Online Gas and Liquid Analyzer Experts

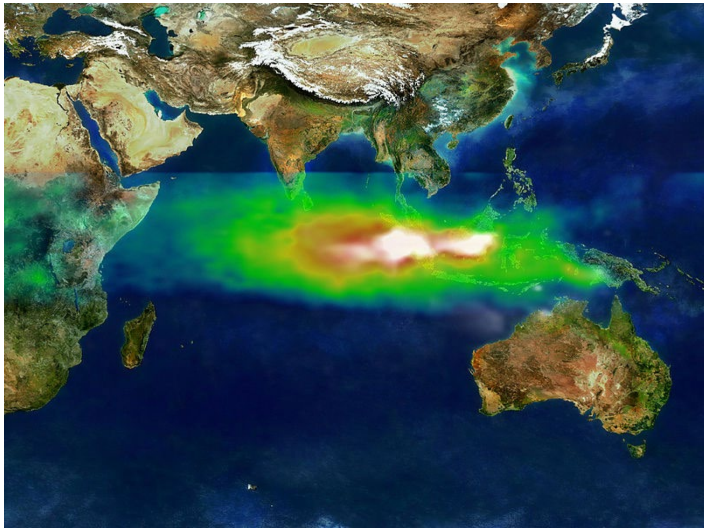
Chromatotec introducing new product range

Portable analyzers and detectors

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

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- 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

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- 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

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A. Objectives

The main objectives of such measurements are to analyze any trend in ozone precursors, to check the efficiency of emission reduction strategies, to check the consistency of emission inventories and to help attribute emission sources to observe pollution concentrations.
An additional aim is to support the understanding of ozone formation and precursor dispersion processes, as well as the application of photochemical models.

B. Substances

Measurement of ozone precursor substances shall include at least nitrogen oxides (NO and NO2), and appropriate volatile organic compounds (VOC such as formaldehyde). A list of volatile organic compounds recommended for measurement is given on next slide.

C. Siting

Measurements shall be taken in particular in urban or suburban areas at any monitoring site set up in accordance with the requirements of this Directive and considered appropriate with regard to the monitoring objectives referred to in Section A.

ANNEX X of European directive 2008/50/EC

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Ozone precursors

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

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PAHs
TO 14
AROMATICS
ODOR
TO 15
AMC
VOCs
PCB
SO_2
OVOCs
HYDRO-CARBONS
SOLVENTS
HALOGENATED
PAMS 56
DIOXINS PRECURSORS
BTEX

microF

Portable Formaldehyde Analyzer

cnrs

Why analyze formaldehyde ?

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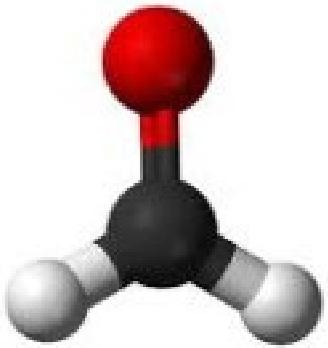
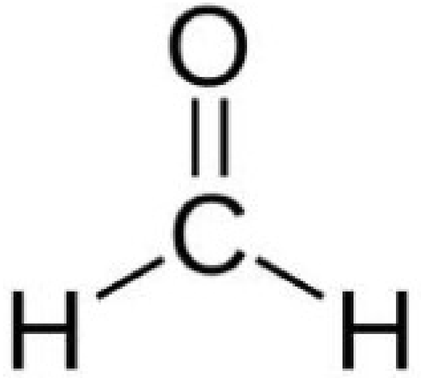
- Formaldehyde is present in :

  - 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/

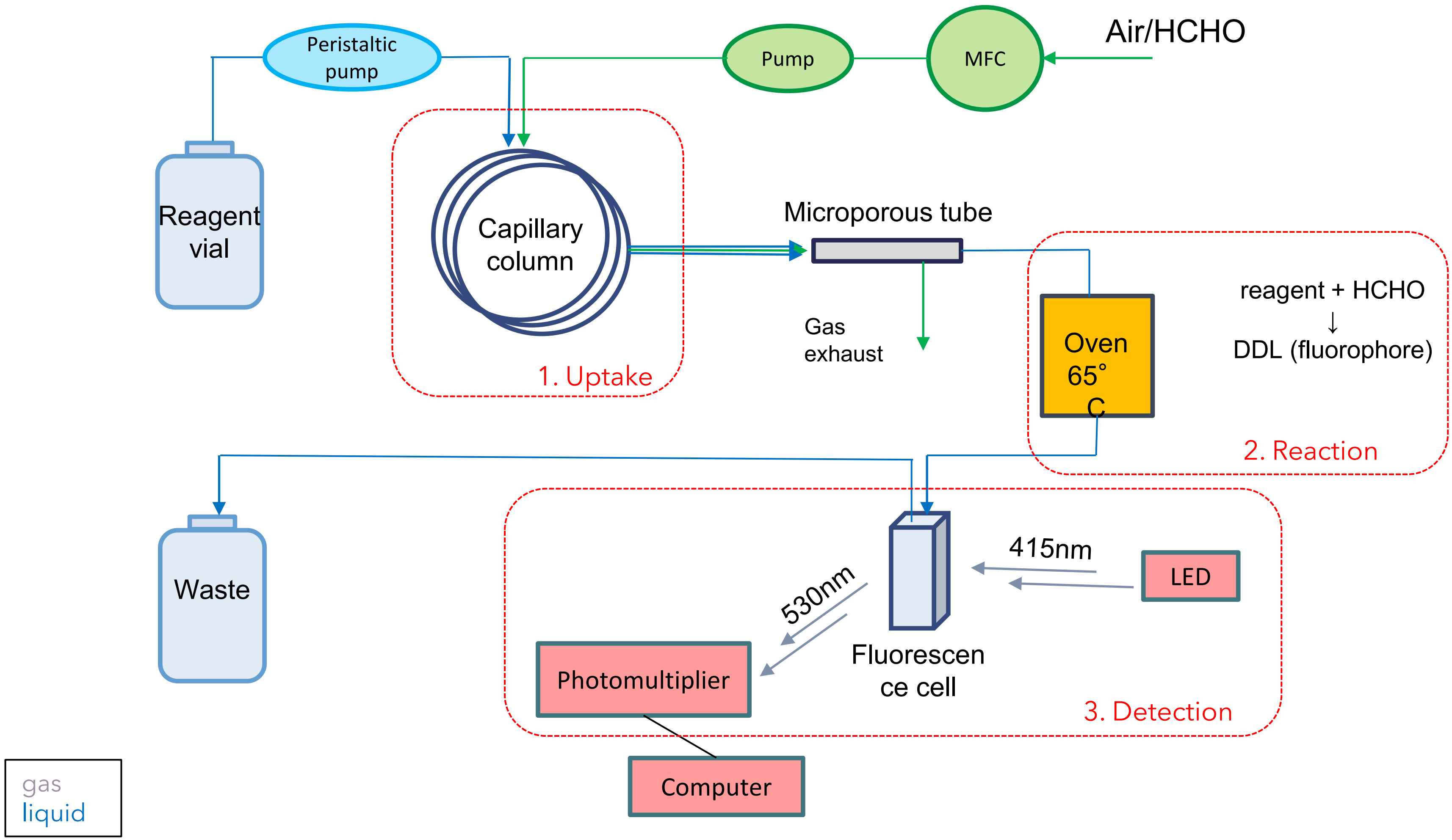
New portable micro Formaldehyde analyzer

Online Gas and Liquid Analyzer Experts

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

Principle Scheme



Full scheme

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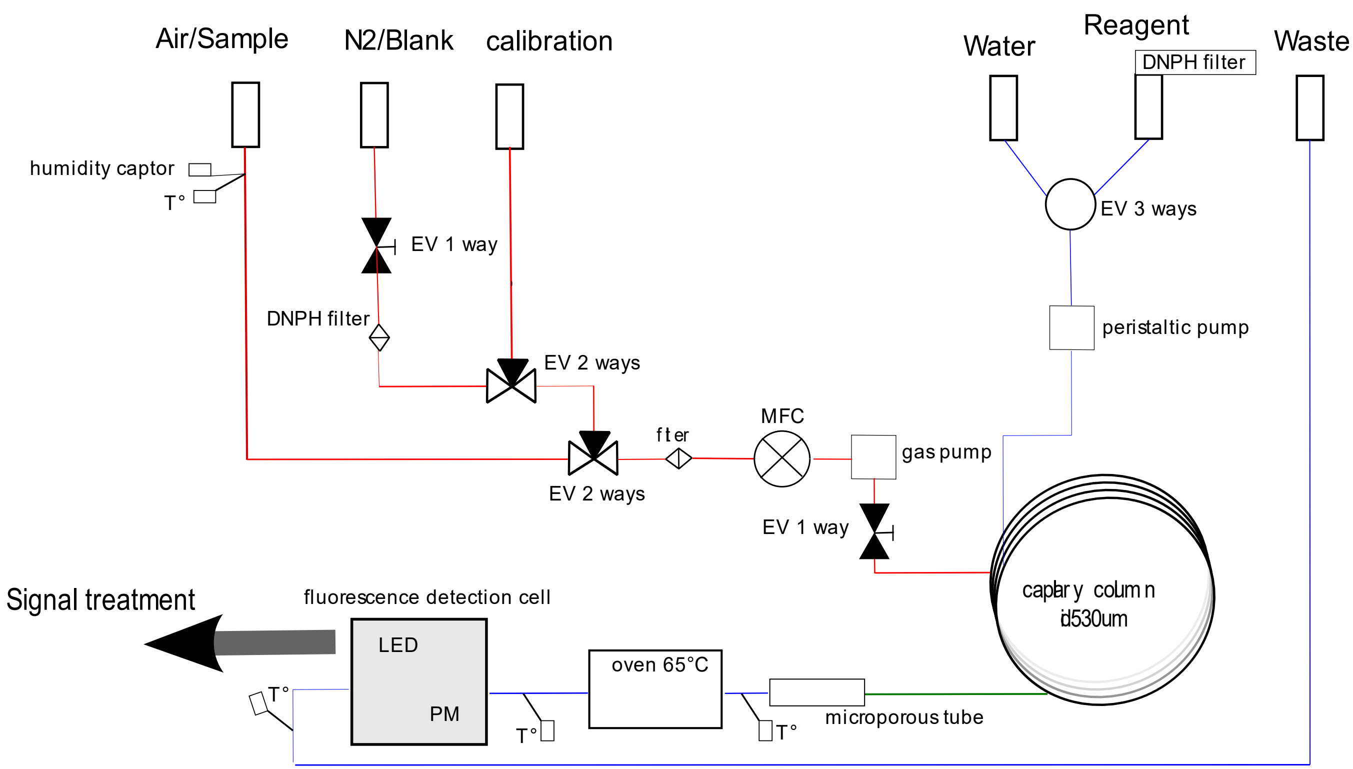
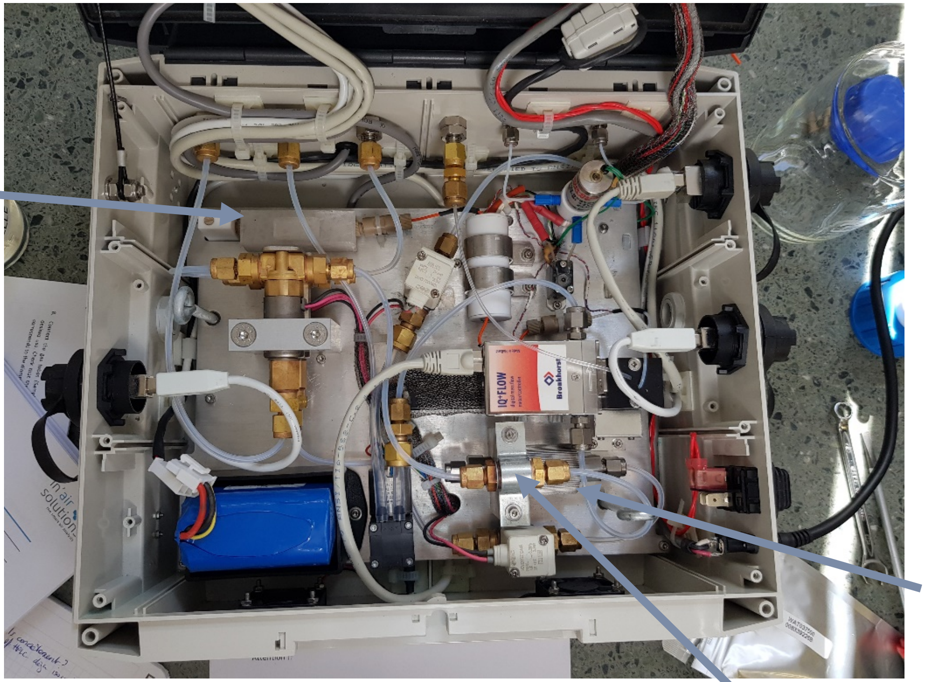


Internal view



Microporous tube

DNPH cartridge

Particle filter

Principle Typical curve

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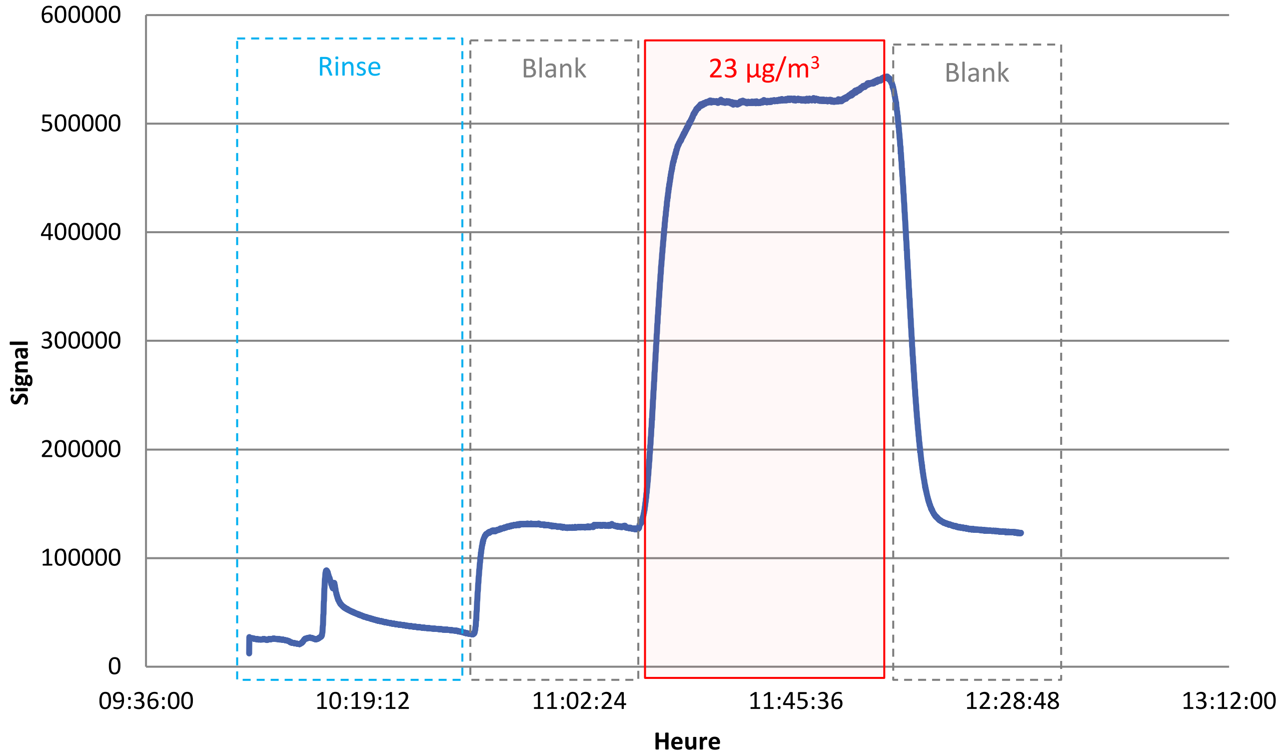


Test parameters :

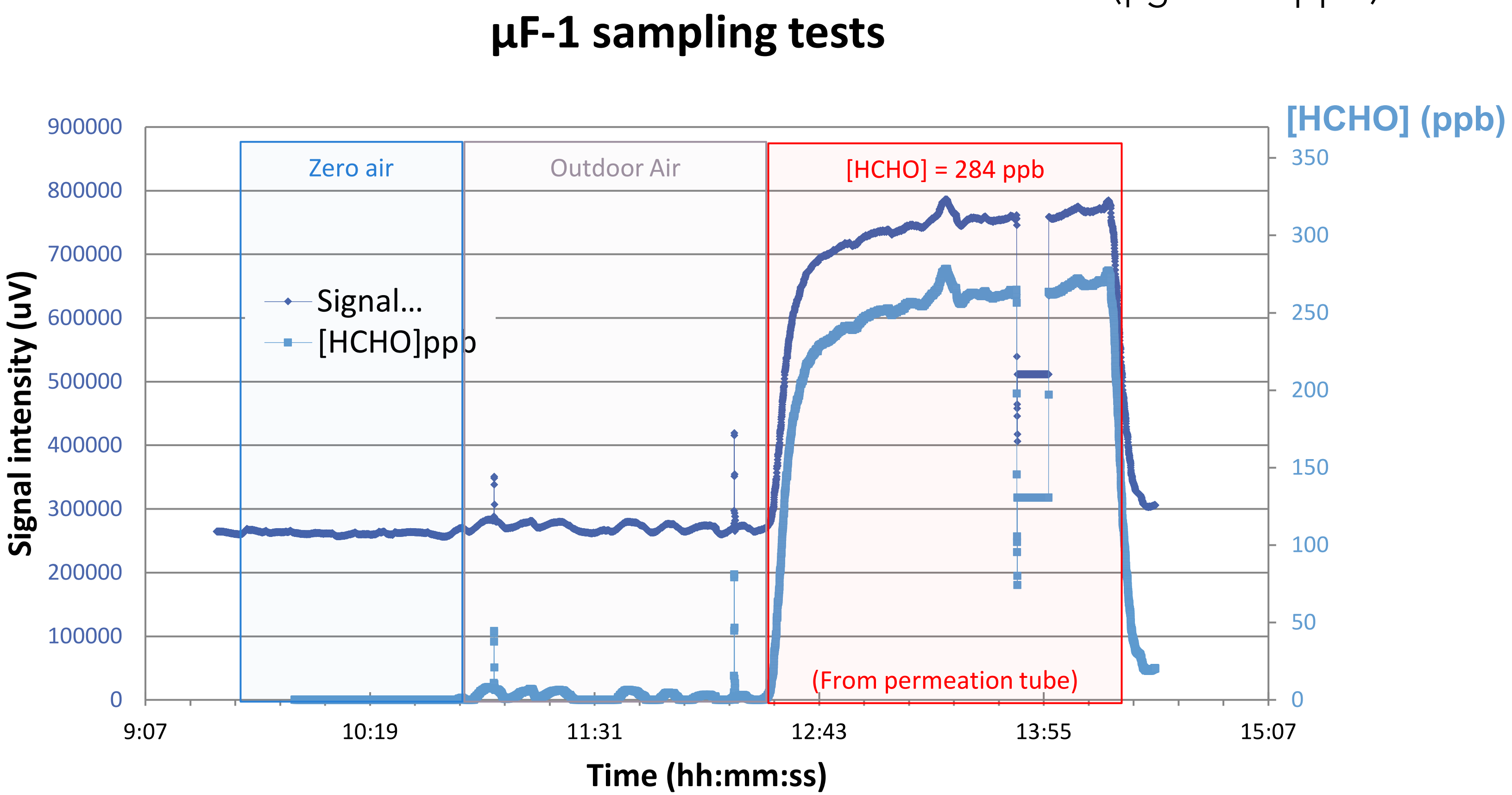
- ***Liquid flow rate*** :17 µL/min
- ***Gas flow rate*** : 250 mL/min
- ***Concentration***: 23µg/m³
- ***Tube length:*** 10 cm

Anaïs Becker's work

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

PrincipleTypical curve

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



Performance

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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 :

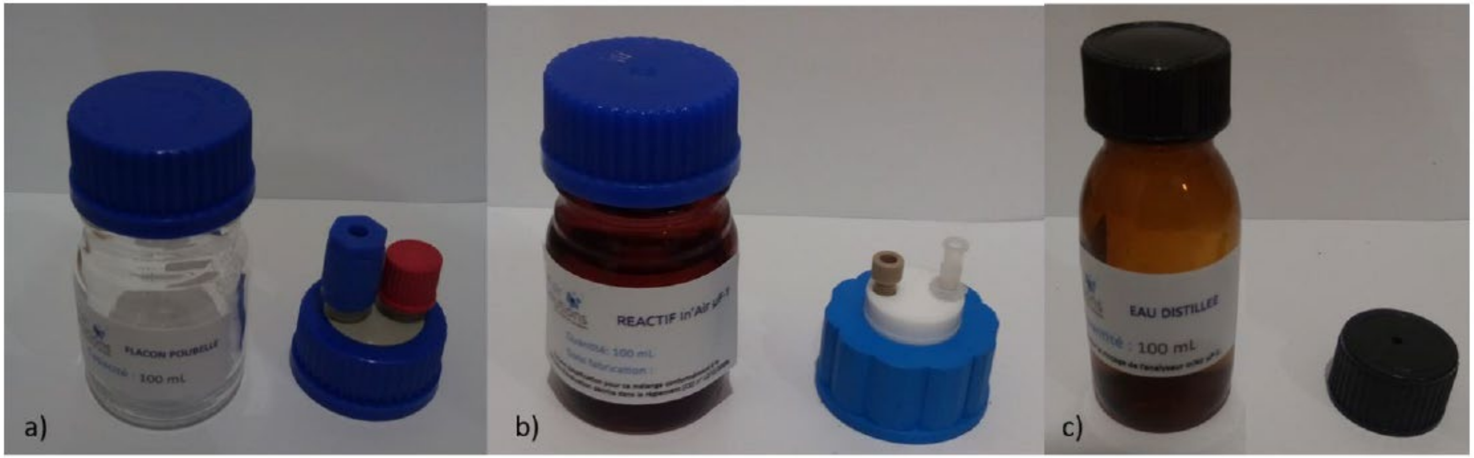
Gas T° : 5 - 40° C;

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

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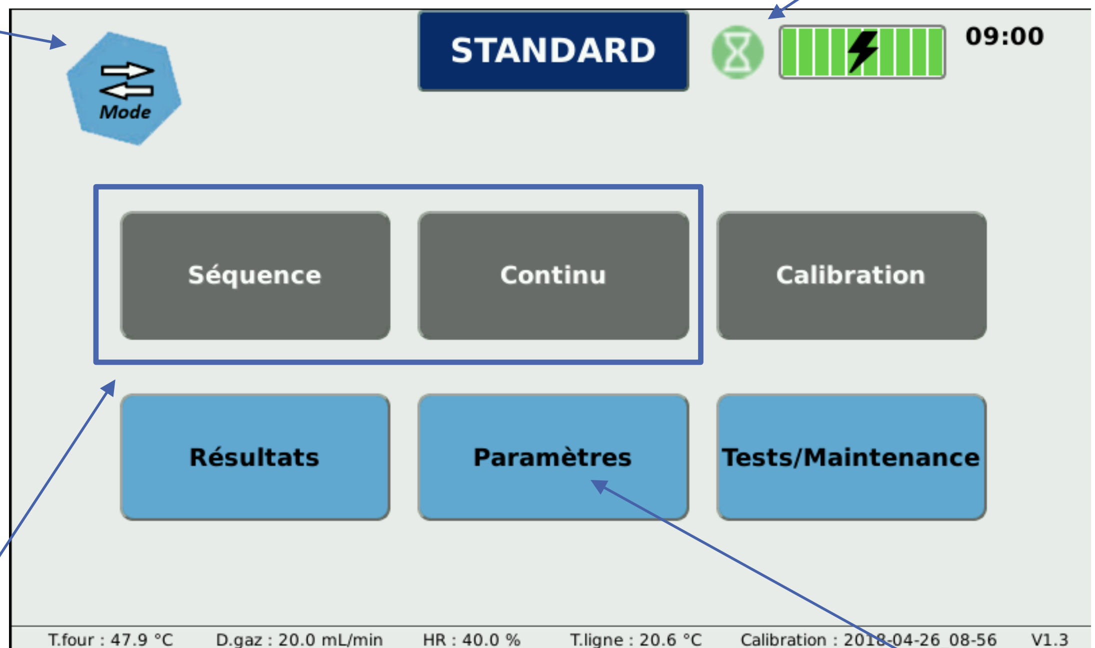
User mode and expert mode

Stabilisation



Analysis

Sequence : Programmable sequence
Continuous : Manual change of modes

General parameters and analysis parameters

Analysis

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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

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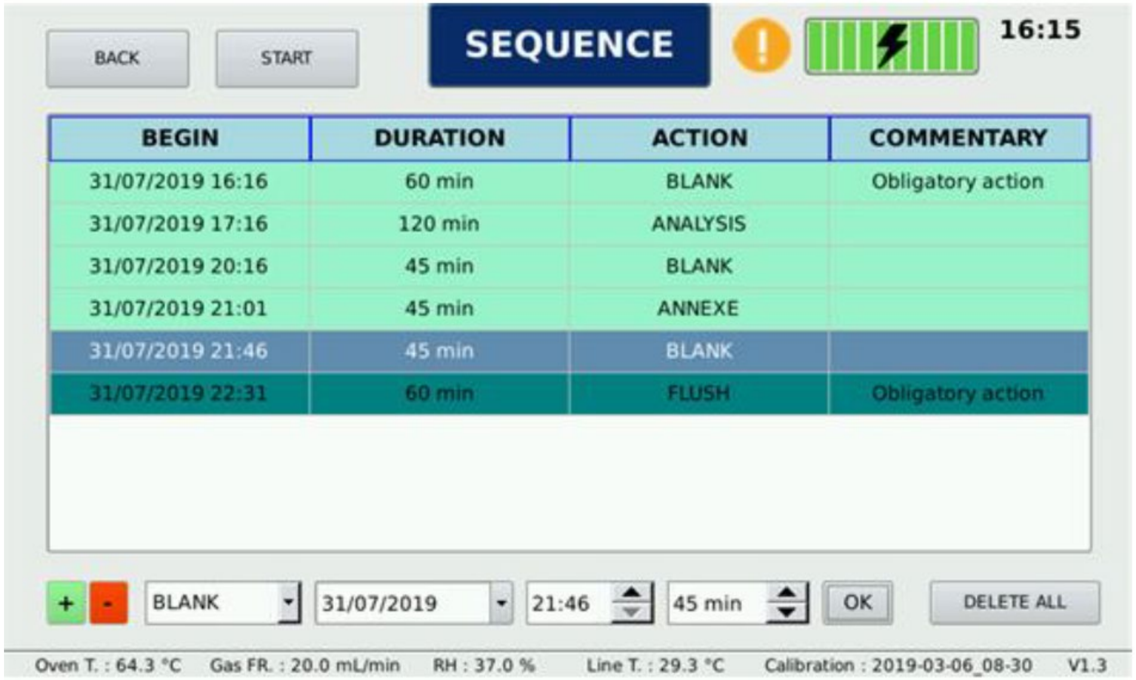
- Sequence programming



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

Results

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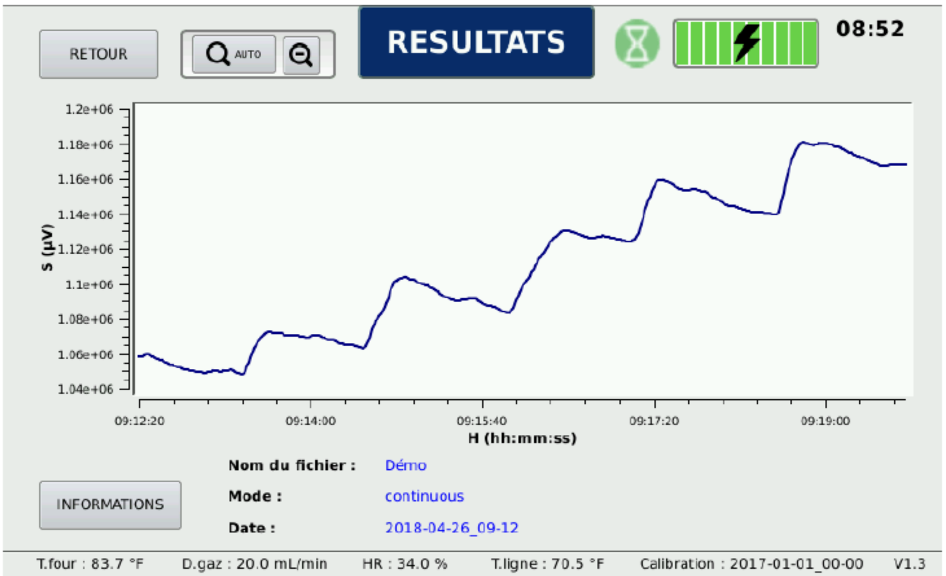

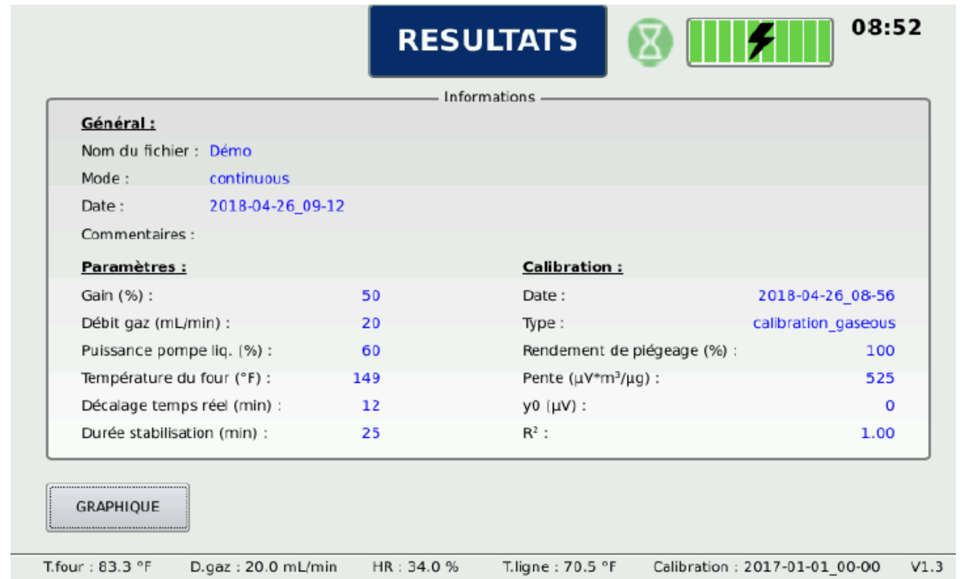

Typical blank baseline : 100,000-150,000 µV

Signal saturation : 2,000,000

Results

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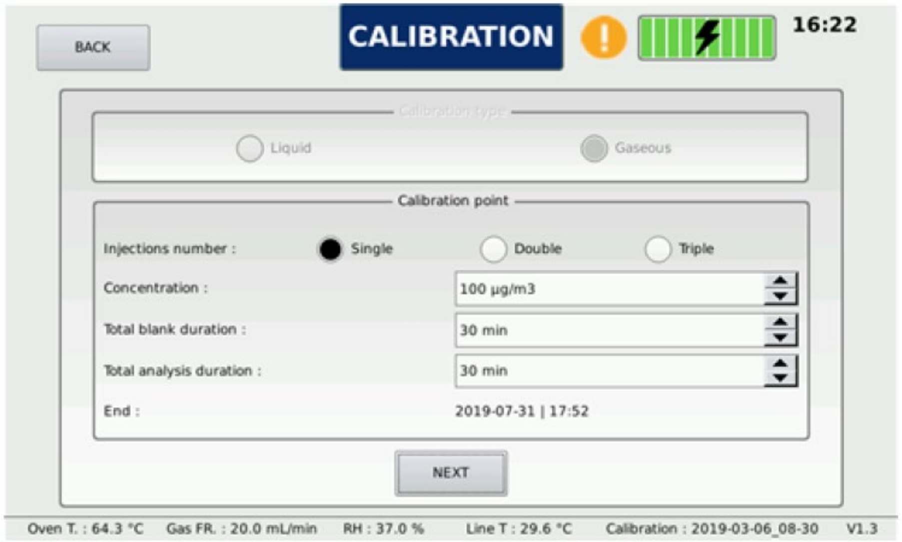
- Direct visualisation
- Exportation as excel file (via USB key)

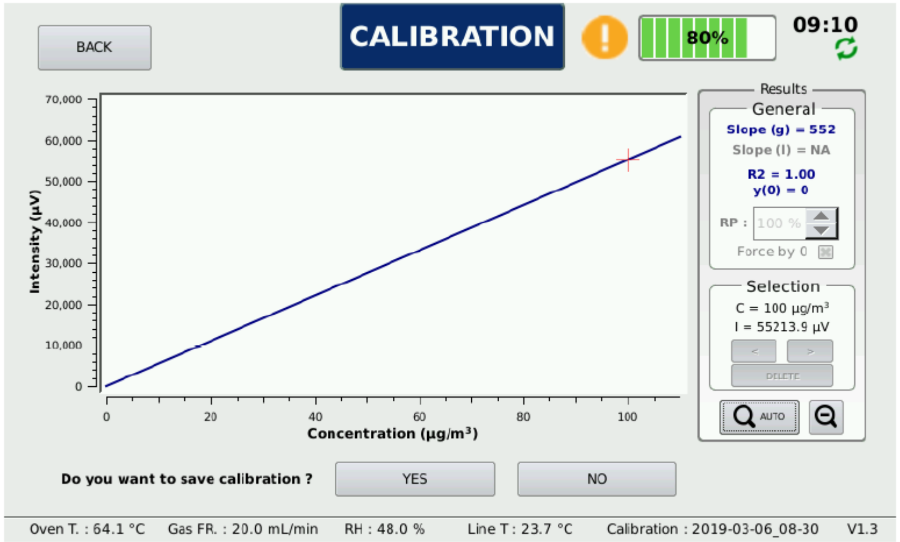
Calibration

1. Connect calibration HCHO to calibration port

2. Program and launch

3. Check before saving





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)

Field campaigns

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- 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.

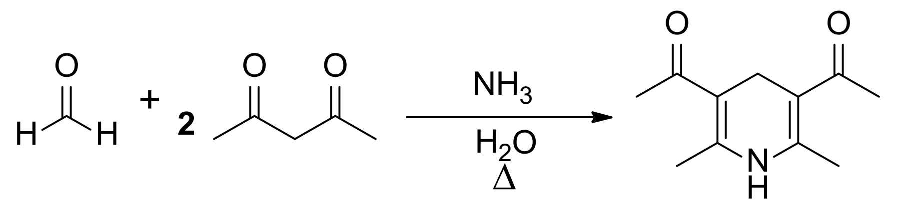
- IMPACT'AIR

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

Strasbourg University – 5/6 june 2019

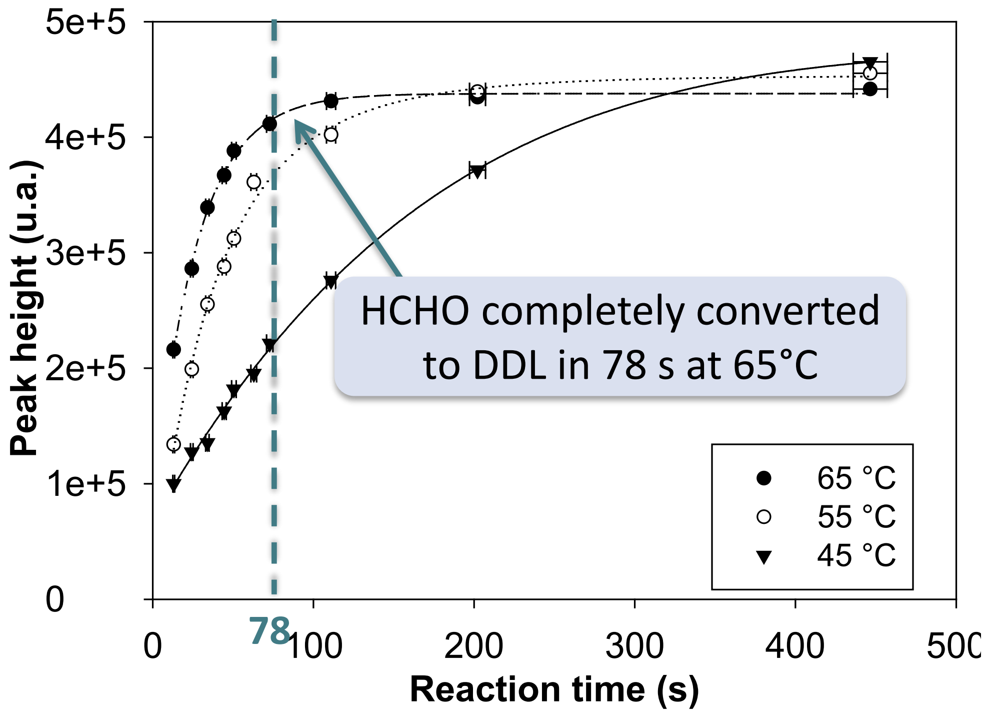
Reaction and kinetic study

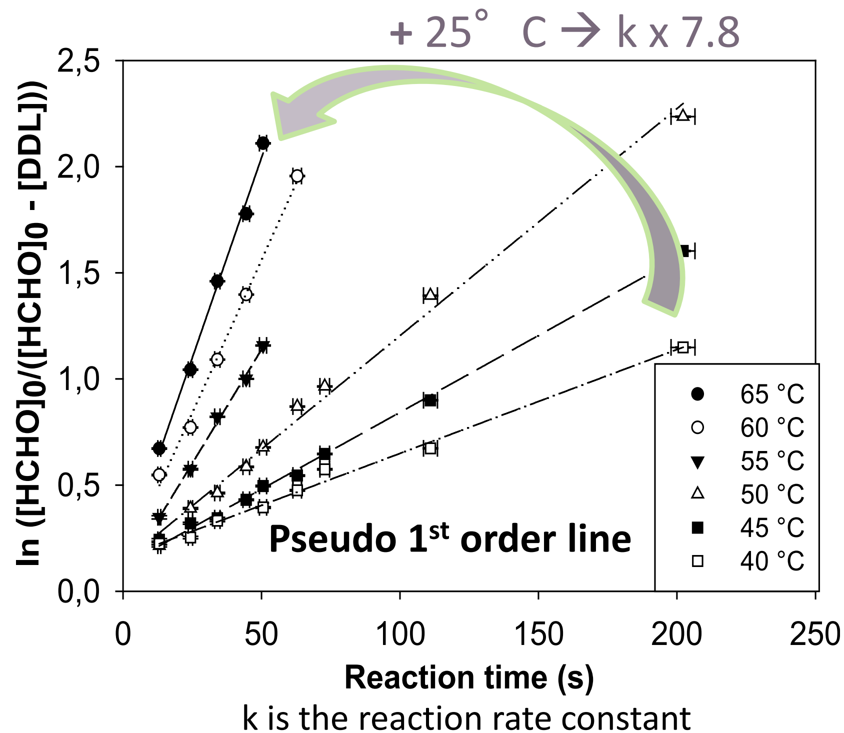
Hantzsch mechanism



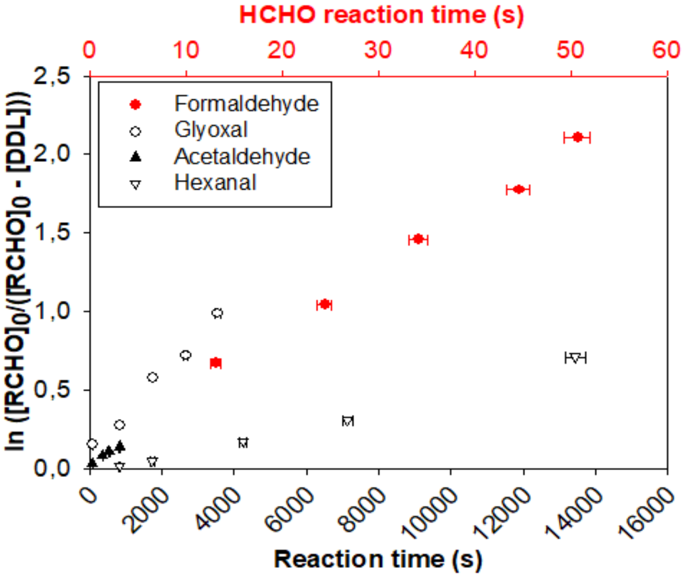
Formaldéhyde Acétylacétone Dihydrolutidine DDL

Kinetic study (Pseudo 1st order reactions)





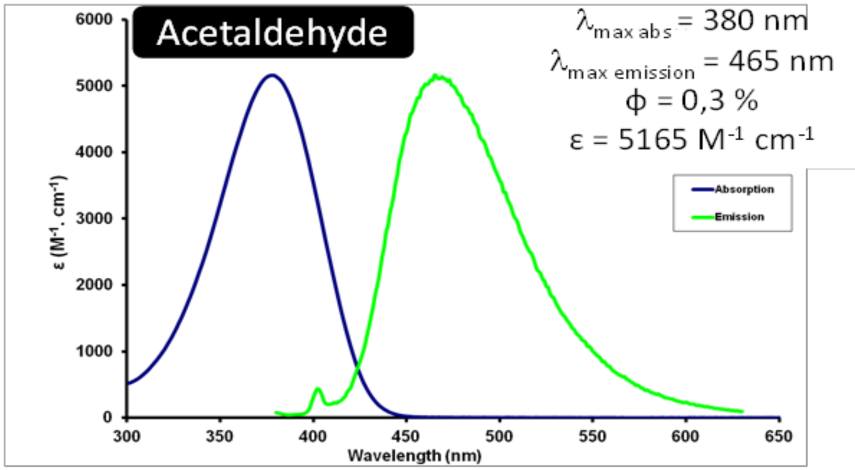
k is the reaction rate constant



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

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

Formaldehyde ϕ = 1,5 %
ε = 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

10

Formaldehyde specificity

<u>Acetaldehyde, Hexanal, Glyoxal</u>

- 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 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
- CSTB (Construction Scientific and technical center)
  - Indoor air control

Online Gas and Liquid Analyzer Experts

MicroGC & microBTEX

Portable Gas Chromatograph Analyzer

Developped in collaboration with CNRS French Research Center

Outline

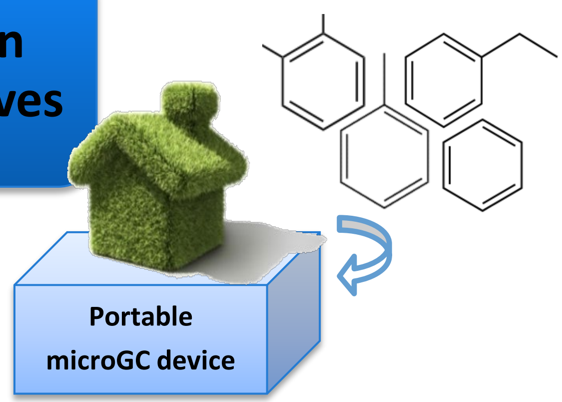
1. General Background

2. Objectives

3.Experimental device

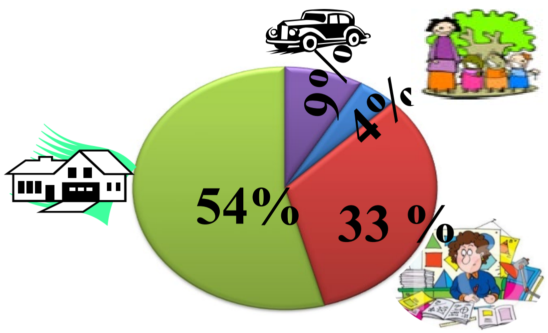
4. Results and discussion

5. Conclusion and perspectives



General background

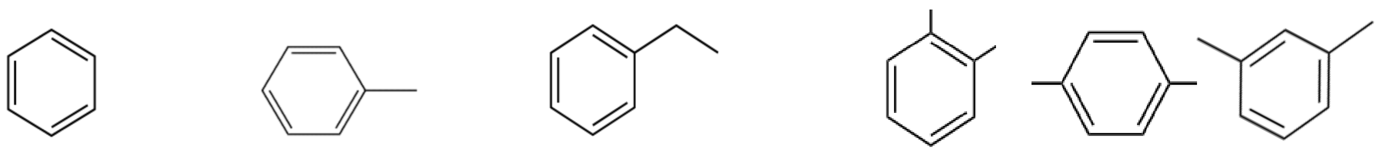
Time spent in enclosed environment can reach 90%



Indoor air quality (IAQ) is responsible of more than 4 millions of premature deaths per year*

Indoor Air is contaminated by a wide variety of Volatile organic compounds (VOCs)

BTEX: Benzene, Toluene, Ethyl Benzene and Xylenes



BTEX emission sources in indoor air

* *World Health Organization*

General background

BTEX effects on health and regulations

Compound	Effect*
Benzene	Human carcinogenic class A (leukaemia)
Toluene	Harmful to Nervous central system
Ethylbenzene	Pneumonitis
Xylenes	Liver and kidney disorder

European Union has fixed a threshold value of **1.6 ppb (5 µg/m³)** in public building since 2013**

In France this threshold value decreased to 0.6 ppb (2 µg/m³) in 2016

This new regulation makes necessary the development of **portable and sensitive instruments** for BTEX and VOCs monitoring in public buildings

** World Health Organisation ** Decret n° 2011-1728 of December 2011 for Indoor air monitoring-French government*

Objectives

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Response in near real time
(10-15 min)

Autonomy
Very low consumption of carrier gas
(few mL/min)

microGC Analyser

Sensitivity
(< 1.6 ppb)

Ultra-Portable
< 5 kg

BTEX & VOCs monitoring in public indoor air starting 2018

Experimental device:

Prototype evaluation

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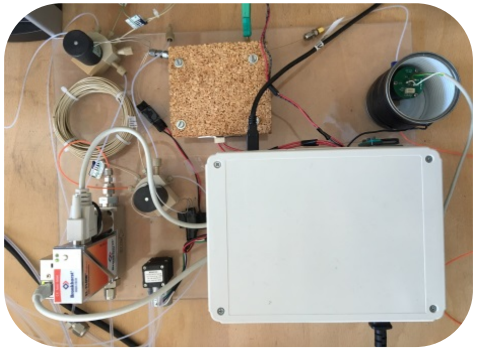
Laboratory prototype 1

Laboratory prototype 2



Industrial prototype

(5 kg including battery)

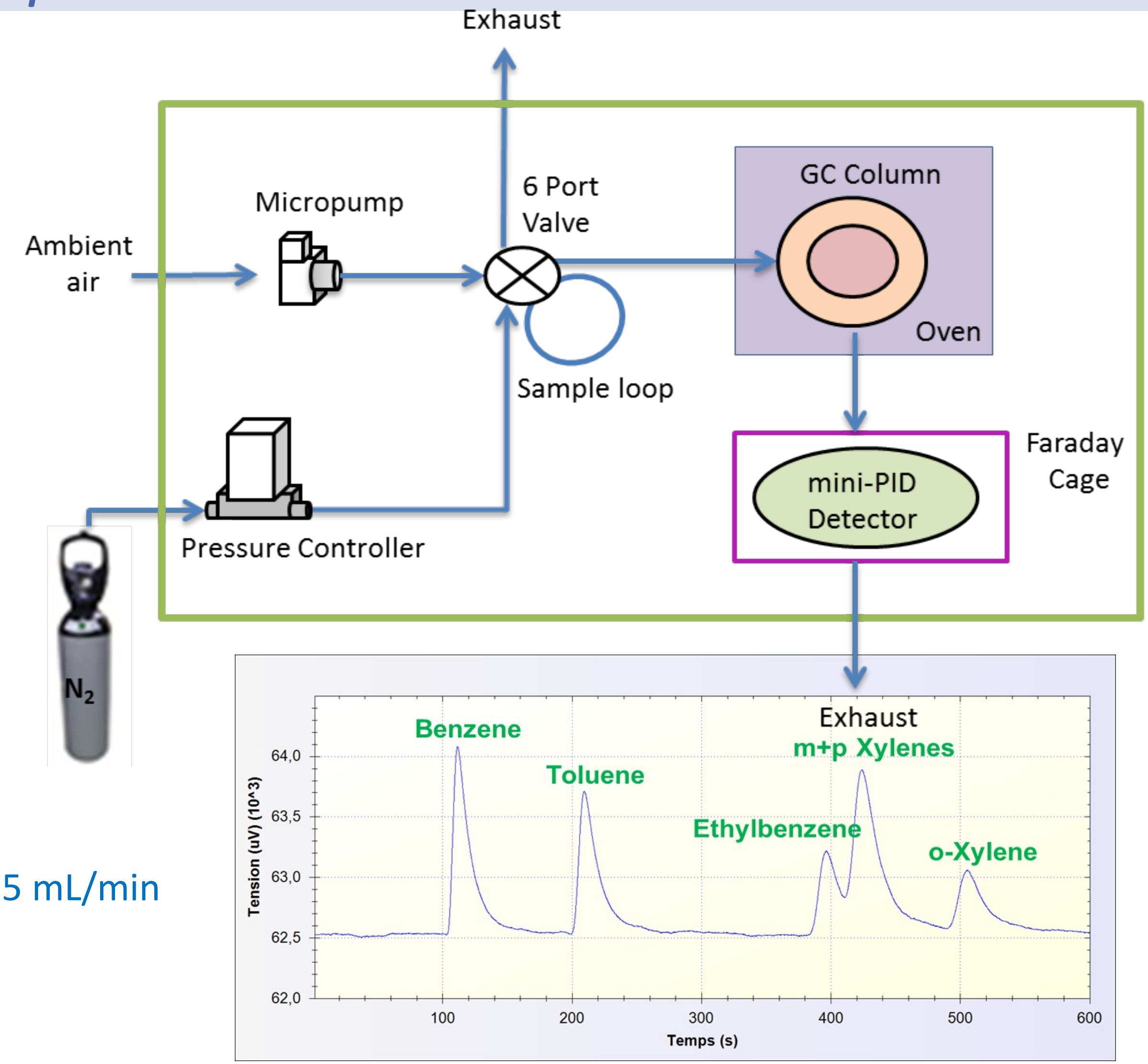
Commercial instrument

Experimental device:

Operating principle

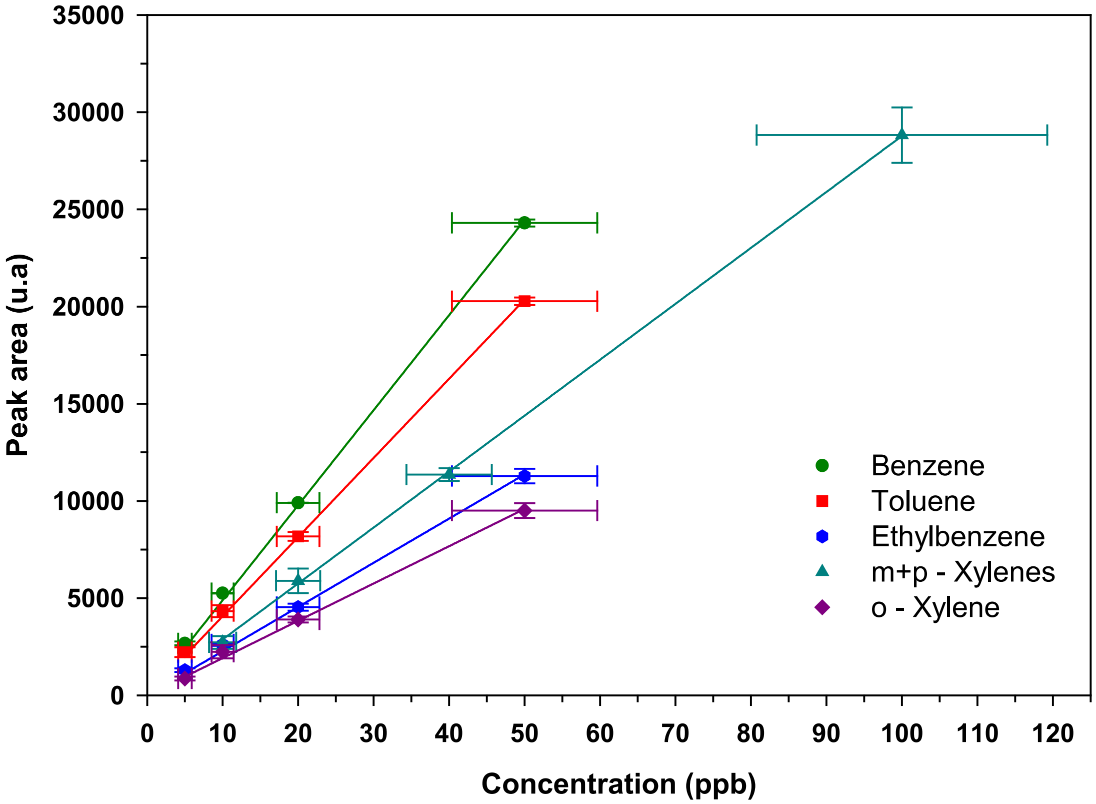
Three steps analysis:

1. Air Sampling
2. Separation
3. Detection



Temperature: 65° C
Carrier gas flow: N2 at 2.5 mL/min
Time of analysis: 10 min

Results and discussion: *Linear range and detection limits*



Compound	LOD (ppb) (S/N=3)
Benzene	1
Toluene	1.6
Ethylbenzene	3.5
m+p - Xylenes	6.7
o-Xylene	6.6

Results and discussion:

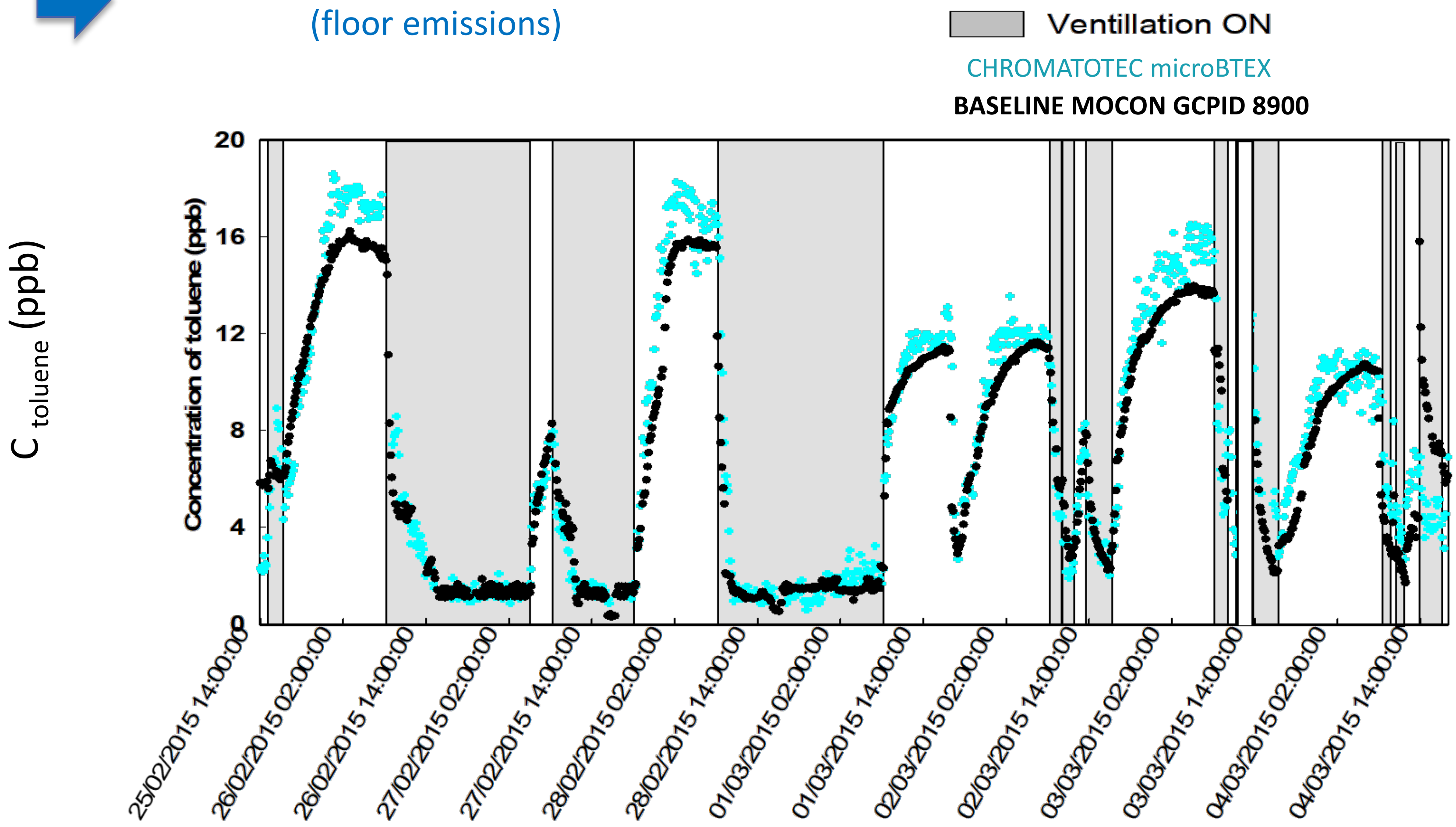
Field campaign MERMAID

- Carried out in a junior high school recently built respecting the thermal regulation of 2005 and equipped with a **modern ventilation**.
- **BTEX concentrations** were continuously **measured** using our new micro-device and a commercial analyzer for **two weeks**, both operating with a **time resolution of 10 minutes**.

classroom

Results and discussion:
Field campaign MERMAID

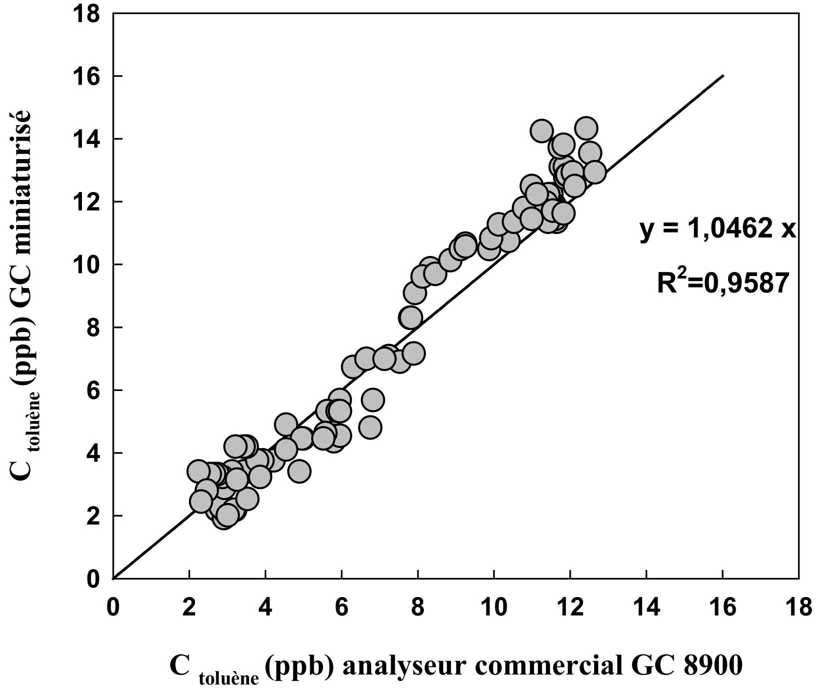
Toluene: major VOC in this classroom
(floor emissions)



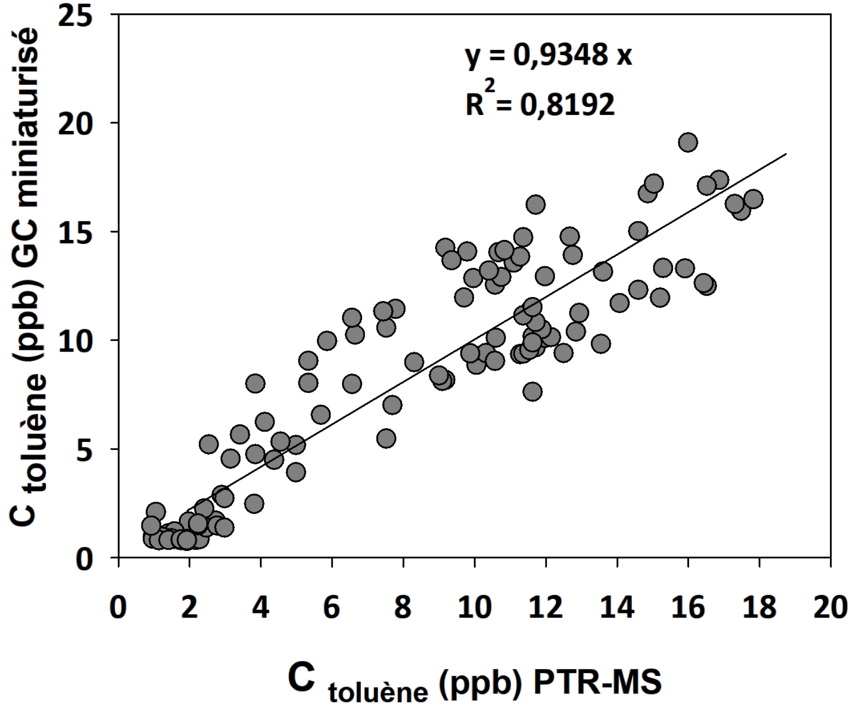
Results and discussion:
Field campaign MERMAID

Online Gas and Liquid Analyzer Experts

Inter-comparaison with other on-line techniques



Deviation: 4.5%



Deviation: 6.5 %

Results and discussion:

Field campaign IMPACT'AIR

Online Gas and Liquid Analyzer Experts

IMPACT'AIR project aims at improving the **indoor air quality in schools**

This project was carried out in two primary schools of La Rochelle (France) for 5 weeks

<u>Main objectives:</u>

- **Monitoring** of regulated **pollutants** (formaldehyde, benzene and CO_2)
- Identification of pollutants **emission sources**

Results and discussion:

Field campaign IMPACT'AIR

	School	Benzene (ppb)	Toluene (ppb)	Ethylbenzene (ppb)	m+p Xylenes (ppb)	o-Xylene (ppb)
Empty Class Week 1	Lavoisier	--	--	--	--	--
	Grandes Varennes	--	--	--	--	--
Furnished Class Week 2	Lavoisier	--	--	--	--	--
	Grandes Varennes	--	--	--	--	--
Normal school activity Weeks 3, 4 and 5	Lavoisier	--	0 – 3.5	0 – 4.4	0 – 10.4	0 – 6.6
	Grandes Varennes	0 – 12.1	0 – 29.5	--	0 – 10.9	0 – 10.5

- Buildings materials and furniture did not emit any BTEX
- All BTEX were detected in the three weeks of normal activity in the classroom
- The major pollutant found in both classrooms was toluene

Conclusions and perspectives

CHROMATOTEC® GROUP
Online Gas and Liquid Analyzer Experts

34L, 0.56kg
28 days
(8h/day)

Autonomy
Very low consumption for carrier gas (few mL/min)

2.5 mL/min

Near real time analysis (10-15 min)

10 min

Limit of Detection (< 1,6 ppb)

1 ppb

microBTEX & microGC analyzer

Ultra-Portable
(weight < 5 kg)

5 kg

- Sensitive, rapid and portable instrument is fully adapted to field measurements for monitoring spatial and time concentrations changes
- Other applications on demand for special compounds and or concentrations
- In the future, addition of a miniaturized preconcentrator (trap) to improve the sensitivity by a factor 10 – 50

Best features microBTEX & microGC

Chromatotec Group
Online Gas and Liquid Analyzer Experts

- Compact size and low weight (<5kg)
- Easy to use with colored touchscreen display
- Deployment in less than 5 minutes
- Powered by mains or battery (>4h)
- Minimal carrier gas consumption
- Rapid calibration with gaseous BTEX mixture or only Benzene

Advantage of this solution

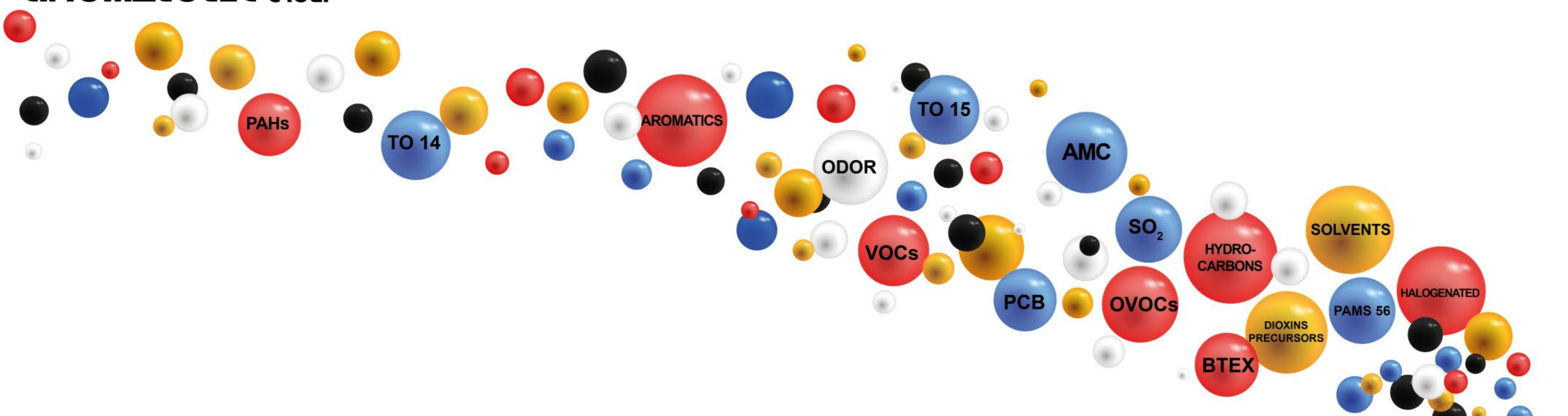
- Short cycle time (15 min) compared to ISO 16000-3:2011
- Automatic solution
- No interferents with chromatography
- Visualization of data

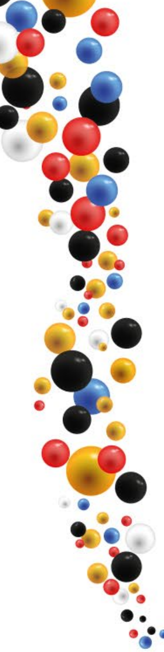
Applications & Markets

- Replacement of Perkin Elmer PhotoVAC Voyager
- Industrial fence line monitoring
- Transportable version for onsite BTEX and VOCs monitoring
- Chemical, pharmaceutical
- Paper plants
- Indoor air (paintings, coatings) & Clean rooms

User profiles

- Customers profiles
  - Governmental agencies (EPA, INERIS)
  - Meteorological institutes
  - Universities and Research centers
  - Industrial consortia
  - Petrochemical groups





µ airTOXIC

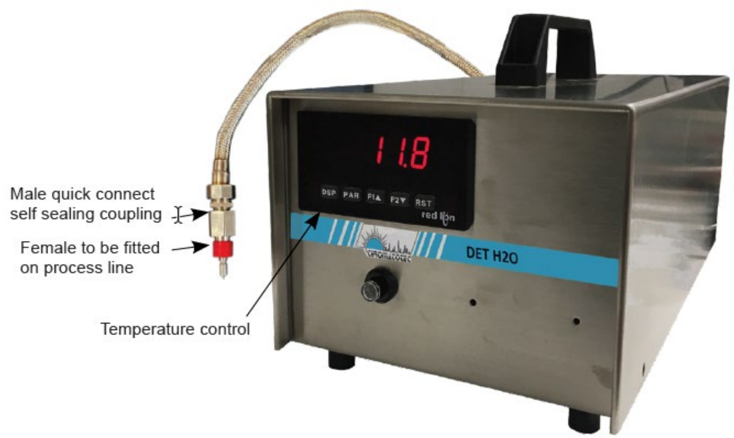
Compact and standalone carrier gas free autoGC

µ airTOXIC

- Wall mounted box µairTOXIC in compliance with mCERTS
- Compact and standalone carrier gas free autoGC for remote air monitoring
- Upcoming product for end of 2021
- Developed thanks to our 30 years experience in autoGC

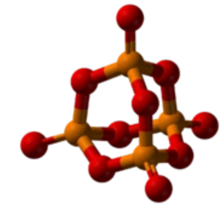
DET H2O

Portable Moisture Analyzer



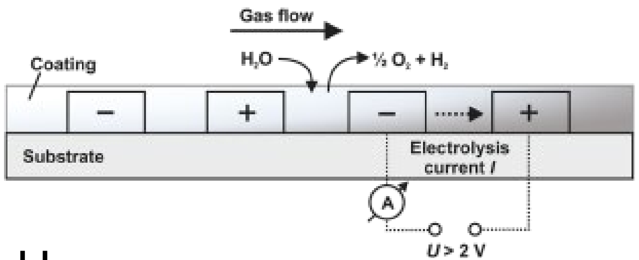
**BATTERY OPERATED
PORTABLE MOISTURE MONITOR**

Technology Principle
Electrolyte Probe

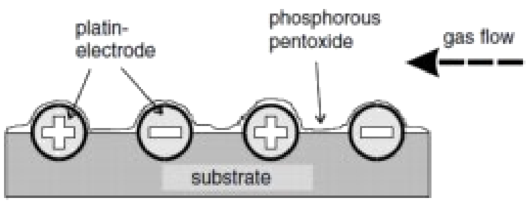


- Method described by Keidel in 1959 : Method for the measurement of H2O in gases
- Technology based on water electrolyze adsorbed by P_2O_5

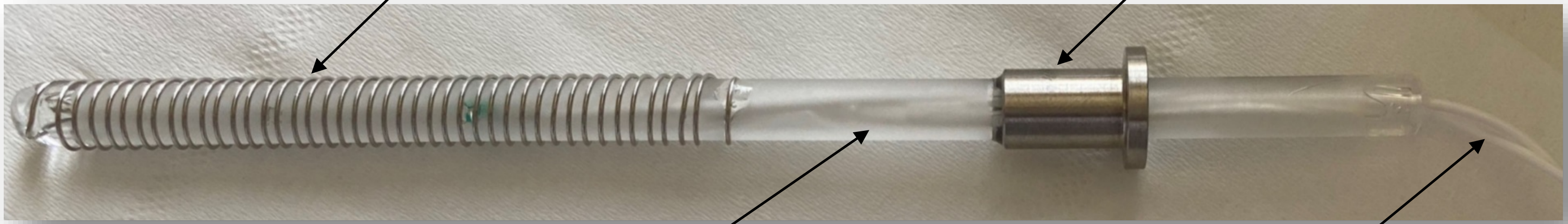
- 2 Pt wires rolled around a glass tube and coated with P_2O_5
- When electrical current is applied, water present in gas is electrolyzed



$$H_2O \rightarrow \tfrac{1}{2} O_2 + H_2$$



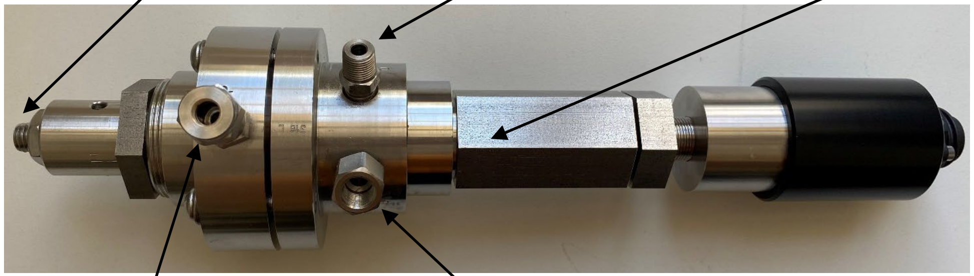
Probe



Pt wires coated with P2O5
Gas outlet
Glass tube
Electrical wires

PORTABLE HYGROMETER :
Probe holder
Pressure and flow regulation systems

Probe inside probe holder



Intrument

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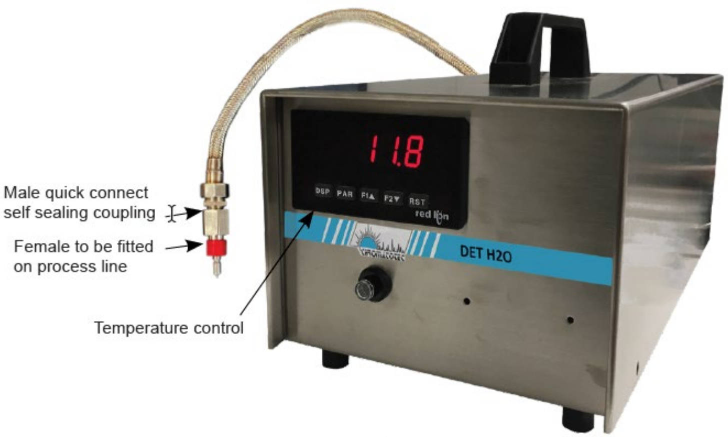
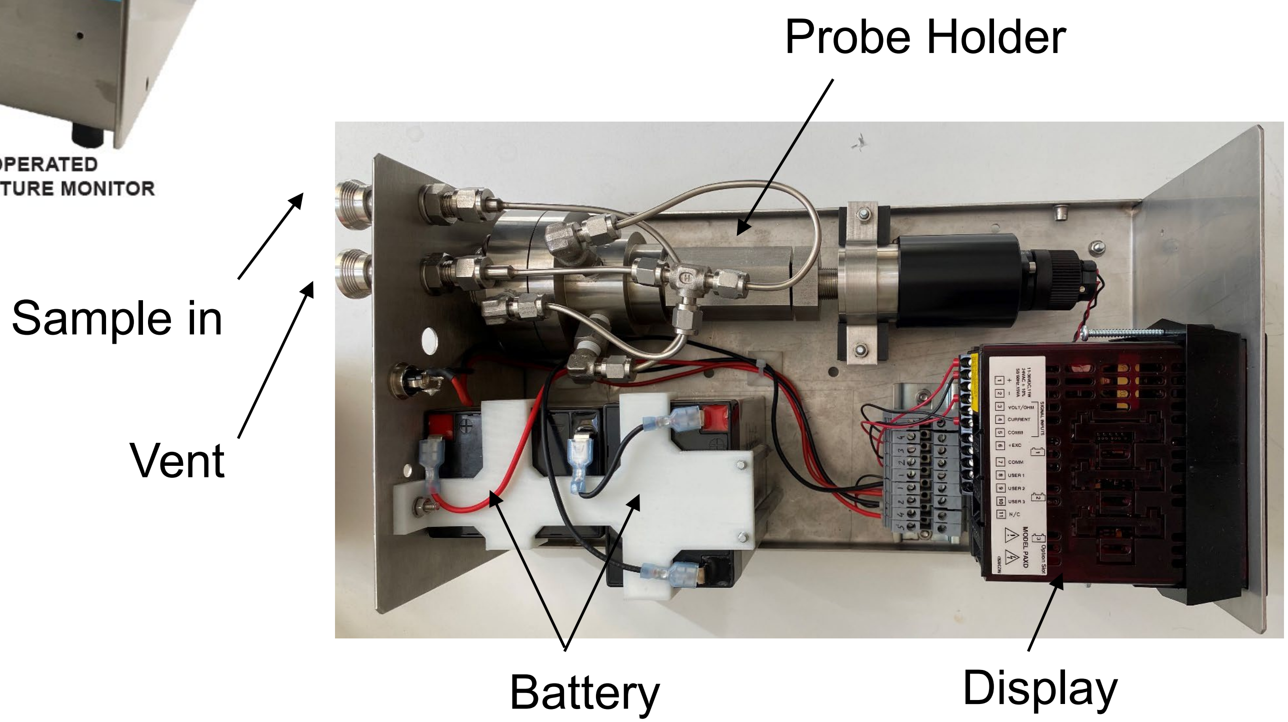
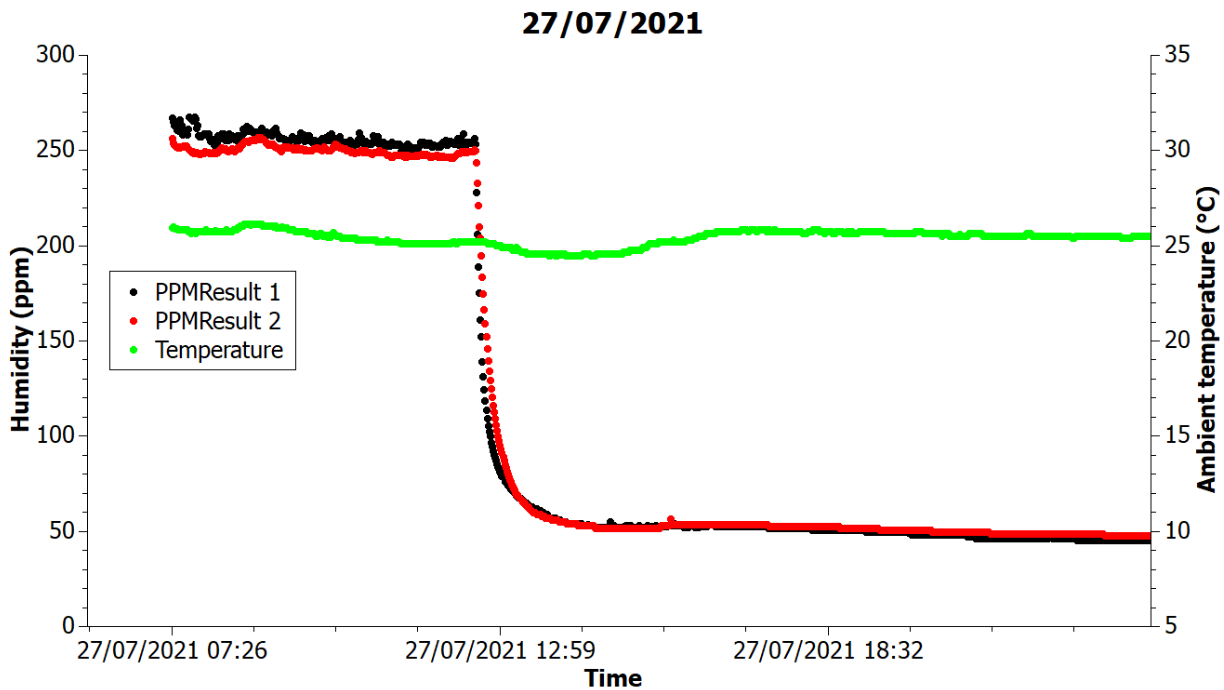


BATTERY OPERATED
PORTABLE MOISTURE MONITOR



Calibration

- 2 calibration points
  - Highest point (humid)
  - Lowest point (dry)



Sensor response time caracterisation

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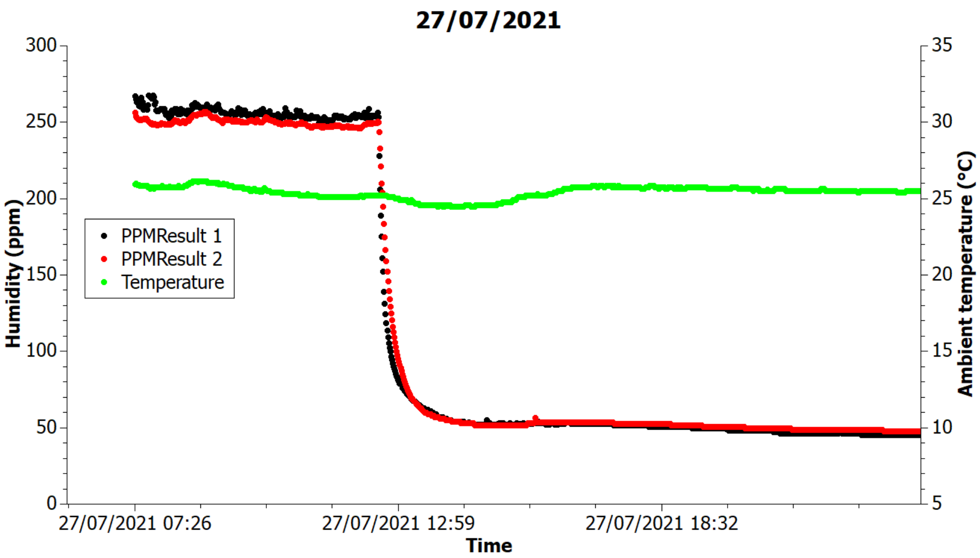
- T90 : Time when 90% of the final value is reached

1) Probe humidification with moisture generator

2) Drying process with dry gas until stabilization of the signal



Applications & Markets

- Medical – moisture analysis in pure gases like O_2
- Industry with corrosive gases
- Chemical, pharmaceutical

Conclusion

Online Gas and Liquid Analyzer Experts

- Technology principle exists since more than 60 years
- Water trapped by P_2O_5 is then electrolyzed and allow a measurement in real time
- Very sensitive technology for multiple gaz analysis
- Moisture in corrosive gases like Cl_2, HCl, H_2... can be analyzed by this technology

Conclusion

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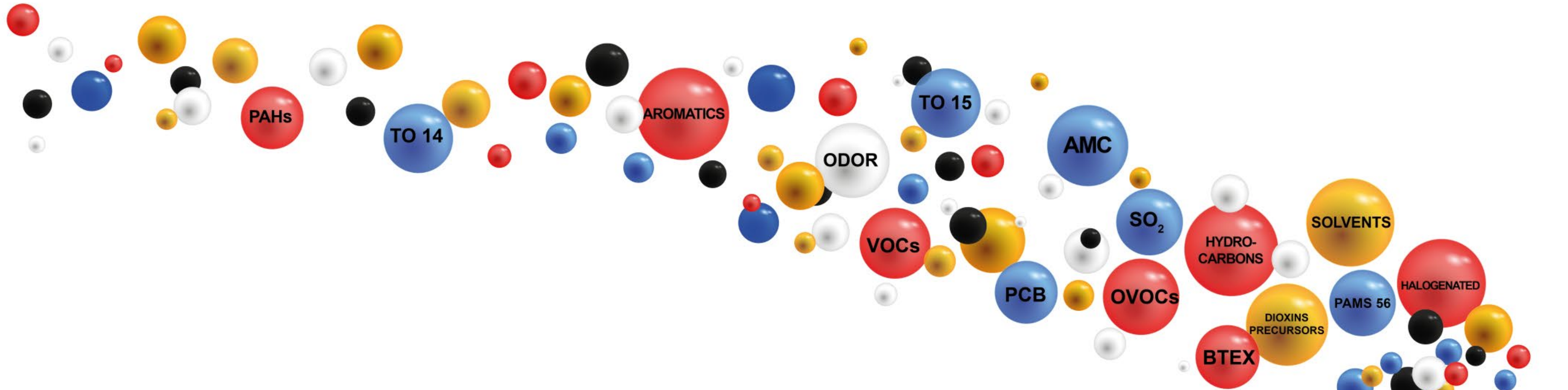
- Stationary or portable hygrometer
- Extended measurement range – from 30ppb to 5000ppm(v) H20
- Capable to measure samples at pressure from 1,4 to 20 barg with pressure reducer – up to 200 barg on request
- ATEX version available



THANK YOU FOR YOUR ATTENTION!

Questions ?