DEVELOPMENT OF A FORMALDEHYDE CHEMICAL SENSOR FOR IAQ MONITORING AND ANALYSIS

- Emmanuel CHEVALLIER
- ETHERA / France

ETHERA : few figures

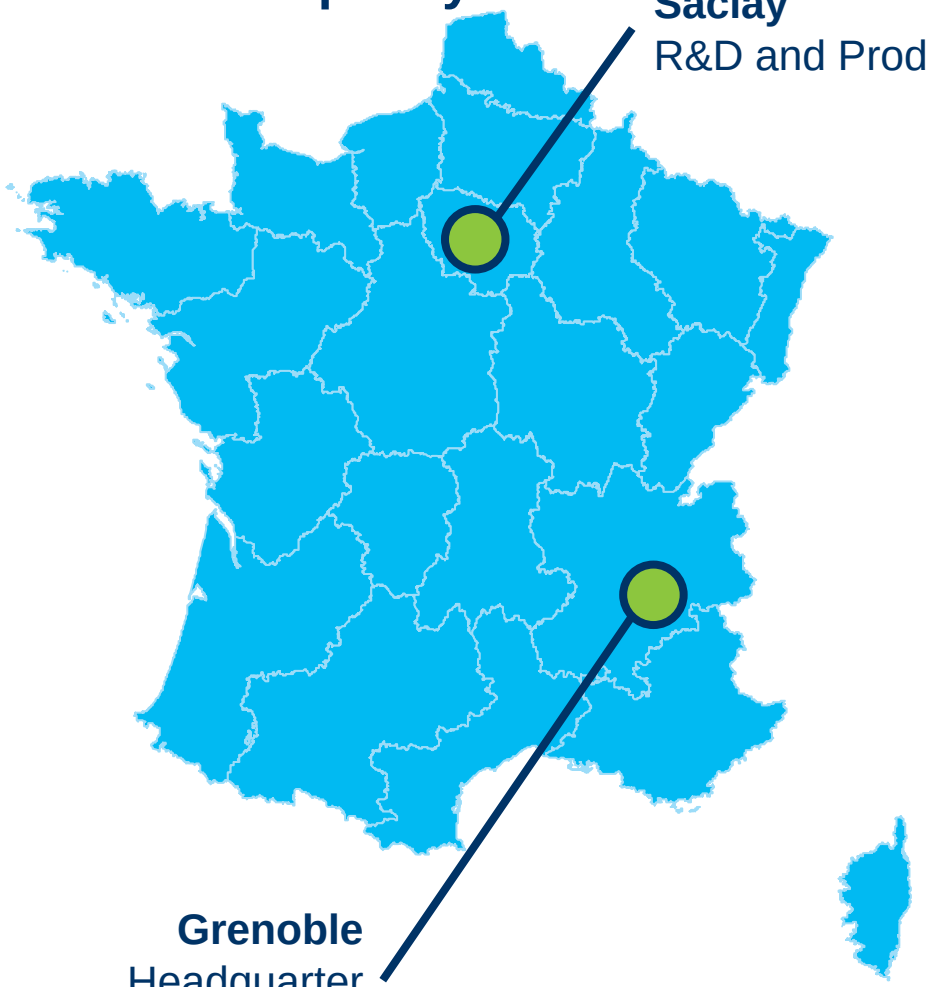
ETHERA develops diagnostic kits for indoor air quality

10 years of research in a common laboratory

energie atomique • energies alternatives

16 people

2 locations



History

LIMPID creation
Common R&D Laboratory
CEA/CNRS/ETHERA

2010

Creation

Financial consolidation

2011

1st fund rise 1.2M€

Product launch

Products qualificationR&D

- *INERIS qualification*
- *Participation in the French campaign in nurseries and schools*

2012

2nd fund rise 3M€

Sales development-R&D

- *Pilot production line*
- *NF and CE qualification*

2013

Europe Development

Sales development Plant ETHERA-R&D

- *Specialised distribution*
- *Reference acquisition and*
- *International development*
- *Consumer*

2014

Consumer

Our markets

Indoor Air Quality

Environment Code

Public buildings (ERP)

IAQ monitoring

Private buildings

LEED building assessment

Industrial Hygiene

Labour Code

Industry

Personal Exposure Limits assessment to chemical risk

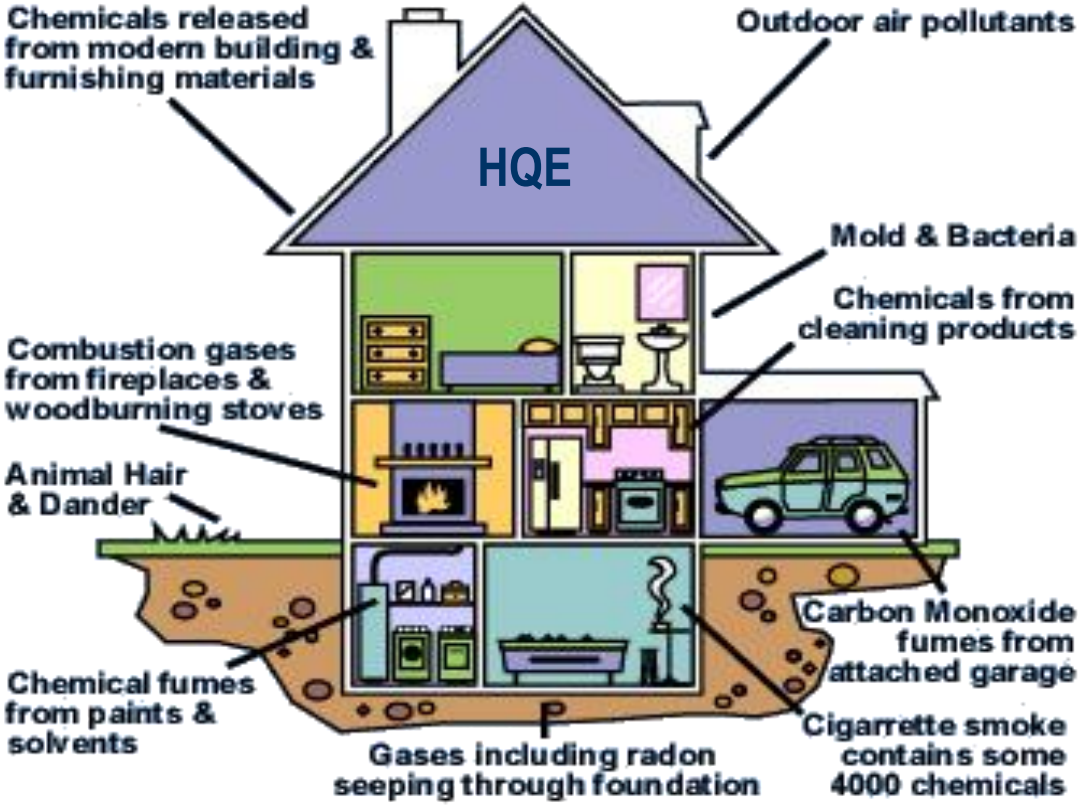
Indoor air pollution

80 up to 90% of our time is spent indoors: homes, workplaces, transport…

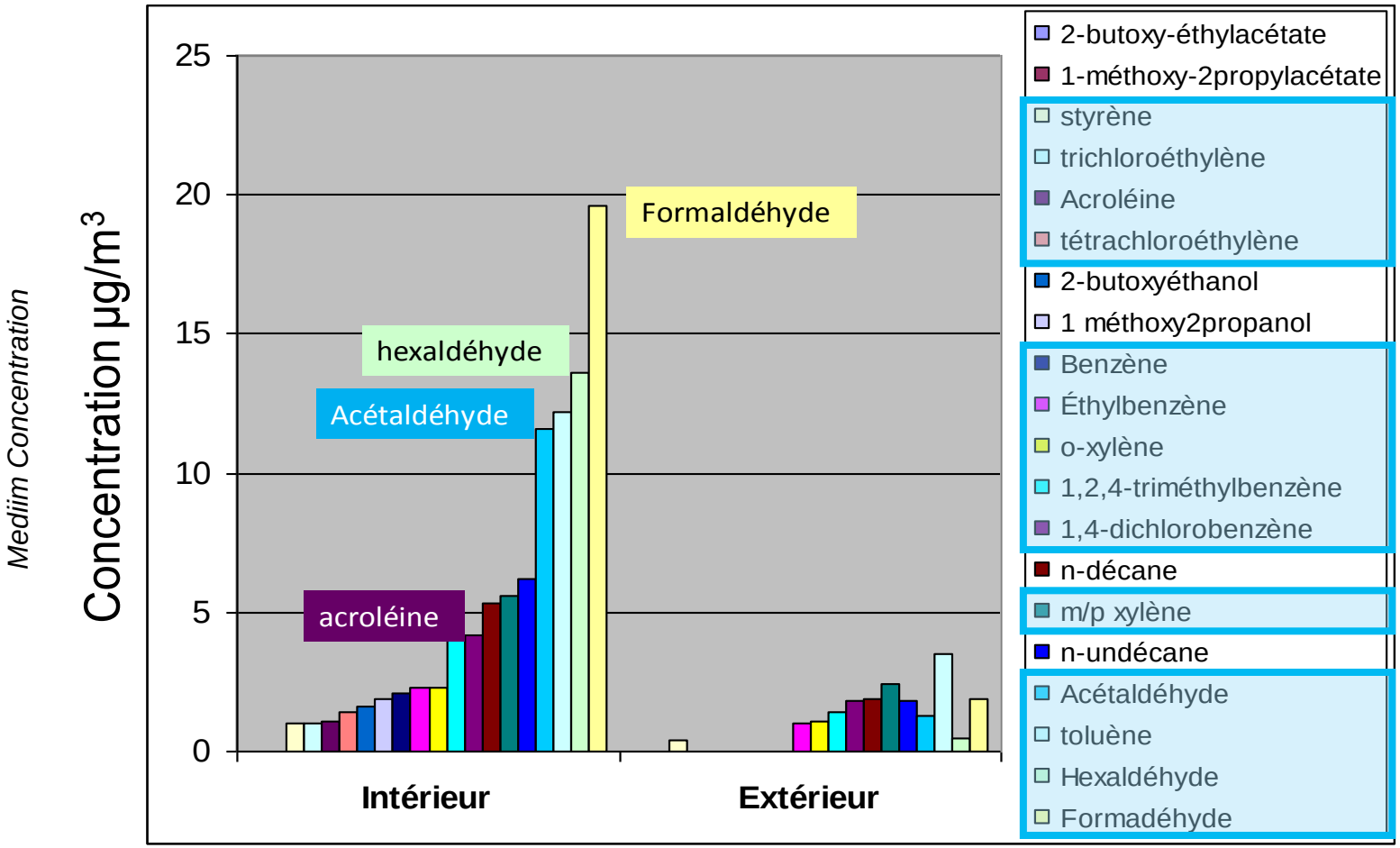
10%

90%

Volatile Organic Compounds



Indoor chemical pollution status



Aldehydes + BTEX = > 80% of total chemical pollution

Source: French Indoor Air Quality Observatory 2006 – Campaign based on 600 French representative dwellings

A stringent regulation in France

- Plan National Santé-Environnement (PNSE 2) + Grenelle
- → 2 new decrees:

Decree n° 2011-321 (march 2011)

Labeling of building products based on their volatile compounds emission

Decree n° 2011-1728 (december 2011)

Monitoring of Indoor Air Quality (IAQ) in public buildings (ERP)
Periodic controls of
Formaldehyde, Benzene and CO_2

The needs

- **Low cost solutions to measure on line pollutants at ppb to ppm levels in public area or in industries**
- Efficient portable instruments to identify the sources of indoor pollution
- New equipments for the treatment of polluted air especially formaldehyde

ETHERA R&D

- **Development, validation and industrialization of new chemical sensors for the measurement of indoor air pollutants**
- Development of new devices for indoor air quality control
- Development of new devices for the purification of indoor air

Ethera research based on an innovative technology
IAQ (Indoor Air Quality) and SH (Safety and Health) measurement and treatment

A nanoporous Sol-Gel material like a « sponge »

Pollutant filtration and concentration

+

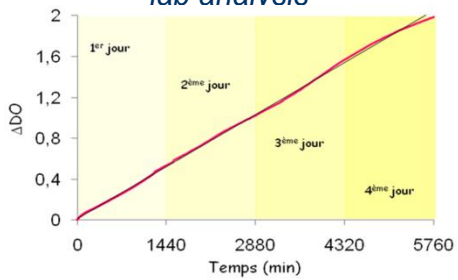
Probe molecule integration

Specific reaction with the pollutant creating a colorimetric reaction

MEASURE

Direct optical detection

Direct ultra-sensitive measurement of pollutant concentration without lab analysis



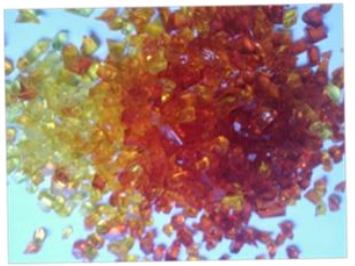
A Simple, Sensitive and Selective technology

- Manufacturing from an industrial **Sol-Gel** process
- Protected with **5 international patents**
- A **operational** pilot production line

EPURATION

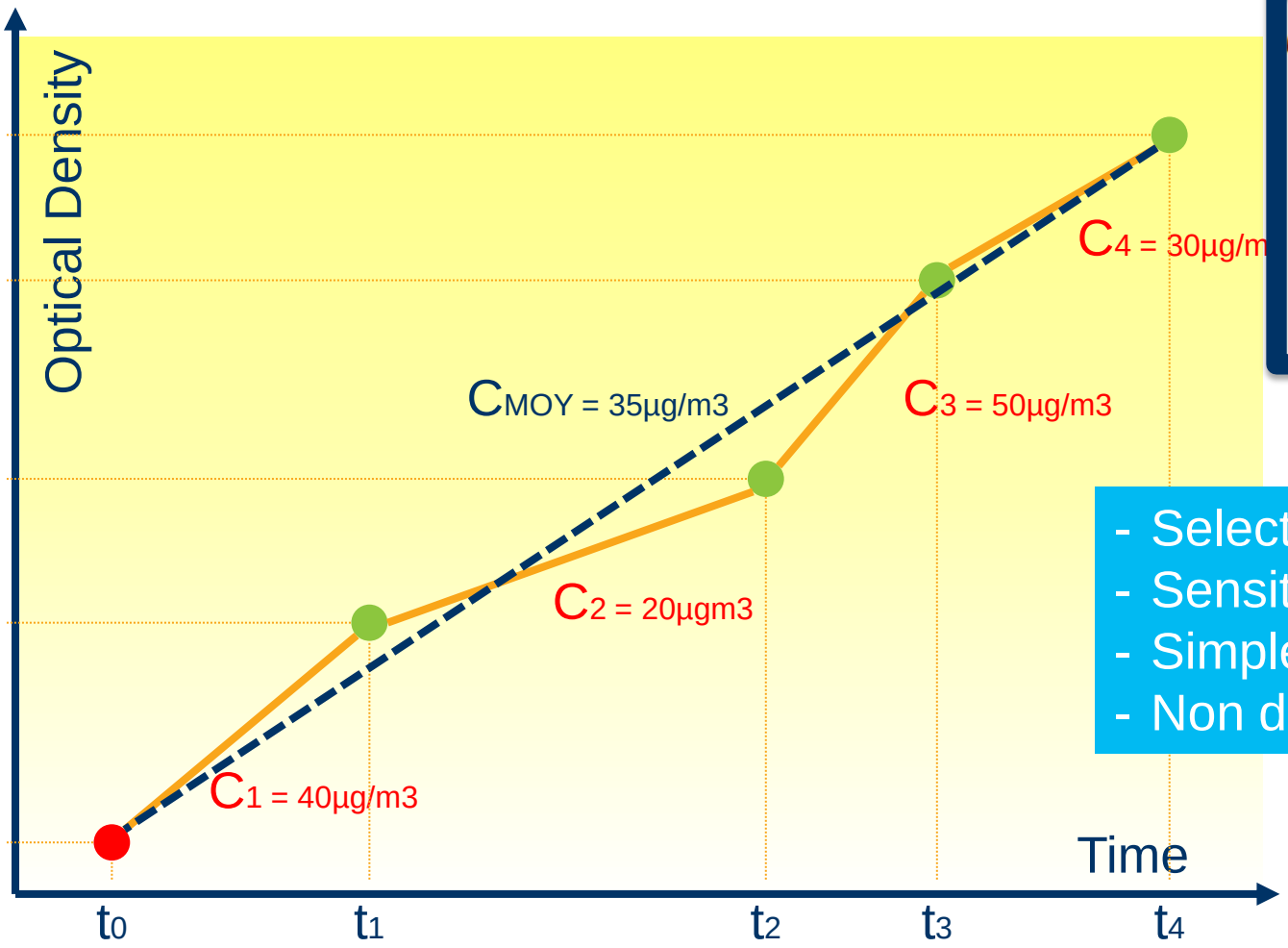
High trapping capacities

Selective and efficient treatment of the pollutant with integrated saturation indicator



ETHERA technology

An innovative material Which optical density is varying **linearly** with the pollutant concentration



$$C(HCHO)ppm = \frac{\Delta DO}{TxK}$$

$$\Delta DO = DOf - DOi$$

$$T\,(\min) = Tf - Ti$$

$$K\,(min^{-1}ppb^{-1})$$

= calibration coefficient

- Selective
- Sensitive(ppb)
- Simple
- Non destructive

Profil'air® product range : a modular approach

Badge for individual dosimetry
PA-SDIxxx

- *Personal Exposure Limits (TWA 8h)*

Dynamic exposure module
PA-MEX001

- *Personal Exposure Limits (STOEL 15min)*
- *Short-term ambiant measurements*

Active sampling

Sensor

Optical reader module
PA-MRF421

Pump module
PA-MPO201

- *Personal Exposure Limits (STOEL 15min)*
- *Short-term ambiant measurements*

Passive sampling

Ambiant diffuser
PA-DFSxxx

- *Long-term ambiant measurements*

Emission measurement chamber
PA-CMExxx

- *Emission source research*

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Competition faces IAQ new expectations

Specificity of Indoor Air Quality Analysis:

- Selective
- Long-term exposure (i.e. 4,5 days for public buildings)
- Very low concentration (few ppb)

deferred analysis!

Current protocol

Sampling on cartouche/tube

Analysis in a laboratory (HPLC-UV)

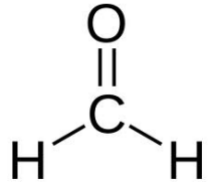
- × Complex
- × Differed results
- × Costly

ethera Breathe Safely

- ✓ Simple
- ✓ Instant results
- ✓ No lab analysis

Standards and regulatory measurements are adapted to the current protocol

Formaldehyde



- Formaldehyde → Carcinogenic to humans, (class 1, IARC), priority substance (OQAI).

- French authorities define three limited value for formaldehyde exposure :

2 Decrees 2011 IAQ

- IAQ : **30 µg/m³** in 2015, **10 µg/m³** in 2022

  (long-term exposure, guideline value for indoor air)

1 Decree 2010 SH

- Time-Weighted Average (TWA, 8h working day) : **0,5 ppm** (0,61 mg/m³)
- Short-Term Exposure Limit (STEL, 15min): **1 ppm** (1,23 mg/m³)

Stages of ETHERA product development

- Sensor development (CEA/CNRS/ETHERA : LIMPID)
- Optimization and adaptation (ETHERA)
- **Calibration in laboratory conditions (ETHERA)**
- **Validation test following a standard (ETHERA)**
- **Correlation test in real conditions**

  (measurement campaign in real conditions) **(ETHERA)**

Main research equipments

Environmental chamber, 1m^3
Pressure, T° (10 - 40°C), RH (20 – 80 %), air velocity (0,1 - 2 m/s), calibrated gas control

Generation of calibrated gas mixtures

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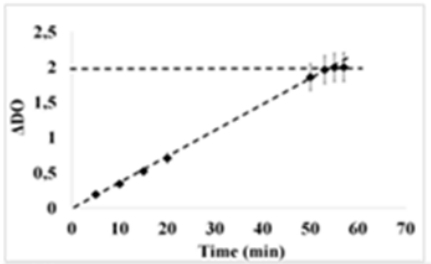
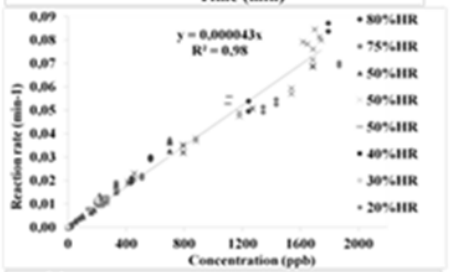
Dynamic exposure : Calibration

in laboratory conditions

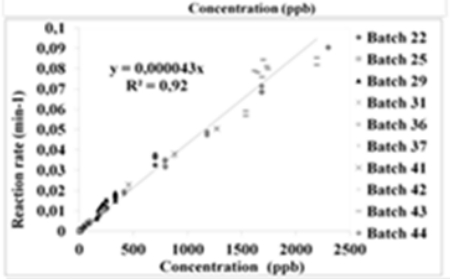
Linearity: sensor response is linear at 7 to 2000ppb of HCHO, 20 to 80%RH



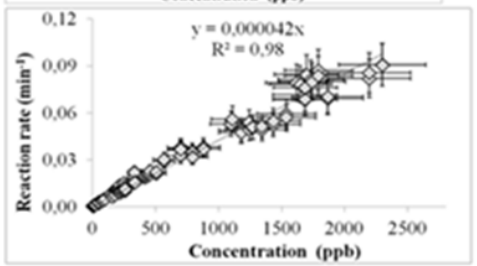
Humidity: No significant influence of humidity on sensor response from 20% to 80% RH



Batch reproducibility: No significant influence of production batches on sensor response



Calibration curve of sensors: linear sensor response from 6 to 2500ppb HCHO and 20 to 80% RH



Other validation parameters: DL =2,5ppb and QL=8ppb (60min expo.)
Uncertainty: ±15% (in the range 6–2500ppb from 20 to 80%HR)

*Average of 4 mesures

Dynamic exposure : Validation

EN1076 Tests results

→4 parameters were investigated:

- 1-Limit of quantification for a 15 min exposure (1 VLE)
- 2-Effect of concentration (0.1, 0.5, 2 VLE, 20C°, 50%RH)
- 3-Influence of the humidity rate (0.1, 2 VLE at 20°C, 20%, 80%RH)
- 4-Influence of the temperature (2 VLE, 50%RH, 15°C, 40°C)

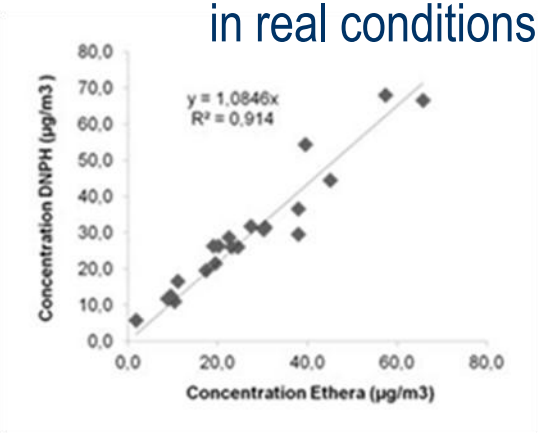
For each tests :
→ 6 to 10 sensors simultaneously exposed
→ comparison with DNPH results

VLE:*« Valeur Limite d'Exposition », i.e. 1230 µg/m³*

ETHERA/DNPH(ref) concentration deviation < 10% ☺

Correlation ETHERA / DNPH

in real conditions



Good correlation for the campaign (LHVP) ☺

Profil'air® product range : a modular approach

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Sensor

Passive sampling

Ambiant diffuser
PA-DFSxxx

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Active sampling

Pump module
PA-MPO201

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- *Short-term ambiant measurements*

Emission measurement chamber
PA-CMExxx

- *Emission source research*

IAQ passive sampling

in laboratory conditions

Calibration

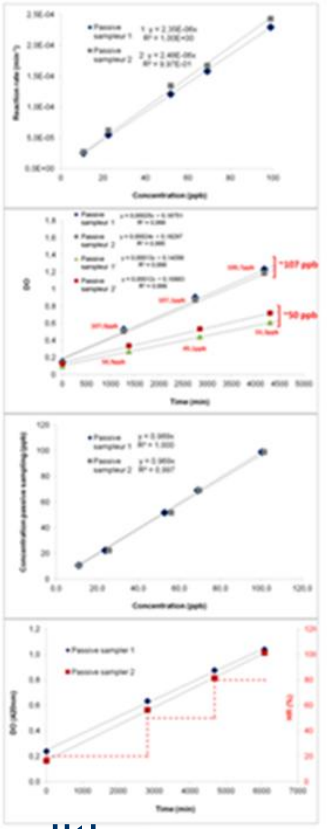
Linearity : sensor response is linear as a function of the formaldehyde concentration of 4.5 days

Linearity : sensor response is linear as a function of time (1, 2, 3 and 4,5 days)

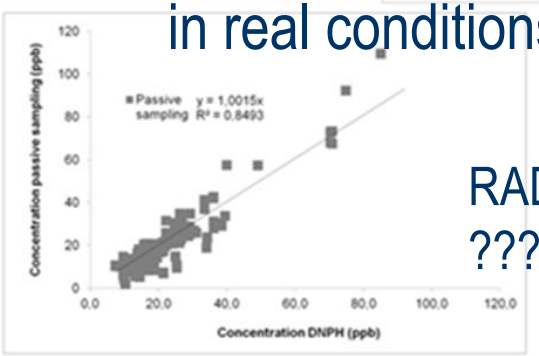
Correlation passive/active : Very good correlation between passive and active ETHERA

Humidity: Little disruption of moisture on sensors

Other validation parameters : DL =0,2ppb and QL=0,8ppb (for 4,5 days exposure)
Uncertainty : ±15% (in the range 6–100ppb from 20 to 80%HR)



in real conditions



RADIELLO ???

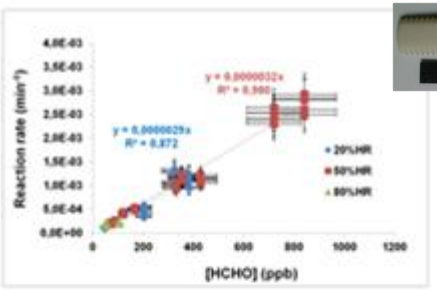
Correlation ETHERA / DNPH

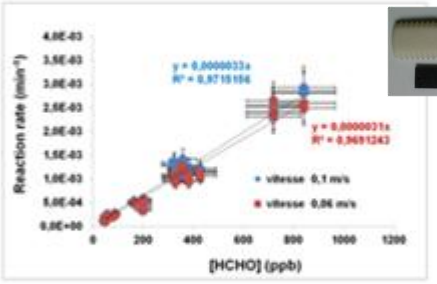
Good correlation for the campaign
→Significant standard deviation
… in progress (+filter)

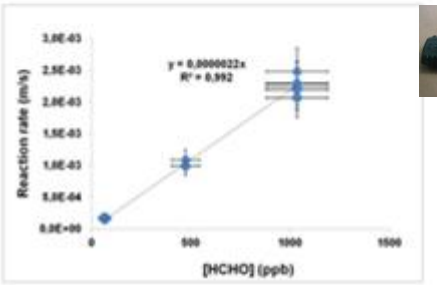
SH passive sampling

Calibration

in laboratory conditions







Linearity: sensor response is linear at 20 to 1000ppb of HCHO, 20 to 80%RH

Humidity: No significant influence of humidity on sensor response from 20% to 80% RH

Speed of air : no significant influence of speed of air on sensor response from 0,06 to 0,1 m/s

Calibration: Validation of the badge definitive 50/500/1000 ppb, 20% to 80% RH and ~0,1 et 0,06m/s, 8h

Other validation parameters : QL= 20ppb (for 8 h exposure)
Uncertainty : ±20% (in the range 25 à 2 000µg/m3 from 20 to 80%HR)

*Average of 6 samples

SH passive sampling : Validation

EN838 Tests results

→6 parameters were investigated:

1. Effect of concentration (0.1, 2 VLE, 20C°, 50%RH)
2. Influence of the humidity rate (0.1, 2 VLE, 20°C, 20%, 80%RH)
3. Effect of exposures time (0.5-8h)
4. Influence of the temperature (2 VLE, 50%RH, 15°C, 40°C)
5. Effect of air velocity
6. LOQ

For each tests :
→6 sensors simultaneously exposed
→Comparison with DNPH results

VLE:*« Valeur Limite d'Exposition », i.e. 1230 µg/m³*

ETHERA/DNPH(ref) concentration deviation < 20% ☺

Overestimation of concentration (10%),

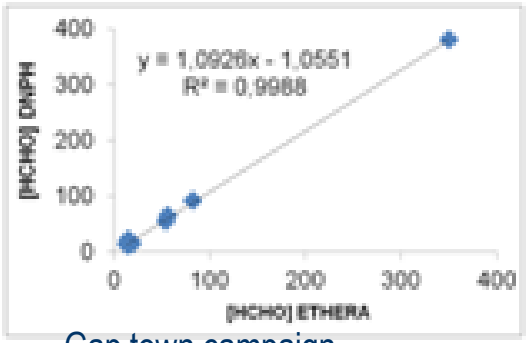
Significant standard deviation (20%)… in progress 😐

Correlation ETHERA / DNPH

Good correlation for the campaign (CHU Grenoble) ☺

→campaign to renew with more measures….in progress 😐

in real conditions



Gap town campaign

Investigation of potential compound interferences

Test dynamic  (30 to 240 min) and static  (24 to 188h) with graded concentrations in the presence and in absence of 50 ppb of HCHO:

- Toluene (500 and 2000 ppb)
- Acetaldehyde / Acrolein / Hexanal (100/50/100 ppb)
- Acetone (several ppm static)

(other vapors: HNO_3, acetic acid, H_2O_2…)

No significant effect on the measurement with a interfering compound on the sensor response with and without of HCHO. ☺

(Exceptional condition : acetaldehyde levels > 100 ppb static > 4 days → overvaluation to 5 ppb of HCHO, unlikely event in indoor air)

Conclusion

ETHERA has developed Profil'air® diagnostic kits designed for professionals

(sensitive, selective, and rapid metering of indoor air pollutants as low as one ppb)

Active sampling, → shorter sampling duration (a few minutes to several hours).

Passive sampling, →of time-weighted averages (a few hours to several days).

validated in the laboratory, according to a standard, measurement campaigns

Conclusion

- A certification ETV (Environmental Technology Verification) with the support of ADEME in order to make the performance of its measuring equipment checked by an ISO17025 laboratory (LNE).

- ETHERA is the first French company to launch a certification ETV!

→ **M. Christian Champion : espace Table Top - ETHERA**

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Profil'air® roadmap

A progressive gas extension

profil air

2011

Formaldehyde

2012

Trichloramine

2013

CO2, T°, HR

Chamber for emission measurements

Badge for personal exposures

Ambiant diffuser

2014

Aldehydes

BTEX