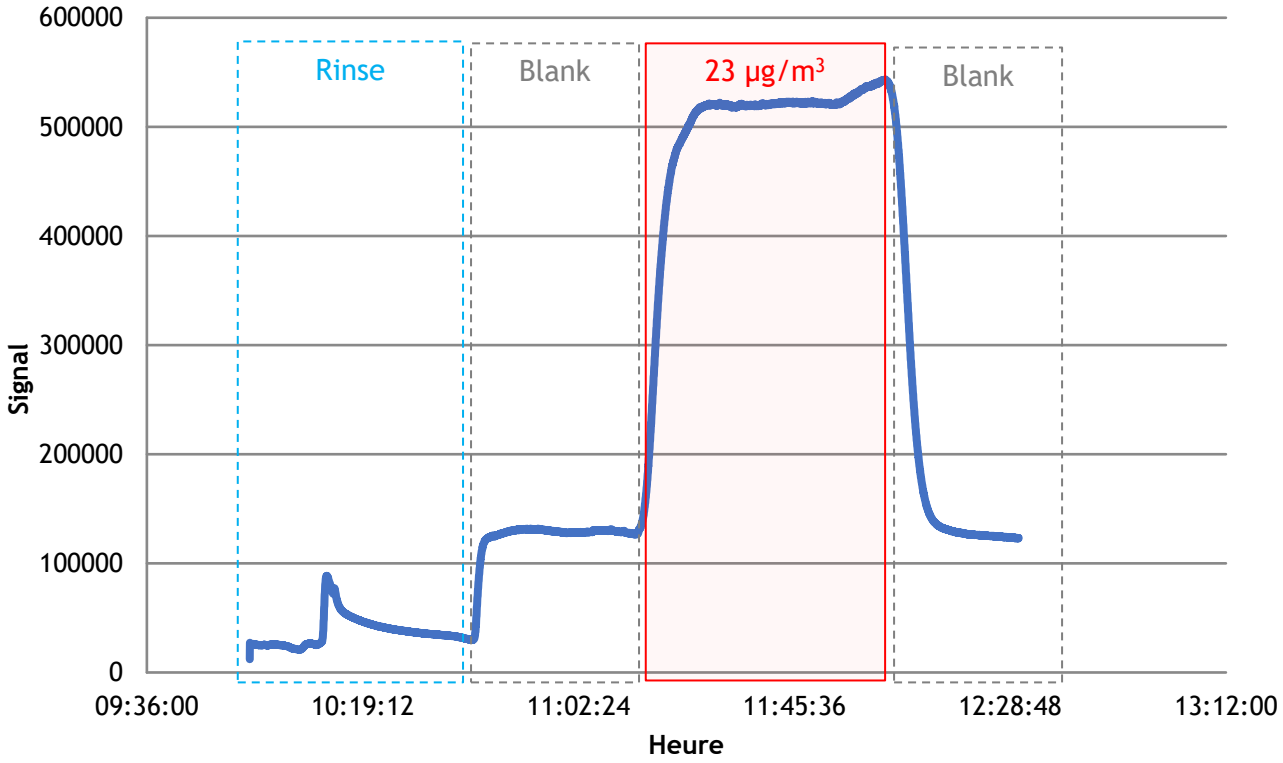
Microporous tube



DNPH cartridge

Particle filter

Principle Typical curve



Test parameters :

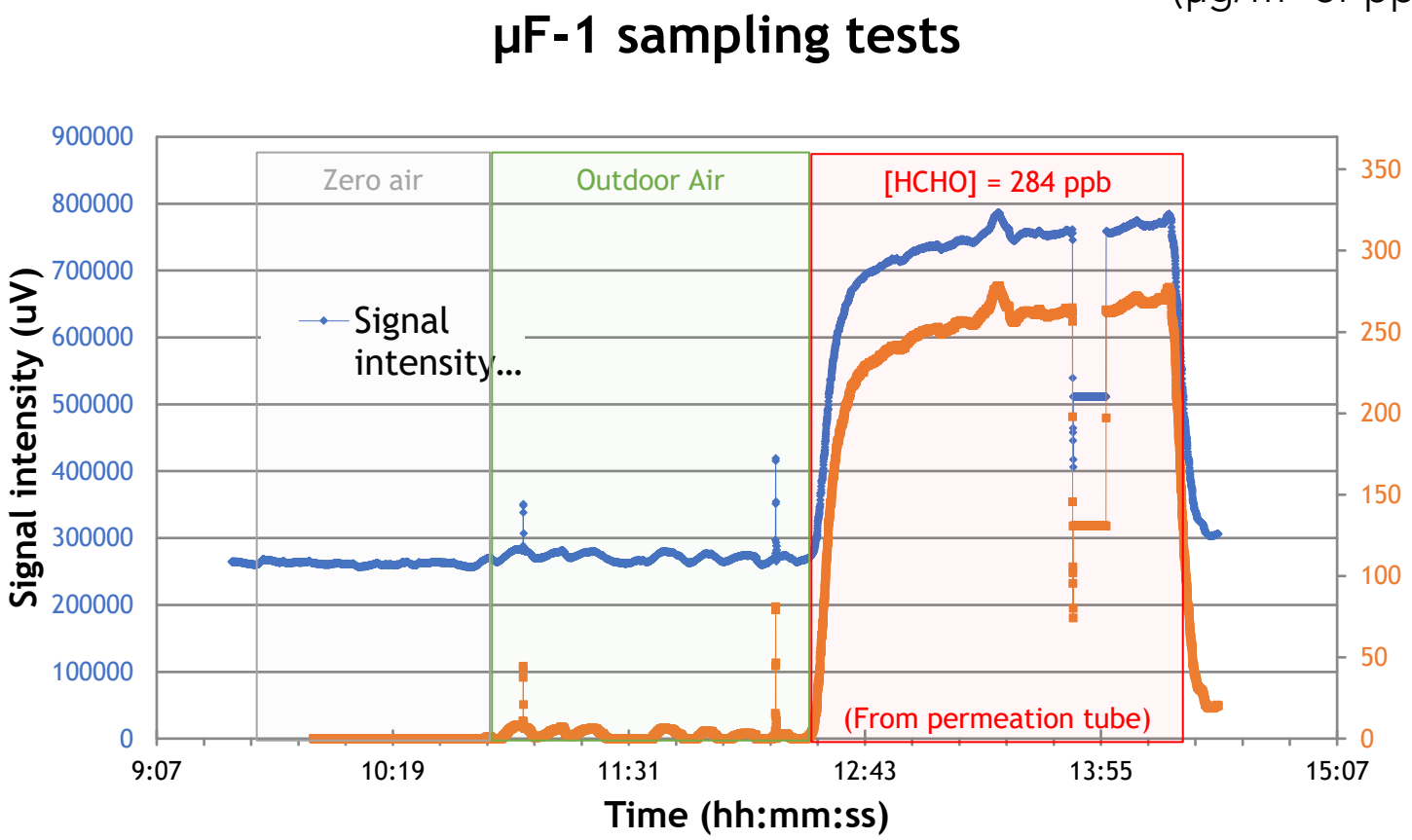
- ***Liquid flow rate*** :17 µL/min
- ***Gas flow rate*** : 250 mL/min
- ***Concentration***: 23µg/m^3
- ***Tube length:*** 10 cm

Anaïs Becker's work

The **intensity of the signal** is **proportional to the concentration** of formaldehyde

PrincipleTypical curve

- Intensity curve
- Concentration curve (μg/m^3 or ppb)



Consumables

- Strainer for particle filter (pore diameter 7 µm) : to change every month
- DNPH tubes and rings : to change every month
  - One for reagent bottle preservation
  - One inside the analyser to filter outdoor air to do blank measurements
  - Storage at 5°C, away from the light
- Microporous tube (10 cm) : to change every month
- Reagent : 100 mL for 80h with analysis caps
  - Storage at 5°C
- Distilled water : 100 mL for 80h
- (Waste bottle to empty after each use)

Performance

Detection range : 0-400 ppb

Detection limit : 1 ppb (1.2 µg/m^3)

Response time : 10 min

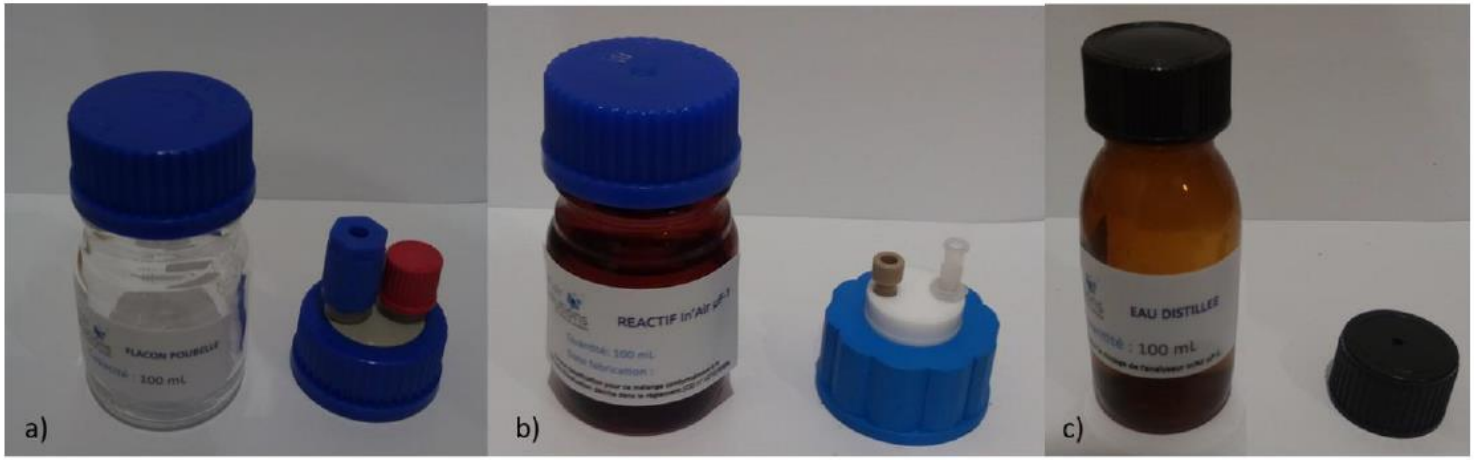
Time resolution : Few seconds to 120 s

Reagent consumption : 1.2mL per 60 minutes

Conditions :

- Gas T°: 5 - 40°C;
- Gas Relative humidity : 20 - 80%
- Atmospheric pressure
- Altitude max : 2000m

Launching and using the device Set-up



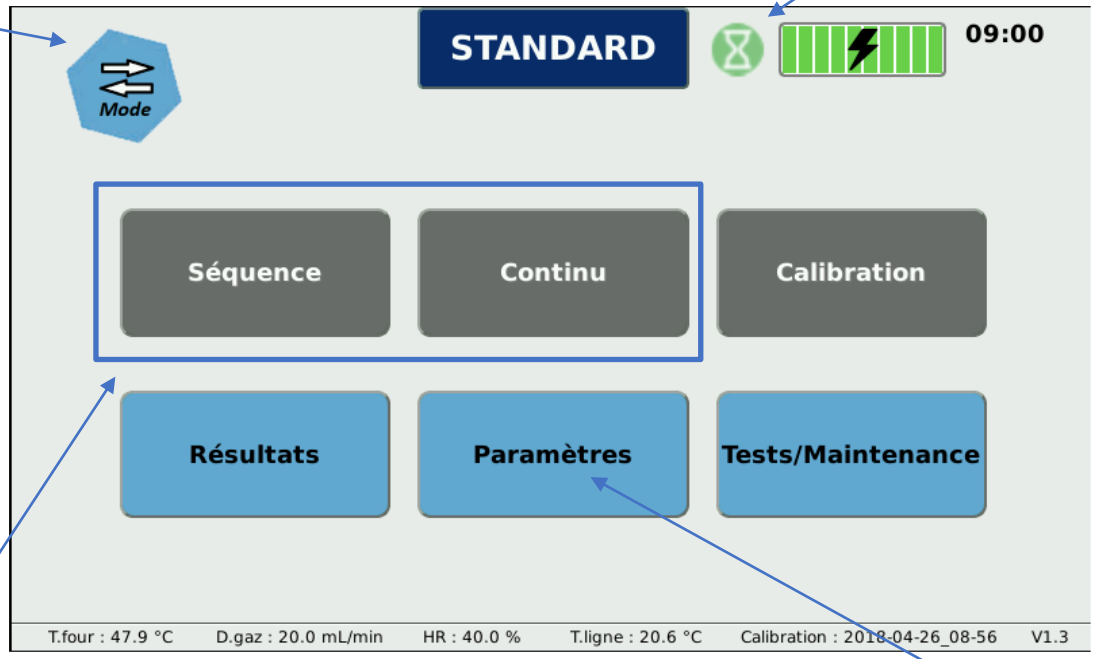
Set-up

Analyser on a flat surface
Caps for liquid and gas connexion removed
Bottles with specific caps in place
Gas at atmospheric pressure
Then turn on the analyser

Analysis

User mode and expert mode

Stabilisation



Analysis

Sequence : Programmable sequence
Continuous : Manual change of modes

General parameters and analysis parameters

Analysis

Before a run, check that the analyser is calibrated

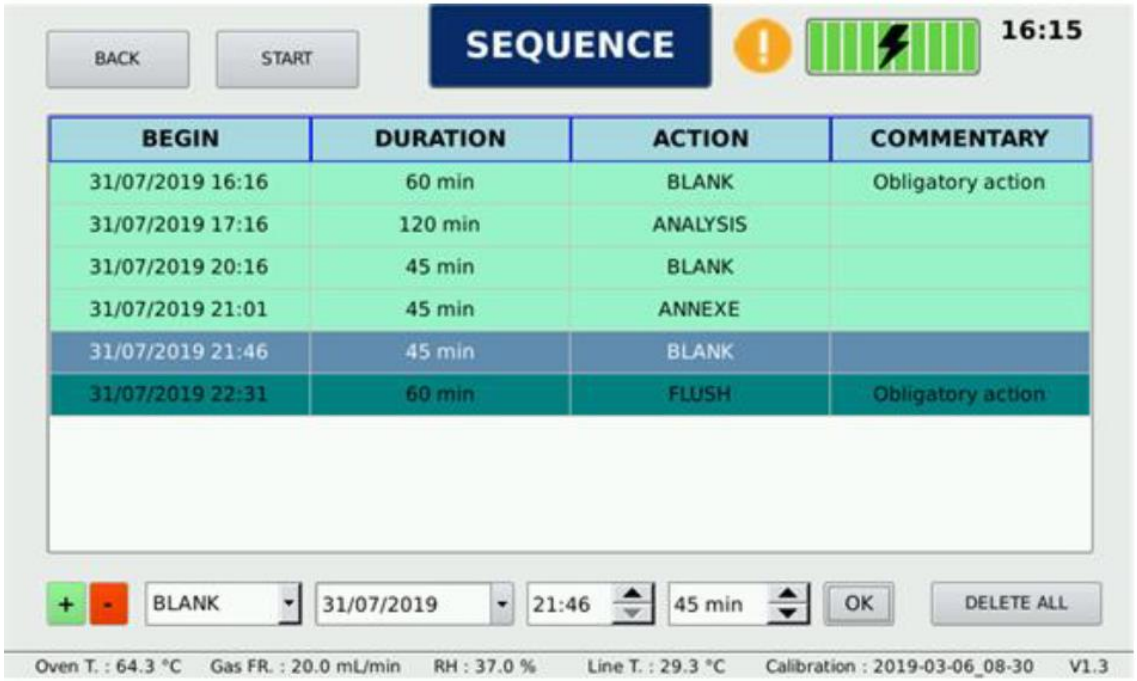
(minimum every 3 months)

- Continuous measurement :

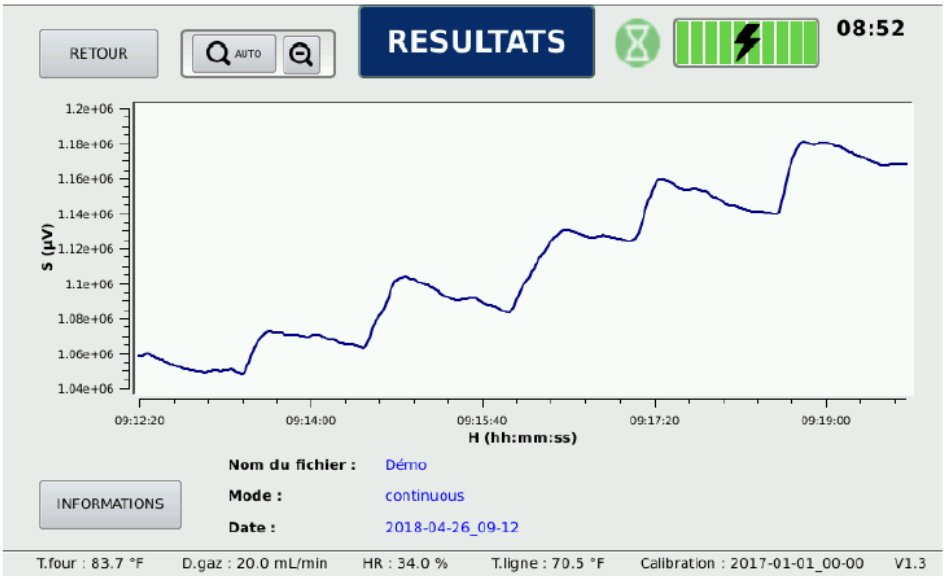
Manual blank, mesure, rincing steps 10min delay when switching from one mode to an other.

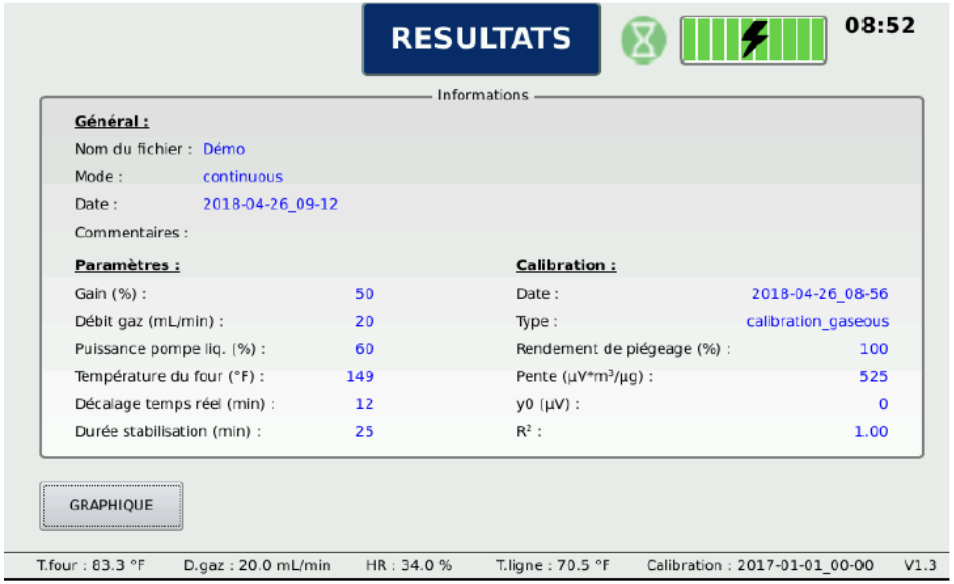
Analysis

- Sequence programming



Results





Typical blank baseline : 100,000-150,000 µV
Signal saturation : 2,000,000

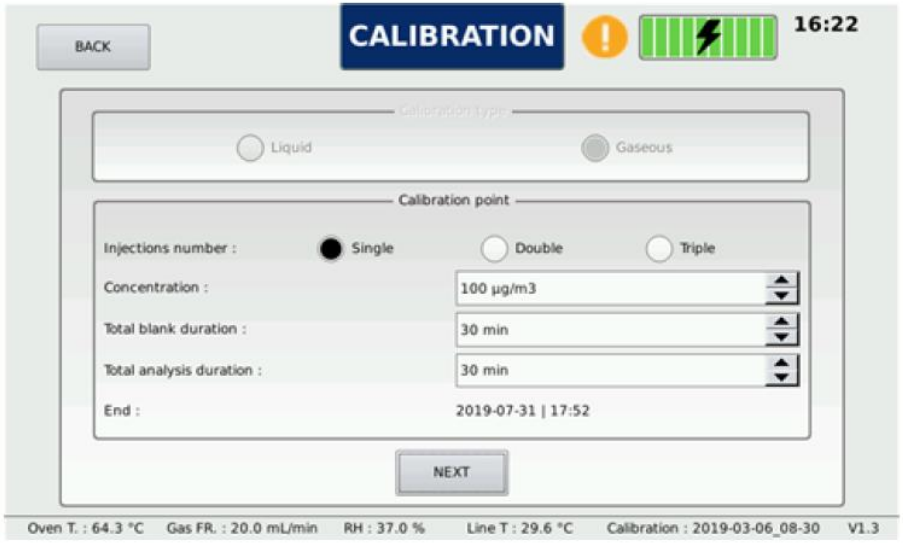
Results

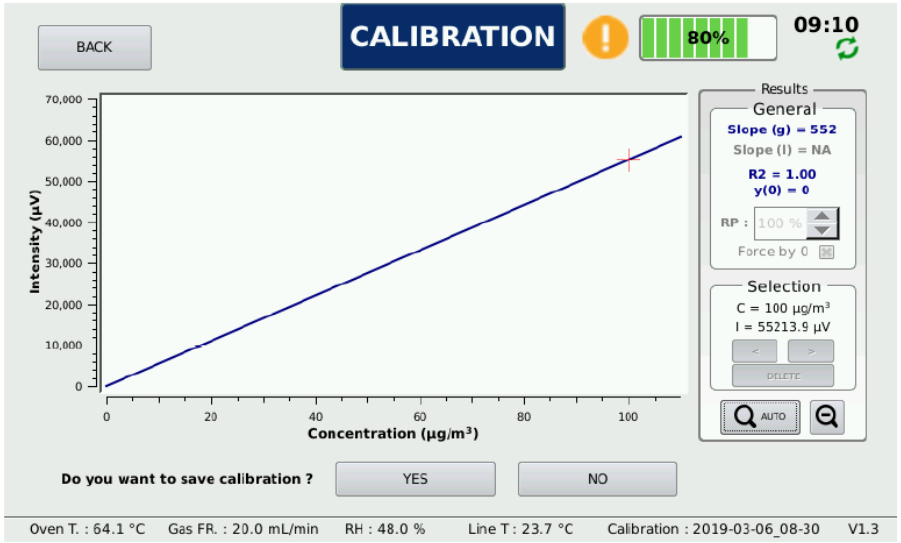
- Direct visualisation
- Exportation as excel file (via USB key)

Calibration

1. Connect calibration HCHO to calibration port

2. Program and launch

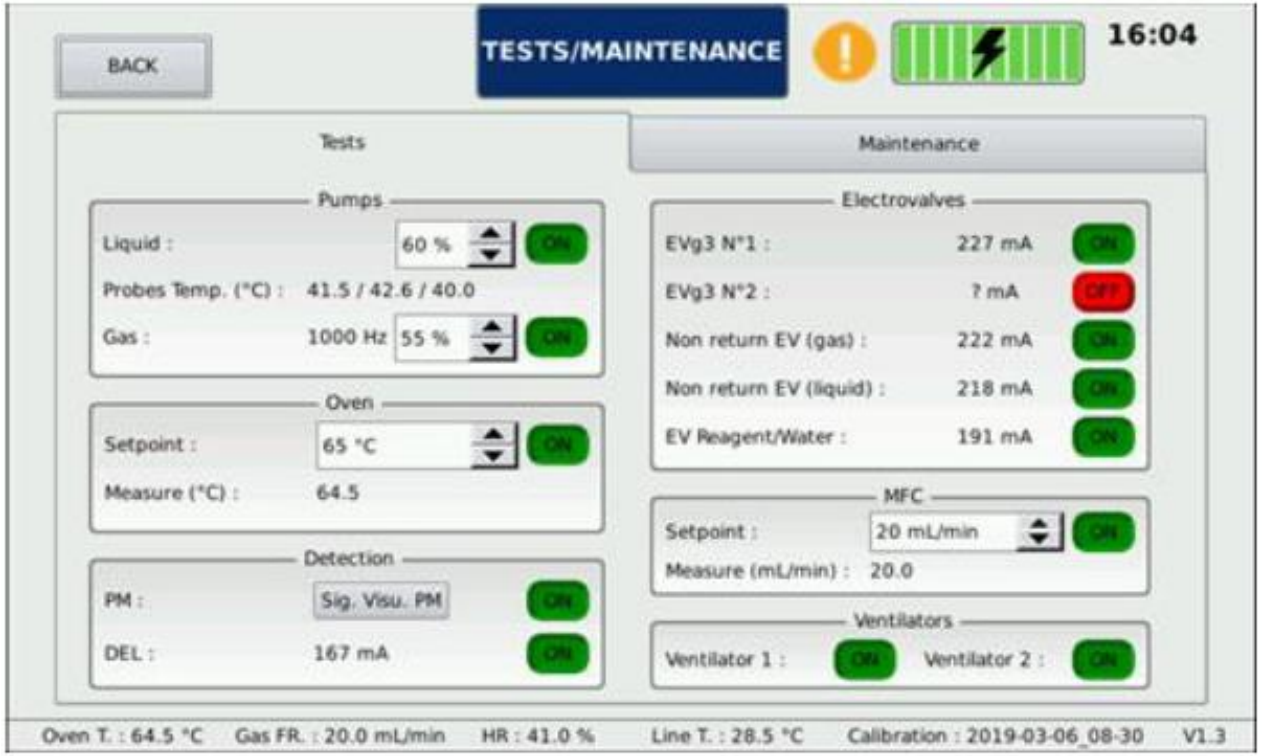




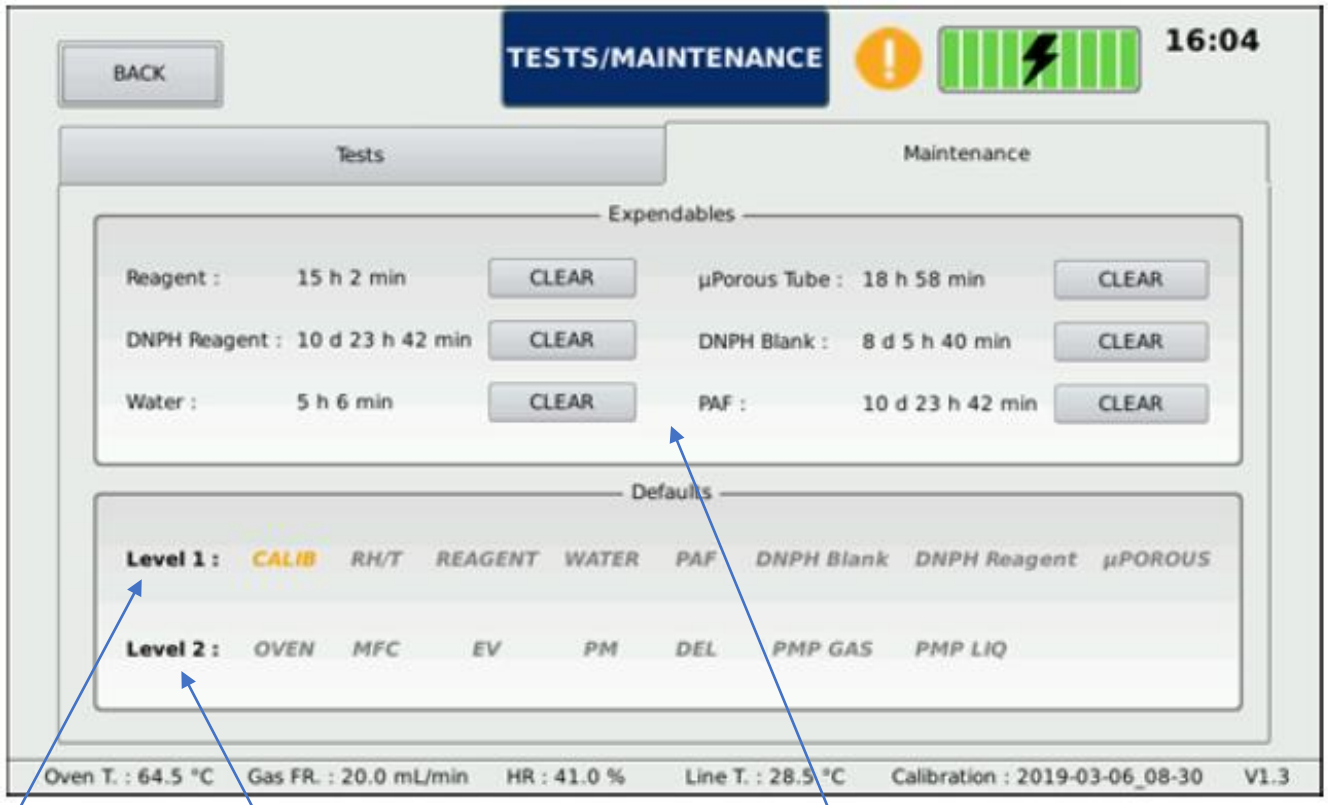
For liquid calibration, connect calibration solution to water port.

The steps are the same as for the gaseous calibration, only the end of calibration screen is different : uptake yield can be changed (gaseous slope vs liquid slope)

Tests/Maintenance



Tests/Maintenance



Level 1 issue :

Device continues to operate

Level 2 issue :

The analyser stops immediately : problem has to be solved and the system has to be restarted

Keep track of the duration of use of each consumable and reset when changed

Field campaigns

- MERMAID project

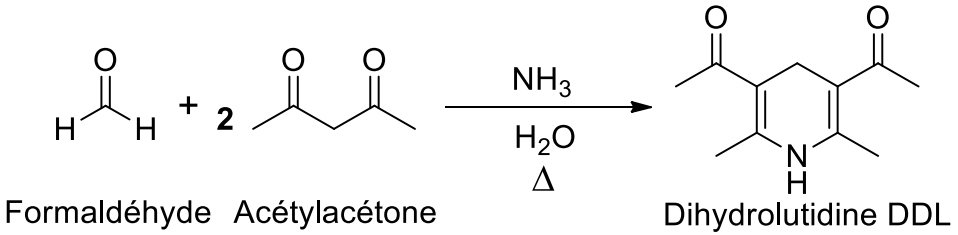
« **Near Real-Time Monitoring of Formaldehyde in a Low-Energy School Building** ». *Atmosphere* 10, nº 12 (décembre 2019): 763. https://doi.org/10.3390/atmos10120763.

- IMPACT'AIR

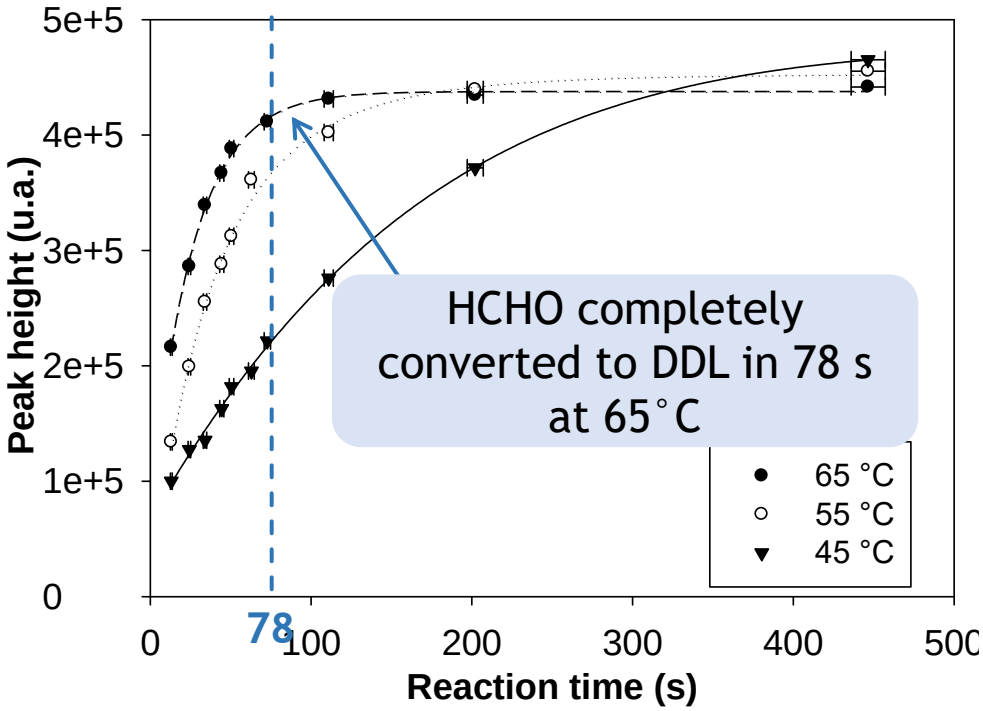
Miniaturized analyzer based on microfluidic technology dedicated to quantification of indoor air pollution

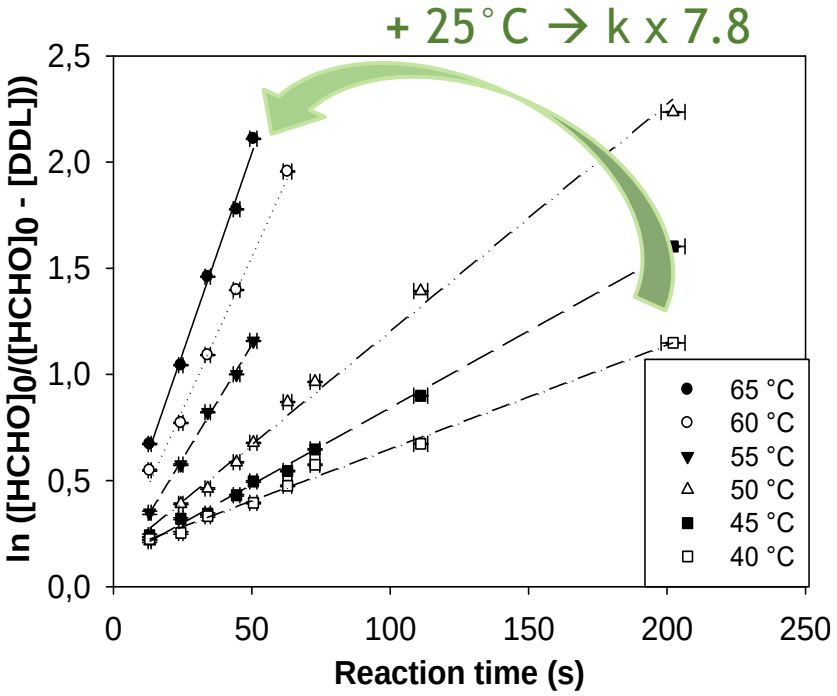
Strasbourg University – 5/6 june 2019

Reaction and kinetic study



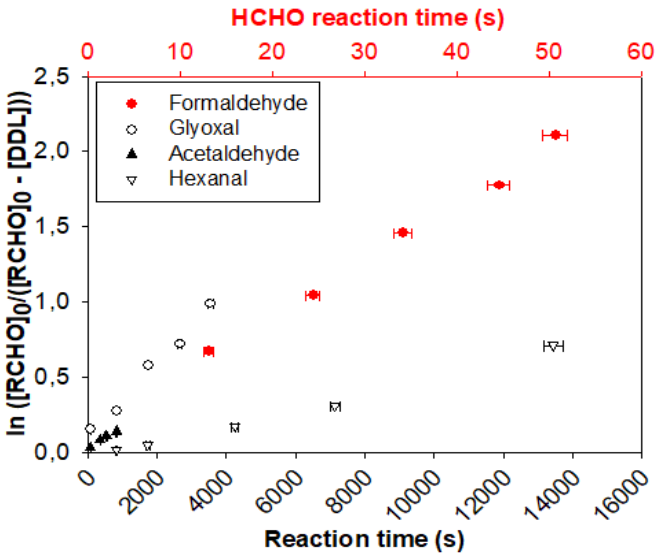
Kinetic study (Pseudo 1st order reactions)





k is the reaction rate constant

Reaction and kinetic study



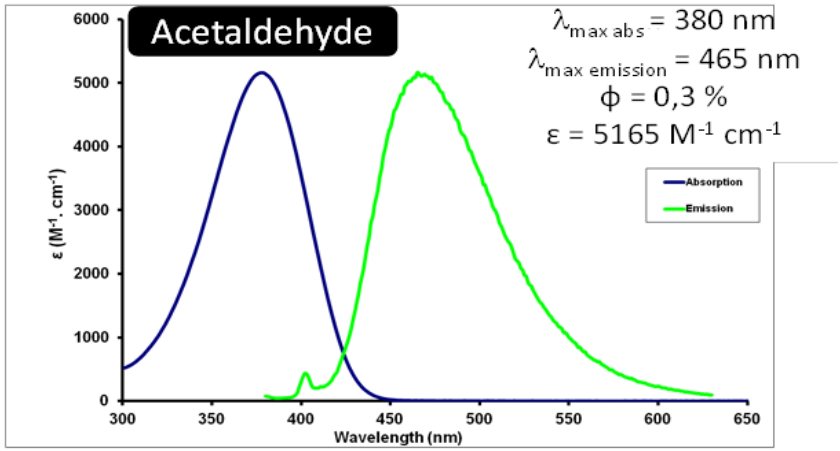
Aldehyde	$10^3 \times k$ ($\pm \Delta k$) ($L^2\ mol^{-2}\ s^{-1}$) at 65°C
Formaldehyde	94000 ± 5000
Glyoxal	31.3 ± 1.6
Acetaldehyde	15.6 ± 0.8
Hexanal	8.7 ± 0.4

$k_{HCHO} >> k_{others\ aldehydes}$

Formaldehyde

ϕ = 1,5 %

$\varepsilon = 6600\ M^{-1}\ cm^{-1}$



Acetaldehyde, Hexanal, Glyoxal

- Low water solubility
- Low fluorescence quantum efficiency
- Low rate reaction constant

No possible interference between these aldehydes and acetylacetone reagent

Formaldehyde specificity

Acetaldehyde, Hexanal, Glyoxal

- Low water solubility
- Low fluorescence quantum efficiency
- Low rate reaction constant

No possible interference between these aldehydes and acetylacetone reagent

Best Features

- Continuous and near real-time measurements

  vs Standard method (ISO: NF ISO 16000-3) : Successive sampling on DNPH cartridge and HPLC analysis – Time consuming and bulky equipment
- Temporal resolution of a few seconds
- High formaldehyde selectivity

  Fluorescence detection excitation and emission wavelength specific to DDL
- No known interference
- LOD 1 ppb
- Portable
- Gaseous or liquid calibration possible

Technology comparison

Specification	Reference method DNPH	aerolaser	Chromatotec airmoHCHO	Chromatotec microF
Detection principle	Derivitization method with DNPH Spectrometer	Thermal desorption and fluorimetric detection (Hantzsch reaction)	GC with FID and methanizer	Derivitization method with DNPH Fluorescence Detector
LDL	Around 10ppb	Around 0,1ppb	Less than 1 ppb in automatic	About 1ppb
Linearity		Linear from 0,1 to 3000ppb with R^2 > 0,999	Linear on peak area R^2 > 0.995 for each compound at ppb or ppm	Linear on 0 - 400 µg/m3 range
Long term stability			RSD on 48 hours < 2% at 2 ppm for all compounds	N/A
Interferences	Other aldehydes	Other aldehydes	Not sensitive to humidity and hydrocarbons.	Specific to Formaldehyde
Compounds measured	Formaldehyde	Formaldehyde	Formaldehyde Methanol Acetaldheyde	Formaldehyde

Feedback from scientific researchers confirm that other solutions are not able to continuously monitor formaldehyde at low ppb (0-30ppb) range accurately

Applications & Markets

- Service study, control laboratory for campaign and **HSE departments**
- Indoor air (paintings, coatings) & Clean rooms
- Ambient air monitoring in urban and rural areas
- Industrial fence line monitoring
- Chemical, pharmaceutical, funeral industries
- Paper plants

User profiles

- Service companies (ex: Bureau Veritas)
- Governmental agencies (EPA, INERIS)
- Meteorological institutes
- Universities and Research centers
- Industrial consortia
- Petrochemical groups

Some reference customer

- La Rochelle University
  - Research studies for indoor air
- CSTB (Construction Scientific and technical center)
  - Indoor air control
- FCBA (Pole Bois Bordeaux)
  - Indoor air control in wood and wood related industries

Online Analytical Solutions Experts

Thanks for your attention