Photocatalyse et traitement d'air
Quels avantages et limitations

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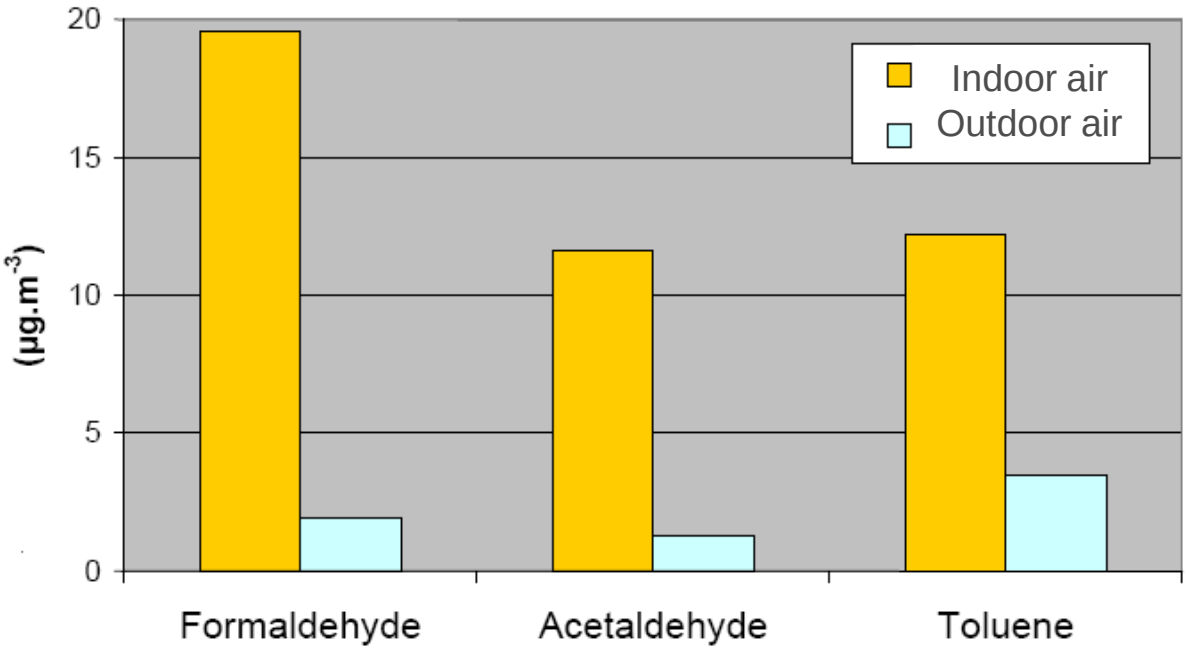
Air pollution: context

Indoor air/ Outdoor air

Main pollutants from outdoor (Motor vehicle emissions, industrial Activities,Residentials activities: SO_2, NOx ($NO + NO_2$); VOC; O3, Particles



(www.oqai.fr)

Indoor air pollution: **construction Materials, Occupants activities**, furniture, equipment

Nowadays, people spend >80% of their time indoors

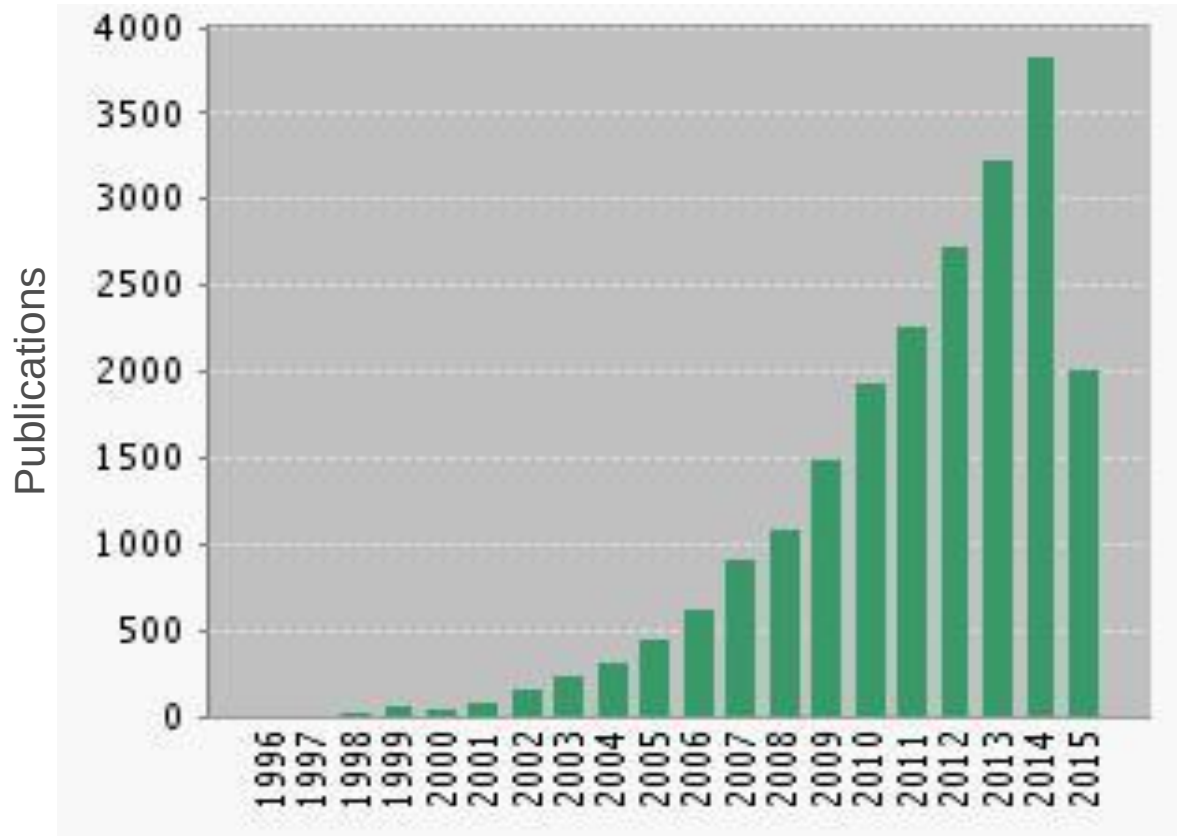
Pollution de l’air intérieur: Quelles solutions

- **Les systèmes air/air du type VMC (Ventilation mécanique forcée) ou CTA(Centrale de traitement d’air) double-flux.**
  - demandent **beaucoup de maintenance**, en particulier au **niveau des filtres et des gaines** qui, encrassées, sont un **milieu de culture bactériologique** privilégié entraînant une perte de débit et une mise en dépression du bâtiment et sont dangereux pour la santé.
  - certaines installations sont **très consommatrices d’énergie** et que les **débits d’air**, dans le cas d’une isolation acoustique insuffisante, **peuvent devenir gênants**.

Pollution de l'air intérieur: Quelles solutions

- **Les traitements plasma (ionisation)**
  - **Très consommatrices d'énergie**
  - **Formation de NOx par dégradation de N2** de l'air
  - **Formation O3**
  - Si **faible ddp** (pour diminuer Nox et O3): uniquement **agglomération** des particules et microorganismes mais **pas de mineralisation**
  - **Formation d'intermédiares réactionnels avant mineralisation**

Air pollution: Potentiality of photocatalysis

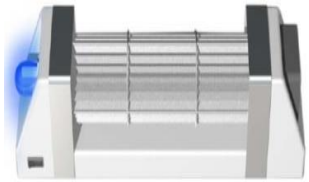


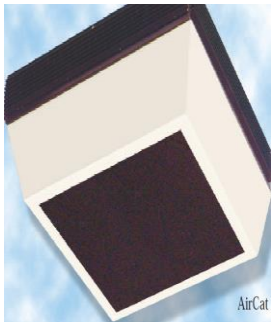
Photocatalytic air pollution: advantages

- **Process active at room temperature: no need of thermal energy**
- **no chemical additives**
- **Elimine pollutant chimique et biologique**
- Possibility of total mineralization of most pollutants (into CO_2, H_2O, Cl^-, NO_3^-, SO_4^{2-}, HPO_4^{2-} ....
- Possibility to use solar energy

Air pollution: Potentiality of photocatalysis

- Passive
- Active





Air pollution: Potentiality of photocatalysis

Is photocatalysis

able to solve

all the cases of pollutions?

Composés inorganiques?

$NH_3 \longrightarrow [\ N_2, N_2O, NO,..\ ] \longrightarrow NO_3^-$

$NO_x \longrightarrow [\ NO, NO_2\ ] \longrightarrow NO_3^-$

$SO_x \longrightarrow SO_4^{2-}$

Pas adapté pour éliminer CO

Ozone (O_3): $2O_3 \longrightarrow 3O_2$

$O_3 + e^- \longrightarrow O_3^{\circ -}$

$O_3 + O_2^{\circ -} \longrightarrow O_2 + O_3^{\circ -}$

$O_3^{\circ -} + H^+ \longrightarrow HO_3^\circ$

$HO_3^\circ \longrightarrow OH^\circ + O_2$

ELECTRONIC AFFINITY
O_3(2,1) > O_2 (0,44)

Hydrocarbures Volatils

Non halogenés

Pas adapté pour éliminer CH_4

Plus la chaine aliphatique, plus la vitesse de disparition est importante
Ex:
$v(C_3H_8) \sim$ 4-5 fois $v(C_2H_6)$
$v(C_3H_8) \sim 200$ fois $v(CH_4)$

M.Kaneko, I. Okura (Eds.);
Photocatalysis
ISSN 161867210

Alcènes plus rapidement éliminé que le alcanes
$v(C_3H_6) \sim 30$ fois $v(C_3H_8)$)

-formation d'intermédiares avant minéralisation (aldehyde, cétone, alcool,…)
-CO peut-être detecté

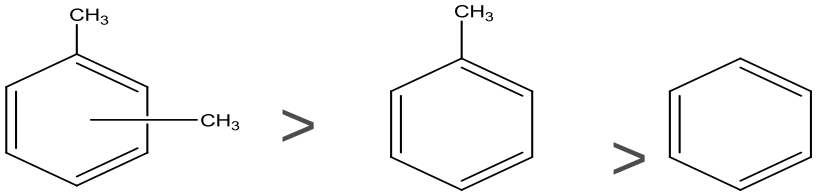
Halogenés

Pas adapté pour dégradation de CCl_4
$V(CH_2Cl_2) \sim 10\,000$ fois $v(CCl_4)$
HCl formé
Formation possible de phosgène

Composés halogénés
plus efficacement dégradés
Que composés non-halogénés

BTEX, COV oxygénés, microrganismes,…?

BTEX:



COV oxidés:

- Alco ol > Aldéhyde > cetone > alcène > alcane

-Composés oxydés > composés hydrocarbonés insaturés

- ASHRAE Manuscript :Evaluation of Photocatalysis for Gas-Phase Air Cleaning – Part 1: Process, Technical and Sizing Considerations; D.T. Tompkins, B.J. Lawnicki, Wa.A. Zeltner, M.A. Anderson,

-O. D'Hennezel; D.F. Ollis, Studies in Surface Science and Catalysis. 1996;101 A:435-442.

-Photocatalytic purification of volatile organic compounds in indoor air: A literature review; Atmospheric Environment 43 (2009) 2229–2246

Microorganisms

virus > cellules bactériennes> spores fongiques

Vera et al 2007: *Proceedings of the 35th Annual Biochemical Engineering Symposium, Rapid City, Dakota. 96-104.*
Huang, et al 2000, *Journal of Photochemistry and Photobiology A: Chemistry, 130(2), 163-170.*

Conclusions intermédiaires

- Dégradation de NH3, NOx et SOx mais formation de NO_3^- et SO_4^{2-}
- Pas adaptés pour CH4, CCL4, CO, CFC
- Adapté pour autres COV mais formation d'intermédiaires avant minéralisation

Intermédiaires formés à la surface du catalyseur donc rapidement dégradés (dépend propriétés d'adsorption, efficacité du catalyseur et conditions expérimentales)

Air pollution:

Is it possible to predict

the efficiency

of photocatalytic

materials or process?

Air pollution: Prediction of efficiency of materials or systems?

- many publications (2014 > 4000 publications) but:
  - The information are not very clear
  - Different conditions of tests whereas many parameters plays an important role
- Some tests are not relevant for the application
  Example material used with indoor light, but tested with UV light

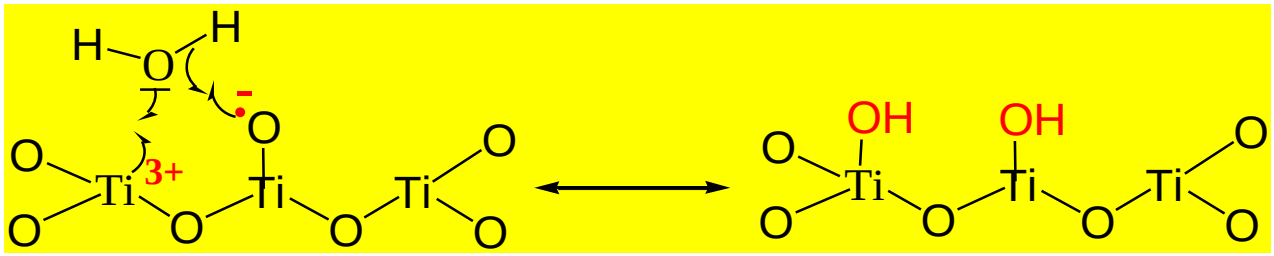
Necessity to develop standardized

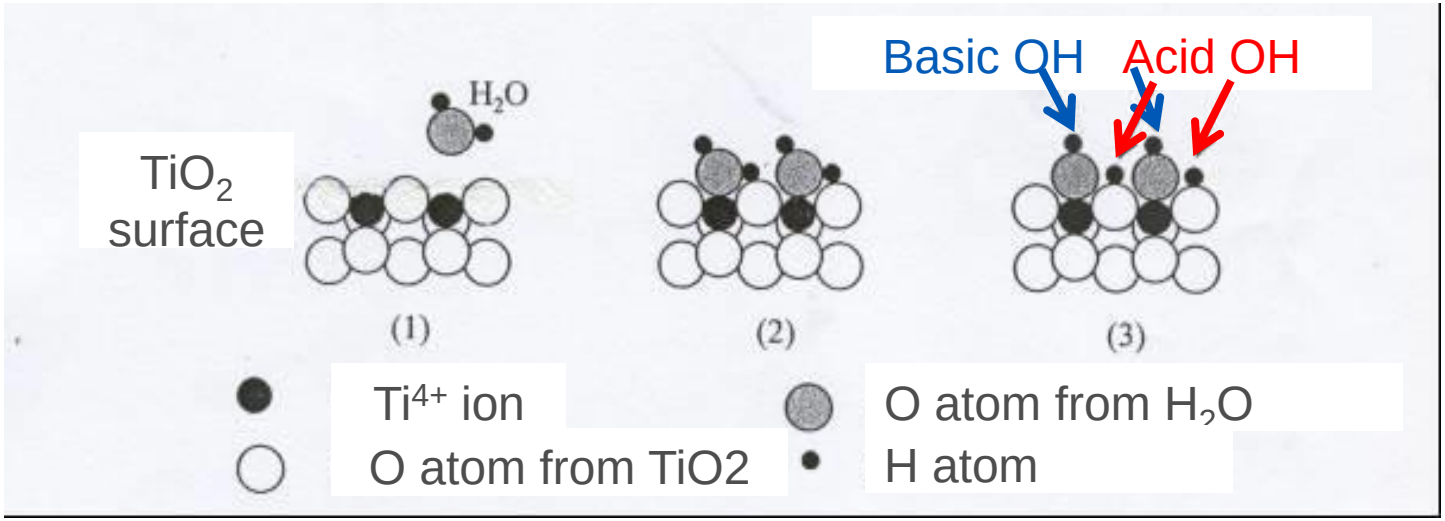
Paramètres à prendre en compte pour l'établissement de standard

- Humidité
- concentration
- simple or mélange de polluants
- Irradiance

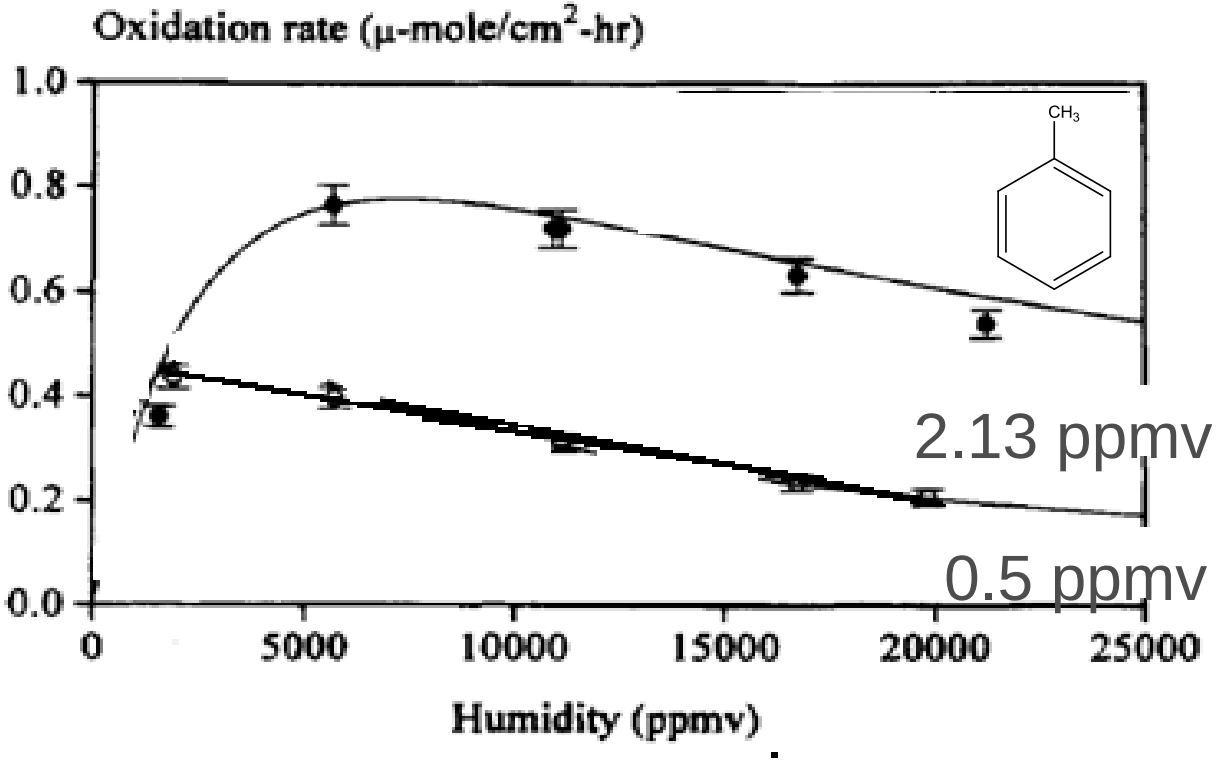
Humidité

Modification des propriétés de surface





Humidité



Dépend :

- % humidité
-Nature et concentration de polluants

A faible %Humidité : $H_20 \longrightarrow OH° + H^+$

Obee et al., VOL. ***29. NO. 5,1995 /ENVIRONMENTAL SCIENCE &TECHNOLOGY 1 1225***

Humidité

❑ By-products

Gas phase

0% RH

Propene
Oxalic acid
Acetone
Benzene
Isopropyl formate
Toluene

TiO_2

Propene
Acetone
Benzene
Methyl glycoxal
isopropyl methyl ketone
Pentanal

Acid acetic
Toluene
Ethyl buthyl cetone
Butyl acetone
Heptanal

Benzaldehyde
methyl isohexyl ketone
Octanal
Hexanol-2-ethyl
Acethyl benzene
Nonanal

60% RH

Toluene
2 Hexanone
Ethyl benzene
3-Heptanone
Heptanal
Octanal
Hexanol-2-ethyl
Acethyl benzene
Nonanal

Propene
Oxalic acid
Acetone
2-Propanol
Butanal
Isobutyl alcohol
1-Butanol
Ethyl acetone
2-Propanone 1 methoxy

Pentanal
Acid acetic
Formic acid butylester
Isopropyl acetate
Hexanal
2-Hexanone
3 hydroxy 3,5 dimethyl
Isopropylformate
Propanal-2-methyl
Cyclohexanone
2-Heptanone-6-methyl
Benzaldehyde

TiO_2

Acetone
Benzene
Toluene
Hexanol-2-ethyl
Nonanal

D. Vildozo, Applied Catalysis B: Environmental 107(2011)347-354

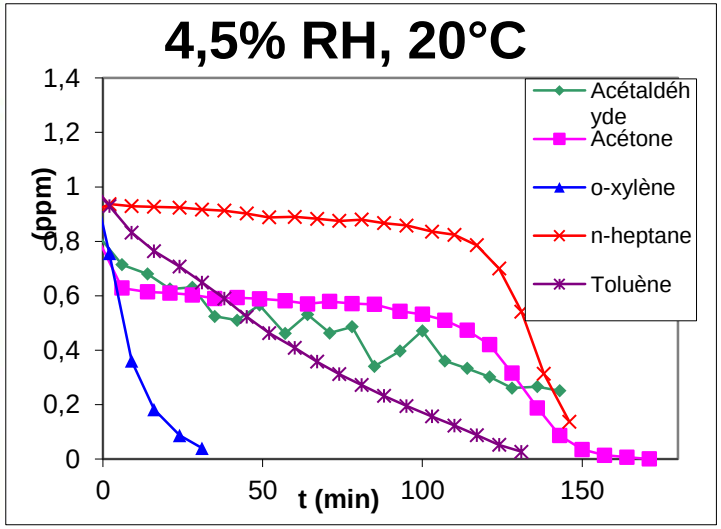
Humidité

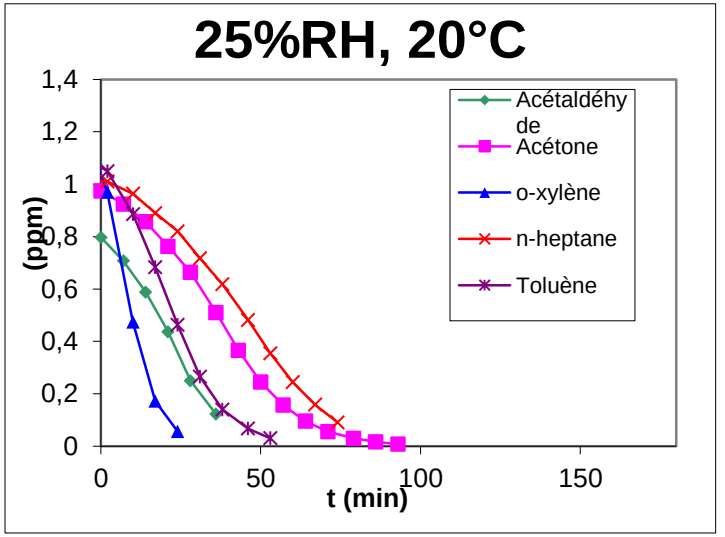
Quelle humidité
dans conditions réelles?

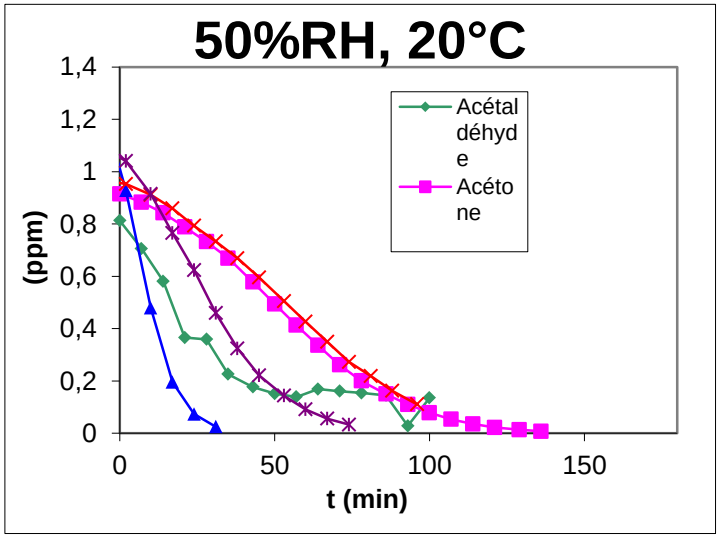
Varie suivant

- l’endroit (pays, pièce,..)
- le jour,

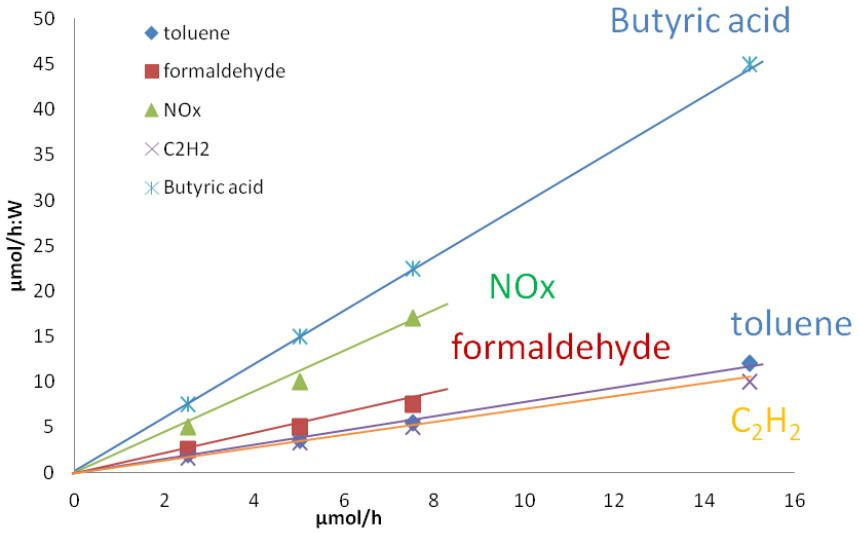
Impact de l'humidité (chambre de 1 m3)







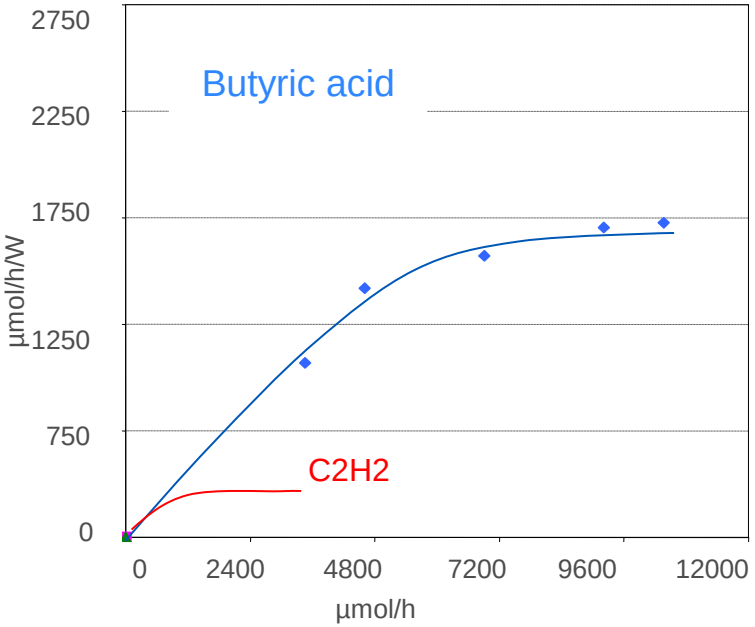
Influence de la concentration (flux molaire)



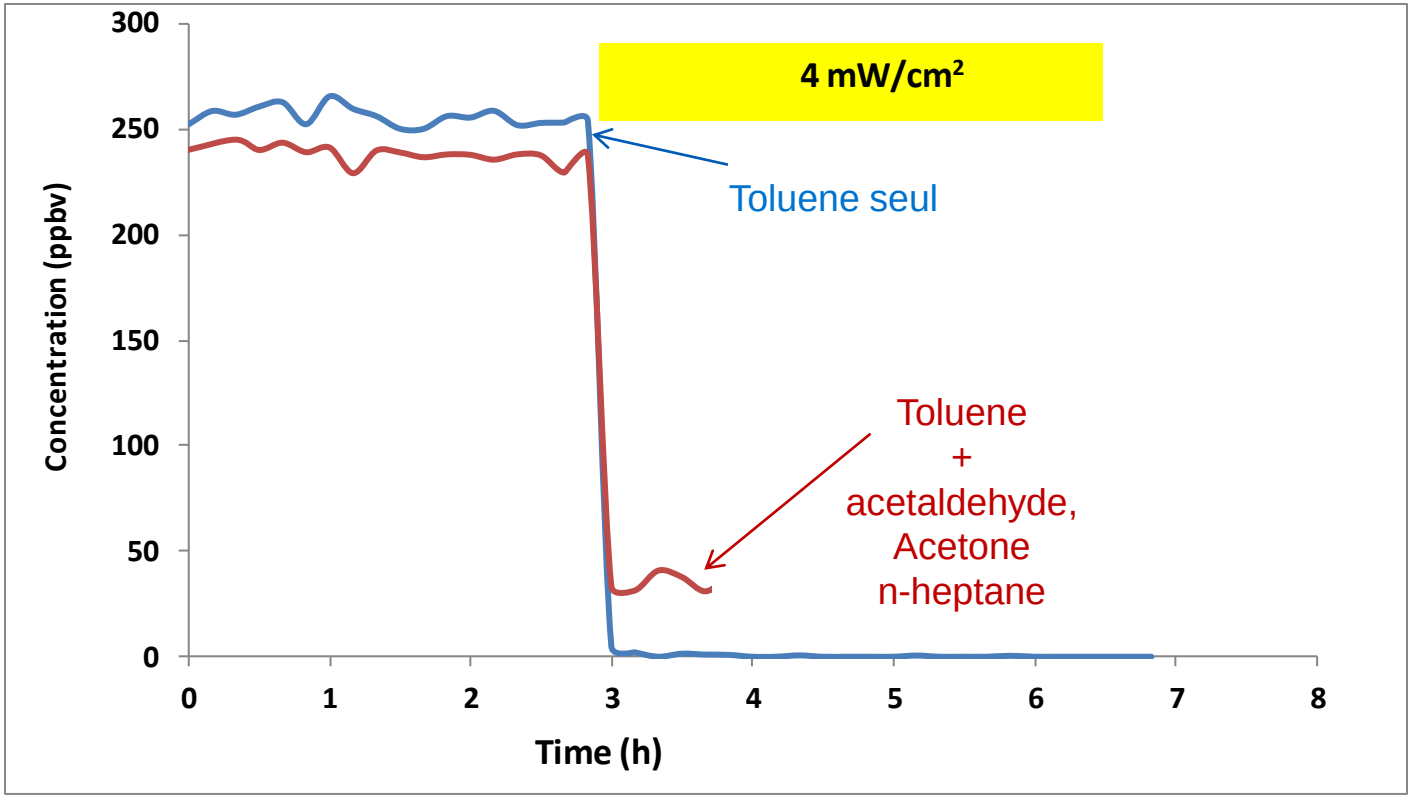
100ppb; 500m³/h

10W/m²

si 1000 cm²
de photocatalyseur
3h à 8h nécessaire



Polluant seul ou mélange de polluants



Impact concentration et déb sur CADR (chambre de 1 m3)

Hypothèse: réaction d'ordre 1

Ln(C/C0)=-(CADR/V)*t

CADR	Acétaldéhyde	Acétone	n-heptane	Toluène	Σ COV
0,5m/s	5,28	1,28	1,24	3,33	1,85
0,2m/s	2,61	0,99	0,94	2,55	1,35

CADR varie avec le débit du dispositif de traitement

Mélange de COV diverses concentrations

en présence HCHO (15 à 60 ppbv)

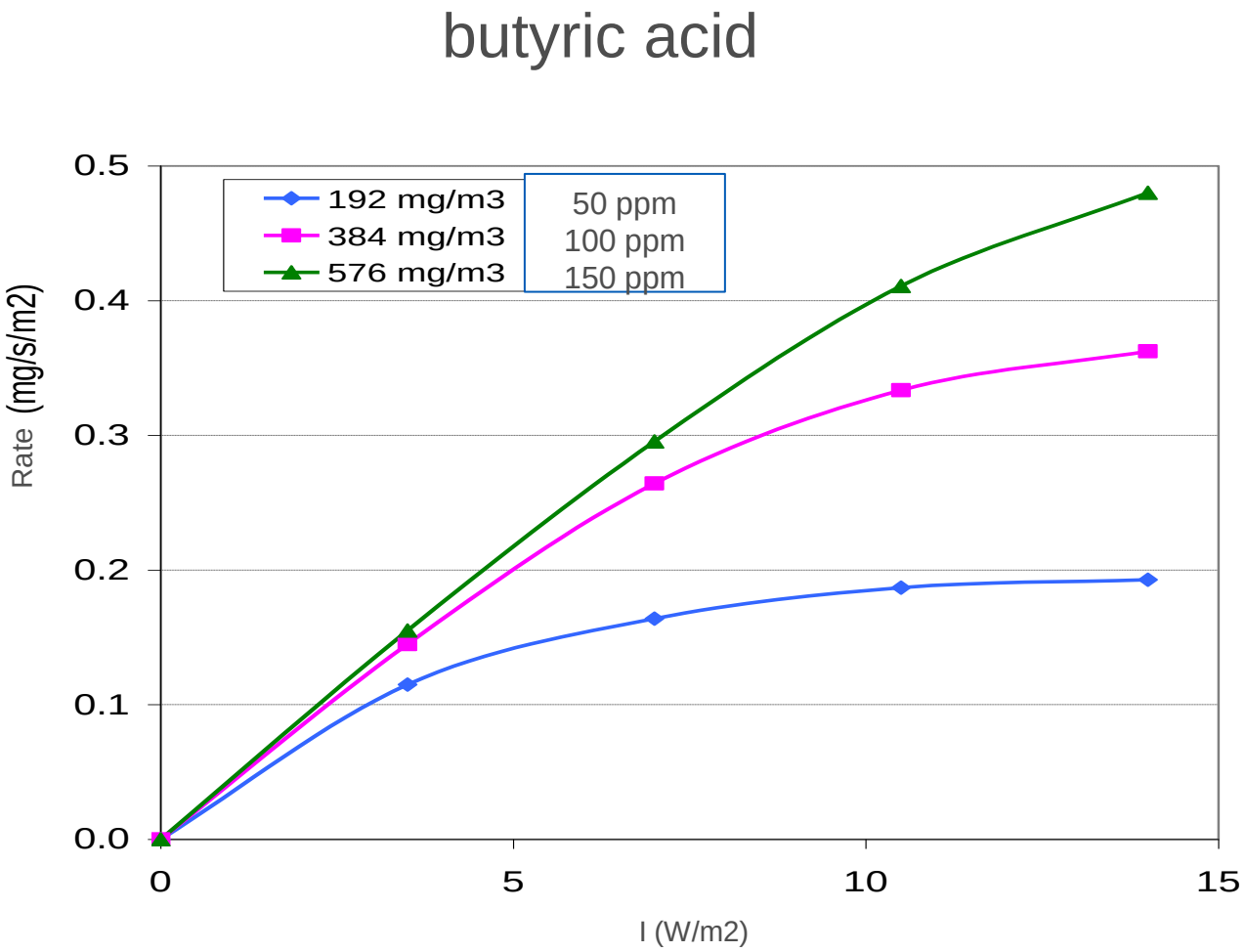
cc (ppbv)	cc formaldéhyde	formaldéhyde	Acétaldéhyde	Acétone	Toluène	n-Heptane	o-Xylène	somme
1100-1400	60	2,6	5,9	2,3	3,2	0,8	8,3	3,7
250	45	7,3	12,8	8,8	3,2	3,4	14,4	8,4
50	45	12,0	15,6	11,1	11,9	7,5	16,2	11,3
35 (moyenne de trois essais)	15-19-35	13,0	17,0	12,7	13,9	9,9	17,8	13,3

CADR varie avec la concentration de polluant

CADR formaldehyde depend [autres COV]

Benoit Kartheuser (CERTECH)

irradiance



Dépend $[conc]_i$:

faible [conc]i ➡ Faible irradiance suffisante

Visible light? What catalyst? Efficiency?

Many publications on active new visible light photocatalysts

- Doping N, Au, C, rare-earth
- New materials: BiOX, …

HOWEVER

- Often tested using dyes as pollutant
- No comparison with TiO2 (ex: P25 (anatase and rutile)
- Irradiance in visible light range + (UV)
- Only few catalyst have efficiency (small) in visible light and most of them are less efficient under UV-A (present in solar light)

Visible light? What type of test?

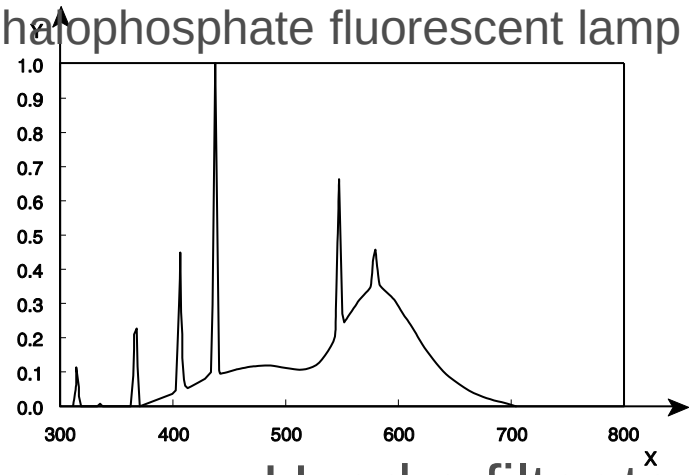
DIRECTLY SOLAR LIGHT?

- The best but difficult to have same irradiance (use energy)
- Always compare with TiO2 P25

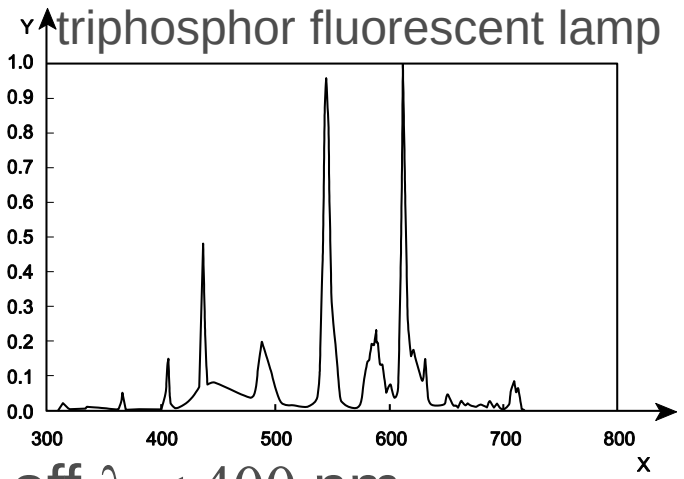
Visible light? What type of test?

ARTIFICIAL LIGHT: MANY POSSIBILITIES

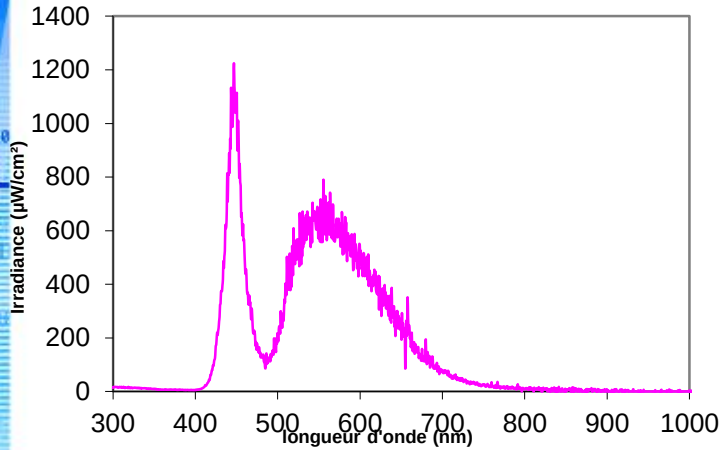
halophosphate fluorescent lamp

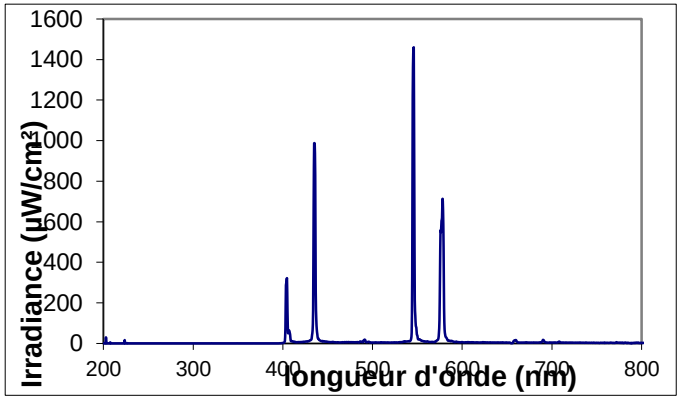


triphosphor fluorescent lamp



Used a filter to cut off $\lambda < 400$ nm





Always compared to the efficiency of TiO2 P25

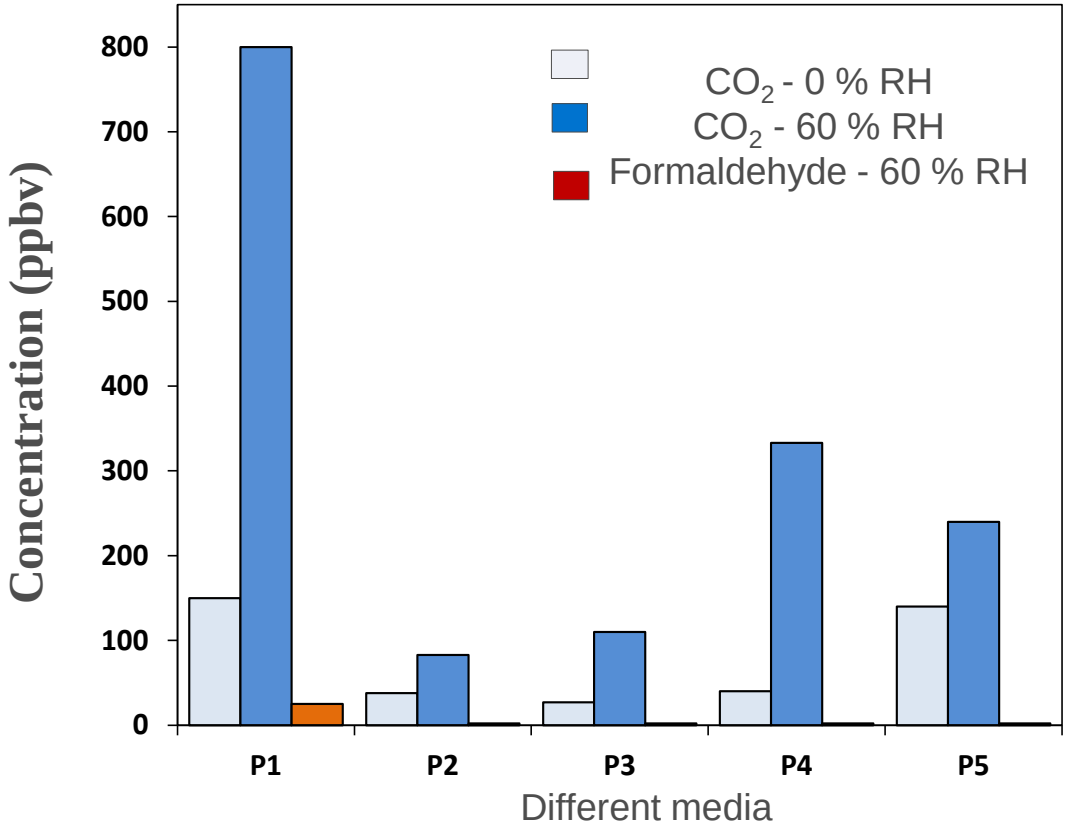
Air pollution:

Other important factor for standardisation

- Stability of photocatalytic materials
- Measure of irradiance
- Ageing

Stability of photocatalytic materials

UV-pretreatment

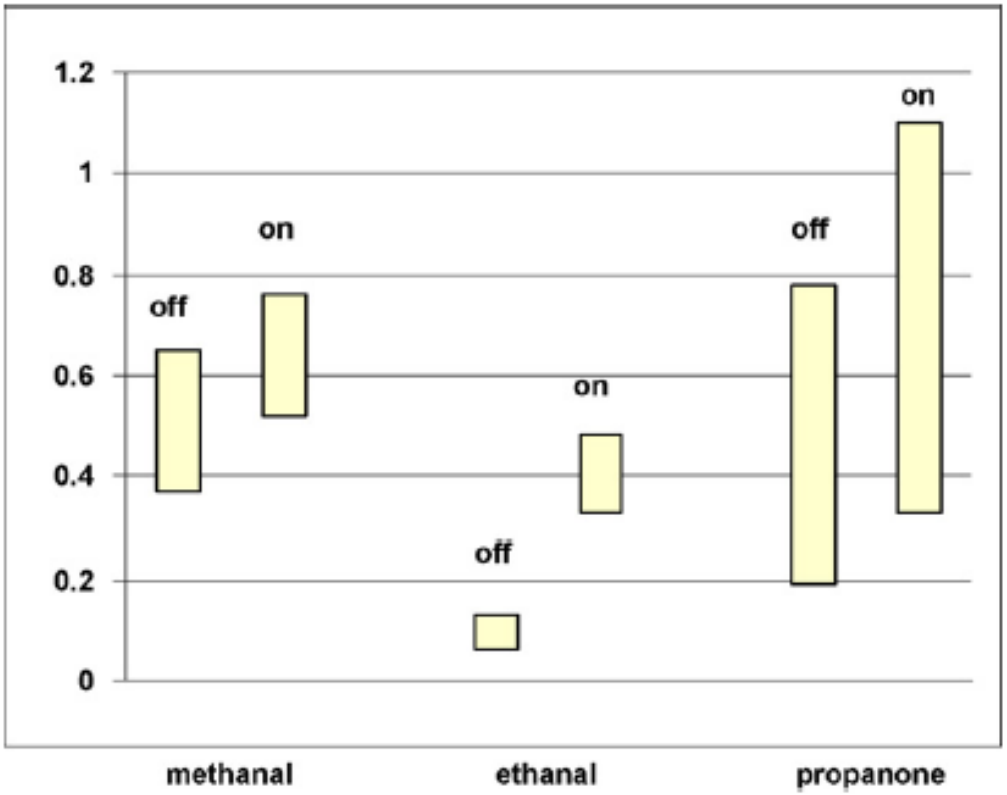


Degradation of media

-Stability has to be check
-preatreatment of media before photocatalytic test

Generation of formaldehyde from media

Stability of photocatalytic system



Generation of formaldehyde, acetaldehyde, propanone

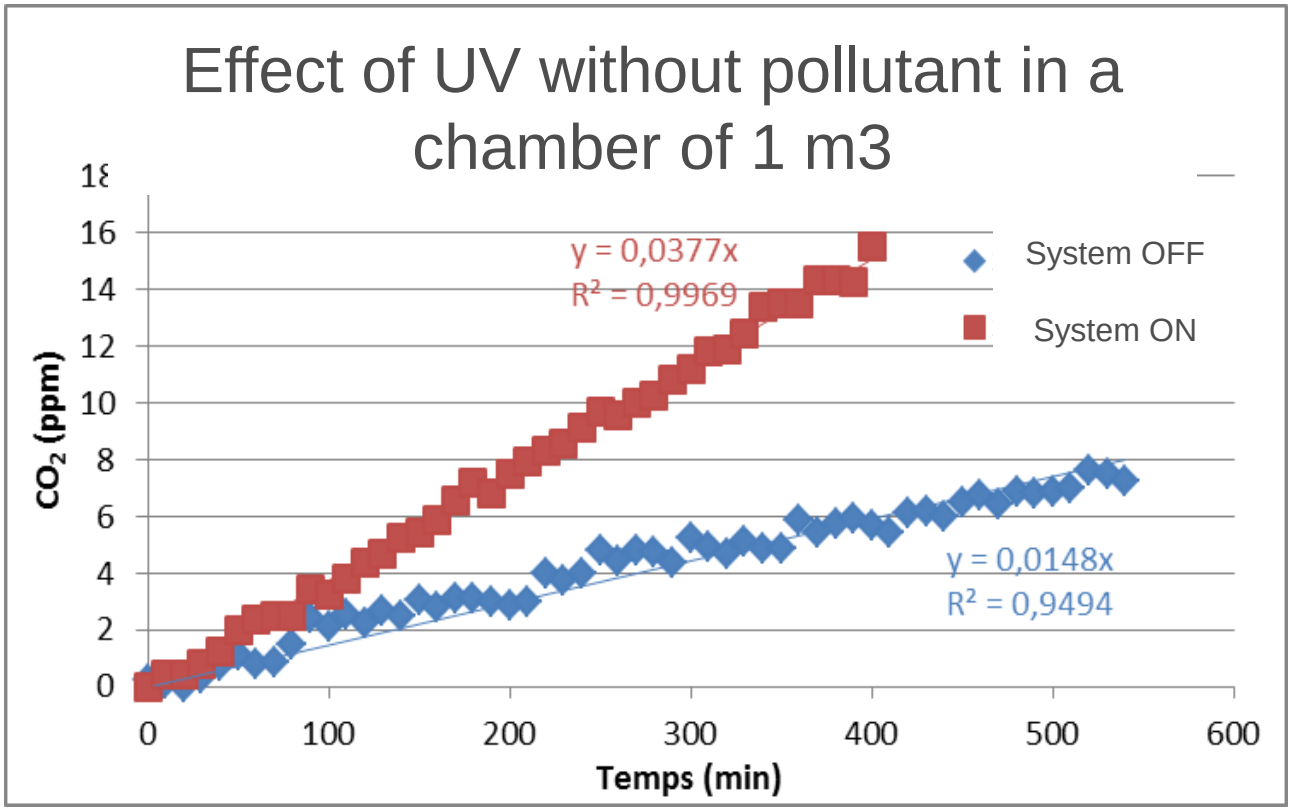
Results obtained in an ordinary room (83 m3) with photocatalytic system

P. Pichat / Applied Catalysis B: Environmental 99 (2010) 428–434

-Stability of media, of system under UV or degradation of pollutant present in the room???

- Stability of system has to be check before using

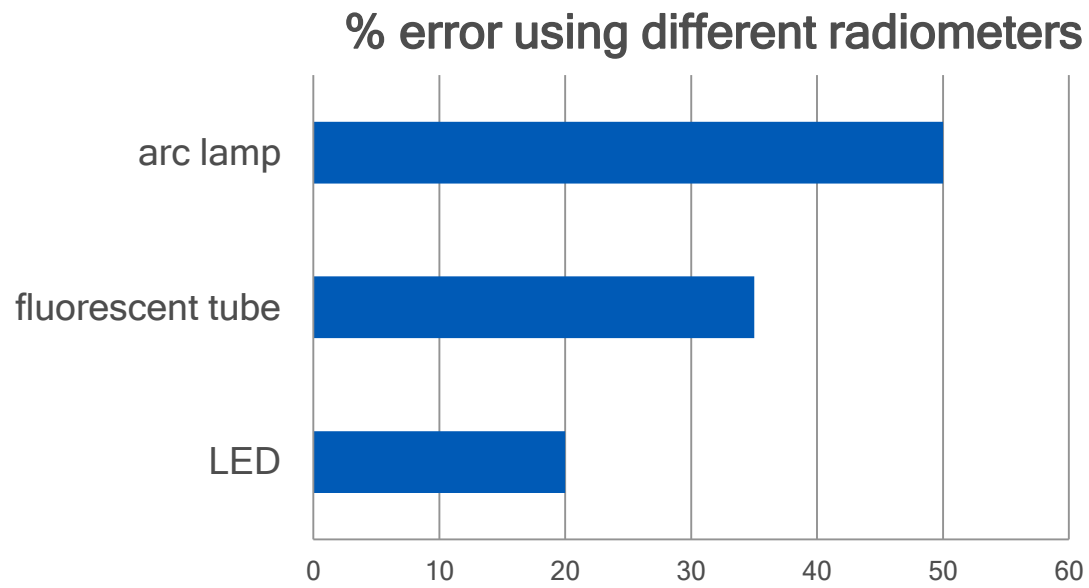
Stability of photocatalytic system



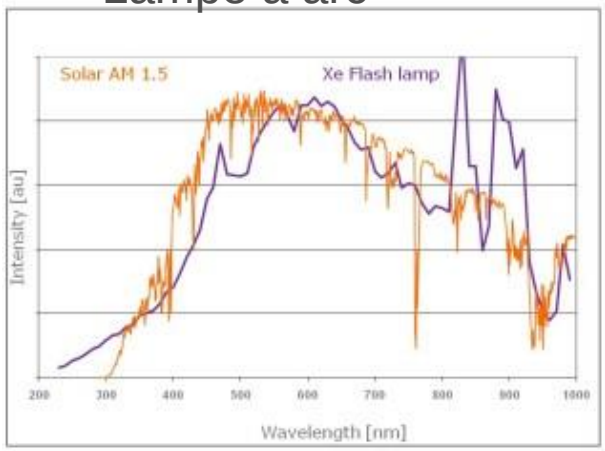
-Non-Stability of media, or system under UV

- Stability of system has to be check before using

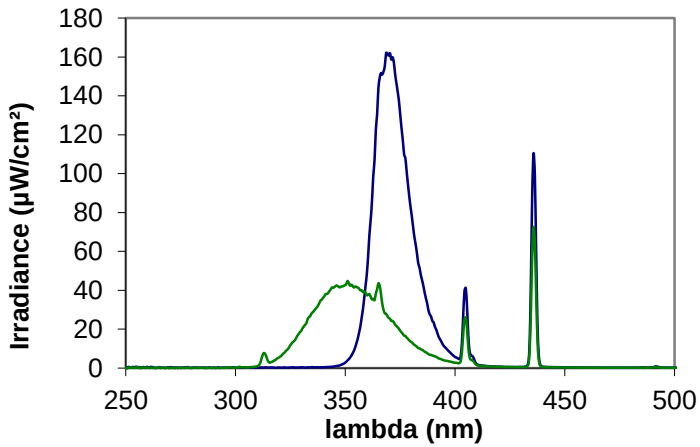
Measure of irradiance



Lampe à arc



fluorescent tube



How to test the efficiency of photocatalytic materials and devices?

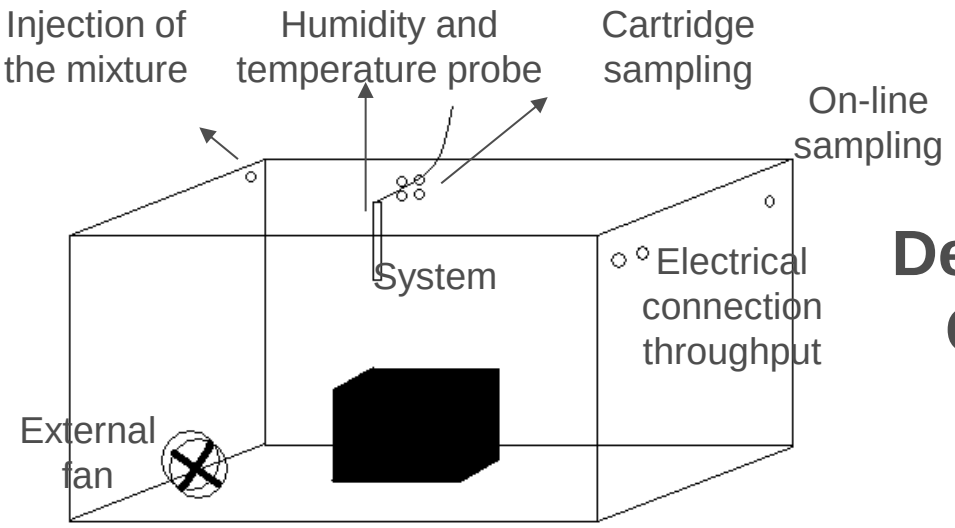
- We have to test the materials and apparatus **in conditions close to reality**
  - humidity
  - concentration
  - irradiance and nature of UV

    (problem to measure irradiance)
  - mixture of compounds
  - *reactor*

-We have to check there are not dangerous
  - -Intermediate / mineralisation
  - -Stability
  - ageing

Standardisation in Europe

WI 386002: Efficiency of photocatalytic devices



Developed by CERTECH

- To test only prototype or commercial photocatalytic air cleaner systems with a maximum flow rate of 1,000 m³/h used for the indoor air remediation.

-To be applied to the treatment of atmospheres that are representative of the air inside buildings and workplaces.

Standardisation in Europe

WI 386002: Efficiency of photocatalytic devices

Conditions

- Pollutants : acetone, acetaldehyde, n-heptane, toluene, formaldehyde

- Indoor air at two concentrations :
  1 : 50 ppbv/pollutants :(check for by-products)
  2 : 1000 ppbv/pollutant : (check for CO_2)

- Initial humidity and T°C: 50 ± 5 % RH; T=22 ± 2 °C

- Ratio Vsystem/Vchamber <= 0.1

Standardisation in Europe

prEN 16846-1:

Efficiency of photocatalytic air cleaners

Efficiency of photocatalytic devices

Has to be demonstrated by verifying the mineralisation of model VOCs to CO_2.

Expression of RESULTS

- Disappearance of VOC: CADR

Comparison graph between the CO_2 produced and the CO_2 expected from the VOC degradation.

- % mineralisation at the end of the test.

Conclusion

Many parameters influence the performance of photocatalytic materials or systems

Establishment of performance is very complex

Necessary to evaluate their performance using conditions closed to real environment

(HR: 40-50%; low concentration; multiple pollutants; irradiance: 10 W/m^2 (passive materials),…

Performance have to be evaluated considering **mineralisation** and **intermediate products** and **not only disappearance** of initial pollutants

Necessity to develop stable materials and system under UV-irradiation

Conclusions

Photocatalyse adaptée pour traiter l'air intérieur en restant concient des limitations

Important

-Poursuivre les études fondamentales pour essayer de prédire leur efficacité

-Développer de meilleurs photocatalyseurs et dispositifs (association de différentes technologies) permettant de limiter les rejets et d'améliorer l'efficacité en lumière visible.