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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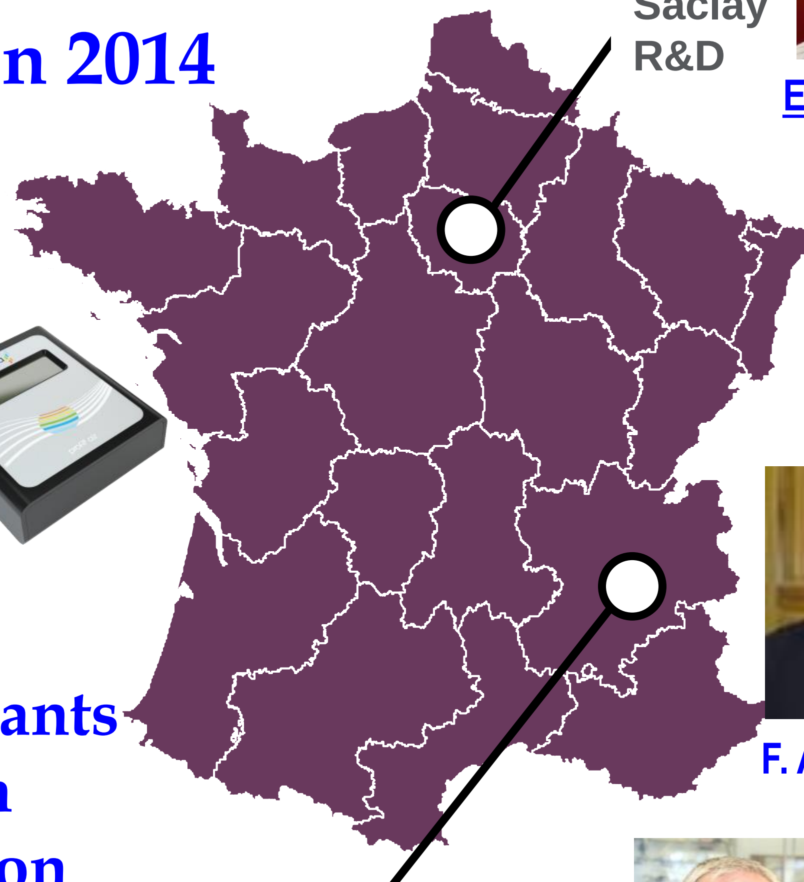
2010: ethera Breathe Safely

17 employees in 2014



Indoor air pollutants
- Quantification
- Source detection
- Depollution

E. Chevallier C. Belon K. Raulin T. Caron

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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?

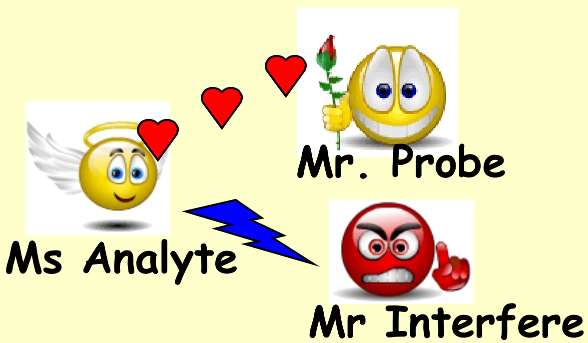
- **Sensitivity**
  - ➢ **ppb level : Pre-concentration**
- **Selectivity**
  - ➢ **micro-chromatography**
  - ➢ **doping, T°**
  - ➢ **molecular recognition**
- **Rapidity**
- **Low cost**

Chemical Sensors

Naporous Sponge
- **Filter**
- **Concentrate**

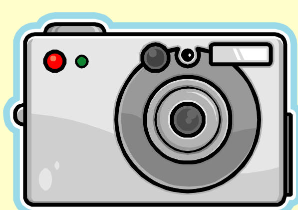
→

Sol-Gel
Simple
Cheap



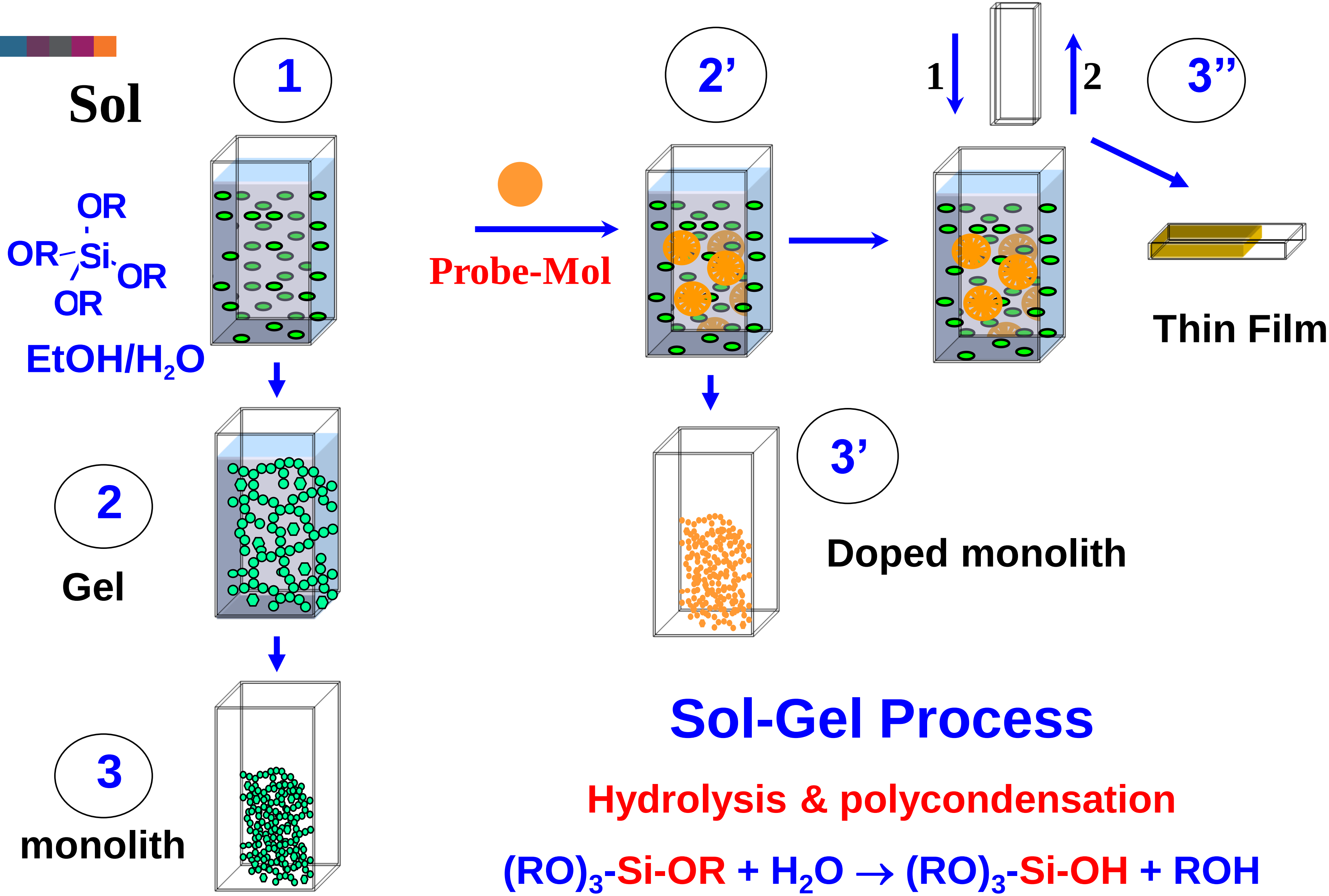
Selectivity

Probe-molecule/Target-analyte



Optical detection: rapidity

Visual detection



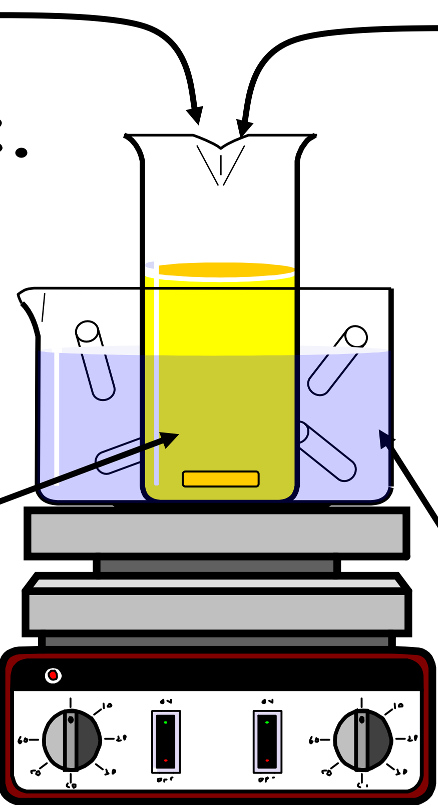
Sol-Gel Process

Hydrolysis & polycondensation

$(RO)_3$-Si-OR + $H_2O \rightarrow (RO)_3$-Si-OH + ROH

$(RO)_3$-Si-OH + OH-Si- $(RO)_3 \rightarrow (RO)_3$-Si-O-Si-$(OR)_3$ + H_2O

Easy-to-do synthesis



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

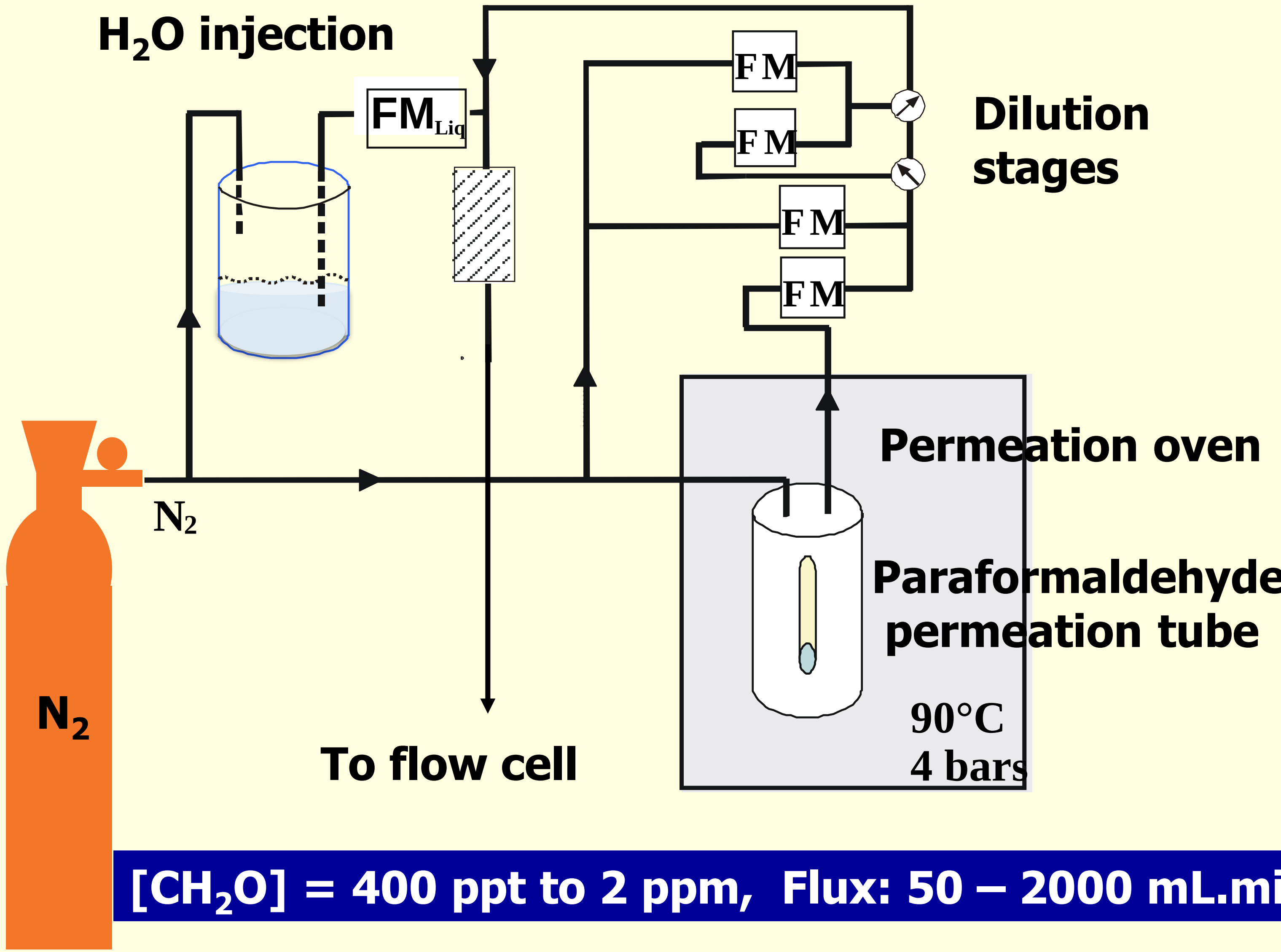
Contact angle, near-IR spectroscopy, TGA

METROLOGY

Generation of calibrated gas mixtures

- Solid compounds (paraformaldehyde)
- Liquid compounds
- Unstable compounds formed in situ (chloramines)

Generation of calibrated gas mixtures



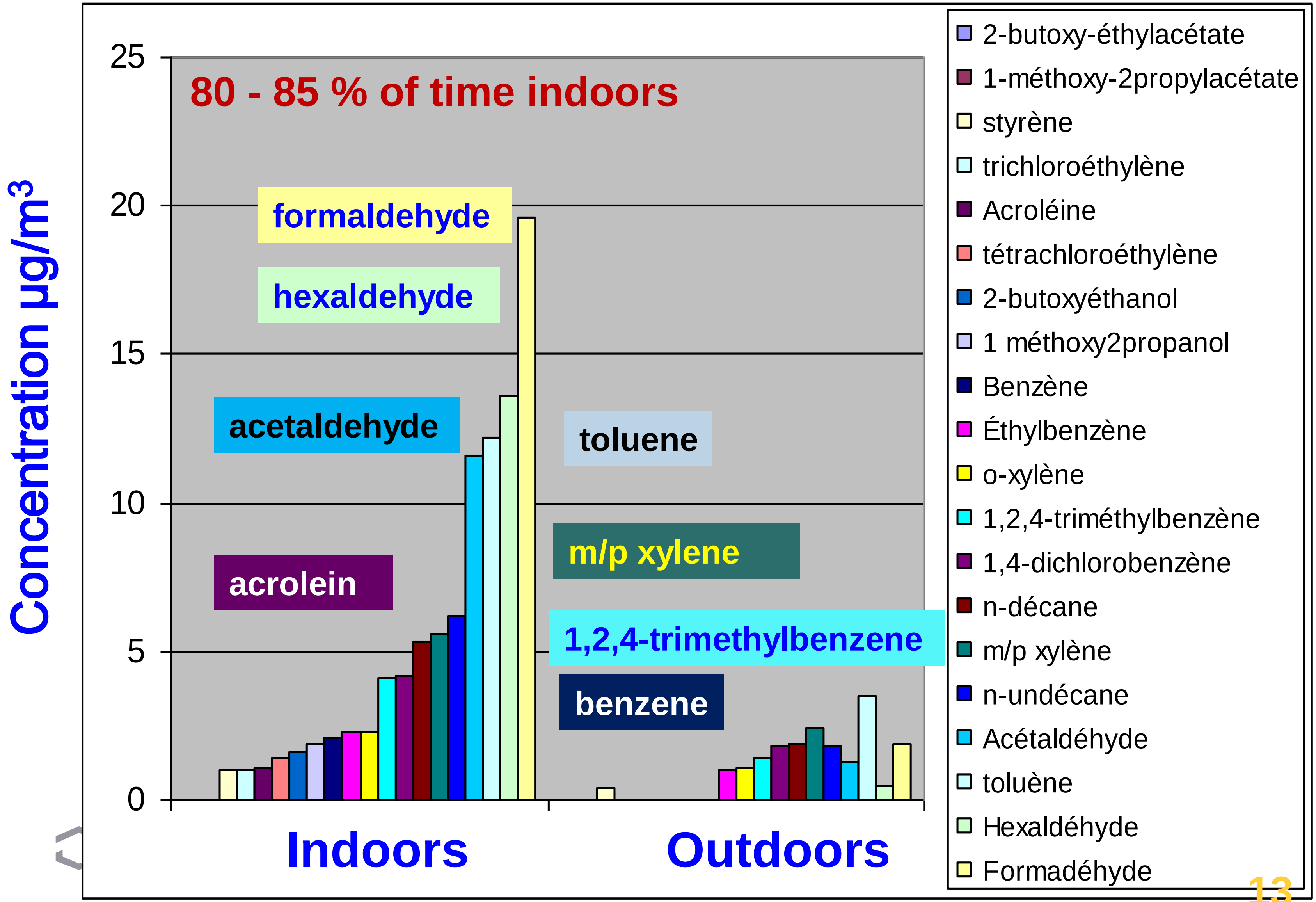
$[CH_2O]$ = 400 ppt to 2 ppm, Flux: 50 – 2000 mL.min^{-1}

Indoor Air Quality

Detection of the ubiquitous formaldehyde

VOC Outdoors and Indoors

French national campaign in 2005 (600 dwelling-houses)

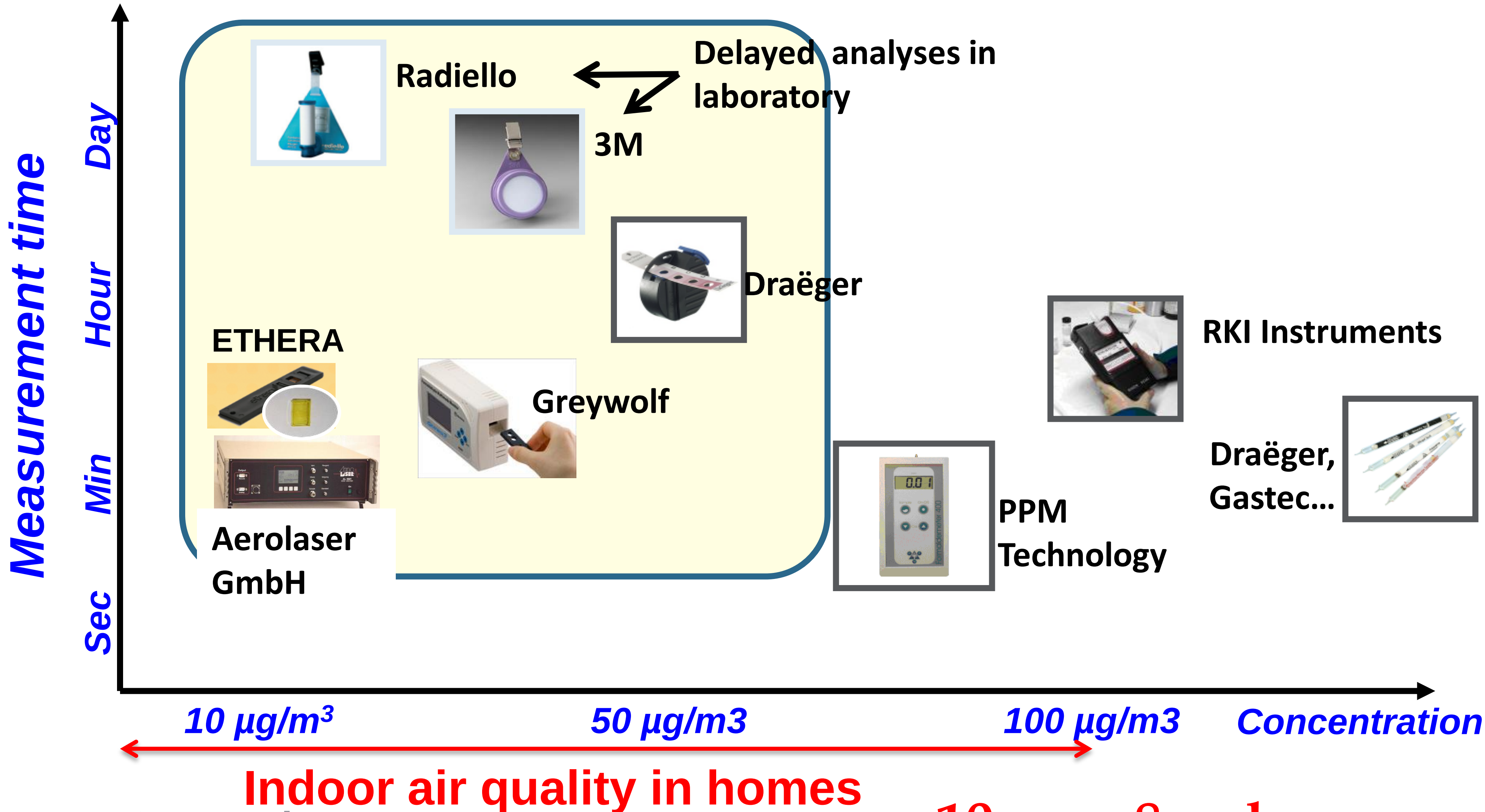


Decisions resulting from the campaigns

- **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/m^3, 30 µg/m^3, 50 µg/m^3
- **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

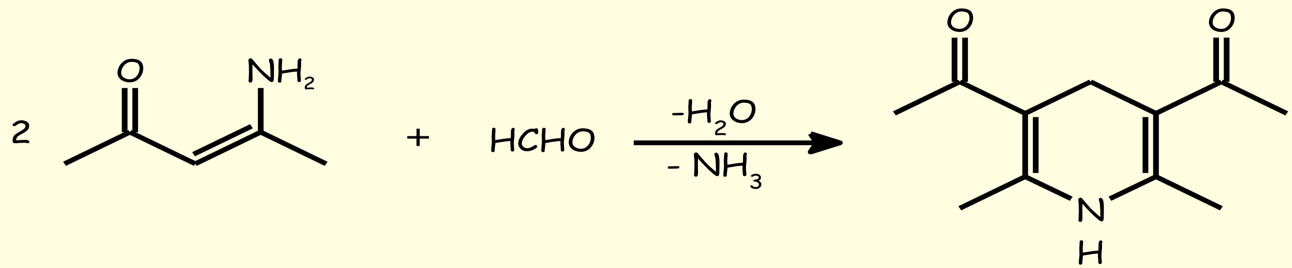
Formaldehyde detection



10 µg = 8 ppb

Chemical Sensor

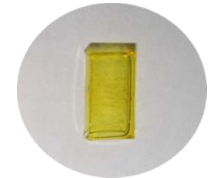
Principle of detection of CH_2O



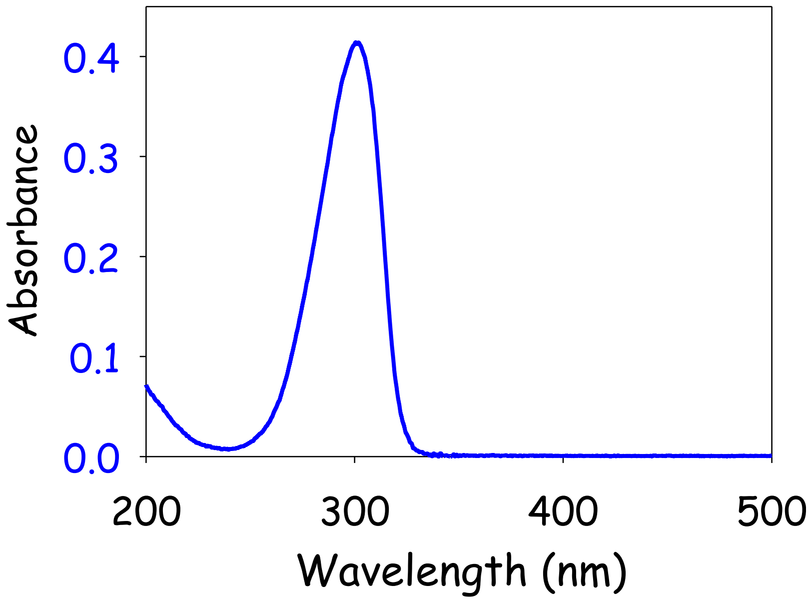
Fluoral P

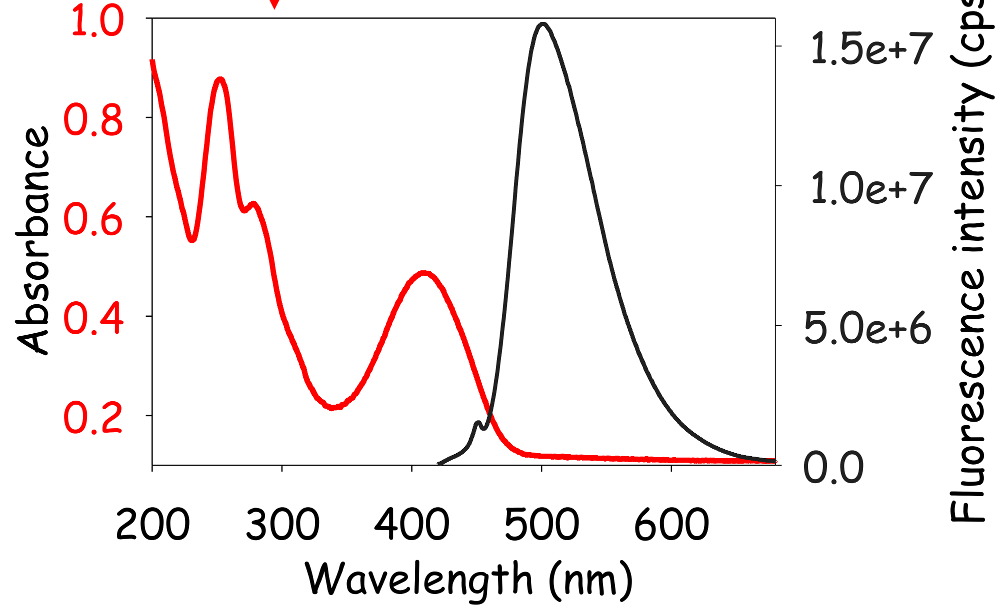
3,5-diacetyl-1,4-dihydrolutidine (DDL)

TMOS/MeOH/ H2O/Fluoral-P



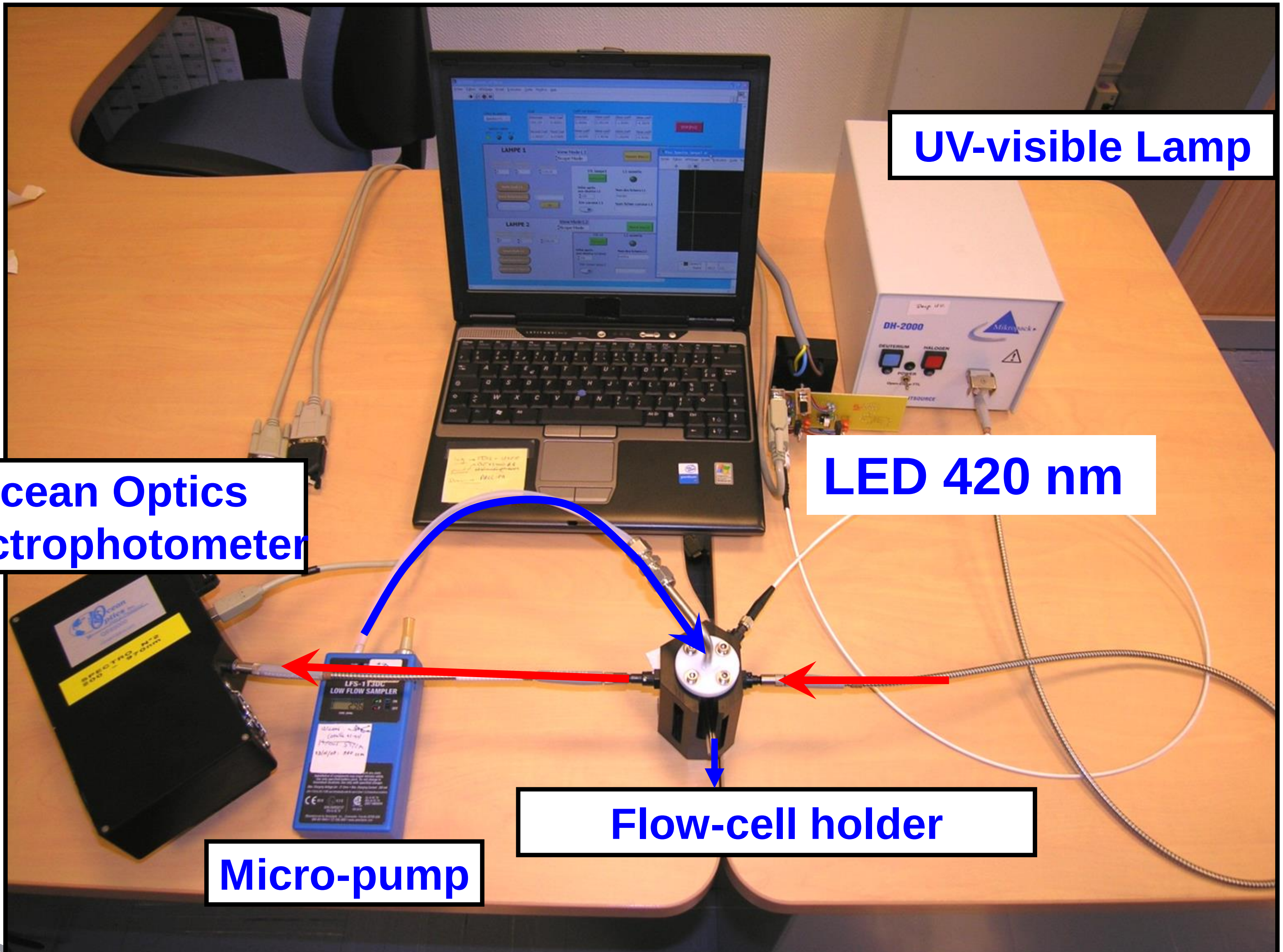
650 m^2/g



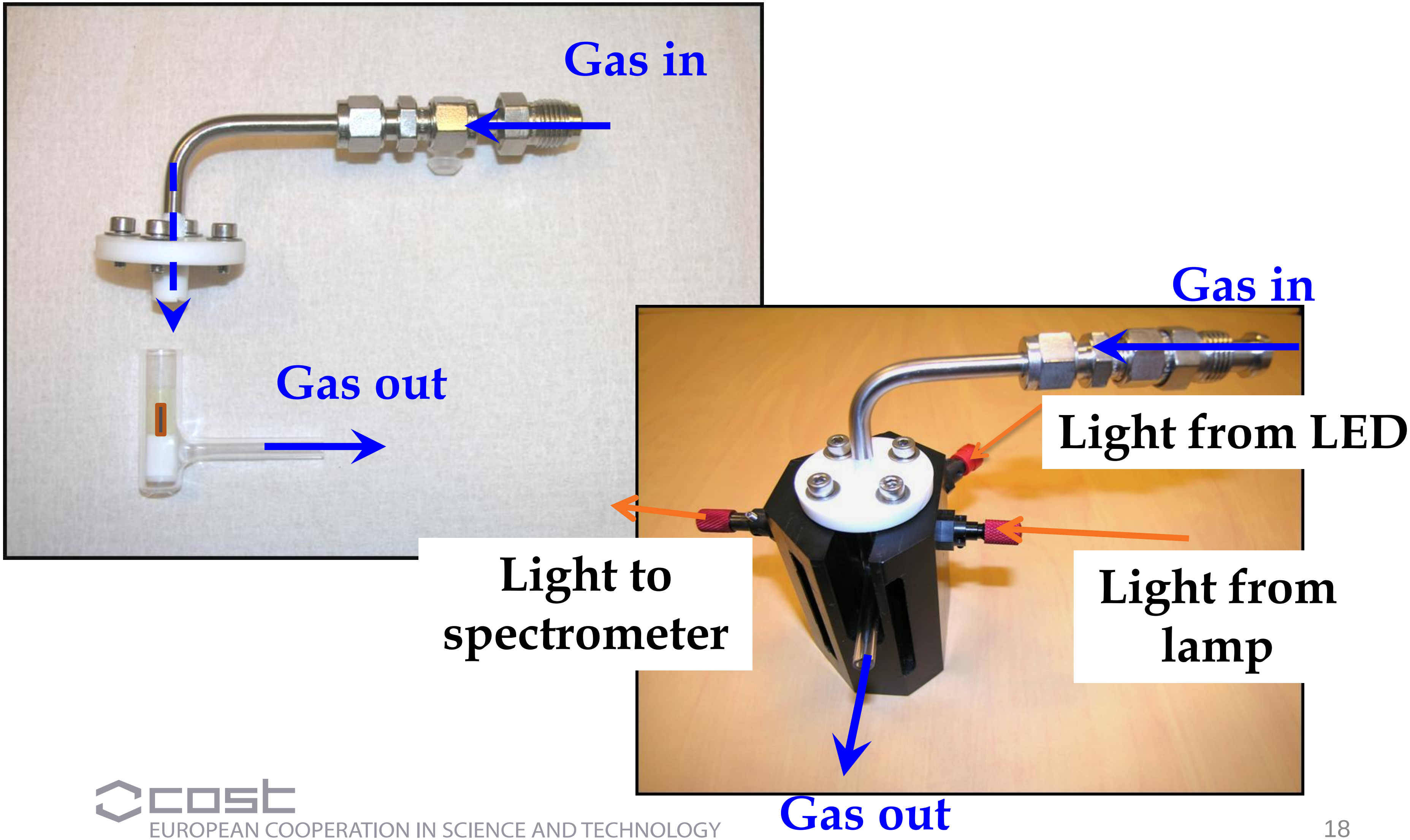


H. Paolacci et al, Sensors & Transducers, 82, 1423-1431, 2007

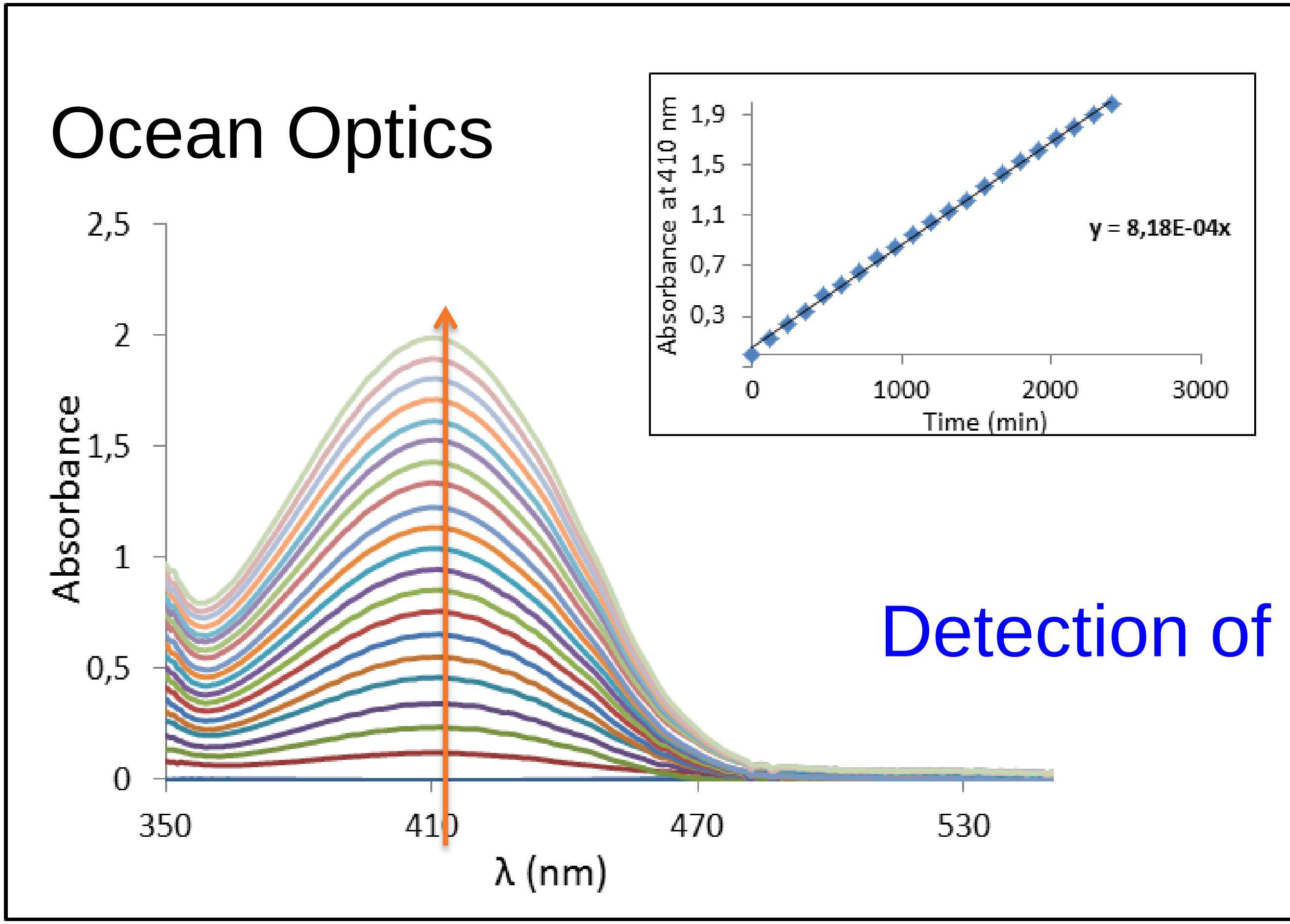
Detection of DDL abs & fluo

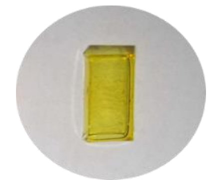


Detection units



Continous exposure of monolith doped with Fluoral-P to CH_2O (40 ppb)



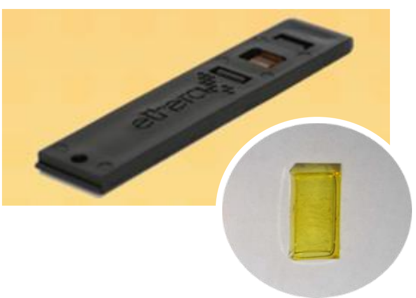


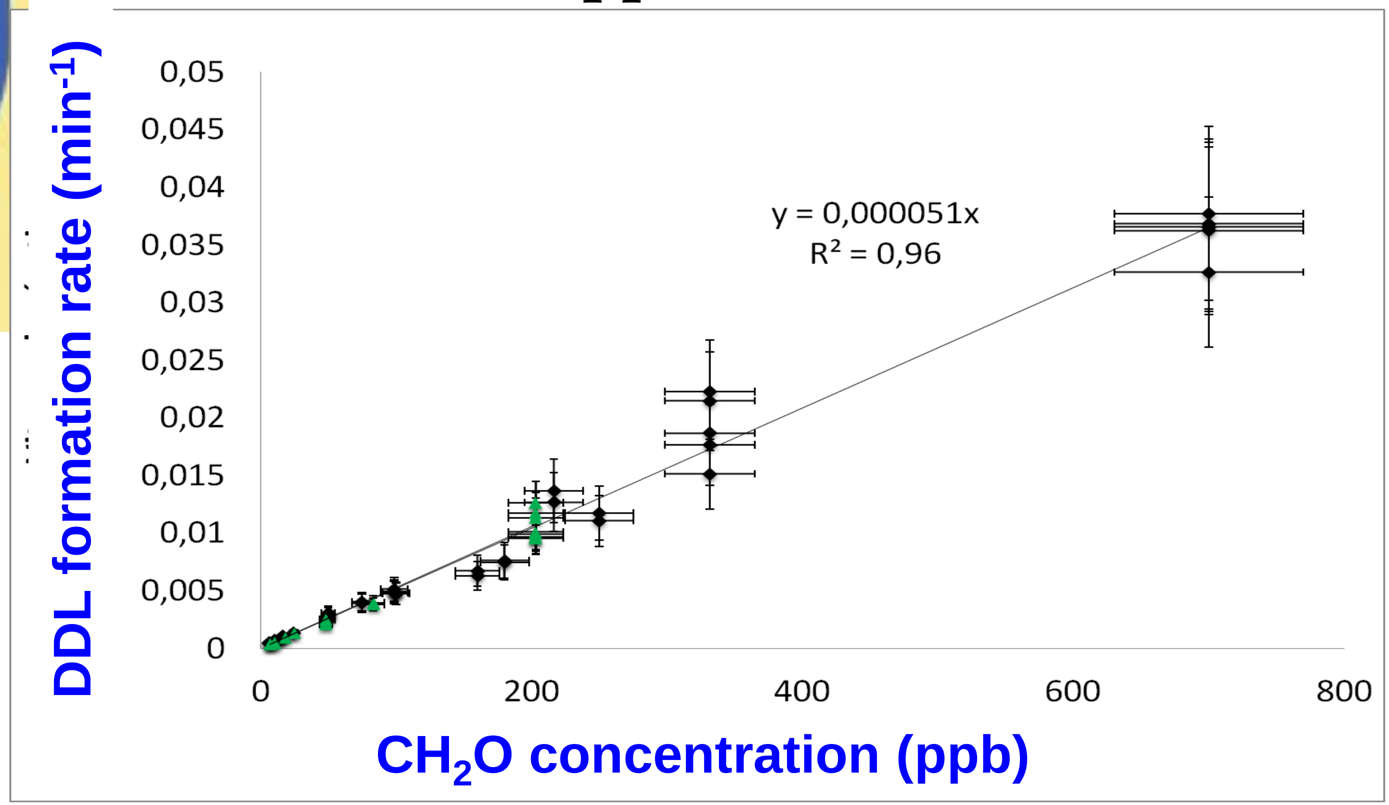
Detection of DDL @ 410 nm

S. Mariano et al, Procedia Engineering, 5 (2010) 1184-1187

PROFIL'AIR of ETHERA

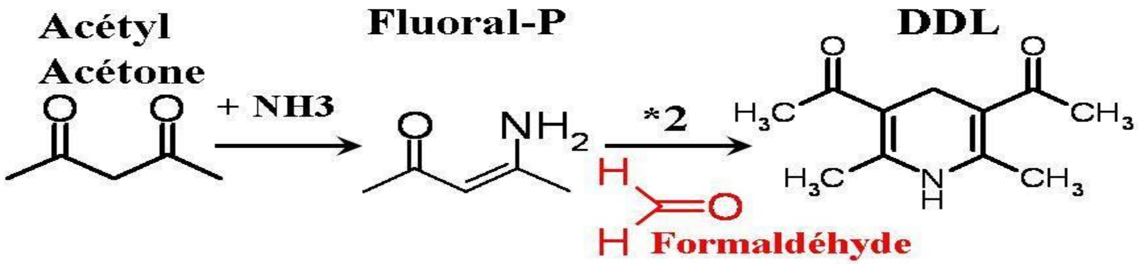
Sampling time: 15 min at 200 mL.min^{-1}
1 ppb -1 ppm, RH = 50 %
5 ppb: 20 min
1 ppb: 90 min





T.-H. Tran-Thi et al., l'actualité chimique, Valorisation de la recherche, N°366, Sept. 2012.

Detection of CH_2O: comparison



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_2O 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 CH_2O measurements in schools

School	Room	[CH_2O]					RH%	T°C	ETHERA	ARB
		average	Lab1	Lab2	Lab3	ARB				
Paul Bert	103	**23,9**	24,2	24,4	23,0	**3,8%**	42,6	22,9	**22,2**	**-7,1%**
Paul Bert	104	**22,9**	24,2	23,0	21,6	**5,7%**	41,9	22,7	**19,8**	**-13,5%**
Paul Bert	105	**17,2**	17,7	18,3	15,6	**9,3%**	43,8	22,7	**14,6**	**-15,1%**
Paul Bert	005	**20,4**	22,1	21,9	17,2	**15,7%**	43,2	21,7	**18,3**	**-10,3%**
Paul Bert	006	**19,4**	19,3	20,7	18,1	**6,7%**	44,2	21,8	**16,9**	**-12,9%**
Ampère	03	**9,7**	9,7				50,0	15,4	**13,0**	**34%**
Ampère	02	**15,0**	15,0				55,6	15,0	**16,0**	**6,6%**
Ampère	01	**15,7**	15,7				53,0	14,9	**16,7**	**6,4%**
Bériat	03	**11,7**	11,7				51,1	15,5	**12,6**	**7,7%**
Bériat	02	**14,2**	14,2				51,8	16,1	**17,0**	**19,7%**
Bériat	01	**16,7**	16,7				52,2	16,0	**19,7**	**18%**
Houille Blanche	05	**10,2**	13,3	8,4	8,9	**30,4%**	56,7	12,4	**6,5**	**-36,3%**
Houille Blanche	04	**8,2**	10,1	7,0	7,0	**23,1%**	55,0	13,1	**5,3**	**-35,4%**
Houille Blanche	03	**11,0**	14,6	8,9	9,6	**32,7%**	52,6	13,6	**6,1**	**-44,5%**
Houille Blanche	02	**8,8**	9,7	8,1	8,7	**10,2%**	52,9	12,8	**7,0**	**-21%**
Houille Blanche	01	**15,4**	17,5	14,3	14,5	**13,6%**	49,2	13,7	**12,0**	**-22%**
Savane	01	**14,6**	17,4	13,4	12,9	**19,2%**	60,0	11,4	**12,1**	**-17%**
Savane	02	**17,8**	21,6	16,1	15,7	**21,3%**				
Savane	03	**18,0**	22,5	15,6	16,0	**25%**				
Savane	04	**8,2**	11,2	6,8	6,5	**36,6%**				
Savane	05	**11,5**	14,0	10,5	10,0	**21,7%**				

$$ARB(\%) = ([CH_2O]_{average} - [CH_2O]_{ETHERA})/[CH_2O]_{average}$$

cost
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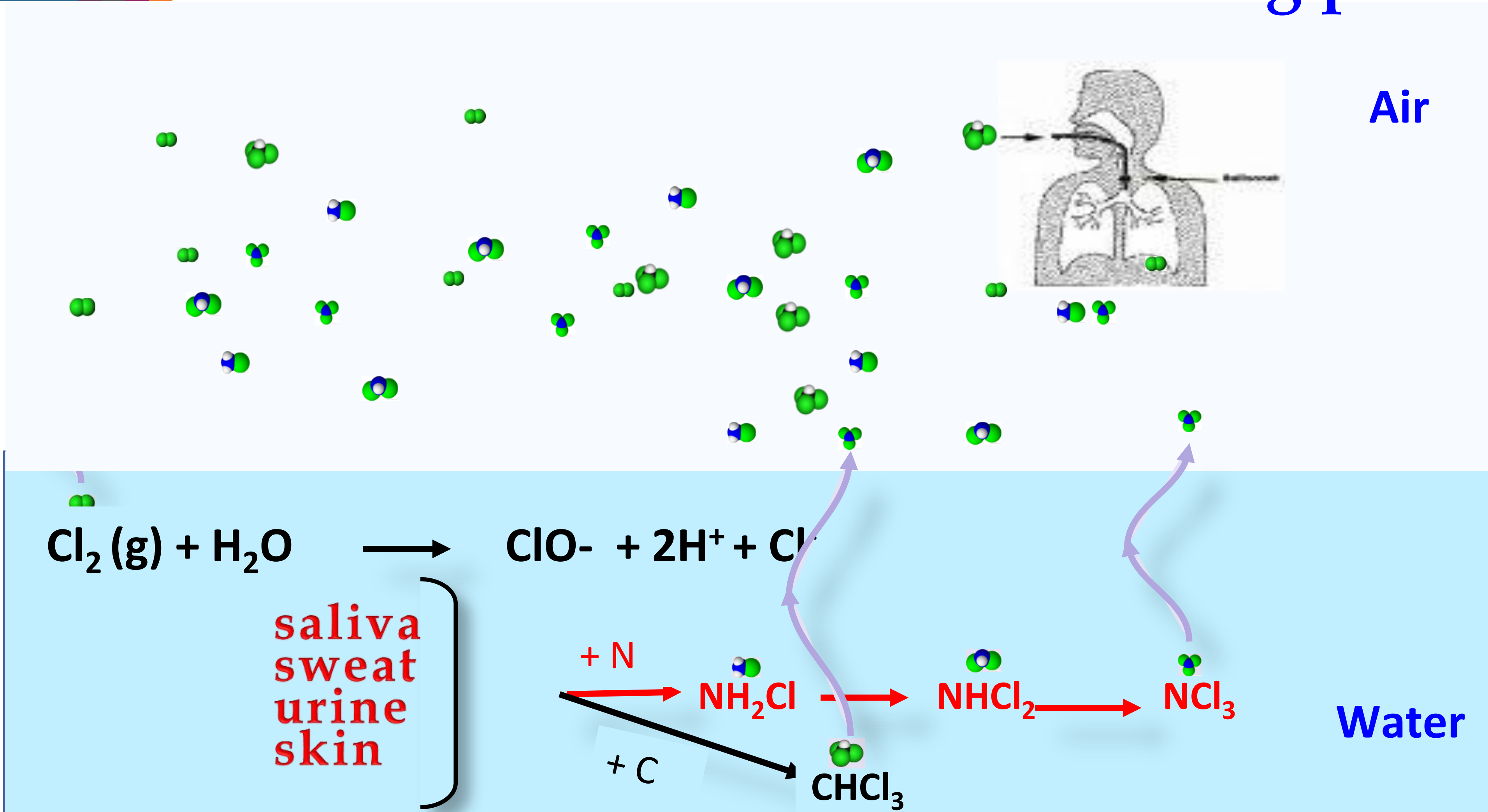
Sensors for Environment

Air quality in swimming pools

Detection of nitrogen trichloride (NCl_3)

What air do we breathe in swimming pools?



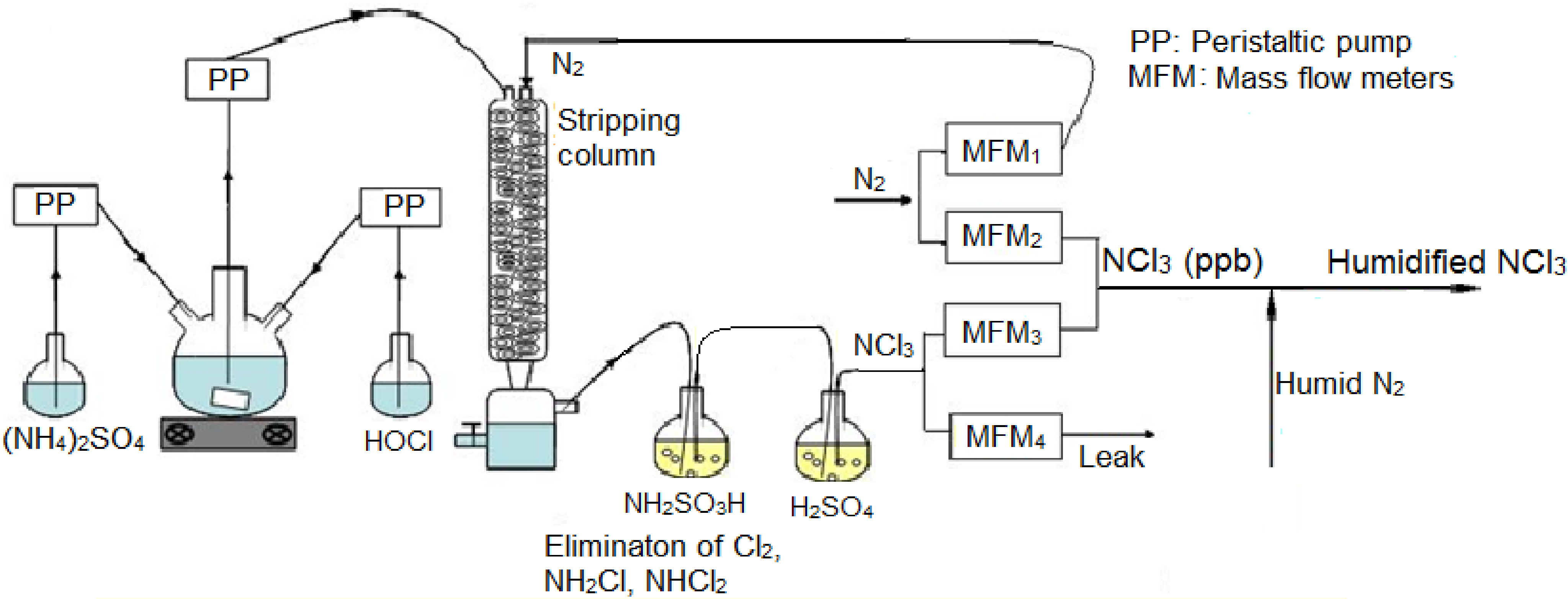
NCl_3 and $CHCl_3$ in air

Toxicity of NCl_3

- 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/m^3 in air = 60 to 100 ppb
- Typical levels measured in swimming-pools
  - 10 to hundreds of ppb (number of swimmers & ventilation system)

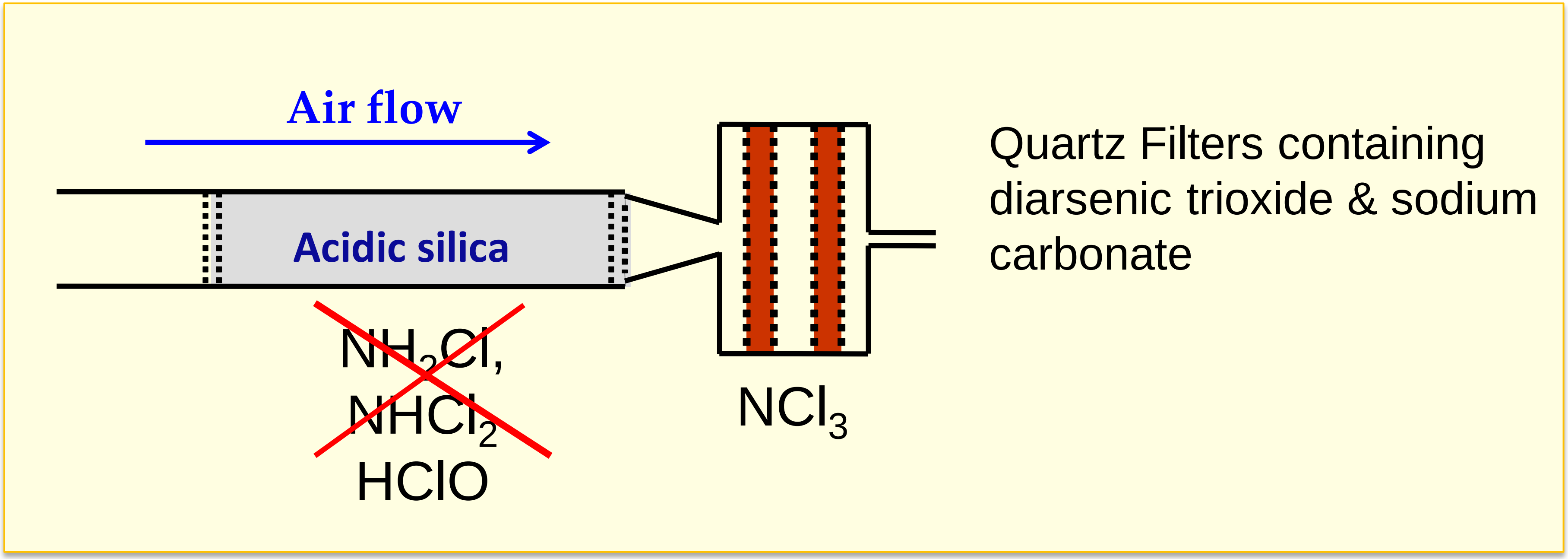
Generation of NCl_3

Reproducing swimming pool atmosphere
Chloramines: NH_2Cl, $NHCl_2$ & NCl_3



$$(NH_4)_2SO_4 + 2\ HClO \rightarrow 2\ NH_2Cl + H_2SO_4 + 2\ H_2O$$
$$NH_2Cl + HClO \rightarrow NHCl_2 + H_2O$$
$$NHCl_2 + HClO \rightarrow NCl_3 + H_2O$$

NCl_3 detection methods



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

Needs : Easy-to-use method

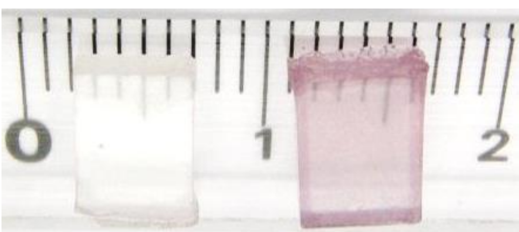
Direct & fast measurements

Principle of NCl_3 detection

$$6\,I^- + NCl_3 + 3\,H^+ \rightarrow 3\,I_2 + NH_3 + 3\,Cl^- \quad (1)$$

$$I_2 + I^- \rightarrow I_3^- \quad (2)$$

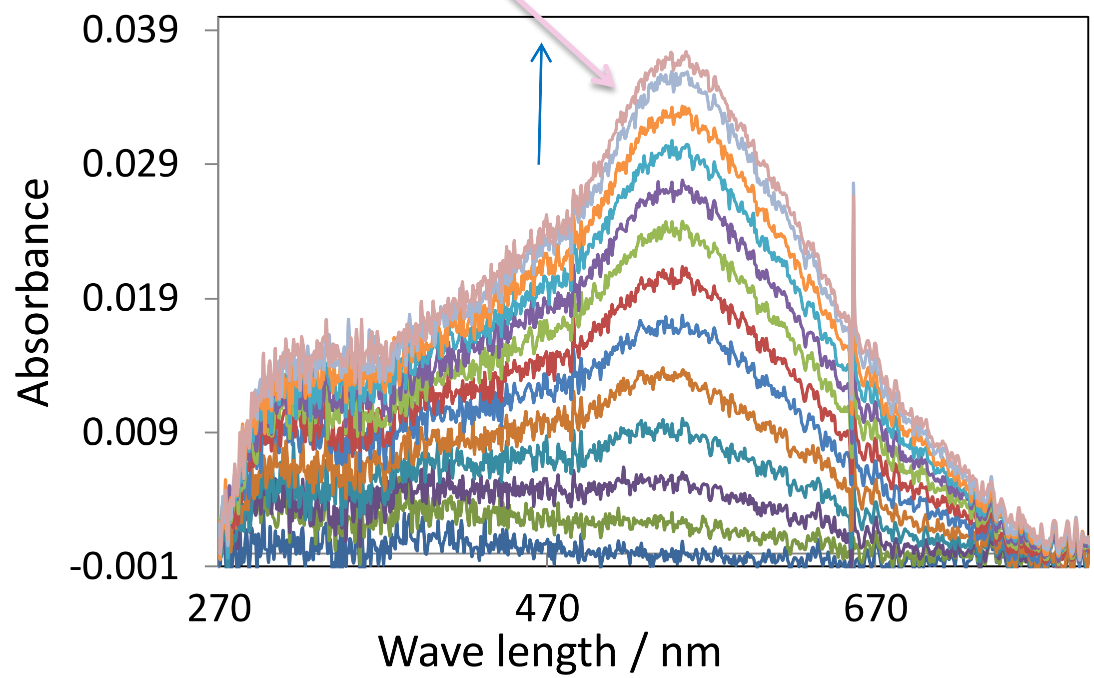
$$I_3^- + \text{Amylose} \rightarrow \text{complex Amylose}/I_3^- \quad (3)$$



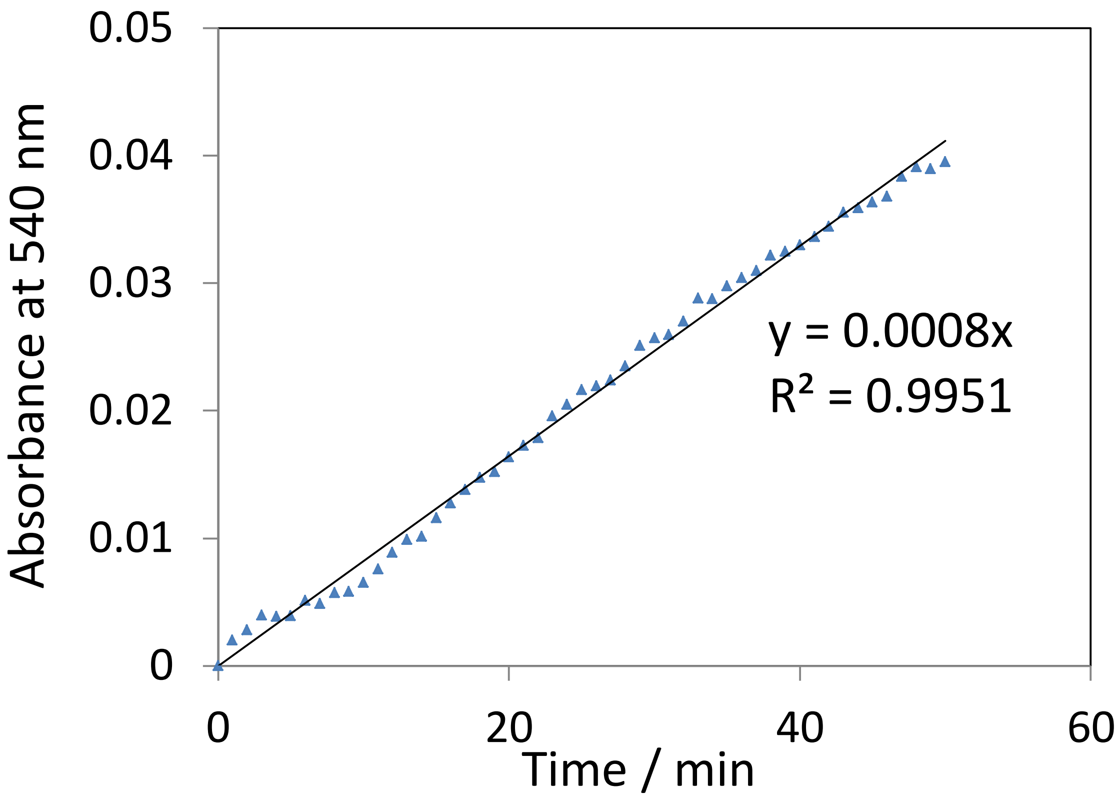
$TMOS/H_2O/Amylose/I^-$

$S_{ads} = 700 \pm 100\ m^2.g^{-1}$

$D_{pore} = 30\ Å$



Kinetics of formation of I_3^-/amylose

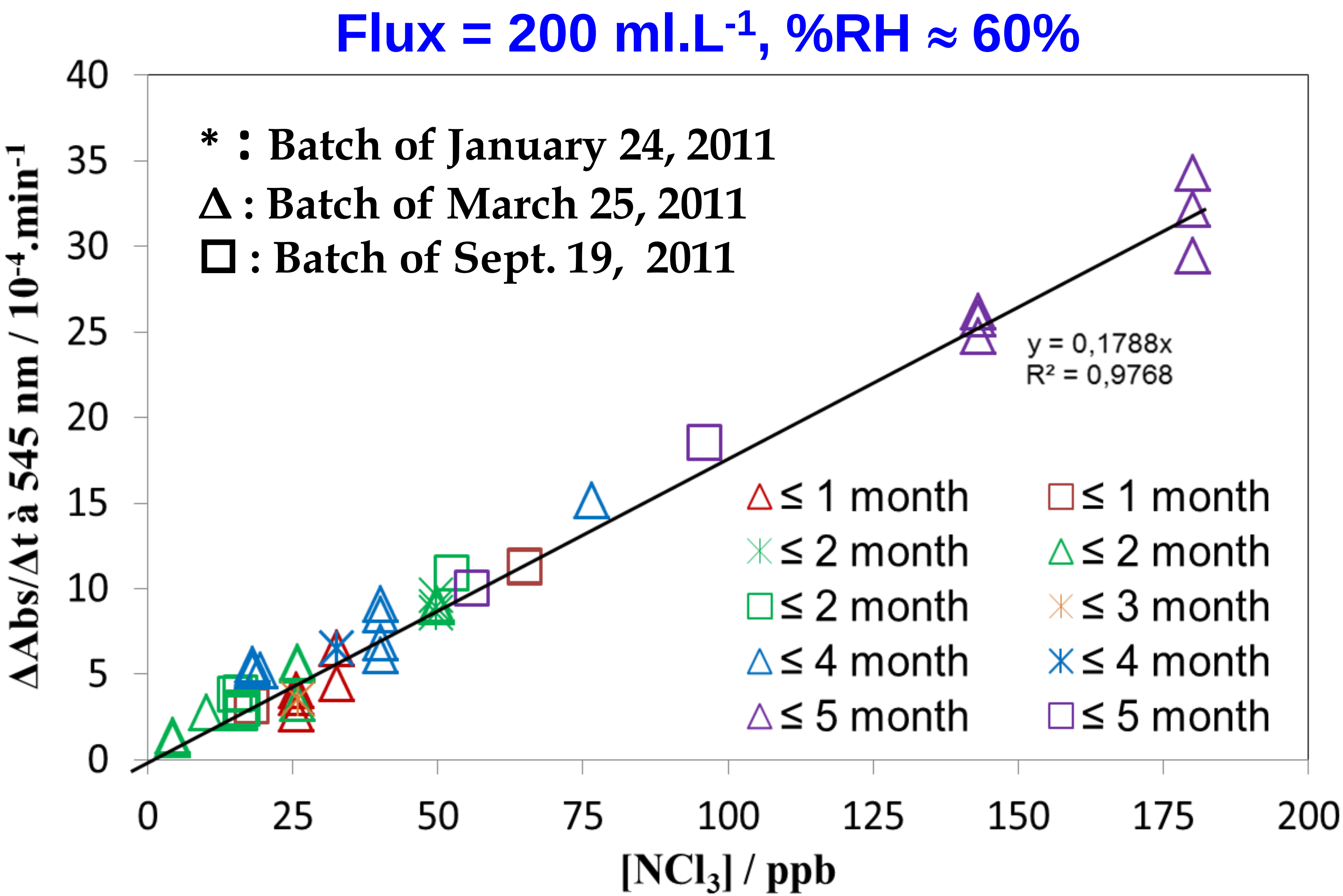


200 mL.min^{-1}

NCl_3 : 50 ppb

Slope proportional to NCl_3 concentration

Calibration curve for NCl_3 detection



cost
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T.-H. Nguyen et al, Sensors & Actuators, 187 (2013) 622– 629

Technology transfer to ETHERA

Commercialized by CIFEC since December 2012

Campaign of NCl_3 measurement in swimming pool

Campaign	Duration	LHVP	ETHERA ppb	ETHERA Time	Population in H_2O	ETHERA average	ARB
March 28	10H-12H	19.1	14.8	10:58	17 children	18.3	4.2%
			21.9	11:32	17 children		
	12H-14H	21.3	18.0	12:00	0	22.0	3.3%
			18.9	12:35	0		
			29.1	12:52	12 adults aquagym		
	14H-16H	19.3	26.8	14:10	11 adults aquagym	18.3	5.2%
			13.3	14:36	11 adult aquagym		
			14.7	15:18	14 children		
April 04	10H-12H	16.7	20.7	10:55	18 children	18.6	11.4%
			19.8	11:27	18 children		
			15.3	11:56	12 children		
	12H-14H	22.4	16.5	12:33	0	16.5	26.3%
	14H-16H	22.8	20.0	14:15	10 adults aquagym	19.8	13.2%
			21.8	14:50	10 adults aquagym		
			17.5	15:35	5 children+3babies		
			19.9	15:37	2nd measurement		

$ARB (\%) = ([NCl_3]_{LHVP} - [NCl_3]_{ETHERA}) / ([NCl_3]_{LHVP})$

Campaign	Duration	LHVP	ETHERA ppb	ETHERA Time	Population in H_2O	ETHERA average	ARB
May 02	10H-12H	3.7	4.9	10:28	0	11.4	208%
			10.6	10:58	0-17 children		
			11.9	11:24	17 children		
			18.2	11:45	17 children		
	12H-14H	14.5	20.8	12:15	17 children	22.9	57.9%
			21.4	12:48	0		
			26.3	14:36	11 adults aquagym		
	14H-16H	16.3	15.2	14:21	7 adults aquagym	14.9	8.6%
			17.2	14:23	2nd measurement		
			12.9	15:08	11 children		
			12.7	15:10	2nd measurement		
			16.6	15:32	10 children+4babies		

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
    specific filters for depollution
  - 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)

Acknowlegments

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