Evaluation of the efficiency and harmfulness of air-purifying photocatalytic commercial devices and materials: VOCs degradation and nanoparticles release

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Normacat project (2010-2013) and SafePHOTOCAT project (2013-2015)

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Normacat project collaborators :

- *TERA ENVIRONNEMENT, project coordinator*
- *Academic laboratories : IRCELYON, IPREM*
- *Technical research center : CERTECH*
- *AFNOR*
- *Private companies : AHLSTROM, CIAT, SAINT-GOBAIN QUARTZ, PHOTOCLEAN QUARTZ, TITANIUM INNOVATIONS*

Public financial support :

SafePHOTOCAT project collaborators :

- *IPREM, project coordinator*
- *Academic laboratories : IPREM, C2MA ARMINES*
- *Technical research center : NOBATEK*

Public financial support :

Context of the study

- A lot of air-purifying devices with photocatalytic functions are now available in the French/European Market
- Are these devices really efficient and safe ?

- How are these systems tested ?
- Information are not very clear in the advertisements
- In some cases, reference to tests carried out in various laboratories, but not **standardized**

Need for normalized tests for photocatalytic air purifiers

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About the standardization : French standard XP-B44-013 and XP-B44-200

- **Standard XP-B44-013** : This protocol applies solely **to photocatalytic systems alone or to combined systems that include a photocatalytic function.**

Measurement of photocatalytic device efficiency used for the elimination of a VOCs mixture and odour in indoor air : Test in air tight chamber in re-circulation mode. The photocatalytic function is demonstrated by verifying the **mineralisation of model VOCs to CO_2**.

→ In project : extension of this standard towards a European Standard

- **Standard XP-B44-200** : This protocol applies **to all kind of autonomous air purifier**.

Mesurement of device efficiency with various contaminants :

- Gas : mixture of 4 VOCs → only contaminants in relation with our project. Continuous contaminants supply. Test in chamber in one-pass mode
- Microorganisms
- Allergens
- Inert particles

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Principle of the standard closed chamber test (AFNOR XP B44-013 – French standard)

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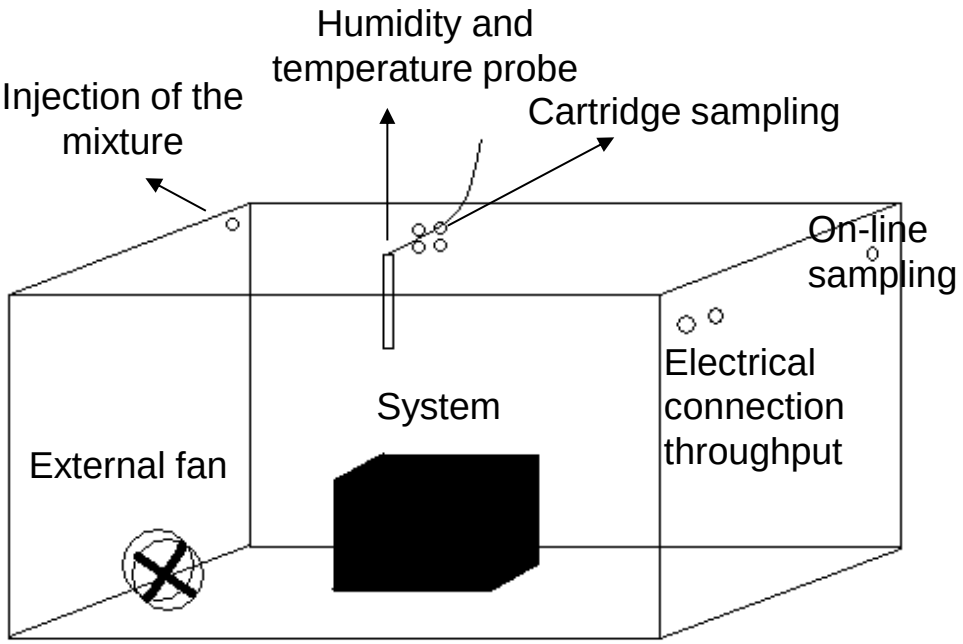
Conditions

- Pollutants : acetaldehyde, acetone, n-heptane, toluene (formaldehyde in project for CEN)
- Indoor air at two concentrations
  1 : 250 ppbv/pollutants
  (check for by-products: O_3, HCHO, other VOCs)
  (50 ppbv in project for CEN)
  2 : 1000 ppbv/pollutant
  (check for CO_2)
- Industrial issue : concentration depends on the application.
- Starting humidity and temperature : 50 ± 5 % RH and 22 ± 2 ° C (may be varied)
- Total sampling volume : < 5% of the total chamber volume (50 L/m³)



Closed chamber : **V >1 m³**
System : flow max **1000 m³/h**
Vsystem/Vchamber ≤ 0.25
(< 0.1 in project for CEN)

Principle of the standard chamber test (AFNOR XP B44-200 – French standard)

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Conditions

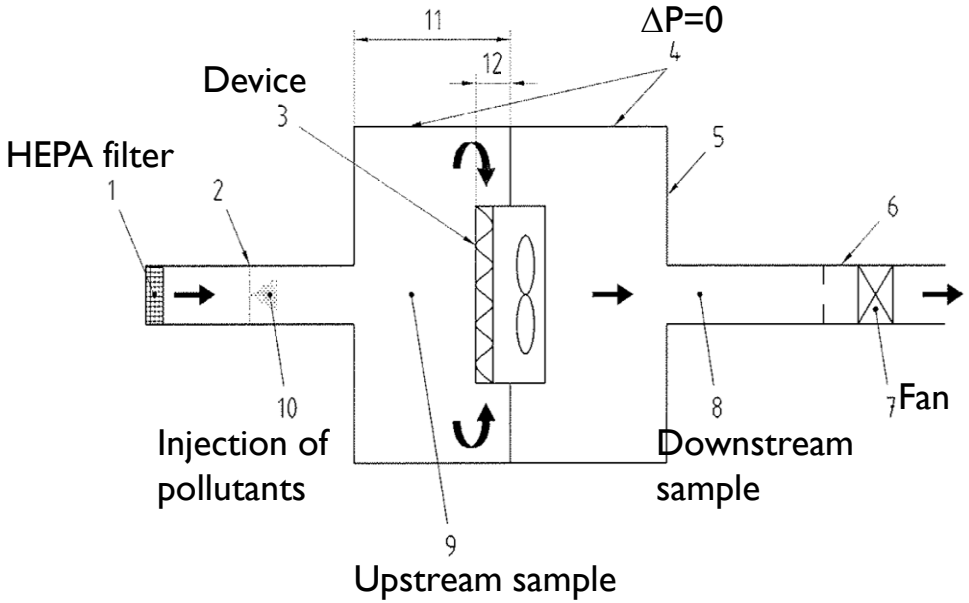
- Pollutants : acetaldehyde, acetone, n-heptane, toluene

  (generated continuously)

- Concentrations : 250 to 500 ppbv/pollutants
  (check for by-products : O_3, HCHO, CO, NO, NO_2)

- Humidity and temperature :
  50 ± 5 % RH and
  22 ± 2 ° C

- Test air filtration : HEPA filter
  (NF EN 1822-1 and CA filter)



Chamber test IPREM-CERTECH

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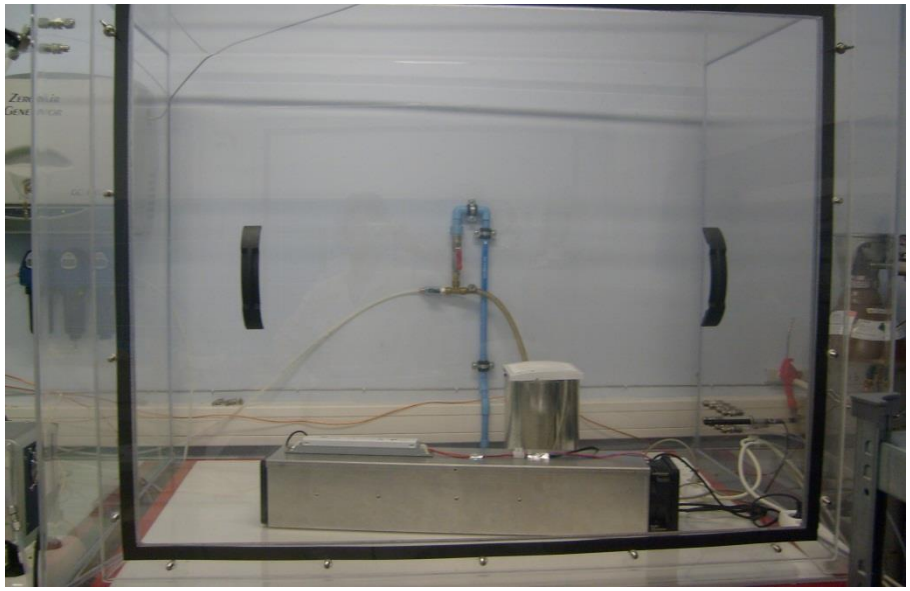
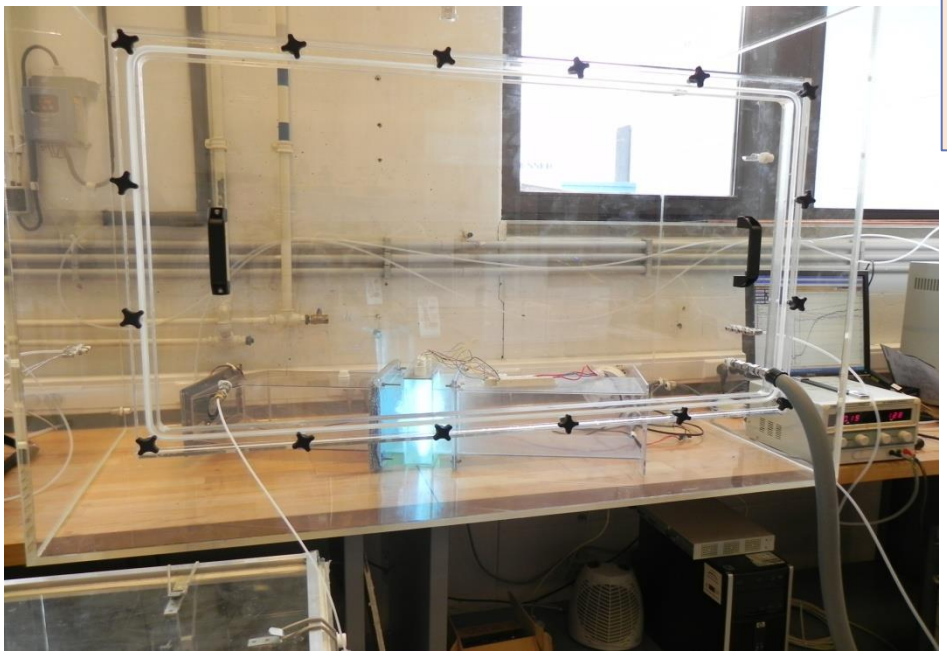


IPREM : 1.17 m^3

Chambers validation :

- No VOCs release : <5 ppbv on 24 h
- Good airtightness : <10% COV leak on 24 h



CERTECH : 1.1 m^3

Analytical equipment used

PARAMETERS	CERTECH	IPREM
Primary VOC (acetaldehyde. acetone. n-heptane. toluene)	**GC-PID (LD < 1 ppb) or IMR-MS /on line** (LD = 1ppb)	**GC-PID /on line** (LD = 2 to 17ppbv)
CO-CO_2 :VOC mineralisation	**CO : photoacoustic** (LD=0,5 ppm) **CO_2 : µGC-TCD** (LD=2 ppmv) **/ on line**	**GC-methanizer-FID / on line)** (LD=1ppmv)
Secondary species	**IMR-MS / on line** (LD = 1 ppb) **HPLC-UV** (LD CH2O = 3 ppbv for 5 L sampling) **& ATD-GC-MS** (LD = 1ppbv) **adsorption on cartridges**	**HPLC-UV** (LD CH2O=4ppbv) **& SPME-GC-FID** (LD CH2O=5ppbv) **ATD-GC-MS** (LD=1ppbv) **adsorption on cartridges**

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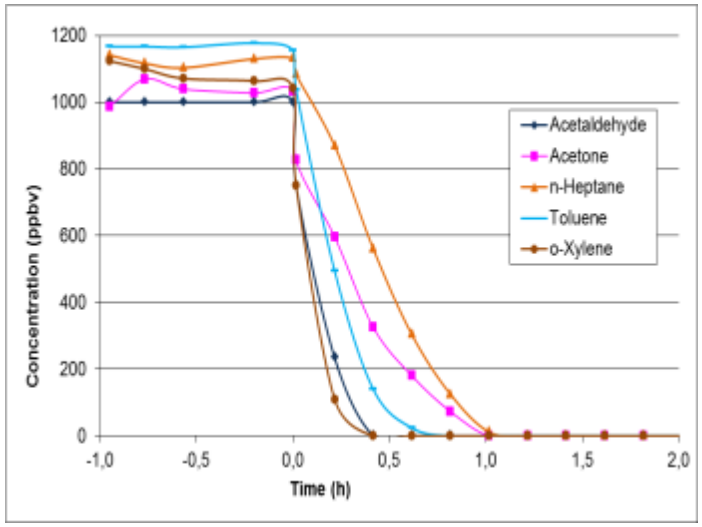
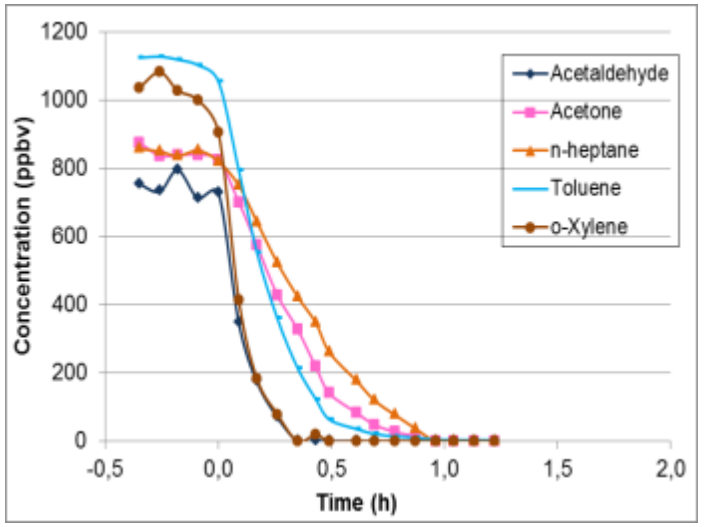
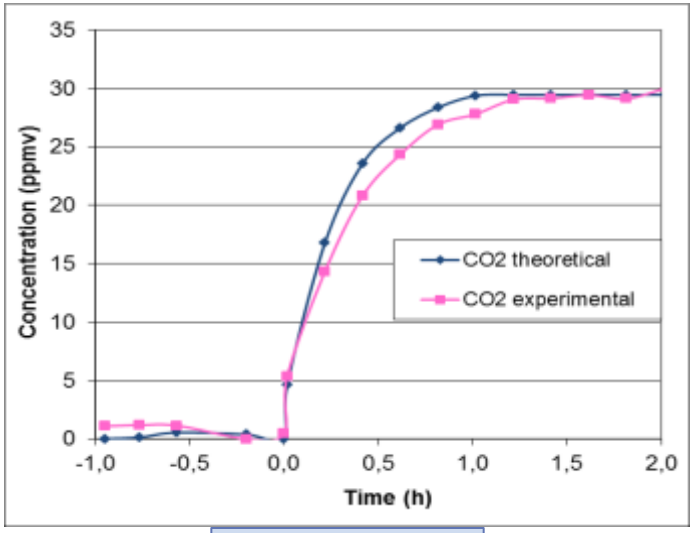
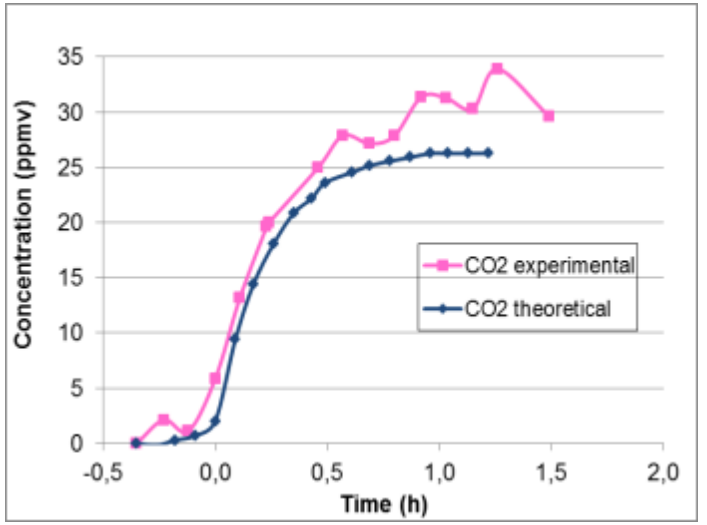
Example of Inter-laboratory study (1)

Similar experimental conditions : same device, each VOC at about 1ppmv, relative humidity 45-55%, temperature 22-28C (standard XP B44-013).









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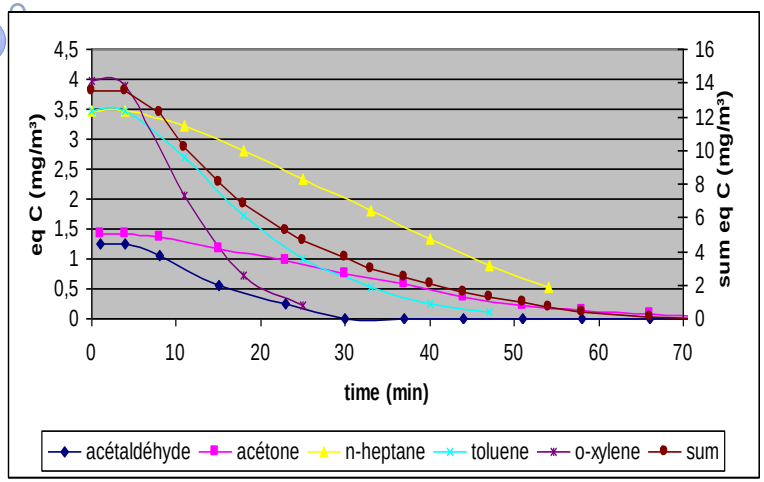
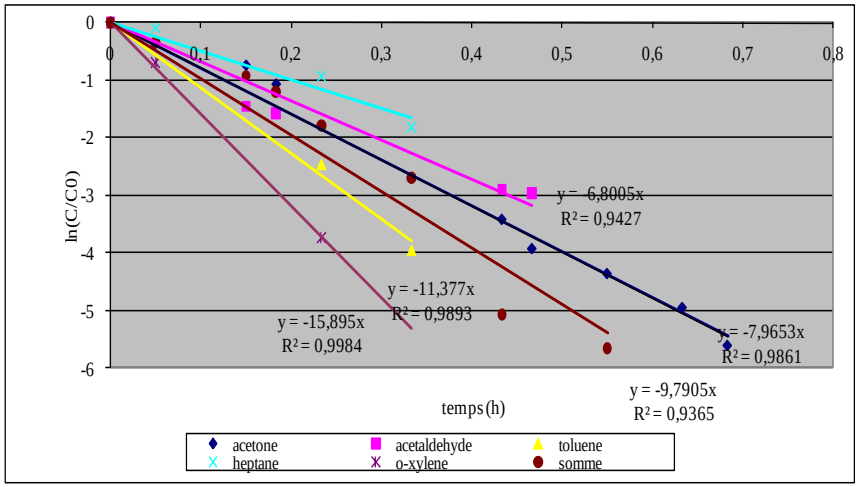
Example of Inter-laboratory study (2)

Results of Clean Air Delivery Rate : CADR





$Ln(C/C0)=-(k_n+CADR/V)*t$ with $k_n = 0$ (no leak)

→ $Ln(C/C0)=f(t)$ → slope= $-CADR/V$

1 ppmv	Acetaldehyde	Acetone	n-heptane	Toluene	o-xylene	∑ VOC
CERTECH (22° C)	10.61±0.21	3.64±0.08	2.65±0.16	5.94±0.24	11.18±0.22	4.51±0.09
IPREM (26 ±2° C)	8.03±1.61	3.18±0.06	2.35±0.07	5.75±0.11	10.30±1.44	4.35±0.09

Kartheuser B., Costarramone N., Pigot T., Lacombe S., *Environ. Sci. Pollut. Res.*, 19:3763-3771(2012)

Standardized tests (AFNOR XP B44-013) with various commercial devices

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8 commercial photocatalytic devices tested + prototype D0

Device	Irradiation source	Photocatalysis only	Control test without VOC		Photocatalytic test with 4 VOC (24 hours maximum)		
			VOC release	CO_2 produced	VOC removal	Mineralization	End by-product
D0	**UVC**	**Yes**	**No**	**No**	**> 99%**	**complete**	**No**
D1	**UVA**	**Yes**	**No**	**Yes**	**> 99%**	**complete**	**No**
D2	**UVA**	**Yes**	**No**	**Yes**	**> 99%**	**complete**	**No**
D3	**UVA**	**Yes**	**No**	**Yes**	**> 99%**	**complete**	**No**
D4	**UVA**	**Yes**	**No**	**Yes**	**> 99%**	**complete**	**No**
D5	**UVC**	**No** (ionization, filtration/activated carbon)	**Yes**	**No**	**0 to 20%**	**No**	**formaldehyde**
D6	**UVC**	**No** (filtration/ activated carbon)	**No**	**Yes**	**> 99%**	not determined	**No**
D7	**UV LED 365 nm**	**No** (filtration/ activated carbon)	**Yes**	**No**	**10 to 30%**	**incomplete**	**formaldehyde**
D8	**unspecified**	**No** (ionization, filtration)	**Yes**	**No**	**48 to 99%**	**No**	**formaldehyde**

Total degradation of 4 VOC – Complete mineralisation – No VOC release for 5 (or 6) devices

Tests according to the AFNOR XP-B44-200 standard

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3 commercial photocatalytic devices tested

Device	Control test without VOC		Test with 4 VOCs added continuously (24 hours maximum)		
	NO_x produced	O_3 generated	VOC removal	Mineralization	By-products
D4	YES	NO	> 99%	Complete	NOx
D8	YES	NO	residual acetone and toluene (≈20 ppb)	No	Formaldehyde NOx
D6	NO	NO	> 99%	Complete	None

2 devices/3 seem efficient for mineralization
Only 1 device release neither VOC nor NO_x (D6)

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Standardized tests (AFNOR XP B44-013) : formaldehyde added in 4 VOCs mixture

certech

4 commercial photocatalytic devices tested

Device	Irradiation source	Photocatalysis only	VOC removal	Formaldehyde removal	By-products	Conclusion
A	UVC	YES	OK	OK	None	OK
B	UVC	YES	OK	OK	None	OK
C	UVC	+ Activated Carbon	OK	OK	None	OK
D	UVA	YES	OK	NO	Formaldehyde /VOC	NO

✓ Total degradation of 4 VOCs for all devices
✓ Formaldehyde and VOC release by device D

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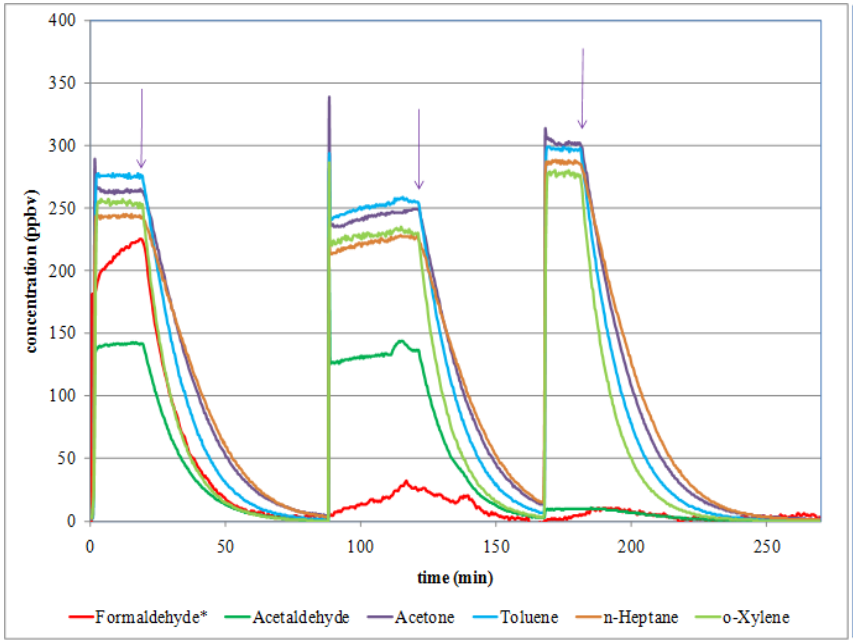
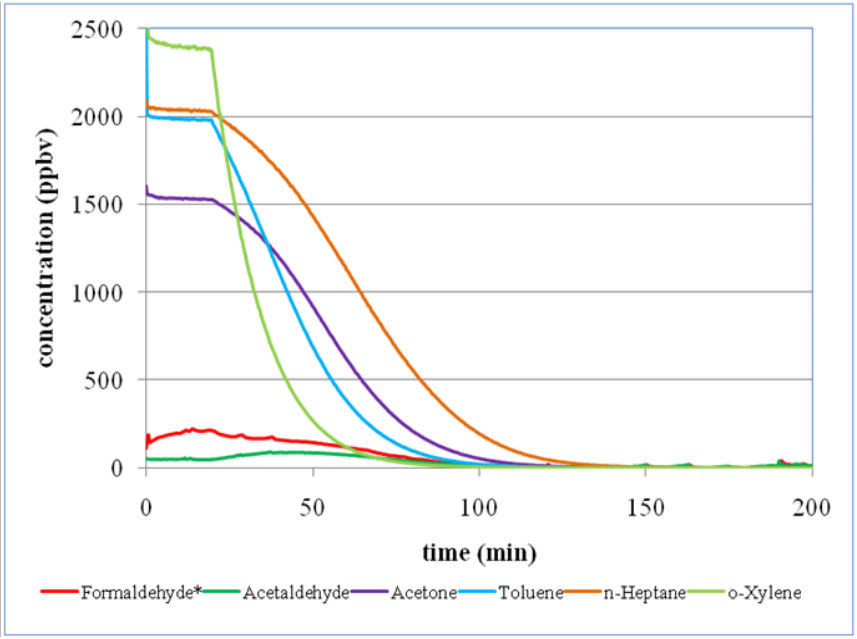
Tests with various photocatalytic devices : formaldehyde added in 4 VOCs mixture

certech : tests of prototype and commercial photocatalytic devices (A/B/C/D)

Device A : VOC evolution as function of different initial formaldehyde concentration.





No formaldehyde increase is detected on line with this device even at high VOC concentration

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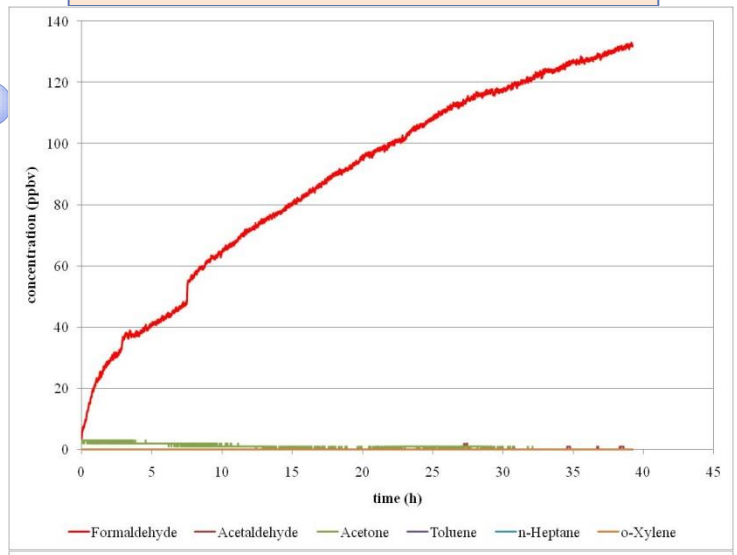
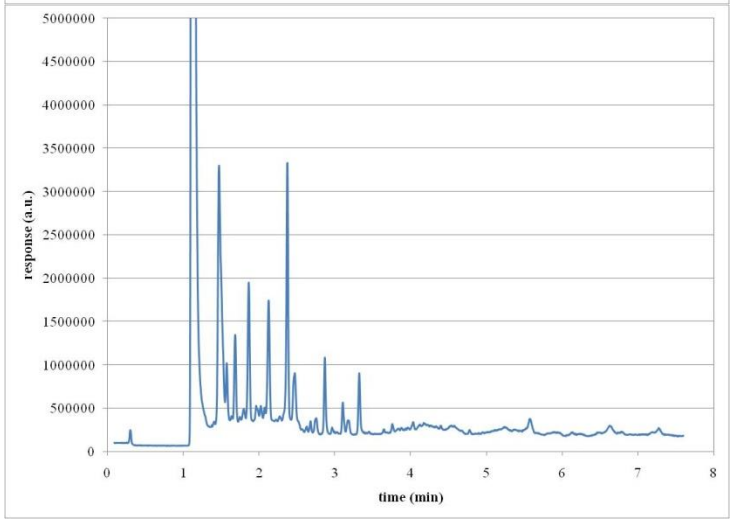
Example of photocatalytic device D

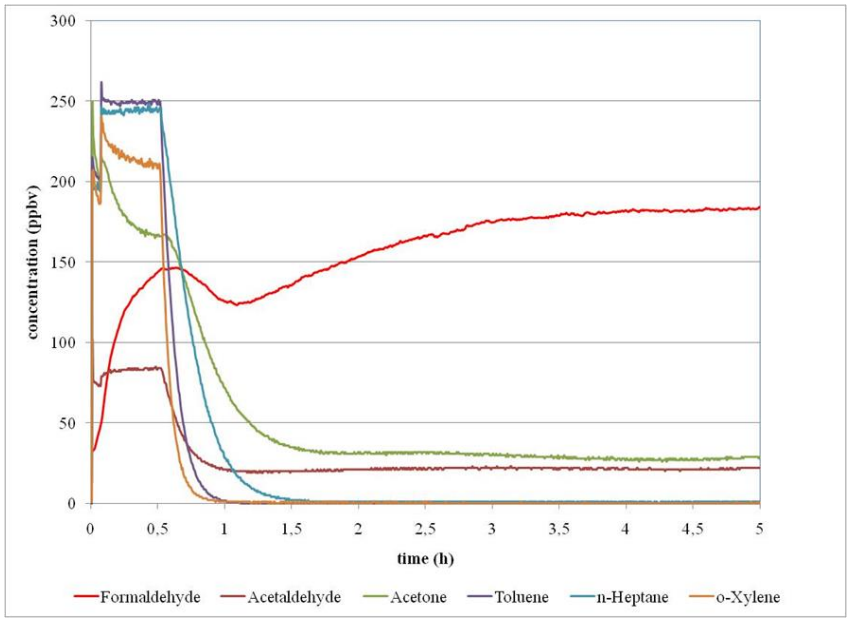
without VOC added





Formaldehyde and unknown VOCs release by the device

with VOC mixture added



No formaldehyde decrease when the device is ON

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First results about system aging

Aging of devices: continuously lighted ON in the laboratory for several days

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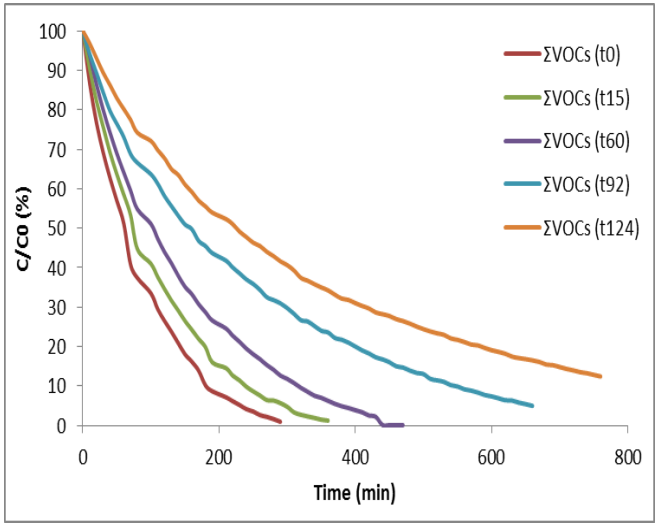
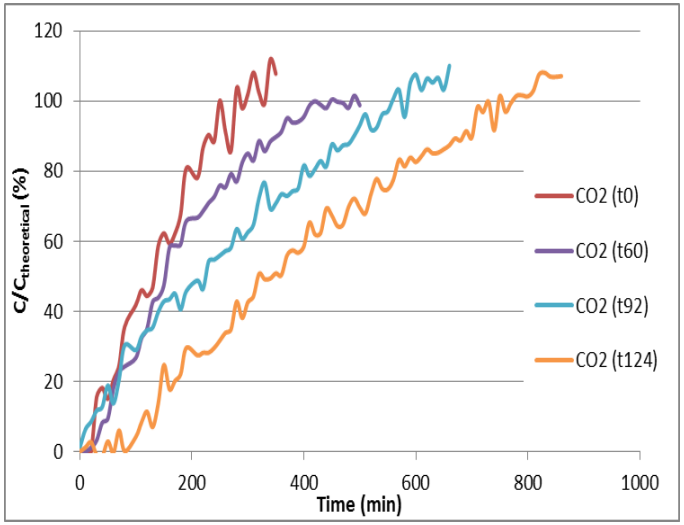
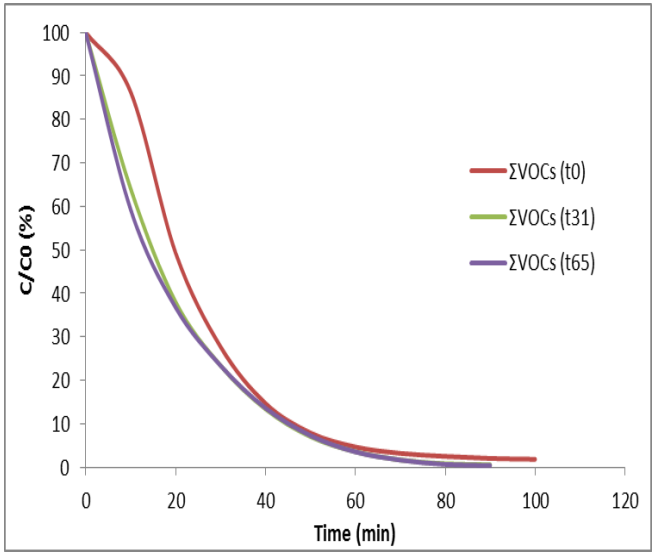
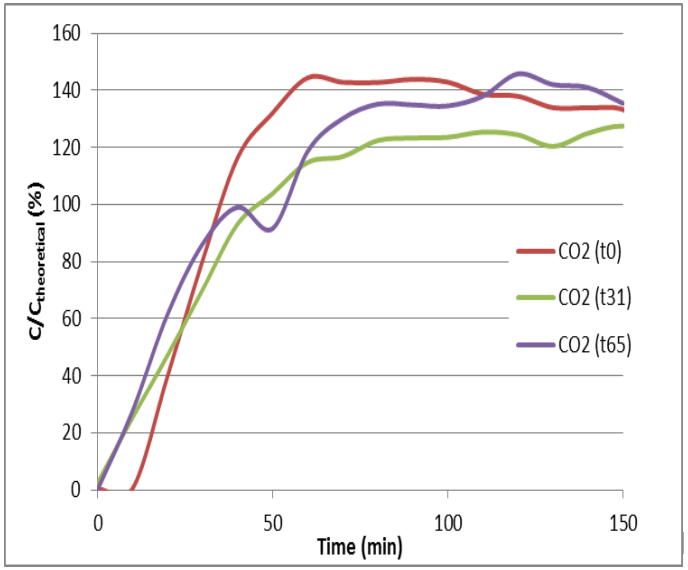
Device D3





Device D4





Equipment for nanoparticles release

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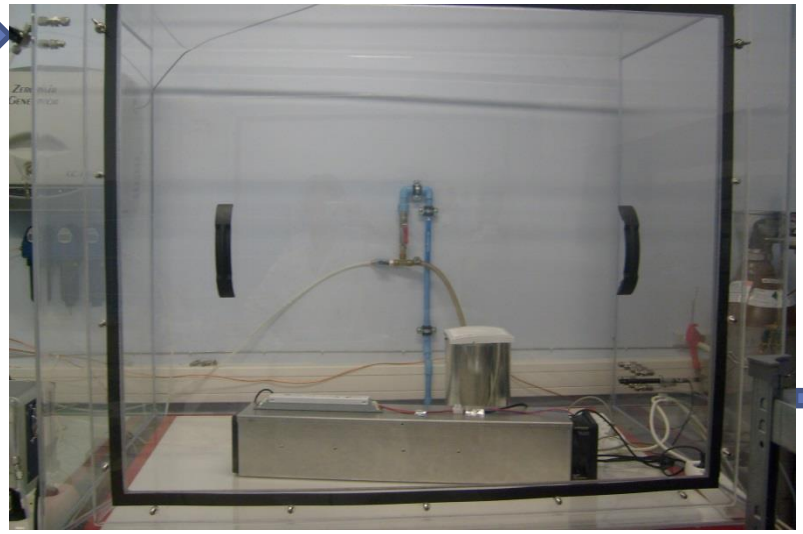
Flow max.: 25 L min^{-1}
Quality ISO8573-1Class1.1.1
Particles < 0.1µm

Filter
0.01µm

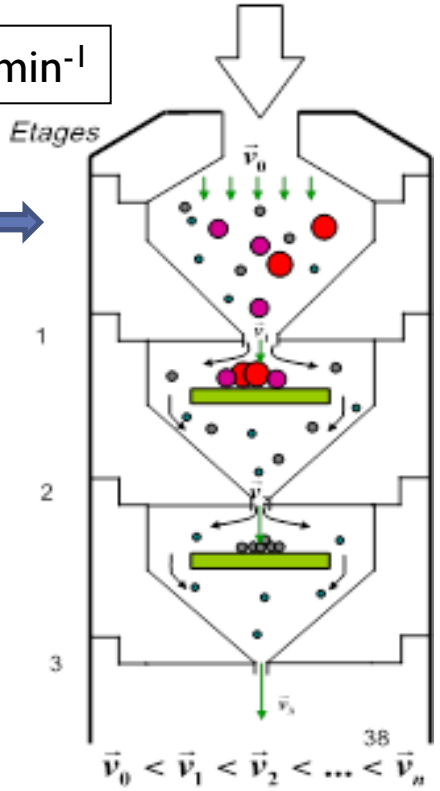


Particles collection according to the size

Electrical Low Pressure Impactor (ELPI)

Flux d' air

10 L min^{-1}



13 stages :
7 nm – 10 µm

First results of nanoparticles release

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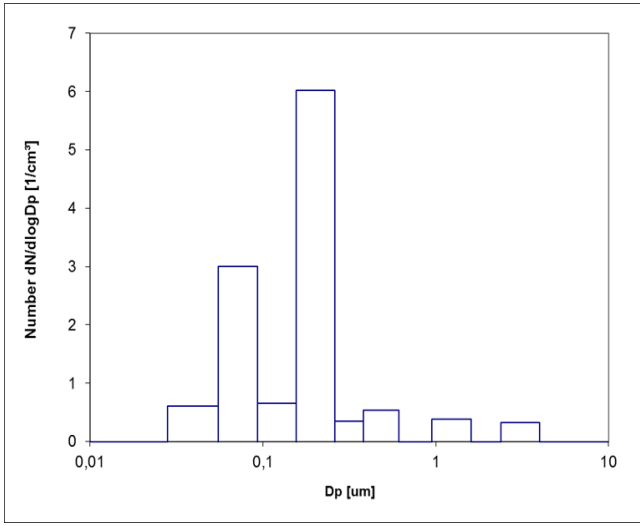
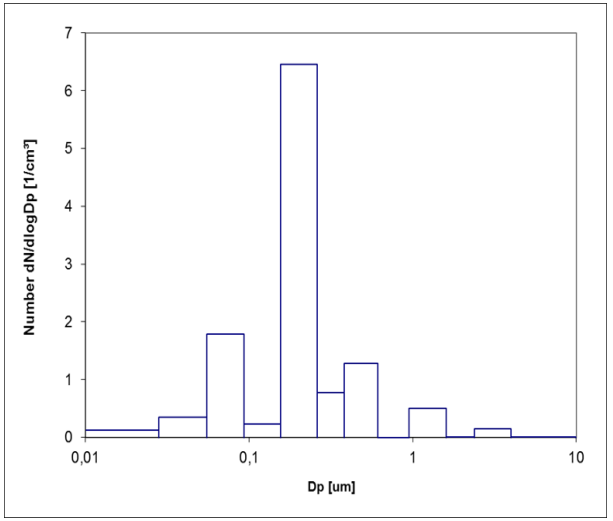
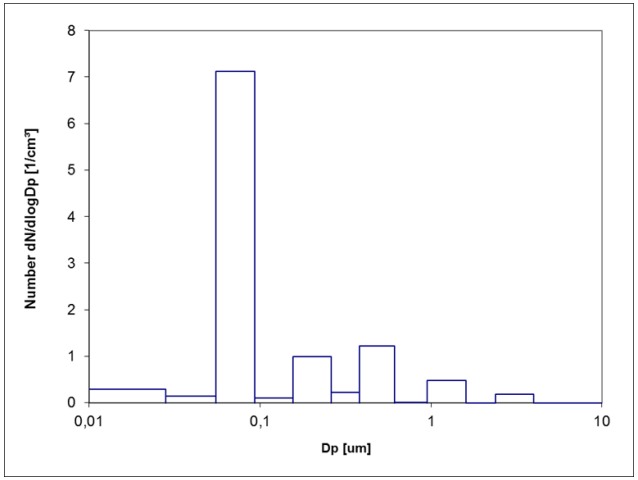
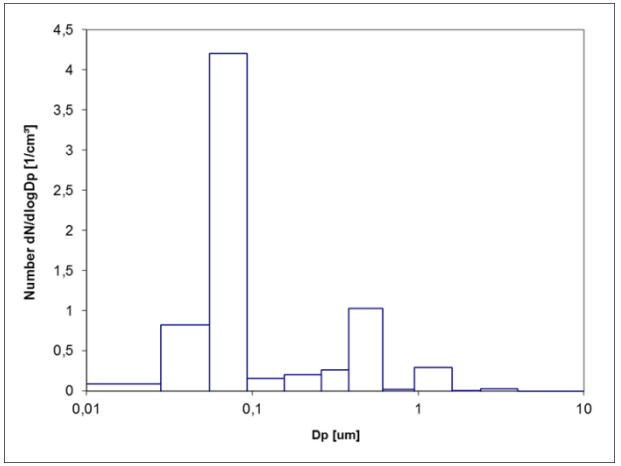
	Distribution average range of the background of the chamber flushed with clean air	Distribution average range with system ON during 3h30 (D4) and 4h30 (D6)
Test D4		
Test D6		

No nanoparticles emitted by 4 devices D4/D5/D6/D8

(Reference : ≈9 000 particles.cm^{-3} collected in the laboratory between 7nm-1µm)

Conclusion

- Satisfactory inter-laboratory results for closed chamber tests.
- Possible comparison of photocatalytic commercial and innovative devices and materials.
- Standardised tests useful to insure that devices found in the market are efficient and safe.
- Following of systems and media aging and batches as well as nanoparticles release useful in the future.
- Following of our project : tests in real conditions in a pilot room (40 m^3) with Nobatek (VOCs efficiency and nano-micro particles release)
- In project : extension from French to European level (CEN TC386 launching the CEN enquiry).

VOC concentrations closer to the indoor air concentration (50 ppbv/product) and add formaldehyde in the mixture.

- Certification needed for these commercial products

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