Příklady testování fotokatalytických produktů z hlediska jejich funkčnosti a vytváření nových standardů

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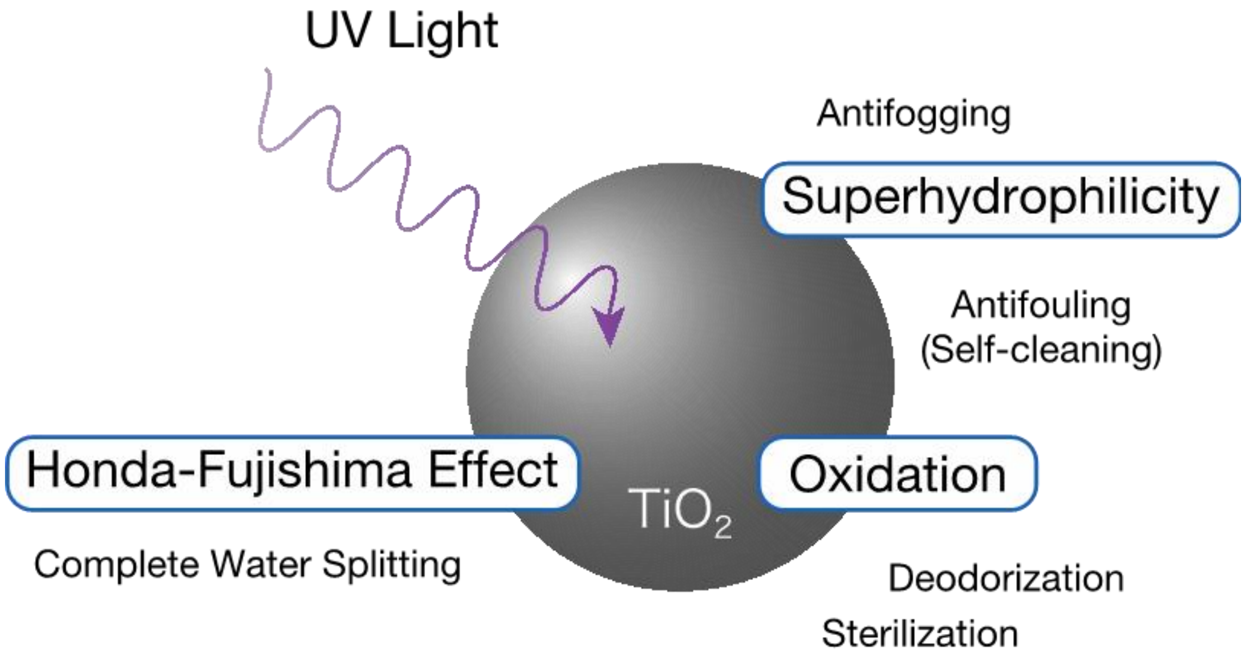
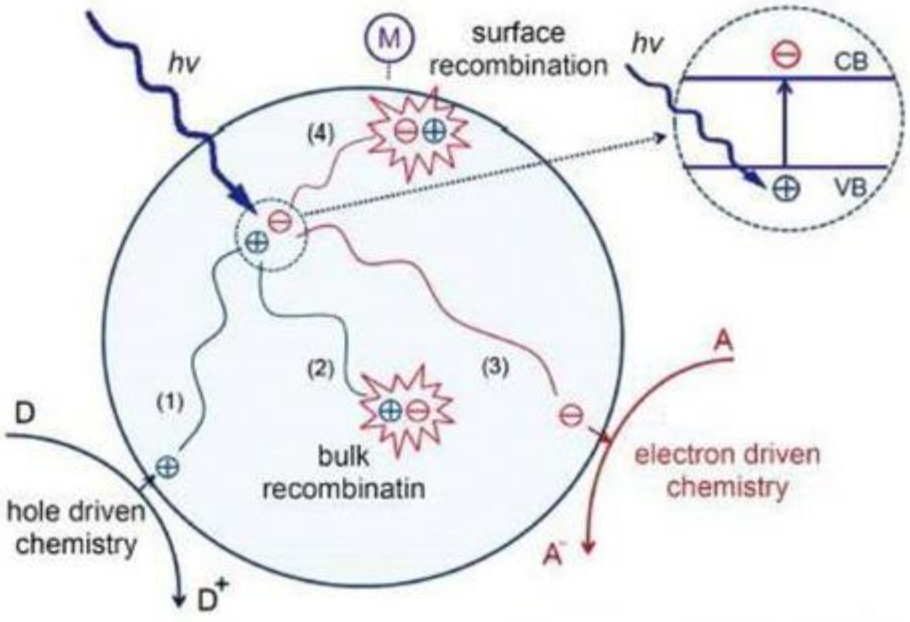
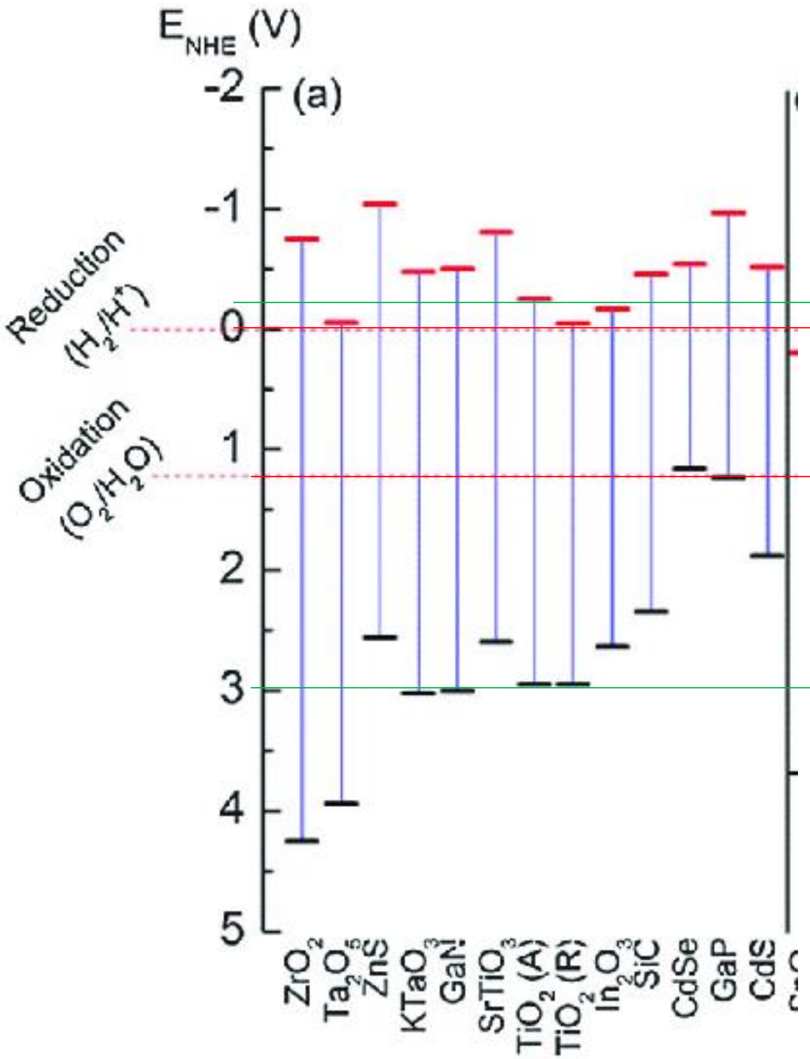
Co je to fotokatalýza?

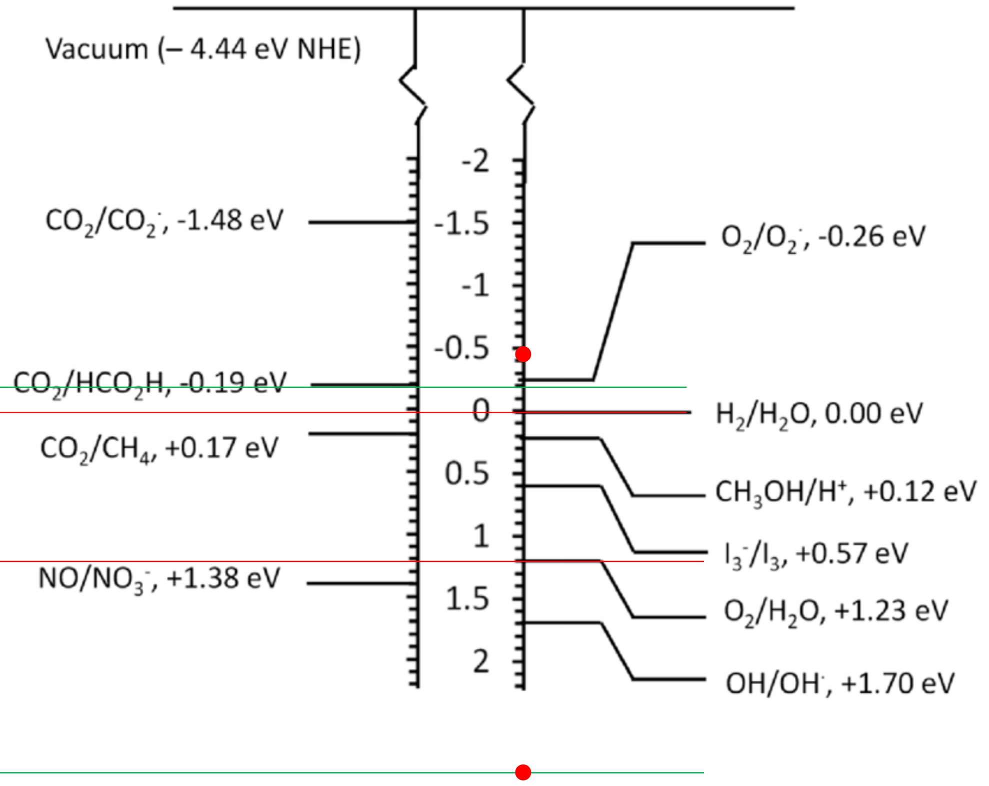
- Radikálový neselektivní redoxní mechanismus.
- Sežere cokoliv pokud jsou energetické potenciály ve správné relativní poloze.





Jak to tedy funguje? Redukce vs. Oxidace





Co je to standard?

- Technická norma či standard je podrobný předpis, který stanovuje důležité parametry či vlastnosti materiálu, výrobku, součásti nebo pracovního postupu, který vede ke *standardizaci*…

- *Standardizace* je proces sjednocení pomocí zavádění standardů. Vede ke koordinaci, kompatibilitě a opakovatelnosti v kvalitě výroby. Standardy se zavádějí buď centrálně (de iure), což je způsob, který převažuje, nebo jde o ustálený převažující standard (de facto), který vznikl z rozšířeného užívání.

K čemu je standard?

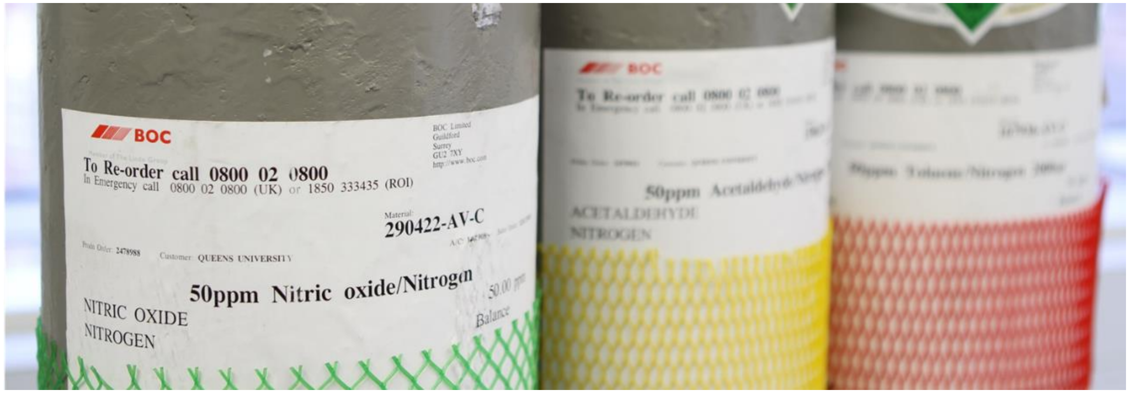
- Zaručení (kontrola) kvality
- Porovnávání produktů za stejných podmínek
- Marketingové využití
- Simulování reálných podmínek?

Fotokatalytické standardy

- Historicky jsou fotokatalytické standardy založeny na japonských normách
- ISO (mezinárodní organizace, hlavně Asie)
- CEN (evropská organizace)
- ISO standardů je spousta nejpoužívanější je jich jen několik
- Kritika ISO standardů – lze aktualizovat
- Nové ISO standardy – hledání kompromisu

(i) air purification

Test pollutant	ISO standard reference number	Suitable sample types and applications
NO	ISO 22197-1	Exterior: NO_x removing paint, concrete and tiles; Interior: odour-removing paint.
Acetaldehyde	ISO 22197-2	
Toluene	ISO 22197-3	
Formaldehyde	ISO 22197-4	



Příklad ISO na odbourávání NOx

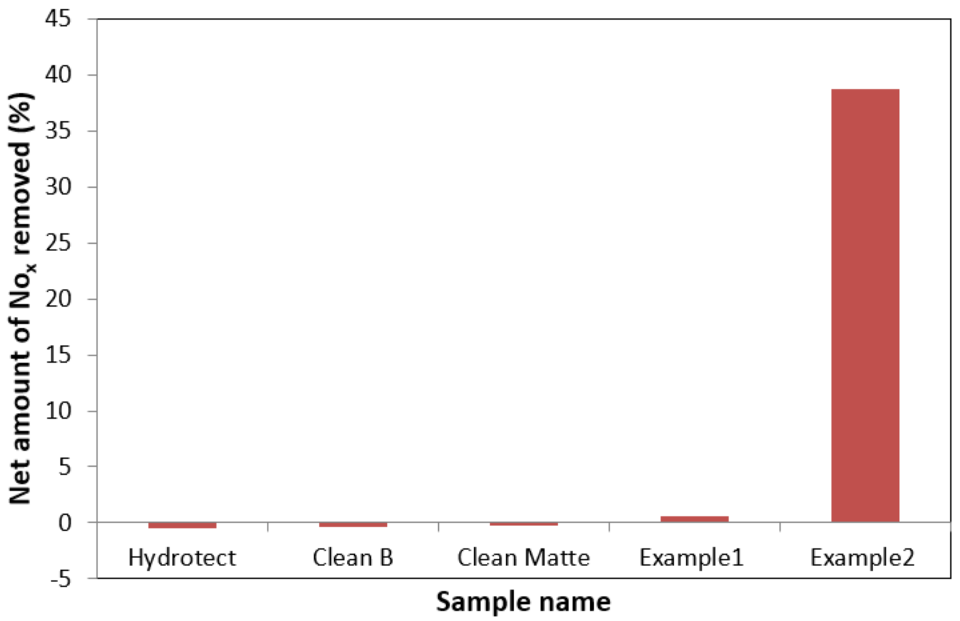


Figure 2 – Histogram illustrating the ability of supplied test pieces, and 2 example test pieces, to remove NO_x from an air stream containing 1 ppm NO over a 5 hour period (units: % of NO supplied to the reactor). All supplied samples are of photocatalytic coating on ceramic tile, whilst example 1 is a sample of TiO¬2 paste dipcoated onto glass, and example 2 is a sample of photocatalytic paper.

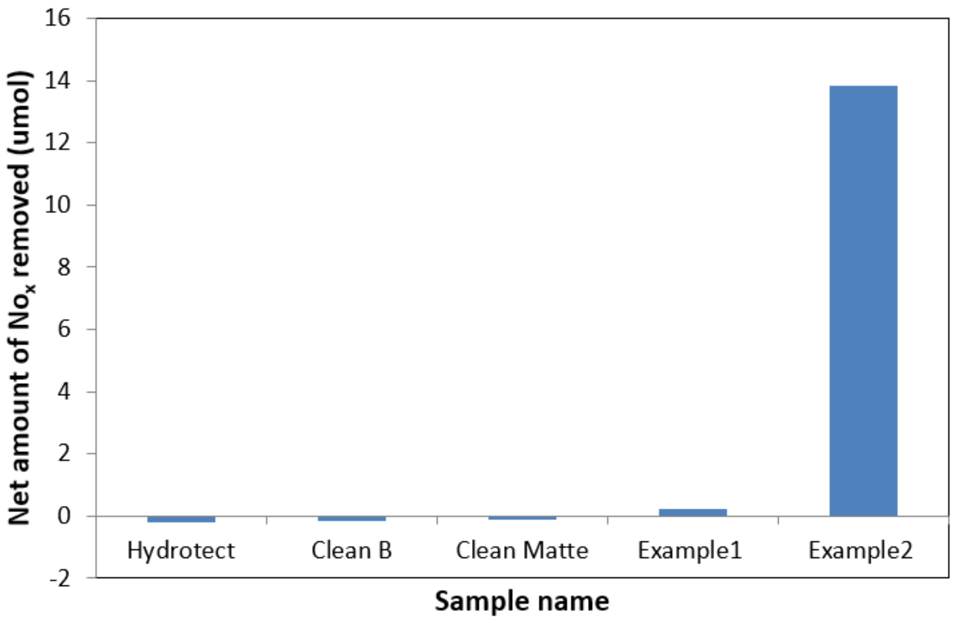


Figure 1 – Histogram illustrating the ability of supplied test pieces, and 2 example test pieces, to remove NO_x from an air stream containing 1 ppm NO over a 5 hour period (units: µmol). All supplied samples are of photocatalytic coating on ceramic tile, whilst example 1 is a sample of TiO_2 paste dipcoated onto glass, and example 2 is a sample of photocatalytic paper.

Sample number (and name)	Units: μmol				
	(i) NO supplied to the reactor	*(ii) NO removed by the test piece*	*(iii) total NO unreacted*	*(iv) amount of NO_2 generated by the test piece*	*(v) net amount of NO_x removed by the test piece = ((ii)-(iv))*
Hydrotect	40.61	-0.24	40.85	-0.02	**-0.22**
Clean B	40.22	0.49	39.74	0.64	**-0.15**
Clean Matte	40.66	-0.13	40.79	-0.02	**-0.11**
Example1 - TiO_2 paste coated on glass	36.86	5.59	31.26	5.38	**0.21**
Example2 - Typical photocatalytic paper	35.69	23.85	11.84	10.02	**13.83**

Table 1 – Summary of (i) NO supplied to the reactor (ii) NO removed by the test piece (iii) total NO unreacted (iv) amount of NO_2 generated by the test piece and (v) net amount of NO_x removed by the test piece = ((ii)-(iv)) for each of the tested samples, and example test pieces, in units μmol.

Sample number (and name)	Units: % of NO supplied to the reactor				
	(i) NO supplied to the reactor	*(ii) NO removed by the test piece*	*(iii) total NO unreacted*	*(iv) amount of NO_2 generated by the test piece*	*(v) net amount of NO_x removed by the test piece = ((ii)-(iv))*
Hydrotect	100	-0.6	100.6	-0.1	**-0.5**
Clean B	100	1.2	98.8	1.6	**-0.4**
Clean Matte	100	-0.3	100.3	0	**-0.3**
Example1 - TiO_2 paste coated on glass	100.00	15.18	84.82	14.60	**0.58**
Example2 - Typical photocatalytic paper	100.00	66.82	33.18	28.07	**38.76**

Table 2 – Summary of (i) NO supplied to the reactor (ii) NO removed by the test piece (iii) total NO unreacted (iv) amount of NO_2 generated by the test piece and (v) net amount of NO_x removed by the test piece = ((ii)-(iv)) for each of the tested samples, and example test pieces, as a % of NO supplied to the reactor.

Customer Name:	n/a
Customer contact:	n/a
Sample name:	**Example 2**
Sample description:	Photocatalytic paper

Testing conditions

Date (dd/mm/yyyy)	05/09/2012
T (°C)	21.1
RH (%)	51
STP flow (L/min)	2.8676
Irradiance (mW/cm^{-2})	0.98
NO supply conc. (ppm)	0.977

Results	Amount (μmol)	Area (%)
(i) NO supplied to the reactor	35.69	100.00
(ii) NO removed by the test piece	23.85	66.82
(iii) total NO unreacted	11.84	33.18
(iv) amount of NO_2 generated by the test piece	10.02	28.07
(v) net amount of NO_x removed by the test piece = ((ii)-(iv))	**13.83**	**38.76**

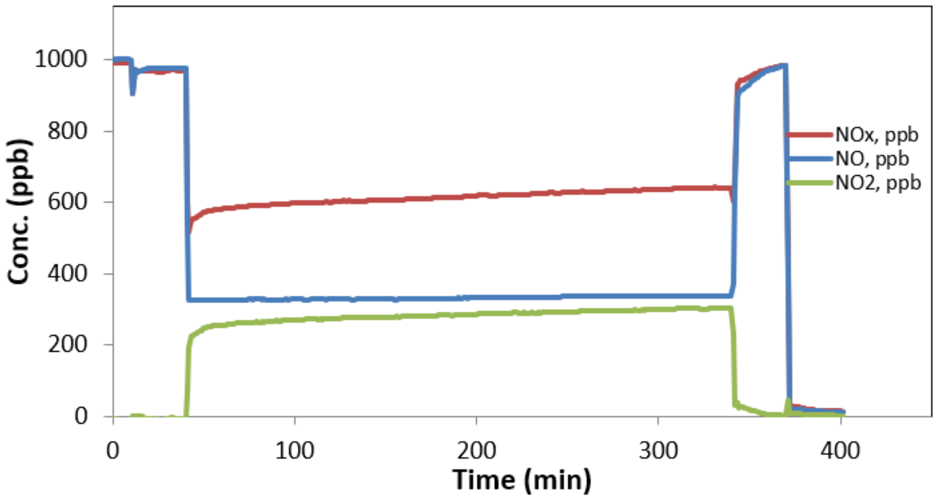


Figure 11 – Trace of NO/NO_x/NO_2 concentration during the ISO test for a typical photocatalytic paper.

Klíčové reakce fotokat. oxidace NO

Key reactions

The titania-sensitised, photocatalytic oxidation of NO proceeds to nitric acid, via nitrous acid and a radical based mechanism.[4-8] The two key photocatalytic reactions are:

$$4NO + O_2 + 2H_2O \xrightarrow[h\nu \geq E_{bg}]{TiO_2} 4HNO_2 \qquad (1)$$

and

$$2HNO_2 + O_2 \xrightarrow[h\nu \geq E_{bg}]{TiO_2} 2HNO_3 \qquad (2)$$

Recent work [4] reveals that the accumulation of nitric acid on the surface promotes its photocatalysed reaction with NO that generates the toxic product NO_2, i.e.

$$2HNO_3 + NO \xrightarrow[h\nu \geq E_{bg}]{TiO_2} 3NO_2 + H_2O \qquad (3)$$

This can lead to an eventual steady state where the rate of NO removal is matched by the rate of NO_2 production; which is clearly highly undesirable. It follows that for any NO_x-removing photocatalyst product to work effectively it is necessary that the HNO_3 photogenerated, via reactions (1) and (2), must be removed at regular intervals, by rinsing with water, e.g. from rain or a damp cloth.

[4] Y. Ohko, Y. Nakamura, N. Negishi, S. Matsuzawa and K. Takeuchi, J. Photochem. Photobiol. A: Chem., 205 (2009) 28.

Příklad ISO na odbourávání VOC - acetaldehydu

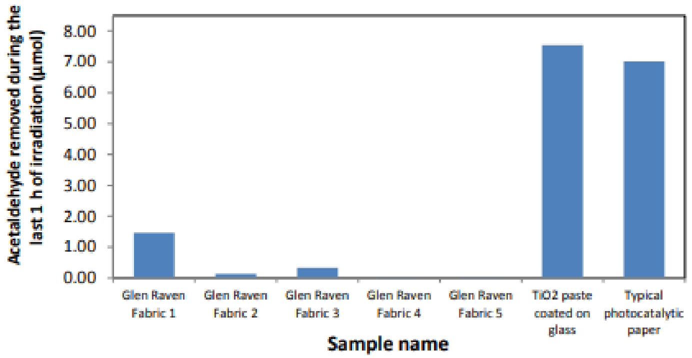


Figure 1 – Histogram illustrating the ability of supplied test pieces, and 2 example test pieces, to remove acetaldehyde from an air stream containing 5 ppm acetaldehyde during the last 1 hour of photoirradiation (units: µmol).

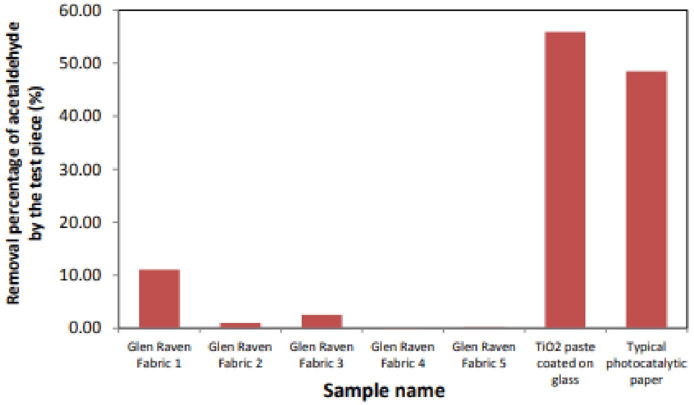


Figure 2 – Histogram illustrating the ability of supplied test pieces, and 2 example test pieces, to remove acetaldehyde from an air stream containing 5 ppm acetaldehyde during the last 1 hour of photoirradiation (units: % of acetaldehyde supplied to the reactor).

Customer Name:	[redacted]
Customer contact:	
Sample name:	**Fabric 1**
Sample description:	White fabric

Testing conditions

Date (dd/mm/yyyy)	28/01/2014
T (°C)	23.0
RH (%)	48
STP flow (L/min)	1.0495
Irradiance (mW/cm^{-2})	1.00
Acetaldehyde supply vol. fraction (ppm)	5.00

Results

(i) Concentration of acetaldehyde supply	**13.17**	µmol
(ii) Acetaldehyde removed by the test piece during the last 1 h of irradiation	**1.46**	µmol
(iii) Removal percentage of Acetaldehyde by the test piece	**11.06**	%

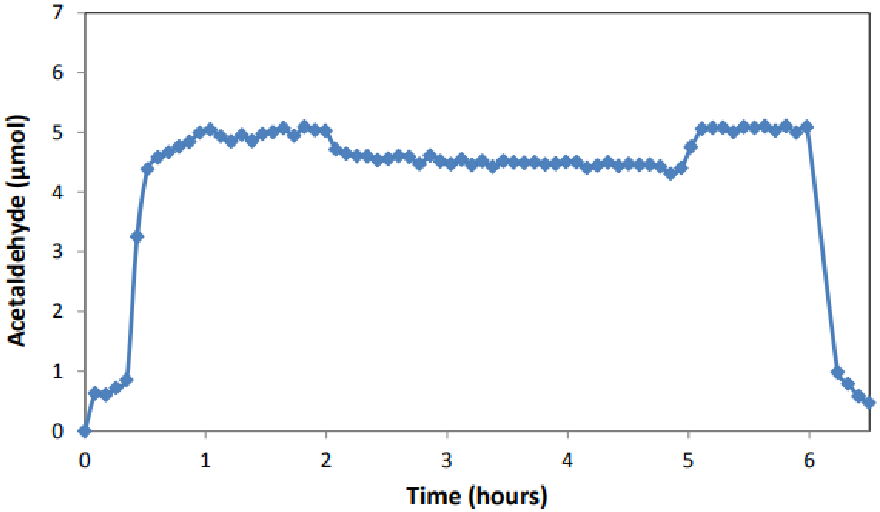
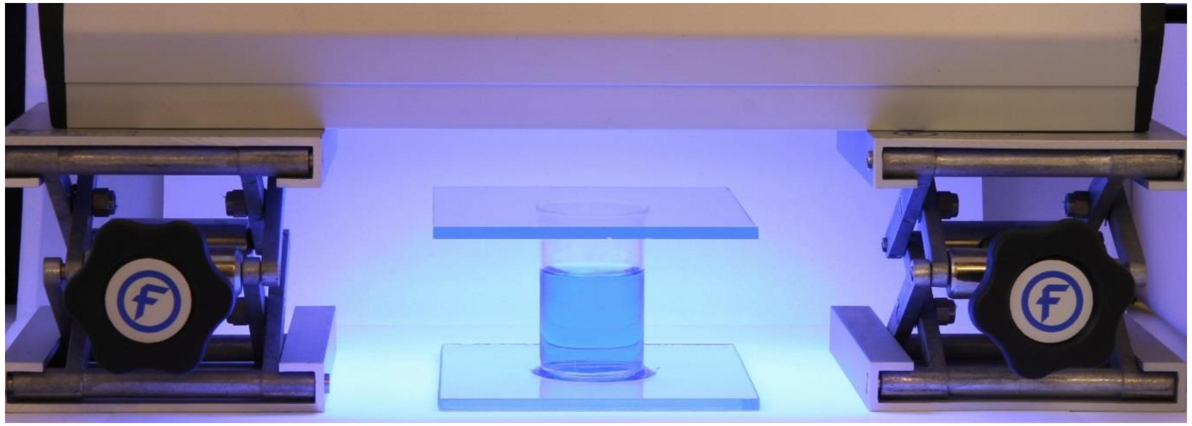


Figure 3 – Trace of acetaldehyde concentration during the ISO test for sample Fabric 1.

(ii) water purification

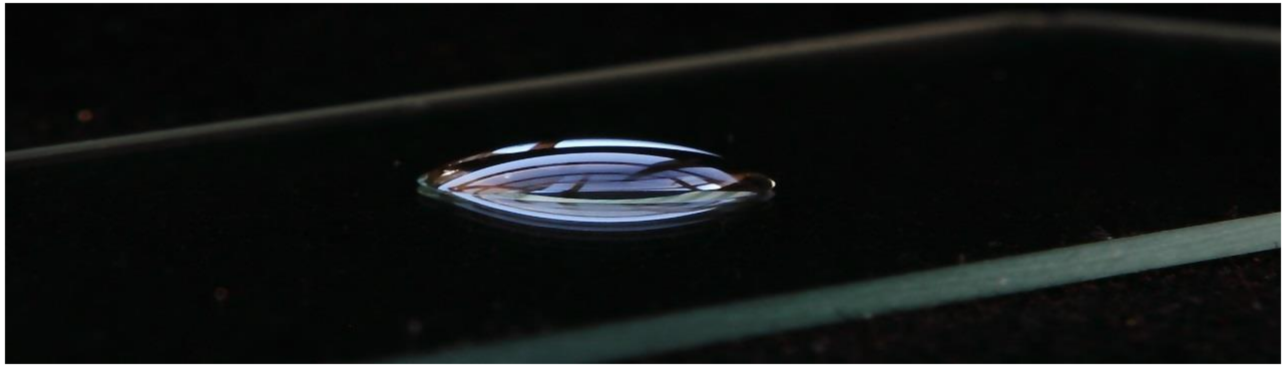
Test pollutant	ISO standard reference number	Suitable sample types and applications
Methylene blue*	ISO 10678: 2010	Water purification units
DMSO	ISO 10676 2010	

* MB not an ISO for water purification by definition, but it is used in that way.



(iii) self cleaning surfaces

Test pollutant	ISO standard reference number	Suitable sample types and applications
Contact angle/Oleic acid	ISO 27448: 2009	Self-cleaning glass, concrete, tent/awning materials and tiles
Methylene blue	ISO 10678: 2010	



Příklad ISO na samočisticí povrch

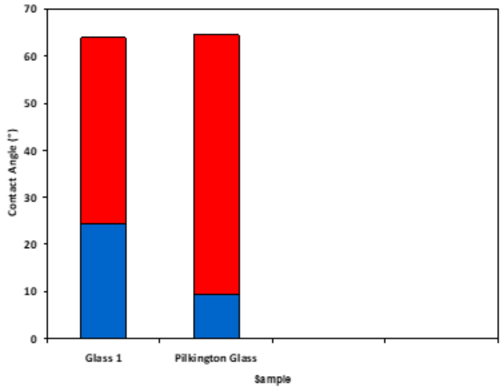


Figure 1 – Histogram illustrating the change in contact angle for Glass 1 and Pilkington Glass after 48h irradiation with 1 mW/cm² UVA. The red bar indicates the starting contact angle and the blue bar indicates the contact angle after 48h.

Table 1 summarises the starting contact angle and contact angle after 3, 24 and 48 h for each of the samples shown in Figure 1, with Table 2 illustrating the water droplet on the surface of each sample at these time periods.

	Contact Angle (°)			
	0 h	3 h	24 h	48 h
Glass 1	63.82	58.32	32.33	24.32
Pilkington Glass	64.39	73.74	26.52	9.48

Table 1 – Initial contact angles for all and for Glass 1 and Pilkington glass, during irradiation with 1 mW/cm² UVA

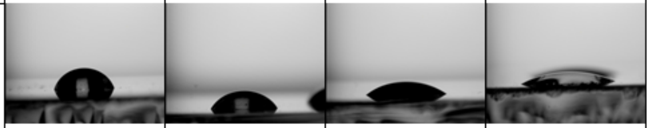
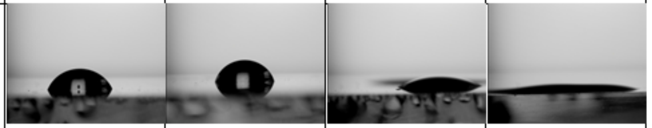
	0 h	3 h	24 h	48 h
Glass 1				
Pilkington Glass				

Table 2 – Photographs to illustrate contact angle measurements over time.

The remainder of this report contains the raw data gathered from the contact angle instrument, along with the original data figure and reaction conditions for each sample under test.

Customer Name:	[redacted]
Customer contact:	
Sample name:	**Glass 1**
Sample description:	Glass

Testing conditions

Date (dd/mm/yyyy)	27/11/2013
T (°C)	20.9
RH (%)	52
Irradiance (mW/cm⁻²)	1.00

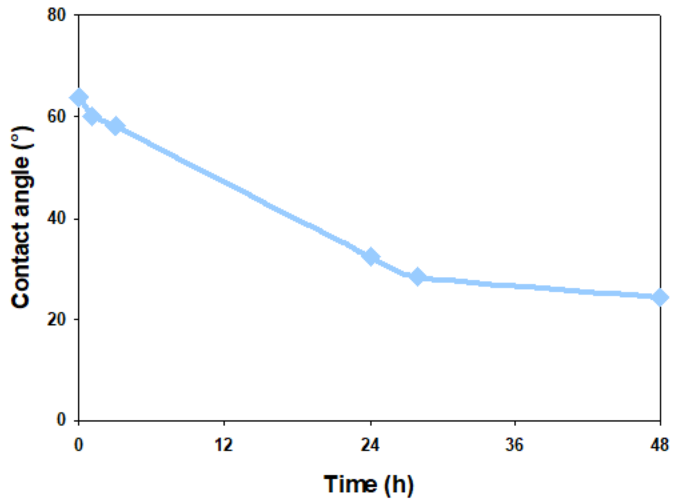


Figure 2 – Trace of water contact angle measured on Glass 1, during 48 h irradiation with 1 mW/cm² UVA light.

Irradiation Time (hours)	0	1	3	24	28	48
Contact Angle (deg)	63.82	59.99	58.32	32.33	28.25	24.32
Contact Angle Left (deg)	63.82	59.99	58.32	32.33	28.25	24.32
Contact Angle Right (deg)	63.82	59.99	58.32	32.33	28.25	24.32
Tilt Angle (deg)	3.14	0.44	0.20	0.86	2.08	0.47
Base (mm)	3.39	3.60	3.80	4.42	4.39	4.82
Base Area (mm^2)	11.55	13.01	14.48	19.6	19.29	23.30
High (mm)	1.05	1.04	0.97	0.61	0.56	0.53
Volume (µl)	5.43	5.94	6.01	4.83	4.35	5.01
Maximum Diameter (mm)	3.78	4.14	4.69	8.63	9.13	5.1
Contrast (cts)	220	221	223	216	221	210
Sharpness (cts)	40	90	62	52	23	21
Black Peak (cts)	0	0	0	3	0	12
White Peak (cts)	220	221	223	219	221	222
Edge Threshold (cts)	91	91	92	92	91	99

Table 3 – Raw data gathered from contact angle instrument for Glass 1, during 48 h irradiation with 1 mW/cm² UVA light.

Příklad ISO na degradaci MB

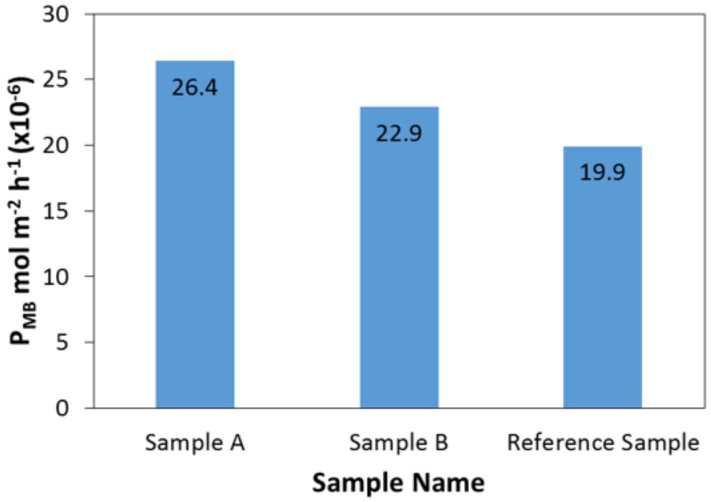


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Fig 1 – Histogram illustrating the specific photoactivity (P_{MB}) of supplied test pieces over a 3 hour period (units: mol m^{-2} h^{-1}).

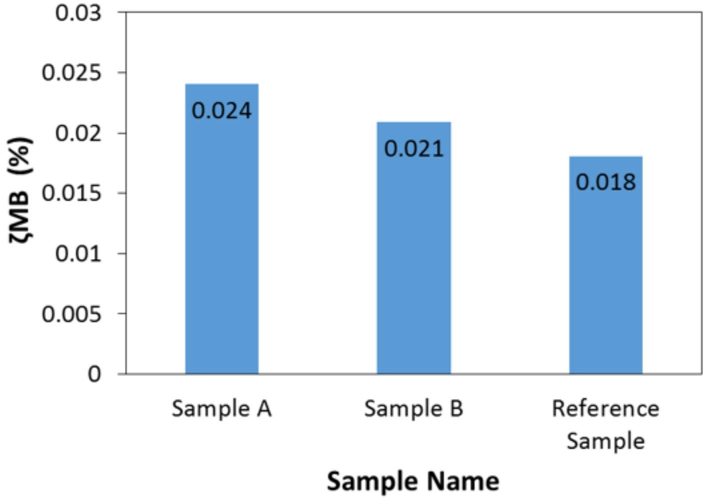


Fig 2 – Histogram illustrating the photonic efficiency of supplied test pieces over a 3 hour period (units: %).

t_m / min	t_m / h	$A_{\lambda,irr}$	$A_{\lambda,dark}$	E, E_{av} / W m^{-2}	E_P, $E_{P,av}$ mol m^{-2} h^{-1}	R_{irr} mol m^{-2} h^{-1}	R_{dark} mol m^{-2} h^{-1}	P_{MB} mol m^{-2} h^{-1}	ζ_{MB} (%)
0	0.00	0.730	0.739	10	0.110				
20	0.33	0.707	0.735	10	0.110	3.22E-05	6.95E-06	2.52E-05	0.022967
40	0.67	0.680	0.736	10	0.110	3.89E-05	-2.05E-06	4.10E-05	0.037300
60	1.00	0.656	0.731	10	0.110	3.36E-05	6.35E-06	2.73E-05	0.024838
80	1.33	0.634	0.733	10	0.110	3.20E-05	-2.68E-06	3.47E-05	0.031604
100	1.67	0.612	0.728	10	0.110	3.00E-05	7.21E-06	2.28E-05	0.020725
120	2.00	0.600	0.730	10	0.110	1.80E-05	-1.86E-06	1.99E-05	0.018116
140	2.33	0.585	0.727	10	0.110	2.03E-05	3.46E-06	1.68E-05	0.015324
160	2.67	0.555	0.726	10	0.110	4.36E-05	2.02E-06	4.16E-05	0.037864
180	3.00	0.555	0.732	10	0.110	2.78E-08	-8.43E-06	8.46E-06	0.007704

Table 1 – Worked results for the BS ISO 10678:2010 test on the test sample A.

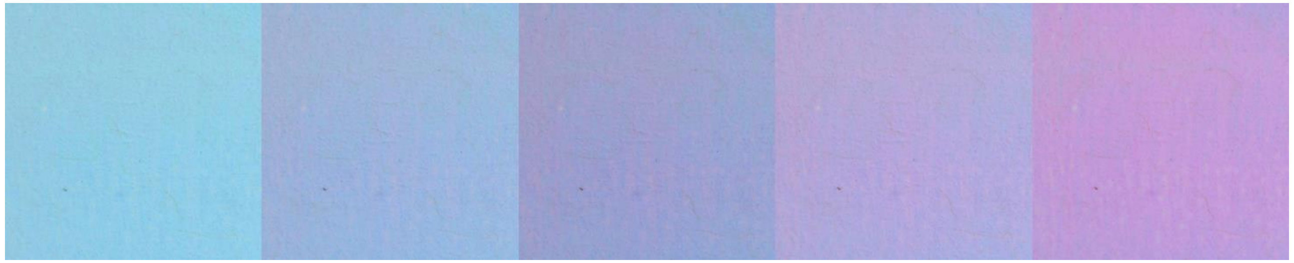
Sample	P_{MB} (mol m^{-2} h^{-1} x 10^{-6})	ζMB (%)
A	26.4	0.024049
B	22.9	0.020896
Reference Sample	19.9	0.018072

Table 2 – Summary of the MB mineralisation test results for the supplied test samples.

The above tables show the results of the test.

(iv) additional tests

Test pollutant	ISO standard reference number	Suitable sample types and applications
Stearic acid	Not ISO	self-cleaning glass, translucent substrates.
Resazurin (PAII)	ISO *21066*	Self-cleaning glass, tiles, paint, textile; samples of low activity. Fast response.



Příklad ISO na odbourávání resozurinu

<u>Results</u>

[redacted] on smooth tile

This sample displayed a good degree of photocatalytic activity, with the Rz film bleaching in an average time of 78 s, a time usually expected from samples of high activity. However the wide difference in how rapidly the two regions tested bleached the Rz would suggest the possibility that the coating is not entirely uniform. The regions were found to reach the end point of the reaction at 109 and 47 s respectively, with these times found from the intercept of the straight line sections of the profiles below (plot 1).

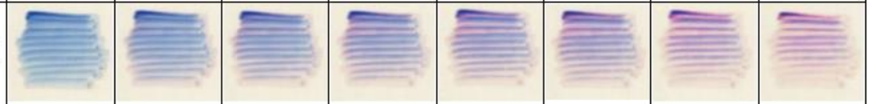
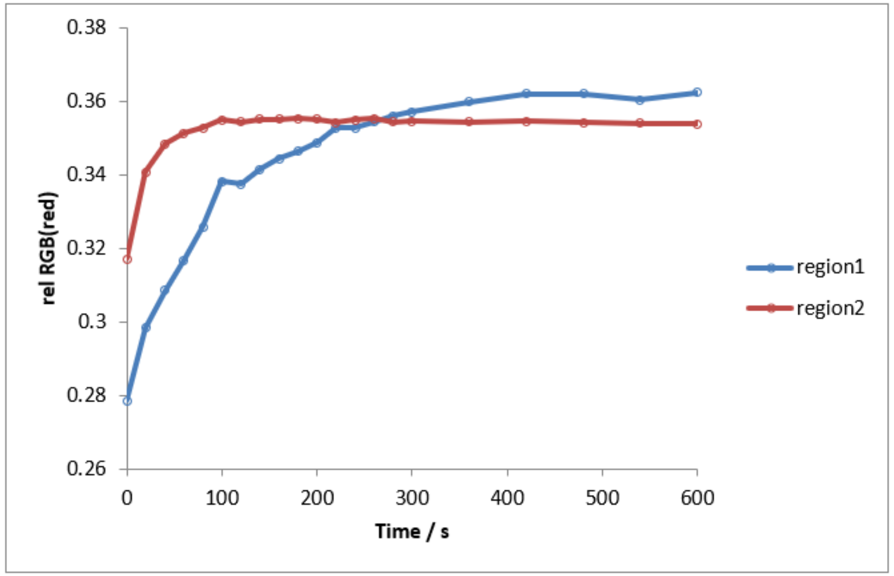
Time / s	0	20	40	60	80	100	200	300
Region 1								
Region 2								

Figure 1 – Visual change in Rz on PURETi Clear smooth tile sample



Plot 1 – Rz breakdown on [redacted] smooth tile sample

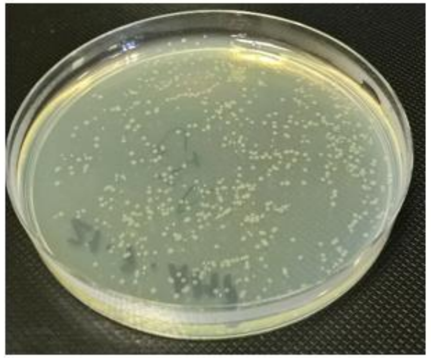
(v) antibacterial activity and antiviral activity

Test pollutant	ISO standard reference number	Suitable sample types and applications
E. coli	ISO 27447: 2009	ceramic materials or other materials that are generated through coating or mixing with photocatalysts.
Bacteriophage Q-beta	ISO 18061:2014(E)	ceramic materials or other materials that are generated through coating or mixing with photocatalysts.

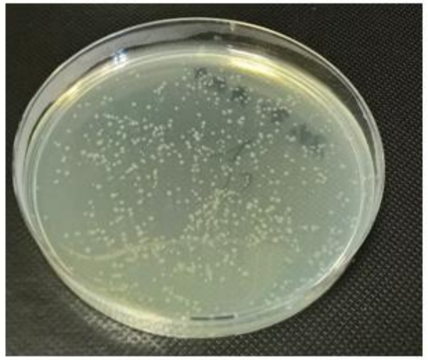
Příklad ISO na antibakteriální aktivitu

Table 2 – Table of results obtained

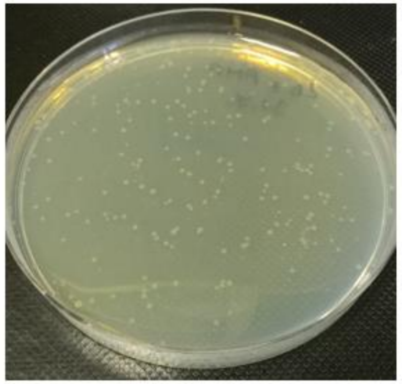
Group	Sample	Condition	Test Duration (hours irradiated)	Average Bacterial Count (CFU mL^{-1})
A	test	Dark	24	964
A	test	UVA	24	0
AB	blank	Dark	24	350
AB	blank	UVA	24	103
B	test	Dark	24	1221
B	test	UVA	24	879
BB	blank	Dark	24	1581
BB	blank	UVA	24	1973
C	test	UVA	24	0
CB	blank	Dark	24	765
CB	blank	UVA	24	188



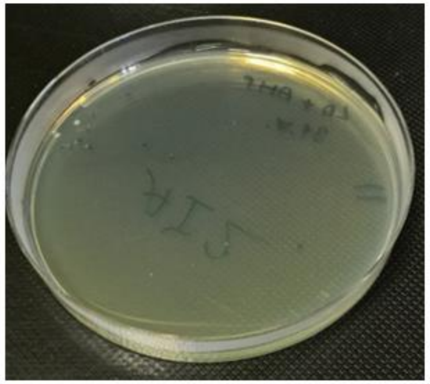
AB dark



AB UVA



A dark

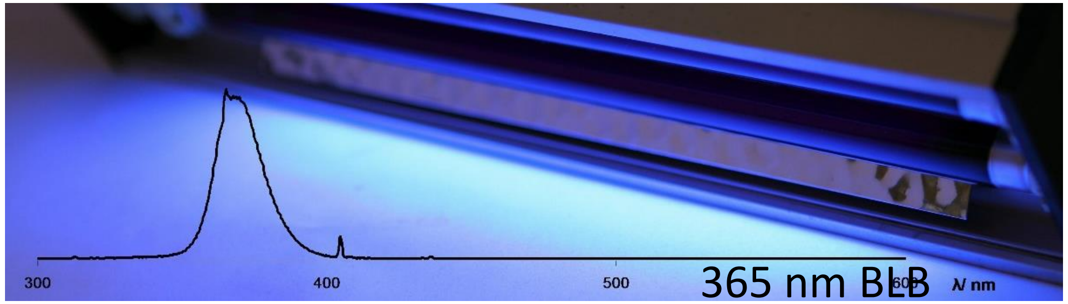


A UVA

Figure 2.- Photographs of final bacteria growth – sample A

(vi) light sources

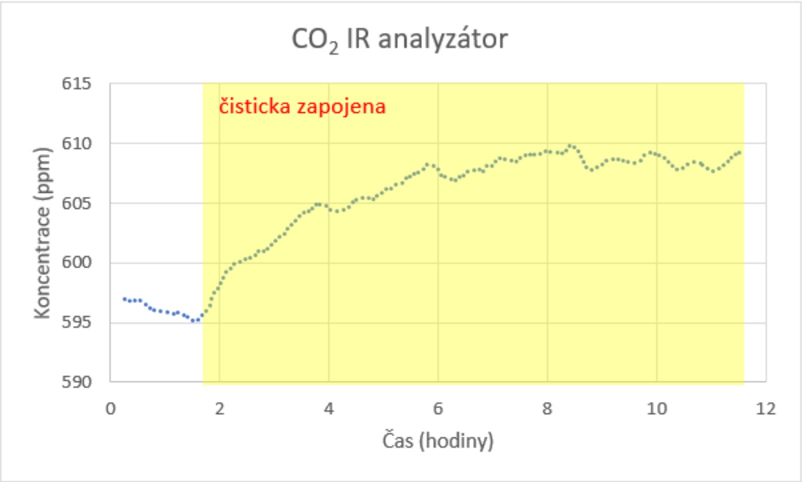
Test pollutant	ISO standard reference number	Suitable sample types and applications
n/a	ISO 10677: 2011	A photocatalyst's performance depends on light irradiation source.



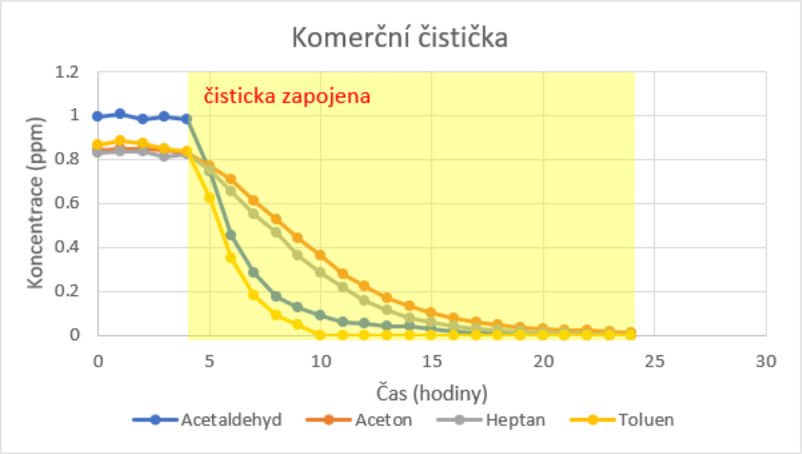
(vii) Chamber test

Test pollutant	CEN standard reference number	Suitable sample types and applications
4 VOC gases	CSN EN 16846-1	Air purifying devices

Příklad CEN testu na účinnost čističky vzduchu



Obrázek 3. Vývoj koncentrace CO_2 podle CO_2 analyzátoru. Celkový nárůst CO_2 byl 15 ppm.

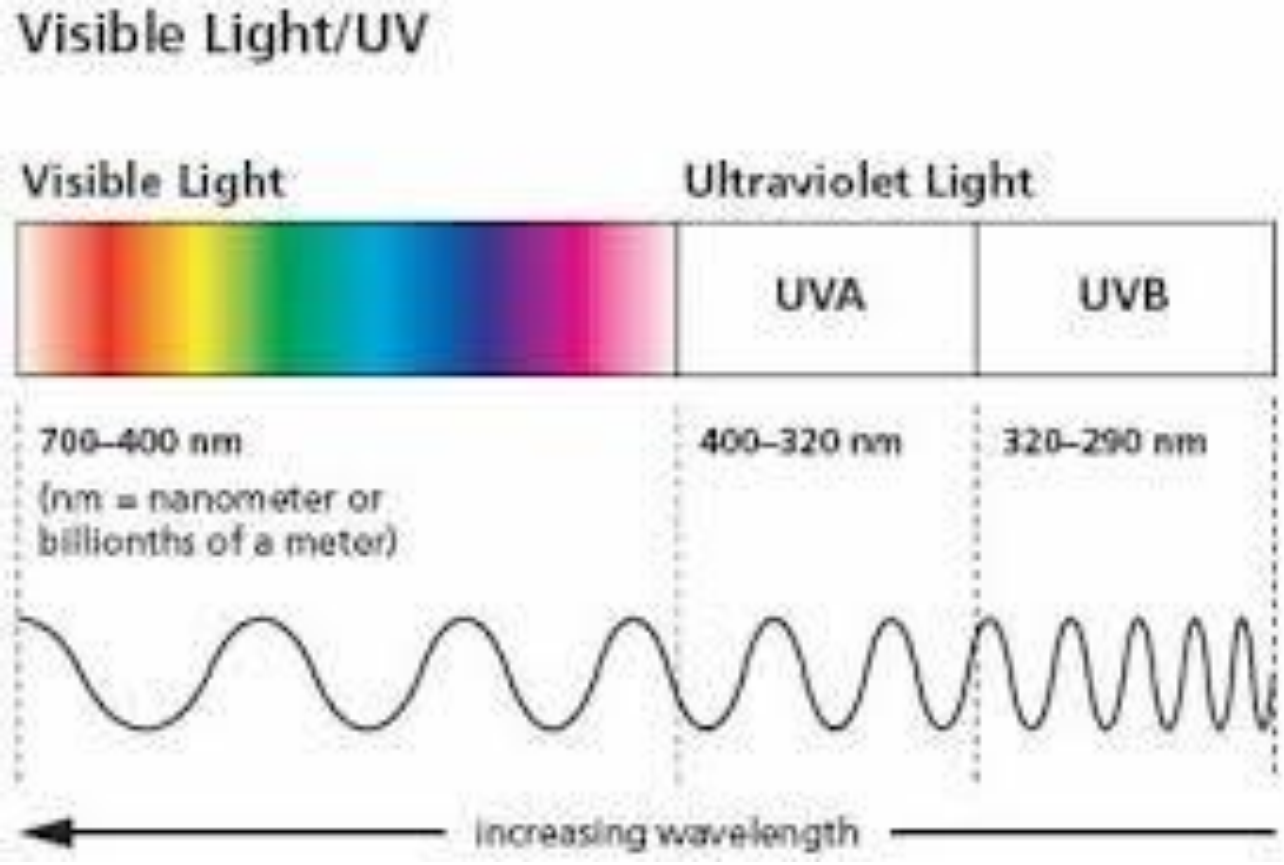


Obrázek 4. Průběh experimentu na odbourávání VOC v boxu při připojení původním krátkým potrubím.
Jedná se o stejnou komerční čističku.

Úskalí a příležitosti při vyvíjení produktů pro odstraňování toxických látek z prostředí (MVP)

- Svatá trojice: záření + fotokatalyzátor + substrát
- Indoor vs. outdoor
- Viditelné světlo vs. UVA záření
- UVA ze slunce nebo z umělého zdroje
- LEDs – energie emise diod je naprosto klíčová
- Trvanlivost vs. pojiva vs. aktivita
- Mít na paměti ‚radikálový neselektivní redoxní mechanismus‘

Poznámka k elektromagnetickému vlnění



Increasing energy

Jak tedy testovat vyvíjené PC produkty

- Základ je mít funkční povrch.
- Vývoj produktu – PAII inkousty.
- Citlivé testy založené na ISO standardech – porovnání s benchmarkem.
- ISO test, vhodný pro zvolenou aplikaci produktu.
- Velice záleží na koncovém využití produktu a substrátu- relativně nízký výsledek ISO testu neznamená tragédii.
- Test, který simuluje reálné podmínky.

The need for a useful association

- PIAJ stamp
- The European Photocatalysis Federation – closed in 2017
- Česká společnost pro aplikovanou fotokatalýzu
- ISO and CEN committees
- Periodic attempts to start one
- Need strong industrial partners with good PC products
- Need independent testing centers with good standards

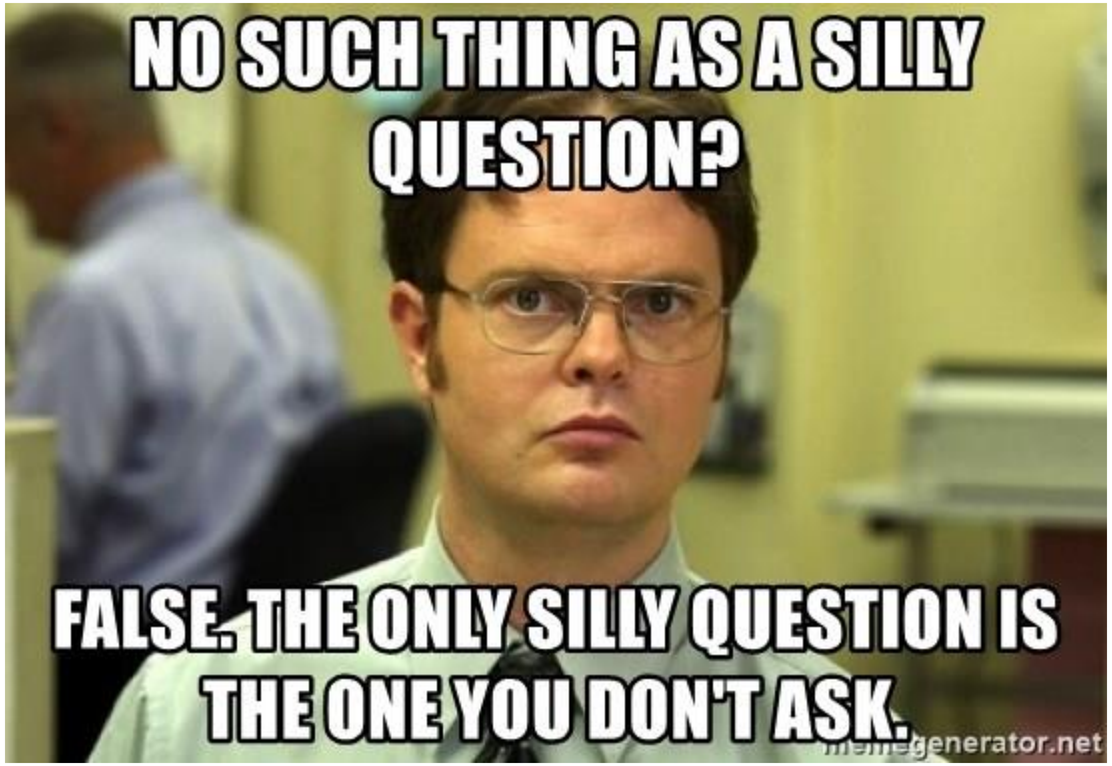
Almost done…

Despite its tempting misinterpretation due to seemingly easy application and relatively uneasy validation, ***photocatalysis offers a realistic and economically viable*** *solution* in line with the idea of sustainable development!

And that is good!

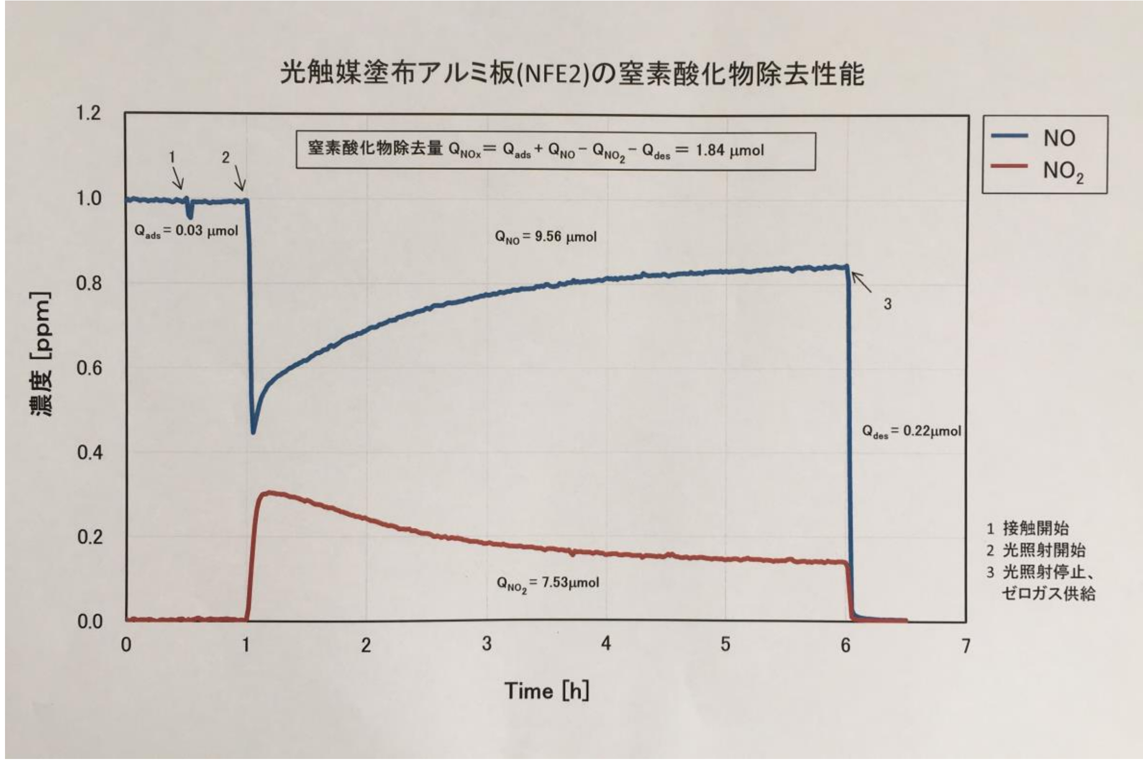
Děkuji za pozornost

- Otázky?

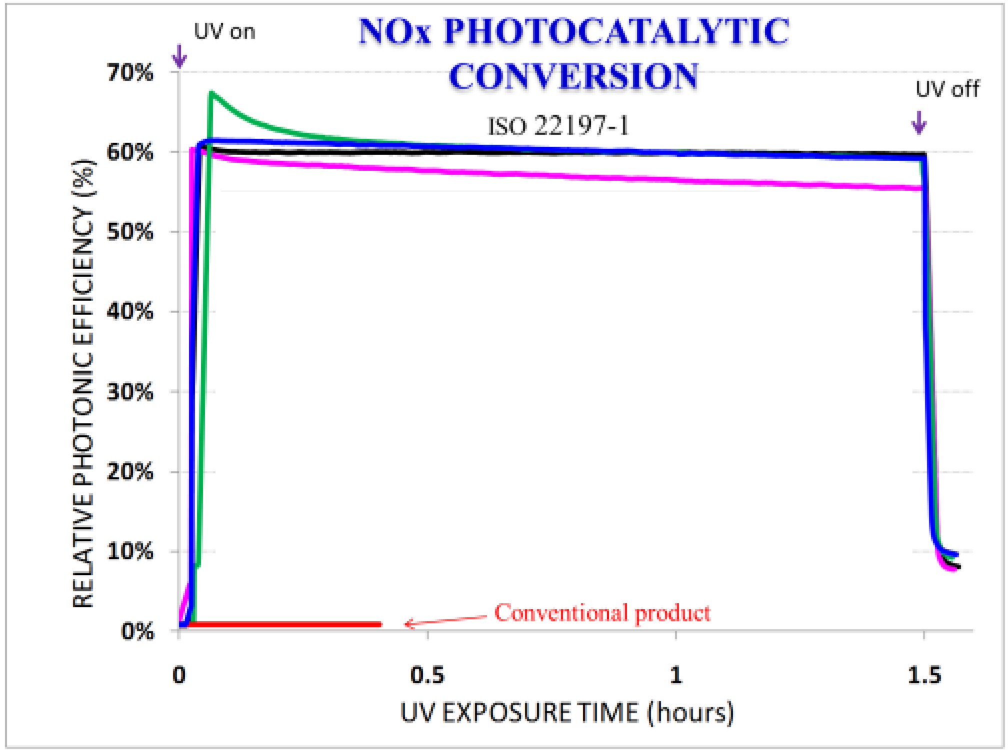


Jak prezentovat výsledek ISO?

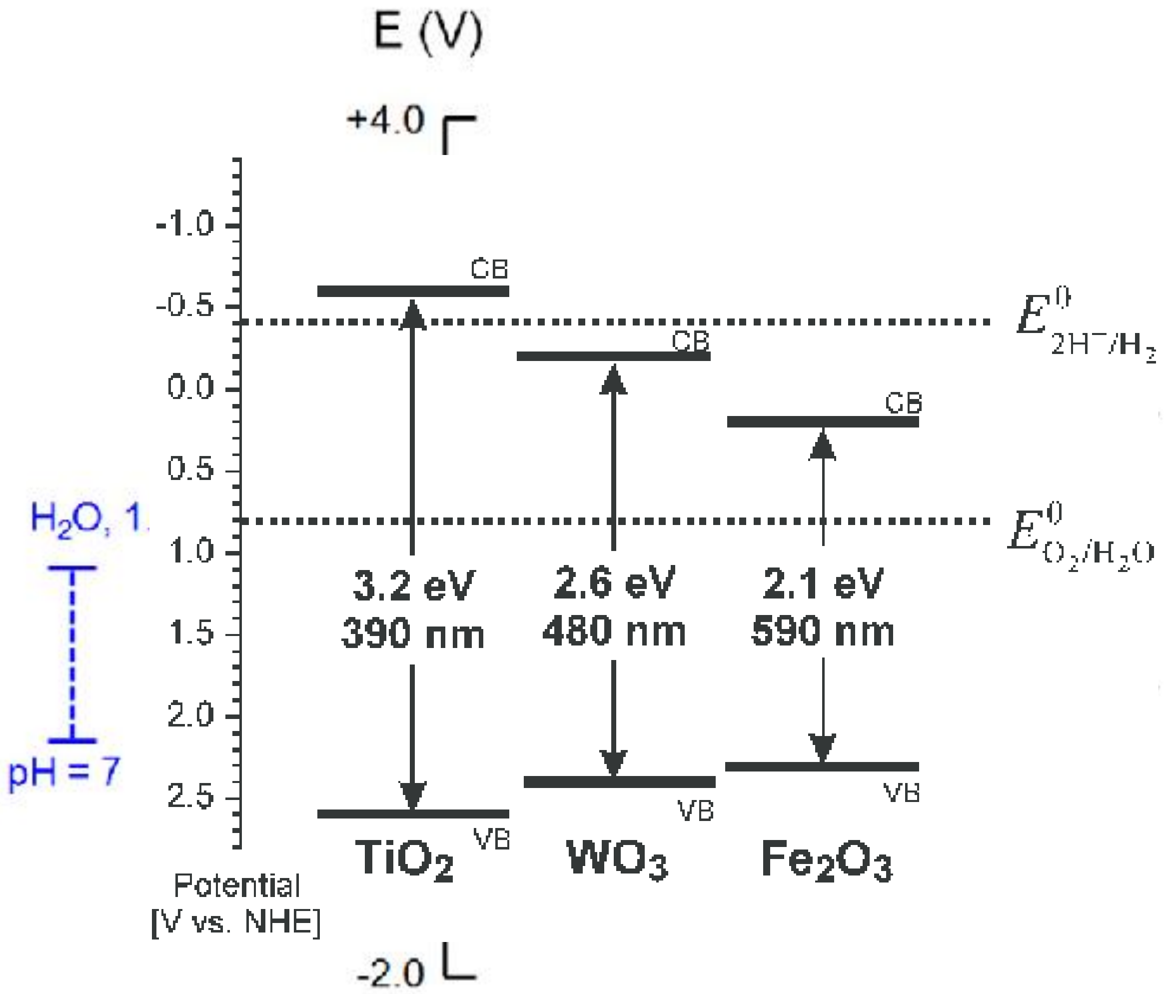
- It’s complicated
- ISO je rigidní… respektujme kolegy v oboru (it’s a niche market).

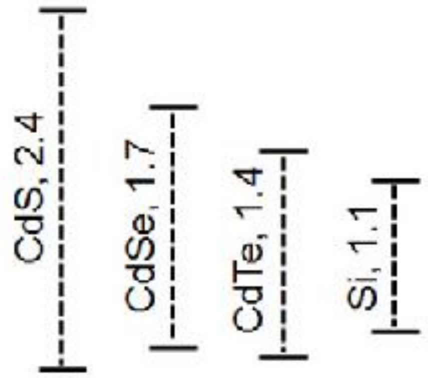


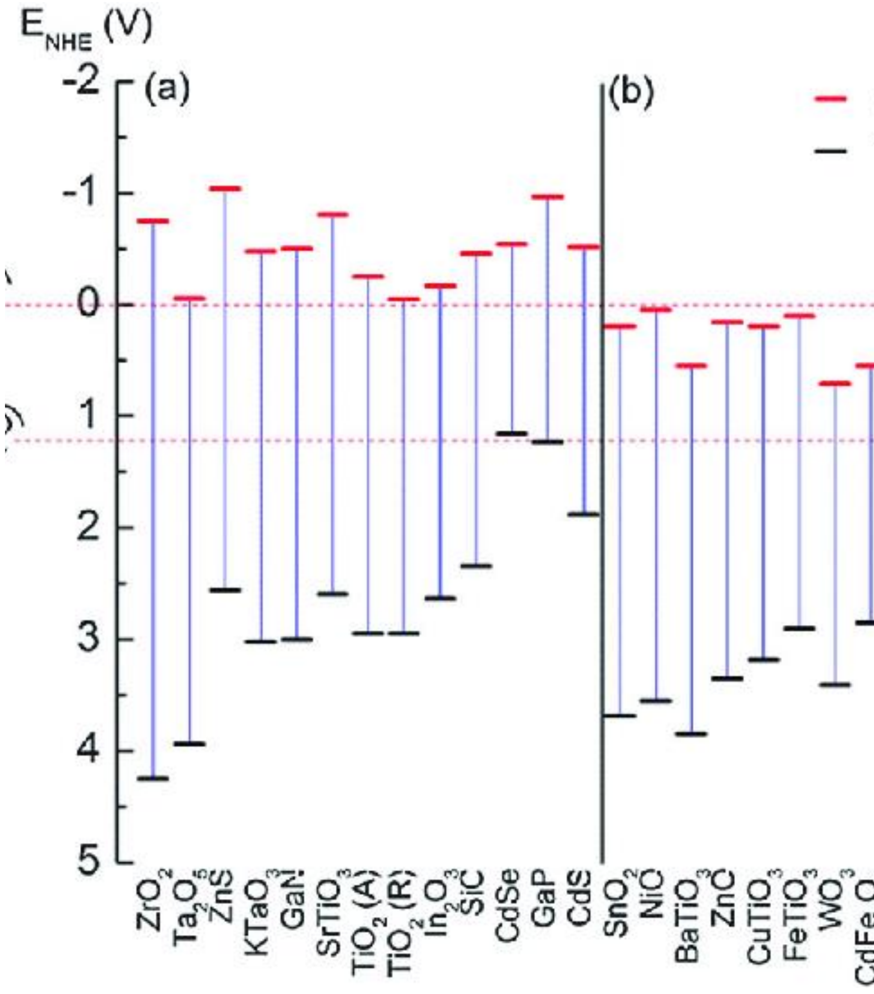
správně



Méně správně


E (V)
+4.0
-2.0
H2O, 1.
pH = 7
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
Potential
[V vs. NHE]
CB
CB
CB
VB
VB
VB
3.2 eV
390 nm
2.6 eV
480 nm
2.1 eV
590 nm
TiO2
WO3
Fe2O3


CdS, 2.4
CdSe, 1.7
CdTe, 1.4
Si, 1.1


ENHE (V)
(a)
(b)
-2
-1
0
1
2
3
4
5
ZrO2
Ta2O5
ZnS
KTaO3
GaN
SrTiO3
TiO2 (A)
TiO2 (R)
In2O3
SiC
CdSe
GaP
CdS
SnO2
NiO
BaTiO3
ZnO
CuTiO3
FeTiO3
WO3