European Network on New Sensing Technologies for Air Pollution Control and Environmental Sustainability - *EuNetAir*

COST Action TD1105

2nd International workshop EuNetAir on

*New Sensing Technologies for Indoor and Outdoor Air Quality Control*

ENEA - Brindisi Research Center, Brindisi, Italy, 25 - 26 March 2014

Chemical Sensors for the Detection and Quantification of Indoor Air Pollutants

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URA CEA-CNRS 2453, 91191 Gif-sur-Yvette/FRANCE
2010: Ethera Breathe Safely

17 employees in 2014

Indoor air pollutants
- Quantification
- Source detection
- Depollution

Crolles Headquarter
Commercial & Marketing Production

Saclay R&D

E. Chevallier C. Belon K. Raulin T. Caron
M. Gallois S. Maurin E. Exposito T-D. Nguyen
F. Abedini A. Gimonet R. François X. Mathiaud

Y. Bigay S. Colomb K. Macquet P. Castaing
Sensors for the Environment

Indoor Air Quality

Formaldehyde (schools)

Nitrogen trichloride (Swimming pools)
SENSORS
which properties are needed?

• Sensitivity
  ➢ ppb level : Pre-concentration

• Selectivity
  ➢ micro-chromatography
  ➢ doping, T°
  ➢ molecular recognition

• Rapidity

• Low cost
Chemical Sensors

Naporous Sponge
• Filter
• Concentrate

Sol-Gel
Simple
Cheap

Selectivity
Probe-molecule/Target-analyte

Ms Analyte
Mr. Probe
Mr. Interfere

Optical detection: rapidity
Visual detection
Sol-Gel Process

Hydrolysis & polycondensation

\[(\text{RO})_3\text{-Si-OR} + \text{H}_2\text{O} \rightarrow (\text{RO})_3\text{-Si-OH} + \text{ROH}\]

\[(\text{RO})_3\text{-Si-OH} + \text{OH-Si-} (\text{RO})_3 \rightarrow (\text{RO})_3\text{-Si-O-Si-(OR)}_3 + \text{H}_2\text{O}\]
Easy-to-do synthesis

1 - organic solvent

2 - Si Alkoxide + Probe molec.

3 - water (pH adjusted)

thermostated bath

Magnetic stirring

4 - Molding

5 - drying

6 - Storage
Characterisations
Monoliths & Films

Porosity
Adsorption/desorption isotherms → $S_{ad}$, $V_{pore}$, distribution of pore size

Film thickness
Profilometry, absorption spectroscopy

Dopant coverage
Thermal Gravimetry Analysis (TGA)

Hydrophilicity or hydrophobicity
Contact angle, near-IR spectroscopy, TGA
Generation of calibrated gas mixtures

- Solid compounds (paraformaldehyde)
- Liquid compounds
- Unstable compounds formed in situ (chloramines)
Generation of calibrated gas mixtures

\[ \text{[CH}_2\text{O]} = 400 \text{ ppt to 2 ppm, Flux: 50} - 2000 \text{ mL min}^{-1} \]
Sensors for Environment

Indoor Air Quality

Detection of the ubiquitous formaldehyde
VOC Outdoors and Indoors
French national campaign in 2005 (600 dwelling-houses)

80 - 85 % of time indoors

Concentration µg/m³

Indoors

Outdoors

- formaldehyde
- hexaldehyde
- acetaldehyde
- toluene
- m/p xylene
- 1,2,4-trimethylbenzene
- benzene
- acrolein

80 - 85 % of time indoors

- 2-butoxy-éthylacétate
- 1-méthoxy-2propylacétate
- styrène
- trichloroéthylène
- Acroléine
- tétrachloroéthylène
- 2-butoxyéthanol
- 1 méthoxy2propanol
- Benzène
- Éthylbenzène
- o-xylène
- 1,2,4-triméthylbenzène
- 1,4-dichlorobenzène
- n-décane
- m/p xylène
- n-undécane
- Acétaldéhyde
- toluène
- Hexaldéhyde
- Formadéhyde

80 - 85 % of time indoors
Decisions resulting from the campaigns

2006: List of 50 indoor air pollutants (INDEX list & ANSES)
2007-2009: Guide Values for Indoor Air (ANSES)
Formaldehyde, Benzene, NO, Naphtalene
Nov. 2009: Values for Risk Management (HCSP)
Formaldehyde: 10 µg/m³, 30 µg/m³, 50 µg/m³
Jan. 2012: Labelling of materials (Law)
Juil. 2012: IAQ monitoring in public buildings (Law)

ANSES = Agence nationale de sécurité sanitaire de l’alimentation, de l’environnement et du travail
HCSP = Haut Conseil de la Santé Publique
Formaldehyde detection

Indoor air quality in homes

10 µg/m³ → 50 µg/m³ → 100 µg/m³

Concentration

Measurement time

Sec → Min → Hour → Day

10 µg = 8 ppb
Chemical Sensor

Principle of detection of CH₂O

\[ \text{Fluoral P} \quad \rightarrow \quad \text{3,5-diacetyl-1,4-dihydrolutidine (DDL)} \]

\[ \text{2 (\text{Fluoral P}) + HCHO \rightarrow NH₃ + (\text{DDL}) - H₂O} \]

Absorbance vs. Wavelength (nm)

Fluorescence intensity (cps) vs. Wavelength (nm)

H. Paolacci et al, Sensors & Transducers, 82, 1423-1431, 2007
Detection of DDL abs & fluo

Ocean Optics Spectrophotometer
UV-visible Lamp
LED 420 nm
Micro-pump
Flow-cell holder
Detection units

Gas in

Gas out

Light from lamp

Light to spectrometer

Gas in

Gas out

Light from LED
Continuous exposure of monolith doped with Fluoral-P to CH₂O (40 ppb)

Ocean Optics

Detection of DDL @ 410 nm

S. Mariano et al, Procedia Engineering, 5 (2010) 1184-1187
PROFIL’AIR of ETHERA

Sampling time: 15 min at 200 mL.min\(^{-1}\)
1 ppb - 1 ppm, RH = 50 %
5 ppb: 20 min
1 ppb: 90 min

\[ y = 0.000051x \]
\[ R^2 = 0.96 \]

Detection of CH₂O: comparison

**Hantzsch reaction**

**Acétyl Acétone** + NH₃ → **Fluoral-P**

Hantzsch reaction

AEROLASER GmbH: 20kg (45*15*56cm), (42 k€)
Reactant solution at 4°C: 5 days max
Fluorimetry: 0.1 ppb to 3 ppm
90 s (10%-90%) every 5 min

NTT technology, GrayWolfSensing FM801 (1.515 £)
Vycor glass doped with acetylacetone
5 cartridges: 530 £
Absorbance @ 420 nm, 20 ppb-1 ppm, 30 min

LFP technology, ETHERA Profil’Air (1.260 €)
Sol-Gel material doped with Fluoral-P
5 cartridges: 225 €
Absorbance @ 420 nm, 5 ppb-1 ppm, 20 min
Campaign of CH$_2$O measurements in schools
Passive mode

Campaign conditions
• Badges hang on the ceiling (3 Radiello, 1 Ethera)
• Duration: Monday morning-Friday afternoon
• RH & T° recorded every day

Analyses of Radiello cartridges by 3 different laboratories:
Quadlab, Tera-Environment, LHVP
Analysis of ETHERA badge on site
### Campaign of CH₂O measurements in schools

<table>
<thead>
<tr>
<th>School</th>
<th>Room</th>
<th>[CH₂O] average</th>
<th>RH%</th>
<th>T°C</th>
<th>ETHERA</th>
<th>ARB</th>
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</thead>
<tbody>
<tr>
<td>Paul Bert</td>
<td>103</td>
<td>23,9</td>
<td>42,6</td>
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<td>-7,1%</td>
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<td>104</td>
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<td>005</td>
<td>20,4</td>
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<td>21,8</td>
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<td>Ampère</td>
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<td>34%</td>
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<td>6,6%</td>
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<td>6,4%</td>
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<td>11,7</td>
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<td>15,5</td>
<td>12,6</td>
<td>7,7%</td>
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<tr>
<td>Bériat</td>
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<td>51,8</td>
<td>16,1</td>
<td>17,0</td>
<td>19,7%</td>
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<tr>
<td>Bériat</td>
<td>01</td>
<td>16,7</td>
<td>52,2</td>
<td>16,0</td>
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<td>18%</td>
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<tr>
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<td>05</td>
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<td>-36,3%</td>
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<td>13,1</td>
<td>5,3</td>
<td>-35,4%</td>
</tr>
<tr>
<td>Houille Blanche</td>
<td>03</td>
<td>11,0</td>
<td>52,6</td>
<td>13,6</td>
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<td>-44,5%</td>
</tr>
<tr>
<td>Houille Blanche</td>
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<td>8,8</td>
<td>52,9</td>
<td>12,8</td>
<td>7,0</td>
<td>-21%</td>
</tr>
<tr>
<td>Houille Blanche</td>
<td>01</td>
<td>15,4</td>
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<td>-22%</td>
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<td>-17%</td>
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<tr>
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<td>02</td>
<td>17,8</td>
<td>60,0</td>
<td>11,4</td>
<td>12,1</td>
<td>-17%</td>
</tr>
<tr>
<td>Savane</td>
<td>03</td>
<td>18,0</td>
<td>22,5</td>
<td>15,6</td>
<td>16,0</td>
<td>25%</td>
</tr>
<tr>
<td>Savane</td>
<td>04</td>
<td>8,2</td>
<td>6,8</td>
<td>6,5</td>
<td>36,6%</td>
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<tr>
<td>Savane</td>
<td>05</td>
<td>11,5</td>
<td>14,0</td>
<td>10,5</td>
<td>10,0</td>
<td>21,7%</td>
</tr>
</tbody>
</table>

**ARB(%) = ([CH₂O]_{average} - [CH₂O]_{ETHERA})/[CH₂O]_{average}**

**Note:** The percentage difference in ARB values indicates the deviation from the average CH₂O concentration.
Sensors for Environment

Air quality in swimming pools

Detection of nitrogen trichloride (NCl₃)
What air do we breathe in swimming pools?

\[ \text{Cl}_2 (g) + \text{H}_2\text{O} \rightarrow \text{ClO}^- + 2\text{H}^+ + \text{Cl}^- \]

**Saliva, sweat, urine, skin**

**Water**

\[ \text{NH}_2\text{Cl} \rightarrow \text{NHCl}_2 \rightarrow \text{NCl}_3 \]

**Air**

\[ \text{CHCl}_3 \]

NCl₃ and CHCl₃ in air
Toxicity of NCl₃

– Classified as « irritant »

– Troubles reported for kids and pool attendants
  – Acute exposure: eye irritation & breathing trouble
  – Long time exposure : asthma

– French regulation for exposed workers (INRS, 2001)
  – 0.3 to 0.5 mg/m³ in air = 60 to 100 ppb

– Typical levels measured in swimming-pools
  – 10 to hundreds of ppb (number of swimmers & ventilation system)
Generation of NCl₃
Reproducing swimming pool atmosphere
Chloramines: NH₂Cl, NHCl₂ & NCl₃

(NH₄)₂SO₄ + 2 HClO → 2 NH₂Cl + H₂SO₄ + 2 H₂O
NH₂Cl + HClO → NHCl₂ + H₂O
NHCl₂ + HClO → NCl₃ + H₂O
**NCl₃ detection methods**

2 hours of pumping + HPLC or
45 min of pumping + liquid phase colorimetry (TRIKLORAM)

Needs: Easy-to-use method
Direct & fast measurements
Principle of NCl$_3$ detection

\[
6 \text{I}^- + \text{NCl}_3 + 3 \text{H}^+ \rightarrow 3 \text{I}_2 + \text{NH}_3 + 3 \text{Cl}^- \quad (1)
\]

\[
\text{I}_2 + \text{I}^- \rightarrow \text{I}_3^- \quad (2)
\]

\[
\text{I}_3^- + \text{Amylose} \rightarrow \text{complex Amylose/I}_3^- \quad (3)
\]

TMOS/H$_2$O/Amylose/I$^-$

$S_{ads} = 700\pm100$ m$^2$.g$^{-1}$

$D_{pore} = 30$ Å
Kinetics of formation of $I_3^-$/amylose

Slope proportional to $NCl_3$ concentration

$y = 0.0008x$
$R^2 = 0.9951$

200 mL.min$^{-1}$
$NCl_3$ : 50 ppb
Calibration curve for NCl$_3$ detection

Flux = 200 ml.L$^{-1}$, %RH $\approx$ 60%

* : Batch of January 24, 2011
$\Delta$ : Batch of March 25, 2011
☐ : Batch of Sept. 19, 2011

$\Delta$Abs/$\Delta$t à 545 nm / $10^{-4}$.min$^{-1}$

$[\text{NCl}_3]$ / ppb

$y = 0.1788x$
$R^2 = 0.9768$

Technology transfer to ETHERA

Commercialized by CIFEC since December 2012
## Campaign of NCl$_3$ measurement in swimming pool

<table>
<thead>
<tr>
<th>Campaign</th>
<th>Duration</th>
<th>LHVP</th>
<th>ETHERA</th>
<th>Population in H$_2$O</th>
<th>ETHERA average</th>
<th>ARB</th>
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</thead>
<tbody>
<tr>
<td>March 28</td>
<td>10H-12H</td>
<td>19.1</td>
<td>14.8</td>
<td>17 children</td>
<td>18.3</td>
<td>4.2%</td>
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<td></td>
<td></td>
<td></td>
<td>21.9</td>
<td>17 children</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>12H-14H</td>
<td>21.3</td>
<td>18.0</td>
<td>0</td>
<td>22.0</td>
<td>3.3%</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>18.9</td>
<td>0</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>29.1</td>
<td>12 adults aquagym</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>14H-16H</td>
<td>19.3</td>
<td>26.8</td>
<td>11 adults aquagym</td>
<td>18.3</td>
<td>5.2%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>13.3</td>
<td>11 adult aquagym</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>14.7</td>
<td>14 children</td>
<td></td>
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<tr>
<td>April 04</td>
<td>10H-12H</td>
<td>16.7</td>
<td>20.7</td>
<td>18 children</td>
<td>18.6</td>
<td>11.4%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>19.8</td>
<td>18 children</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>15.3</td>
<td>12 children</td>
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<td></td>
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<tr>
<td></td>
<td>12H-14H</td>
<td>22.4</td>
<td>16.5</td>
<td>0</td>
<td>16.5</td>
<td>26.3%</td>
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<tr>
<td></td>
<td>14H-16H</td>
<td>22.8</td>
<td>20.0</td>
<td>10 adults aquagym</td>
<td>19.8</td>
<td>13.2%</td>
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<td></td>
<td></td>
<td></td>
<td>21.8</td>
<td>10 adults aquagym</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>17.5</td>
<td>5 children+3babies</td>
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<td>19.9</td>
<td>2nd measurement</td>
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</table>

**ARB (%) = ([NCl$_3$]$_{LHVP}$-[NCl$_3$]$_{ETHERA}$)/([NCl$_3$]$_{LHVP}$)**
<table>
<thead>
<tr>
<th>Campaign</th>
<th>Duration</th>
<th>LHVP</th>
<th>ETHERA ppb</th>
<th>Time</th>
<th>Population in H₂O</th>
<th>ETHERA average</th>
<th>ARB</th>
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<tr>
<td>May 02</td>
<td>10H-12H</td>
<td>3.7</td>
<td>4.9</td>
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<td>11.4</td>
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<td>10.6</td>
<td>10:58</td>
<td>0-17 children</td>
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<td>11.9</td>
<td>11:24</td>
<td>17 children</td>
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<td>14:36</td>
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<td>16.6</td>
<td>15:32</td>
<td>10 children+4 babies</td>
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</tbody>
</table>
CONCLUSIONS

• Sol-Gel nanoporous materials well-suited for:
  – Selective and sensitive sensors (nanoreactors with specific probes)
  – Analyte preconcentration (sponge, high $S_{ad}$)
  – Analyte filter (tailored pores)

• Many domains of application
  – Environment: chemical sensors for air quality
  – Health: Microbiology, food industry (discrimination of bacteria)
    Non-invasive diagnosis of diseases

• Other potential uses
  – Filtering membranes for other sensors (pore size monitoring)
  – Up-stream specific filters trapping of undesired pollutants)
Acknowledgments

A-M. Laurent        C. Beaubestre

Laboratoire d’Hygiène de la Ville de Paris