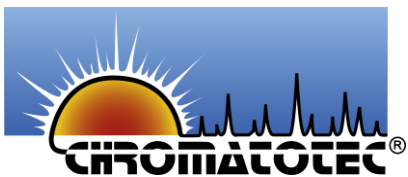


Online Analytical Solutions Experts



Chromatotec Sales Meeting

France, Saint-Antoine, July 5 to 7



Online Analytical Solutions Experts

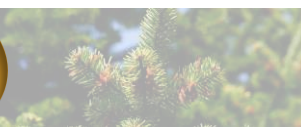
Micro Formaldehyde

Portable analyzer for continuous formaldehyde monitoring
in ambient air

Industrial
applications



Ambient
Air



Oil & Gas



Water /
Liquid samples



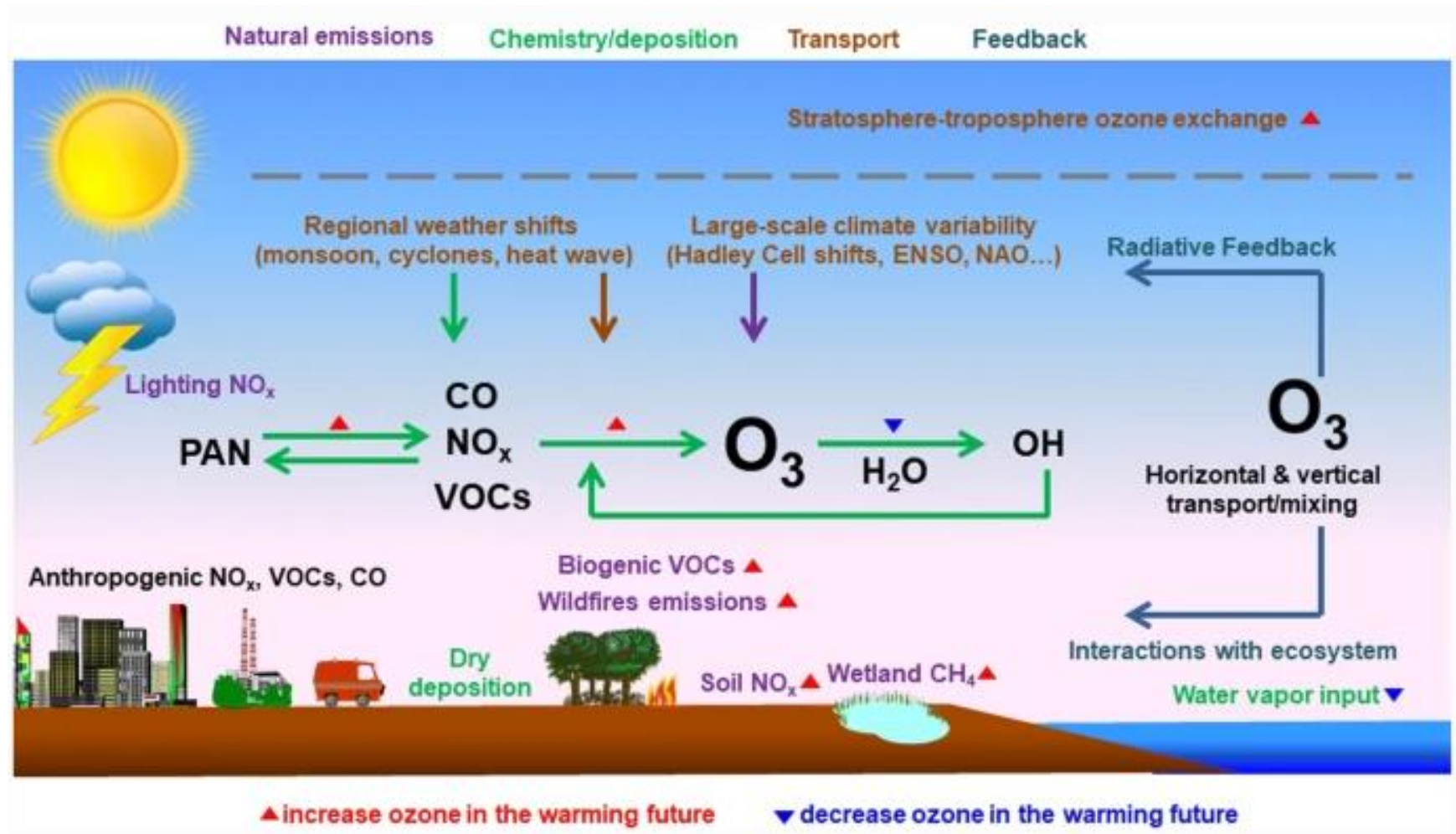
Odor



Process

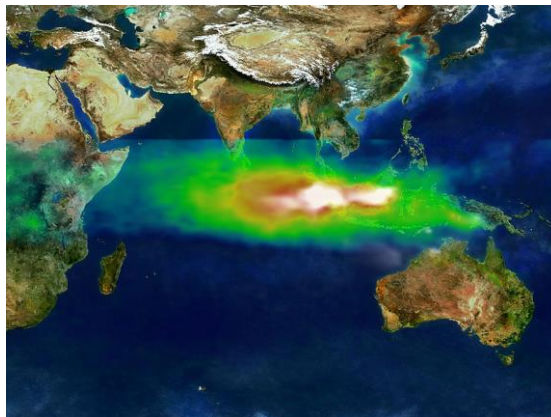


Ozone precursors



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 (NO_x, VOC like formaldehyde) to define national emission maxima.



¹The International Geosphere-Biosphere Program -
World Climate Research Program

²http://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 $\mu\text{g}/\text{m}^3$
- 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

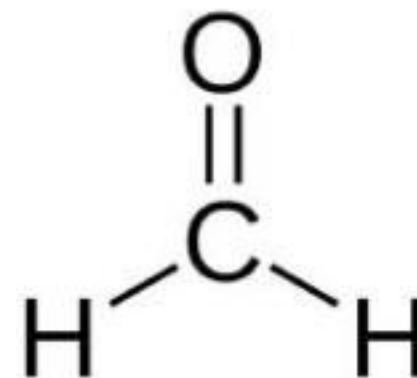
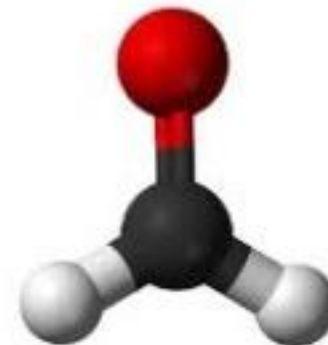
1. Official method with HPLC and DNPH cartridges
2. Online autoGC-FID with methanizer : airmoHCHO
3. Laser technology
4. Portable microfluidic technology

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.atusante.com/risques-professionnels/cmr-cancerogenes-mutagenes-toxiques-reproduction/formaldehyde/formaldehyde-effets-sante/>

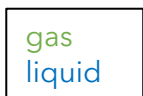
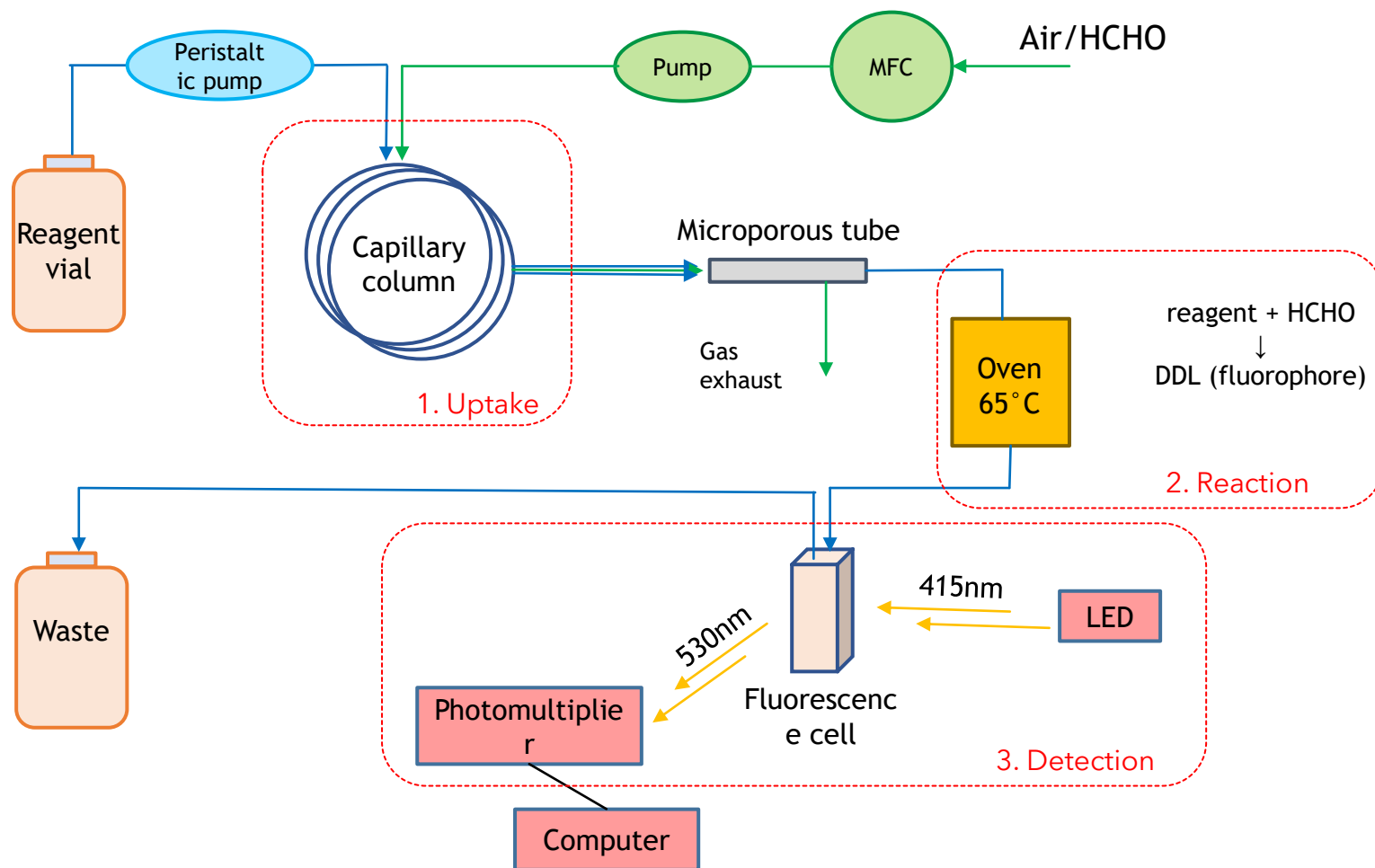
New portable micro Formaldehyde analyzer

Dimension	32 cm × 28 cm × 15 cm
Weight	6,5kg
Limit of detection	1 µg/m ³
Linearity range	0 - 400 µg/m ³
Trapping type	Microfluidic annular flow
Derivatization reagent	Fluoral-P (acetylacetone)
Detection type	Fluorescence

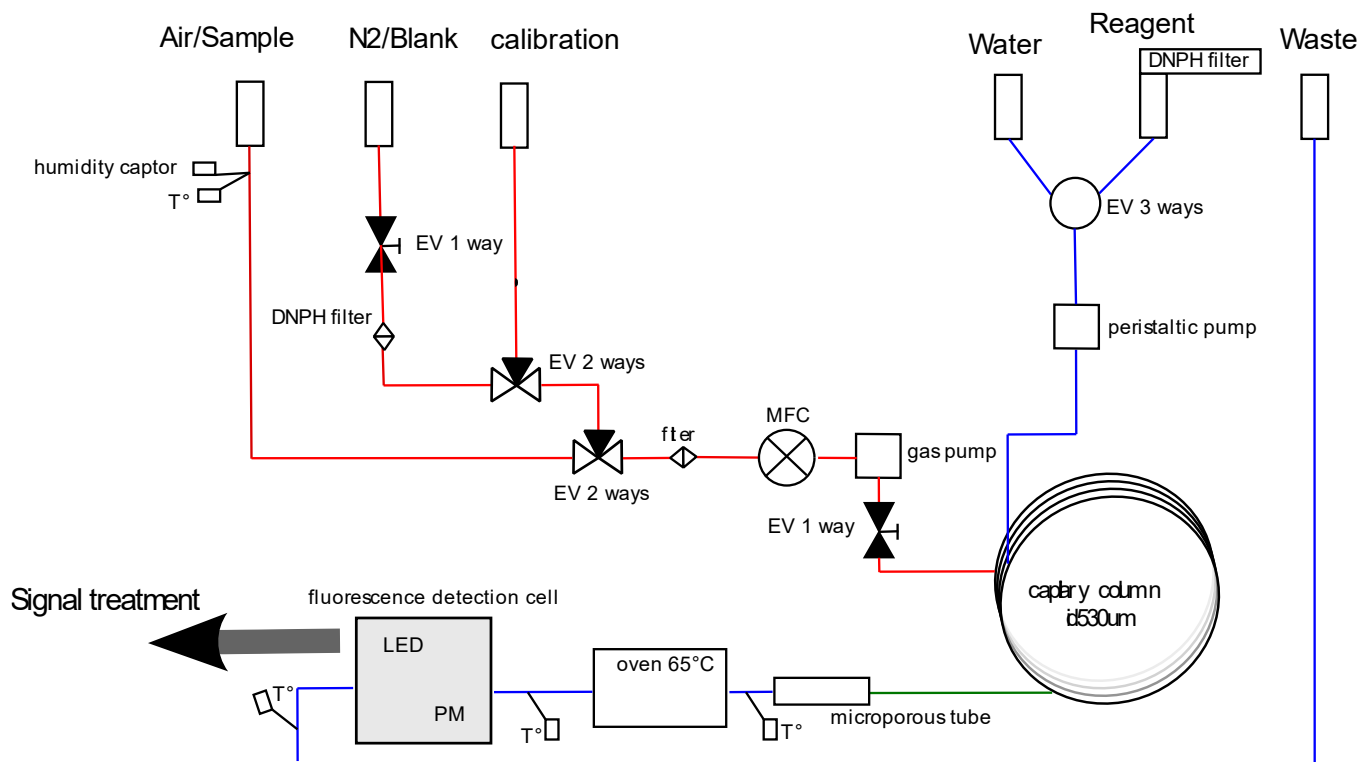


Developped in collaboration with CNRS French Research Center

Wall mounted autoGC

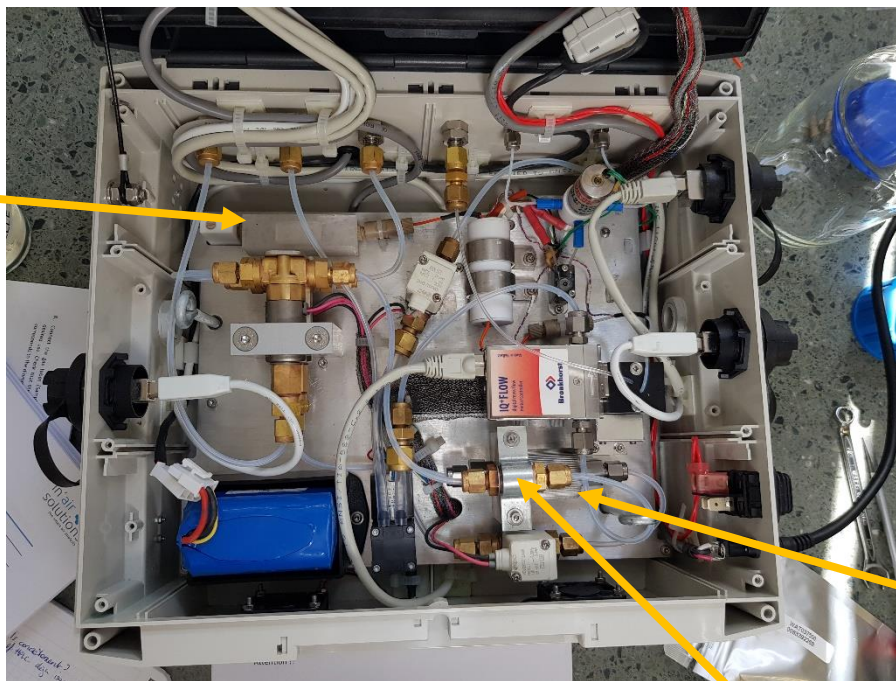


Full scheme



Internal view

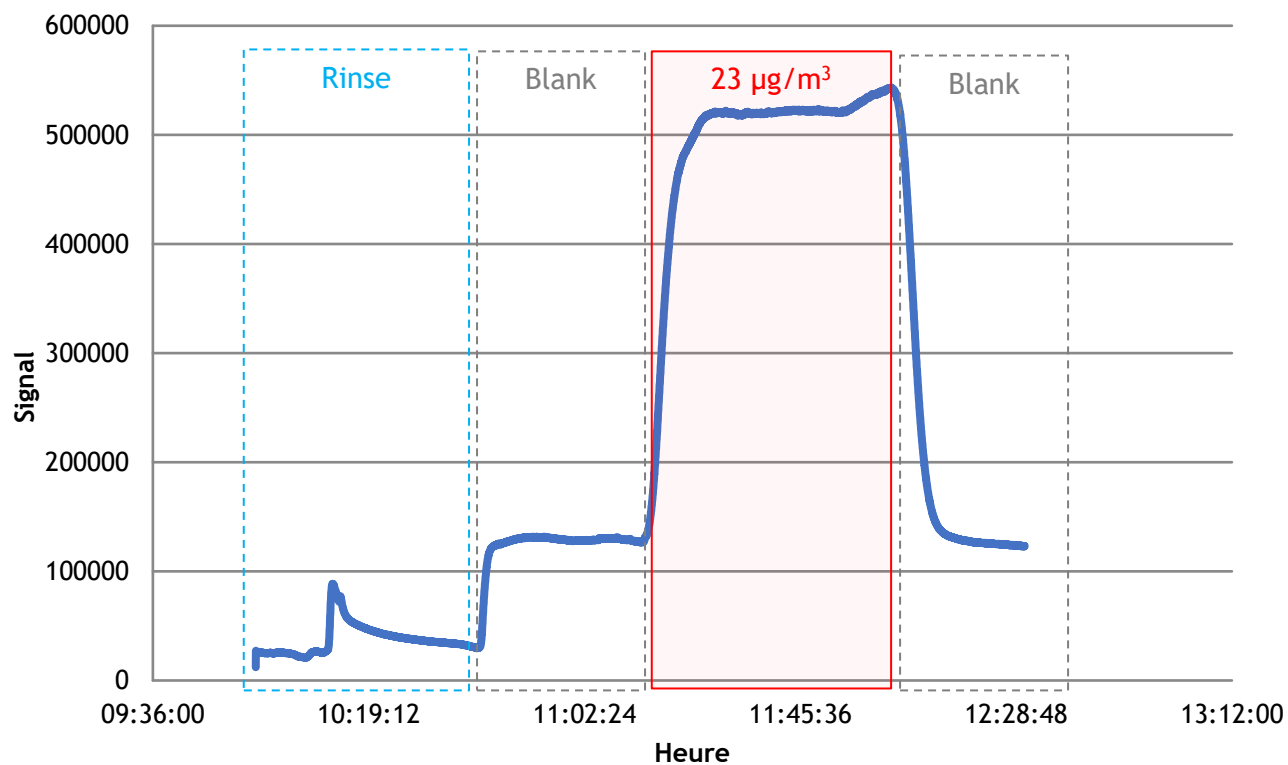
Microporous tube



DNPH cartridge

Particle filter

Principle Typical curve



Test parameters :

- **Liquid flow rate** : 17 $\mu\text{L}/\text{min}$
- **Gas flow rate** : 250 mL/min
- **Concentration** : 23 $\mu\text{g}/\text{m}^3$
- **Tube length** : 10 cm

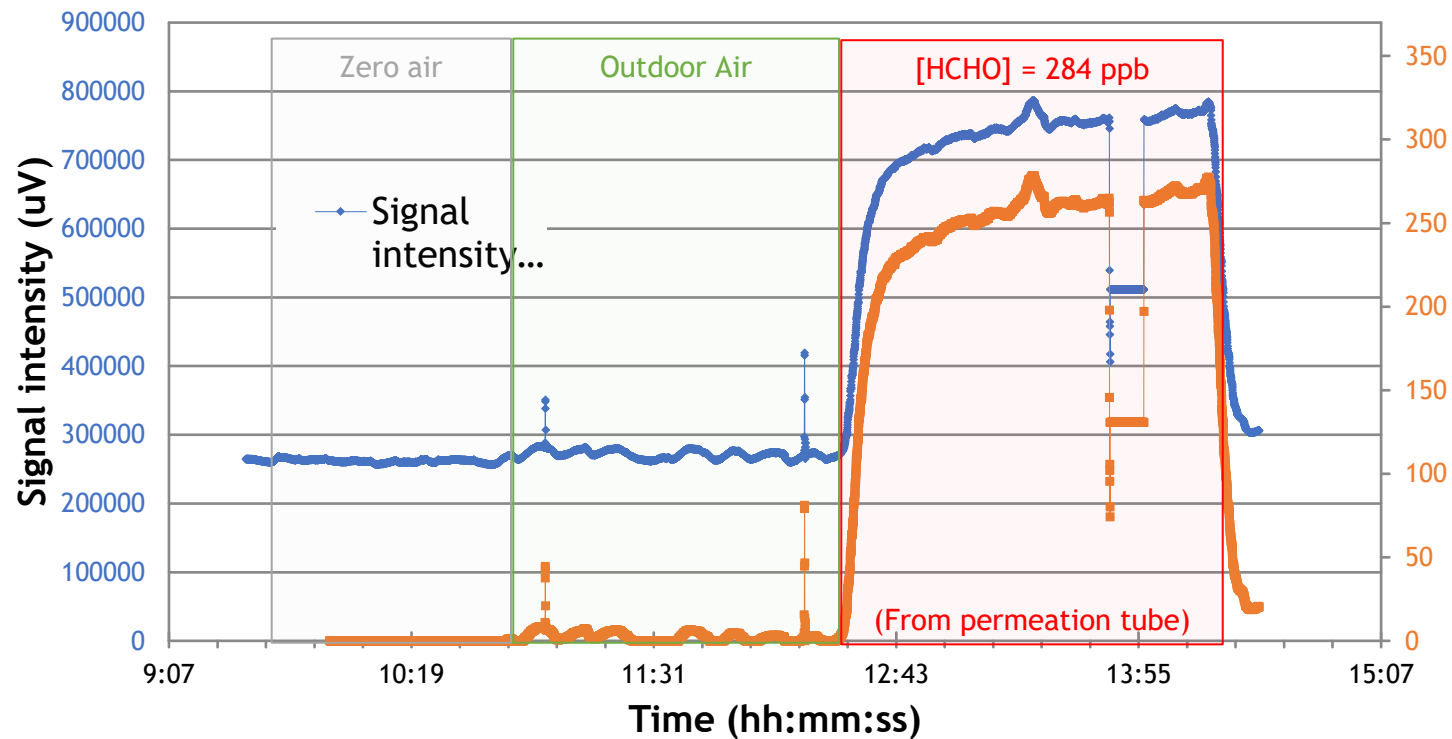
Anaïs Becker's work

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

PrincipleTypical curve

- Intensity curve
- Concentration curve ($\mu\text{g}/\text{m}^3$ or ppb)

$\mu\text{F}-1$ sampling tests



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 ($1.2 \mu\text{g}/\text{m}^3$)

Response time : 10 min

Time resolution : Few seconds to 120 s

Reagent consumption : 1.2mL per 60 minutes

Conditions :

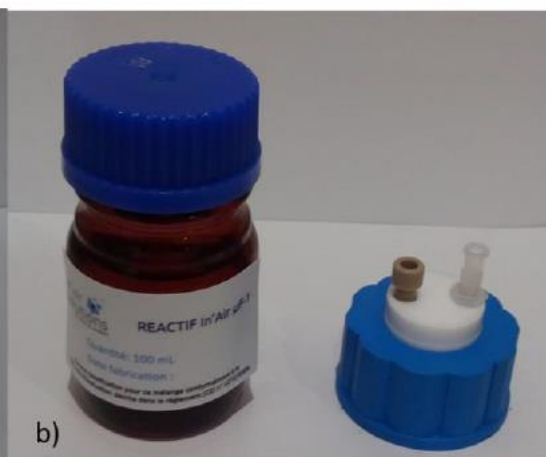
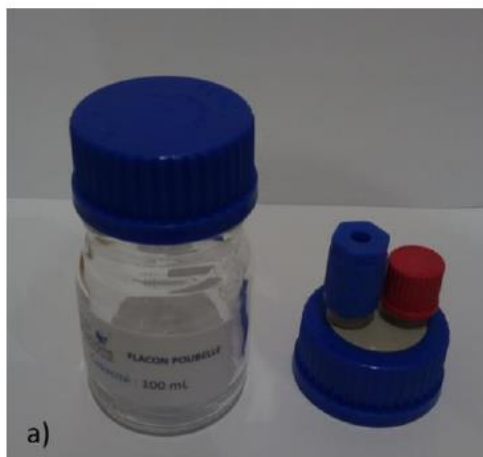
Gas T°: 5 - 40°C;

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

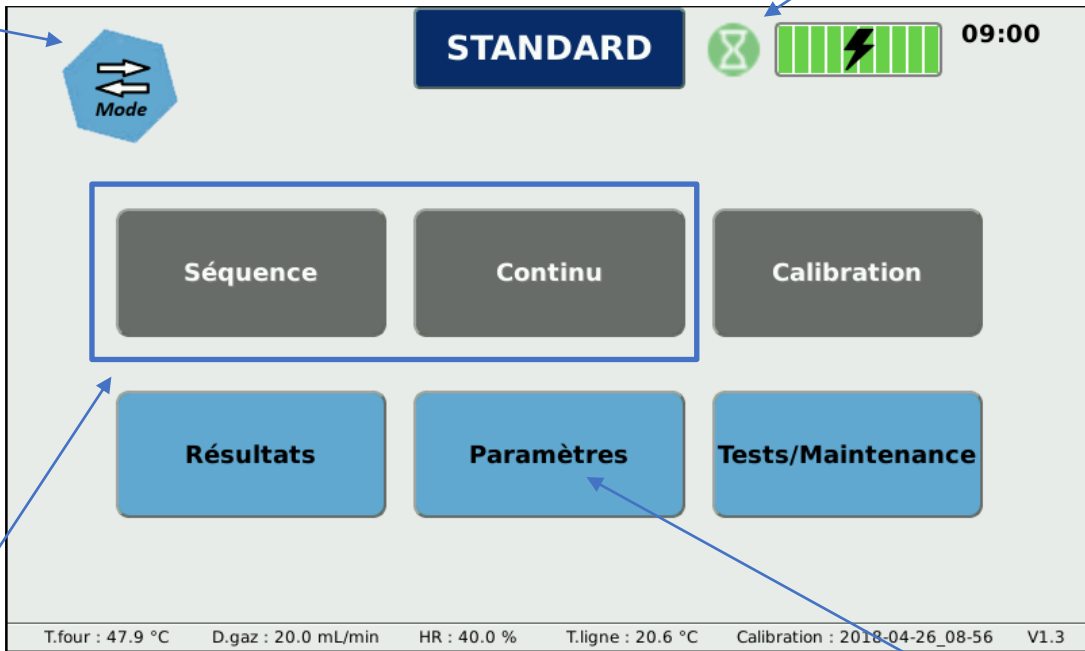
User mode and expert mode

Stabilisation

Analysis

Sequence : Programmable sequence
Continuous : Manual change of modes

General parameters and analysis parameters



The screenshot displays the Chromatotec control interface. At the top, there is a 'Mode' button with a double arrow icon, a 'STANDARD' button, a green hourglass icon, a battery status indicator with a lightning bolt, and a digital clock showing '09:00'. Below these, there are six main function buttons arranged in two rows: 'Séquence', 'Continu', and 'Calibration' in the top row; 'Résultats', 'Paramètres', and 'Tests/Maintenance' in the bottom row. A blue box highlights the 'Séquence' and 'Continu' buttons. At the bottom of the screen, a status bar displays various parameters: 'T.four : 47.9 °C', 'D.gaz : 20.0 mL/min', 'HR : 40.0 %', 'T.ligne : 20.6 °C', 'Calibration : 2018-04-26_08-56', and 'V1.3'. Arrows from the text labels point to specific elements: 'User mode and expert mode' points to the 'Mode' button; 'Stabilisation' points to the green hourglass icon; 'Analysis' points to the 'Séquence' and 'Continu' buttons; 'Sequence : Programmable sequence' and 'Continuous : Manual change of modes' point to the 'Séquence' and 'Continu' buttons respectively; and 'General parameters and analysis parameters' points to the 'Paramètres' button.

Analysis

Before a run, check that the analyser is calibrated
(minimum every 3 months)


► Continuous measurement :

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



Analysis

- Sequence programming

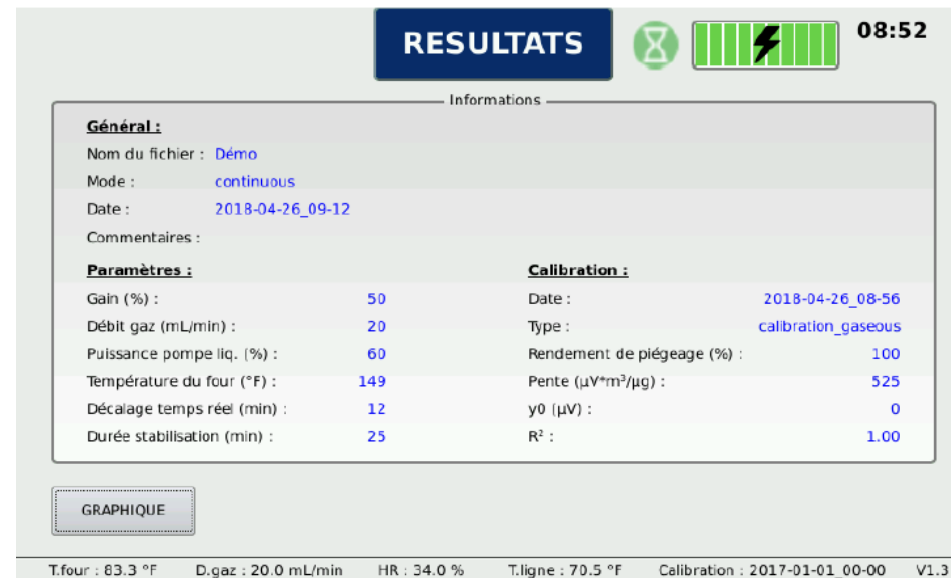
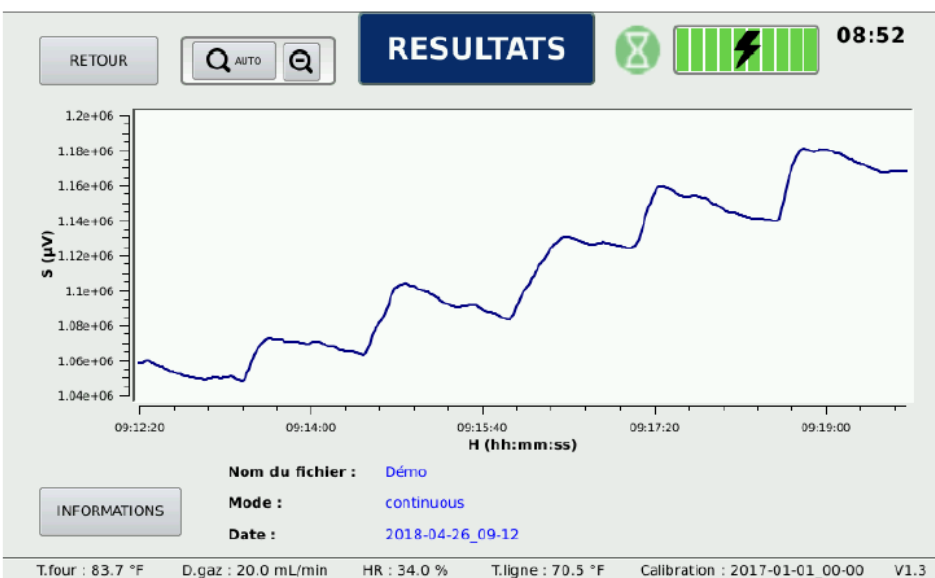
BACK START **SEQUENCE** !  16:15

BEGIN	DURATION	ACTION	COMMENTARY
31/07/2019 16:16	60 min	BLANK	Obligatory action
31/07/2019 17:16	120 min	ANALYSIS	
31/07/2019 20:16	45 min	BLANK	
31/07/2019 21:01	45 min	ANNEXE	
31/07/2019 21:46	45 min	BLANK	
31/07/2019 22:31	60 min	FLUSH	Obligatory action

+ - BLANK 31/07/2019 21:46 45 min OK DELETE ALL

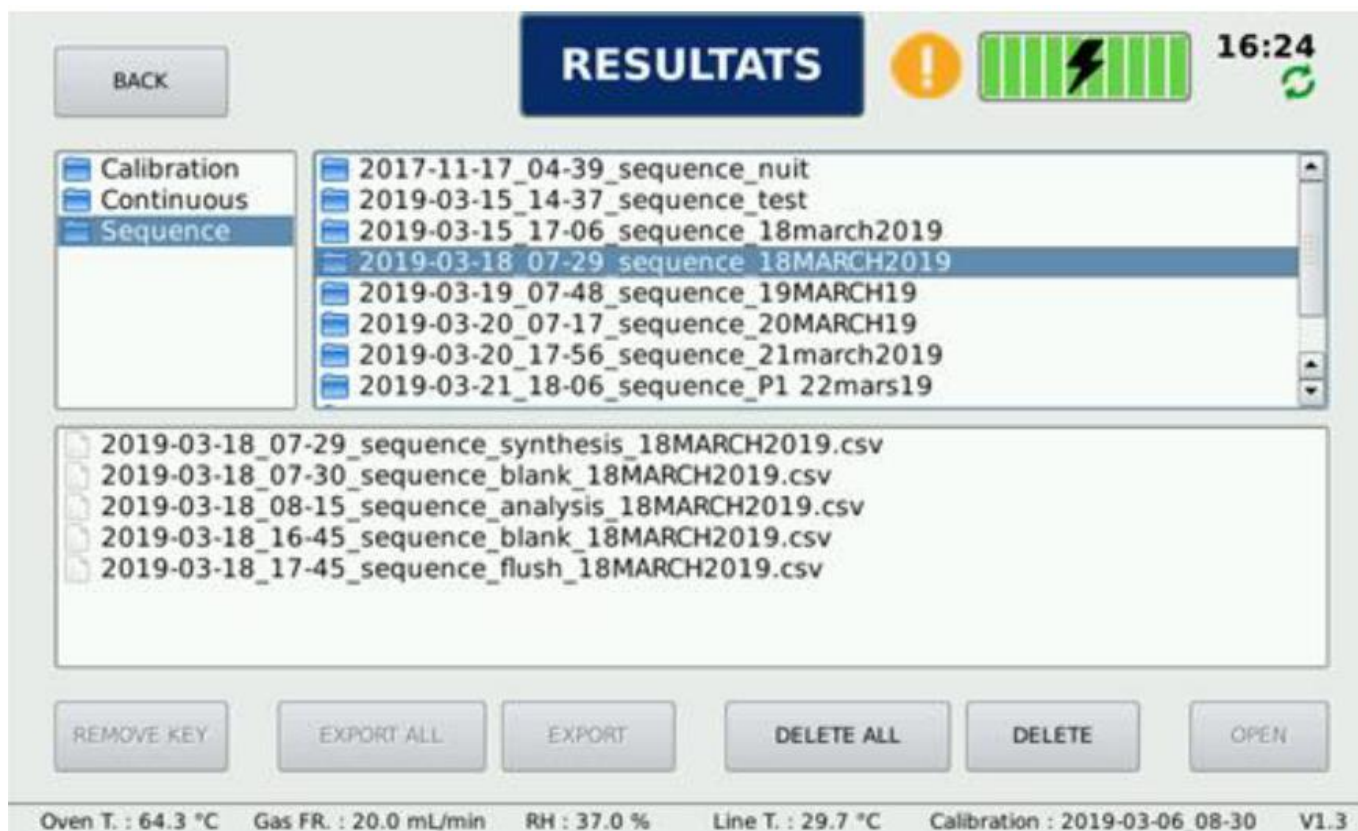
Oven T. : 64.3 °C Gas FR. : 20.0 mL/min RH : 37.0 % Line T. : 29.3 °C Calibration : 2019-03-06_08-30 V1.3

Results



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

Results

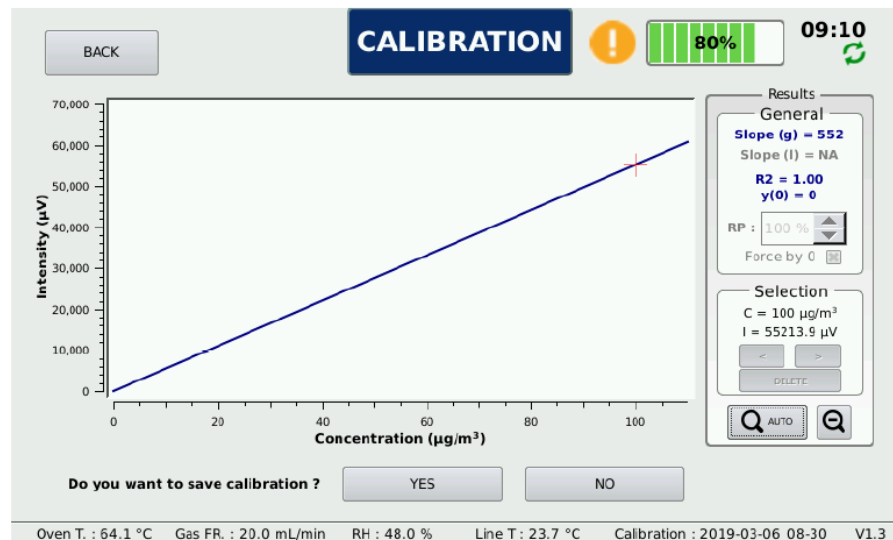


- ▶ Direct visualisation
- ▶ Exportation as excel file (via USB key)

Calibration

1. Connect calibration HCHO to calibration port
2. Program and launch

The screenshot shows the 'CALIBRATION' screen with a 'BACK' button and a battery icon. The 'Calibration type' is set to 'Liquid'. Under 'Calibration point', 'Injections number' is set to 'Single', 'Concentration' is '100 µg/m³', 'Total blank duration' is '30 min', and 'Total analysis duration' is '30 min'. The 'End' time is '2019-07-31 | 17:52'. A 'NEXT' button is at the bottom. The status bar at the bottom shows: Oven T.: 64.3 °C, Gas FR.: 20.0 mL/min, RH: 37.0 %, Line T.: 29.6 °C, Calibration: 2019-03-06_08-30, V1.3.




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

BACK

TESTS/MAINTENANCE







16:04



Tests

Maintenance



Pumps

Liquid : 60 %  

Probes Temp. (°C) : 41.5 / 42.6 / 40.0


Gas : 1000 Hz 55 %  


Oven

Setpoint : 65 °C  


Measure (°C) : 64.5


Detection


PM : Sig. Visu. PM 


DEL : 167 mA 


Electrovalves

EVg3 N°1 : 227 mA 



EVg3 N°2 : ? mA 

Non return EV (gas) : 222 mA 

Non return EV (liquid) : 218 mA 



EV Reagent/Water : 191 mA 

MFC

Setpoint : 20 mL/min  

Measure (mL/min) : 20.0

Ventilators

Ventilator 1 :  Ventilator 2 : 

Oven T. : 64.5 °C Gas FR. : 20.0 mL/min HR : 41.0 % Line T. : 28.5 °C Calibration : 2019-03-06_08-30 V1.3

Tests/Maintenance

The screenshot shows a control panel interface for a chromatography system. At the top, there is a 'BACK' button, a 'TESTS/MAINTENANCE' title bar, a warning icon (exclamation mark in a circle), a battery level indicator (green bars with a lightning bolt), and the time '16:04'. Below the title bar, there are two tabs: 'Tests' and 'Maintenance'. The 'Expendables' section lists various consumables with their remaining time and a 'CLEAR' button for each: Reagent (15 h 2 min), DNPH Reagent (10 d 23 h 42 min), Water (5 h 6 min), µPorous Tube (18 h 58 min), DNPH Blank (8 d 5 h 40 min), and PAF (10 d 23 h 42 min). The 'Defaults' section shows two levels of settings: Level 1 (CALIB, RH/T, REAGENT, WATER, PAF, DNPH Blank, DNPH Reagent, µPOROUS) and Level 2 (OVEN, MFC, EV, PM, DEL, PMP GAS, PMP LIQ). At the bottom, a status bar displays: Oven T. : 64.5 °C, Gas FR. : 20.0 mL/min, HR : 41.0 %, Line T. : 28.5 °C, Calibration : 2019-03-06_08-30, and V1.3. Blue arrows point from the explanatory text below to the 'CALIB' button in Level 1 and the 'PAF' entry in the Expendables list.

Expendables	
Reagent : 15 h 2 min	<input type="button" value="CLEAR"/>
DNPH Reagent : 10 d 23 h 42 min	<input type="button" value="CLEAR"/>
Water : 5 h 6 min	<input type="button" value="CLEAR"/>
µPorous Tube : 18 h 58 min	<input type="button" value="CLEAR"/>
DNPH Blank : 8 d 5 h 40 min	<input type="button" value="CLEAR"/>
PAF : 10 d 23 h 42 min	<input type="button" value="CLEAR"/>

Defaults	
Level 1 :	CALIB RH/T REAGENT WATER PAF DNPH Blank DNPH Reagent µPOROUS
Level 2 :	OVEN MFC EV PM DEL PMP GAS PMP LIQ

Oven T. : 64.5 °C Gas FR. : 20.0 mL/min HR : 41.0 % Line T. : 28.5 °C Calibration : 2019-03-06_08-30 V1.3

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, n° 12 (décembre 2019): 763.

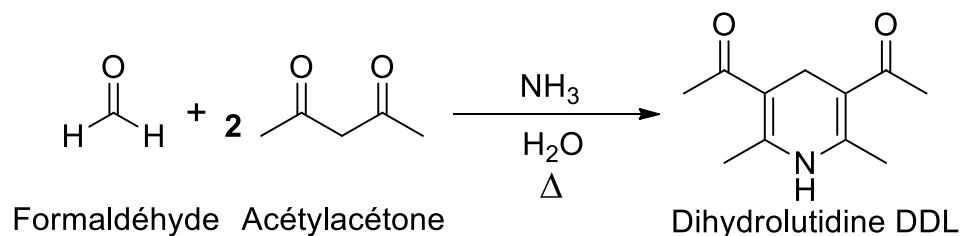
<https://doi.org/10.3390/atmos10120763>.

► IMPACT'AIR

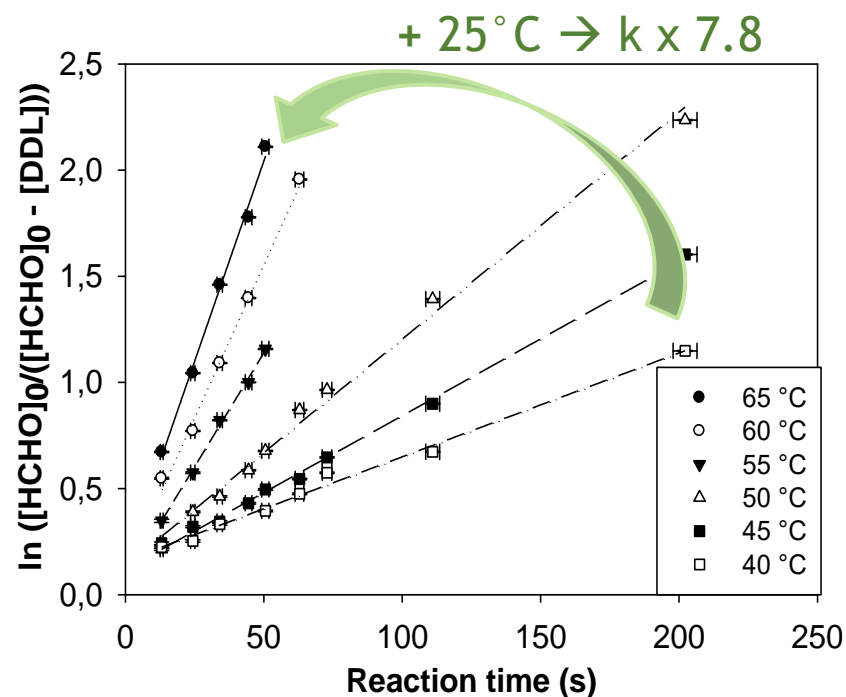
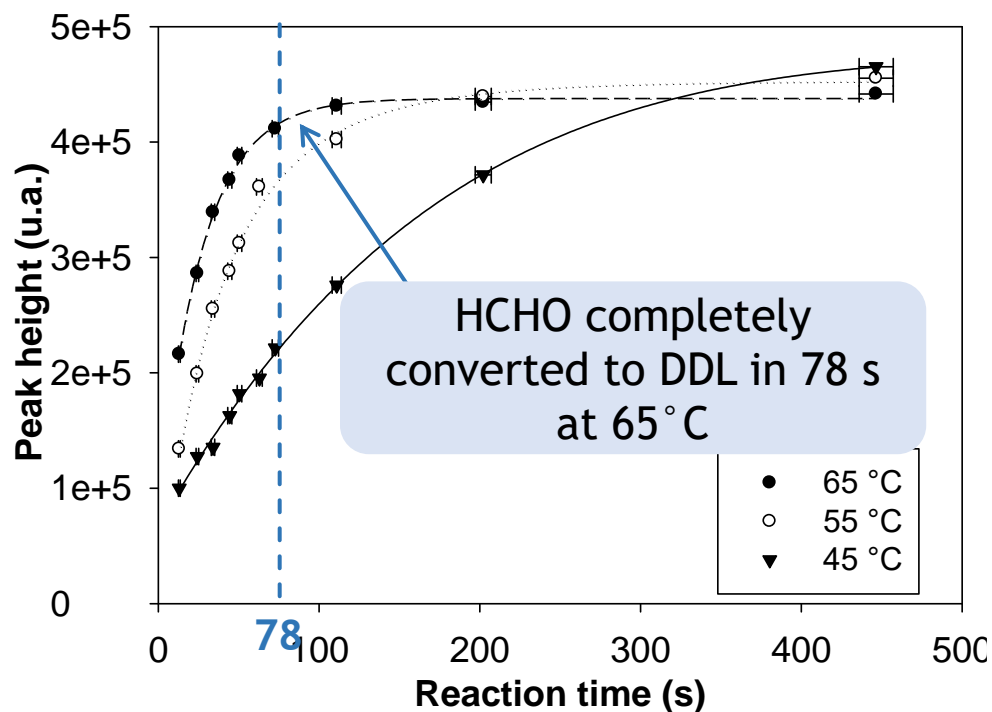
Miniaturized analyzer based on microfluidic technology dedicated to quantification of indoor air pollution

Strasbourg University - 5/6 june 2019

Reaction and kinetic study

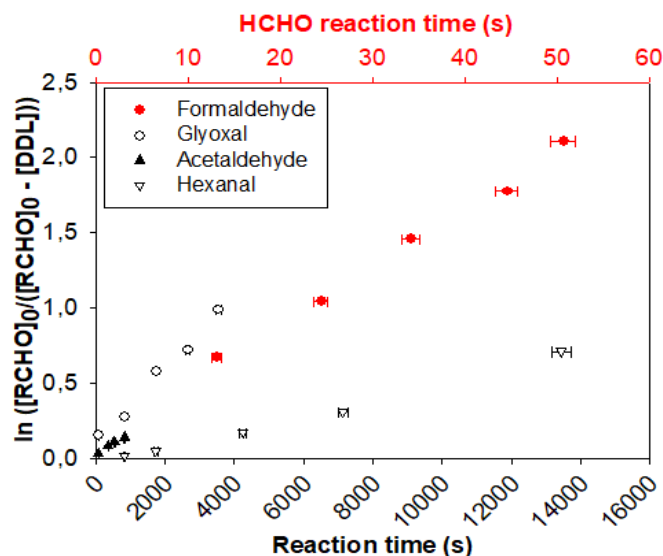


Kinetic study (Pseudo 1st order reactions)



k is the reaction rate constant

Reaction and kinetic study



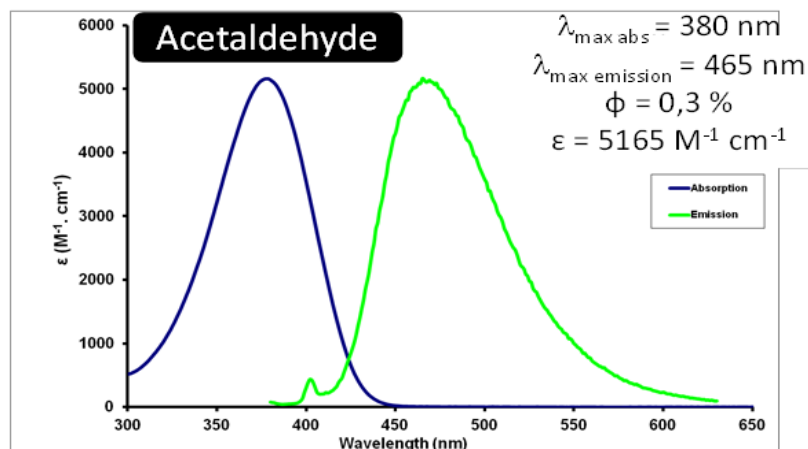
Aldehyde	$10^3 \times k (\pm \Delta k)$ ($L^2 \text{ mol}^{-2} \text{ s}^{-1}$) at 65°C
Formaldehyde	94000 ± 5000
Glyoxal	31.3 ± 1.6
Acetaldehyde	15.6 ± 0.8
Hexanal	8.7 ± 0.4

$$k_{\text{HCHO}} \gg k_{\text{others aldehydes}}$$

Formaldehyde

$$\phi = 1,5 \%$$

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



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**

10

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 $\mu\text{g}/\text{m}^3$ 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

Chromatotec Sales Meeting, France, 5-7 July 2022



Applications & Markets

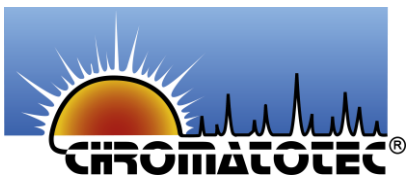
- ▶ Service study, control laboratory for campaign and **HSE departments**
- ▶ Indoor air (paintings, coatings) & Clean rooms
- ▶ Ambient air monitoring in urban and rural areas
- ▶ Industrial fence line monitoring
- ▶ Chemical, pharmaceutical, funeral industries
- ▶ Paper plants

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