Standard method for testing photocatalytic materials for water treatment

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Photo-Catalytic Processes & Environmental Analysis,

INN, NCSR "DEMOKRITOS"

EUROPEAN STANDARD | EN 17120

NORME EUROPÉENNE

EUROPÄISCHE NORM | February 2019

ICS 25.220.20

English Version

Photocatalysis - Water purification - Performance of photocatalytic materials by measurement of phenol degradation

Training School "AOPs for water T&O"

5-9 Sep 2022, Athens, Greece

Photocatalytic materials

Applications:

Self-cleaning surfaces, air purification / sterilization and water treatment

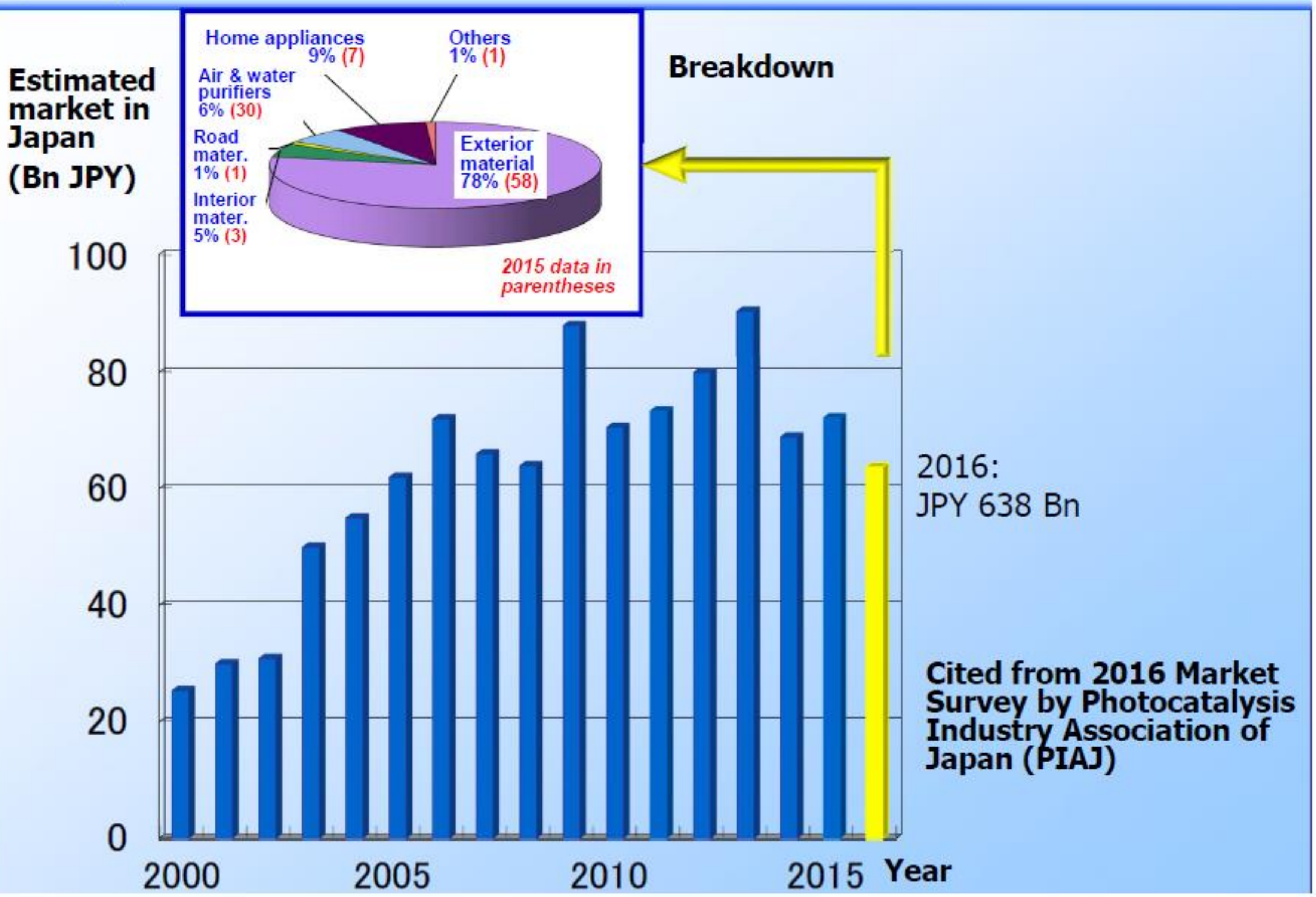
Advantages:

- **No use of chemicals (regeneration of catalyst)**
- **Low energy consumption using LED light sources or sensitized materials in visible or solar light**

Global market:

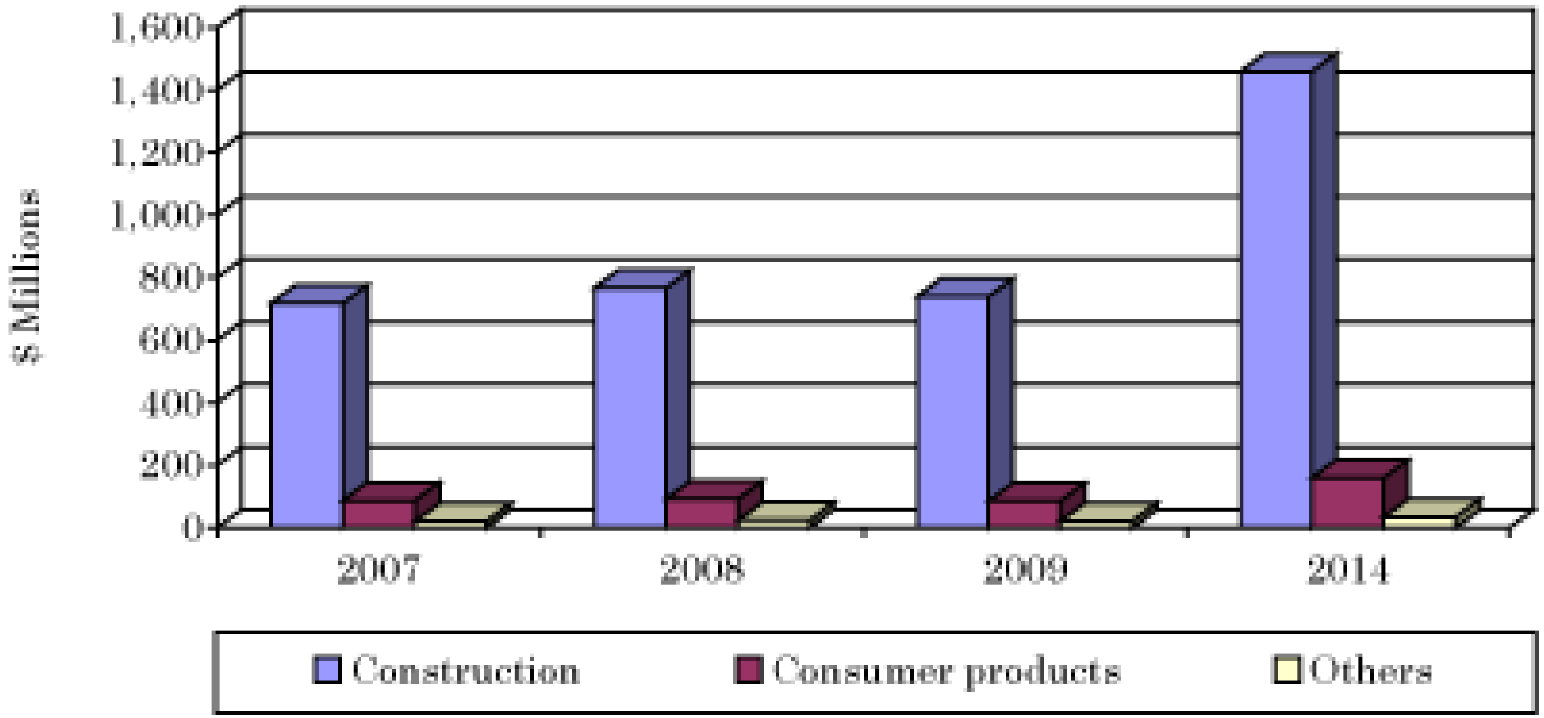
- **It is expected to exceed the 1.5 billion $ with an annual growth rate grater than 14% during the last 5 years**
- **Photocatalytic products market includes construction materials and surfaces as well as water treatment applications**

Estimated Photocatalyst Market in Japan



Cited from 2016 Market Survey by Photocatalysis Industry Association of Japan (PIAJ)

SUMMARY FIGURE
GLOBAL MARKET FOR PHOTOCATALYST PRODUCTS
2007–2014
($ MILLIONS)



Source: BCC Researc

Photocatalysis – Water Purification
Need for a standard method

A large number of photocatalytic materials enter in the global market

and

There is a lack of an appropriate standard method for assessing the performance of photocatalytic materials

→

The development of a standard test method is needed in order to asses the photocatalytic activity of materials and enable comparisons between them

Photocatalysis – Water Purification
Groups needed standards

Research Organizations – Academia	*Development of photocatalysts*
Industry (1)	*Production of photocatalytic materials, sales*
Industry (2)	*Manufacturing of water treatment equipment (large scale, small scale)*
Water utilities	*Treatment of drinking water, waste water*
Health organizations	*Safety of treated water*
Consumers – citizens	*Safety of treated water*

Probably at present researchers and producers of materials are the most important stakeholders, because of small number of applications in water treatment.

Photocatalysis – Water Purification
What standards are needed?

- **A standard procedure for assessing the photocatalytic activity of materials with regards to water purification**
- ***Assessment of the catalyst (material) – not of the process.***
- **Is this covered by ISO TC 106 and ISO 19722 standards?**
  - ISO 10676:2010 Fine ceramics (advanced ceramics, advanced technical ceramics) Test method for water purification performance of semiconducting photocatalytic materials by measurement of forming ability of active oxygen.
  - ISO 10678:2010 “Fine ceramics (advanced ceramics, advanced technical ceramics) Determination of photocatalytic activity of surfaces in an aqueous medium by degradation of methylene blue.
  - ISO 19722:2017 “Fine ceramics (advanced ceramics, advanced technical ceramics) — Test method for determination of photocatalytic activity on semiconducting photocatalytic materials by dissolved oxygen consumption”

Development of standards

European Committee for Standardization
Comité Européen de Normalisation
Europäisches Komitee für Normung

CEN/TC 386 "Photocatalysis" - WG3 : "Water Purification"

Convener of WG3: Dr. Anastasia Hiskia, NCSR "Demokritos"

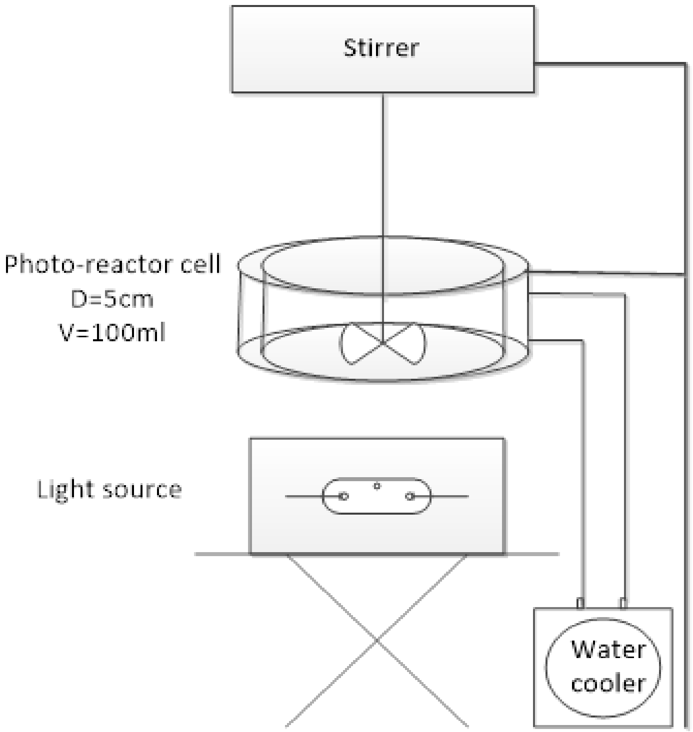
Development of a standard procedure for assessing the photocatalytic activity of materials with regards to water purification

The standard should:

- Consider but not duplicate ISO standards.
- Consider all stakeholders' needs.
- Be conceptually valid, reproducible, suitable for accreditation, add value to stakeholders.
- Consider all parameters that affect test results, i.e. nature of catalyst, type of test (batch-continuous flow), light sources, geometry, type of water, substrate compounds, pH, oxygen, agitation, expression of results.
- Be in line with TC386-WGs, e.g. WG1 "Terminology", WG6 "Light Sources".

Test method description

- The irradiation source must yield an average irradiance of (10±5%) W/m^2, according to CEN/TS 16599
- No significant degradation of phenol takes place (<5% degradation) over the time of the test due to direct photolysis.
- High Performance Liquid Chromatography system with UV detection (e.g. 270-280 nm) suitable for the quantitative determination of phenol in water.
- Total Organic Carbon analyser capable for determinations of TOC/DOC in water (optional).
- Plots of phenol concentration (C) vs time, under irradiation, under dark, and under irradiation in the absence of the test material.
- Observed rate constant (k) can be calculated from a graphical plot of ln(C) vs time, assuming first-order kinetics
- The test is carried out also with a reference material and the ratio of the rate constants ($k_{sample}/k_{reference}$) is reported



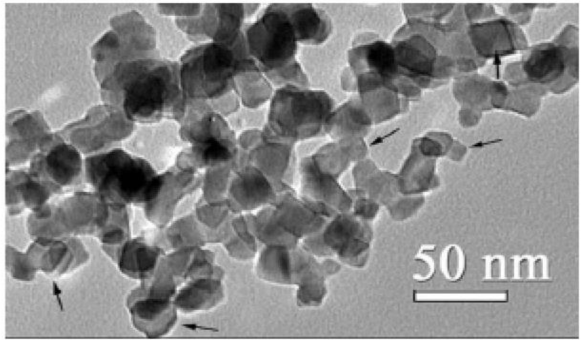
NIST reference TiO_2 material

National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 1898

Titanium Dioxide Nanomaterial



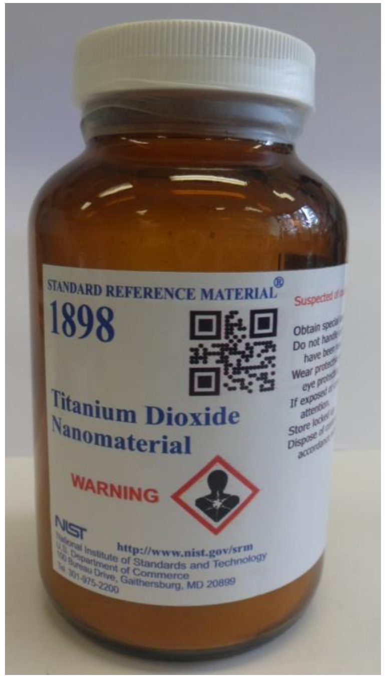


Table 1. Certified Values for BET Specific Surface Area

Measurement Technique	Specific Surface Area Value[a] (m^2/g)
MP	55.55 ± 0.70
SP	53.85 ± 0.78

Table 2. Information Values for Relative Phase Fractions Determined by Rietveld Refinement of Two-Phase Mixture

Phase	Relative Fraction[a]
Anatase	0.76 ± 0.03
Rutile	0.24 ± 0.03

Table 3. Information Values for Average Volume-Weighted Crystallite Size Based on Analysis of Multiple Reflections[a,b]

Phase	Size (nm)
Anatase	19 ± 2
Rutile	37 ± 6

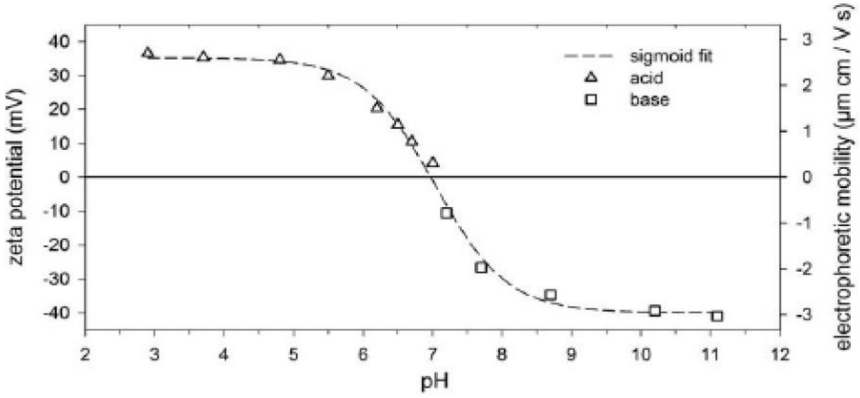
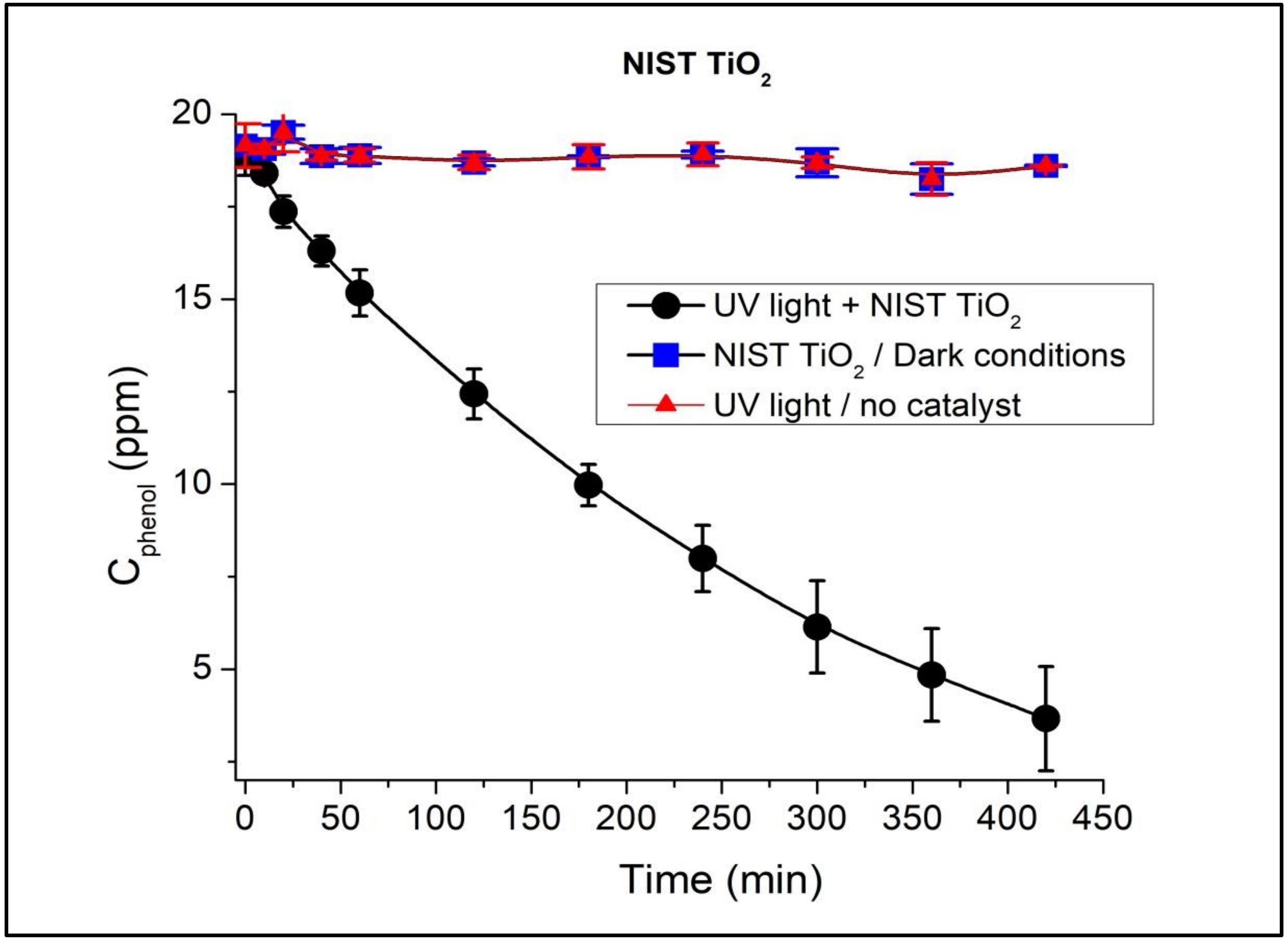


Figure 3. Acid-to-basic (Δ) and basic-to-acid (□) titrations of SRM 1898 suspensions. The five-parameter sigmoidal fit yields an isoelectric point at pH 7.0.

Phenol photodegradation with NIST reference TiO_2 material



Experimental conditions

- C_{phenol}= 20 ppm
- C_{TiO2} = 0.5 g L^{-1}
- Suspension volume: 100 ml
- Light irradiance: 10 W/m^2
- Stirring for 30 min before irradiation
- air saturation

Photocatalysts tested

CRISTALACTiV

PC500

PRODUCT DATA SHEET

CRISTAL

Typical Properties: This information does not constitute a specification. Product Specifications are available on request.

- Crystal form: anatase
- TiO_2 content: ~ 85 wt%
- Surface area: ~ 350 m^2/g

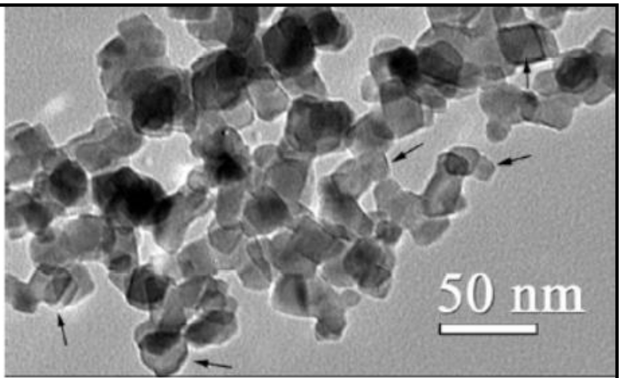
	CristalACTiV™ PC-105	CristalACTiV™ PC-500	CristalACTiV™ S5-300A	CristalACTiV™ S5-300B	CristalACTiV™ PC-S7
Crystallographic Structure	Anatase	Anatase	Anatase	Anatase	Anatase
TiO_2 Content (wt%)	~ 95	~ 85	~ 20	~ 18	~ 10
Surface Area (m^2/g, by 5-point BET)	~ 90	~ 350	~ 330	~ 330	~ 300
pH			~ 1.0	~ 11.0	~ 8.5
Density			~ 1.2	~ 1.1	~ 1.1

National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 1898

Titanium Dioxide Nanomaterial



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Round robin test protocol

CEN TC 386 WG 3 Round Robin " Photocatalysis — Water purification — Performance of photocatalytic materials by measurement of phenol degradation"										
Phenol stock solution concentration:	**1,0 g/L**									
Initial phenol concentration, Co:	**20 mg/L**									
Photocatalyst concentration:	**0,5 g/L**									
Volume of reactor :	**100 ml**									
Actions:										
Enter or edit values (min, pH, mg/L)		Check 1	Check 2	Check 3	Sample test	Sample test	Sample test	Sample test	Sample test	Sample test
Enter or edit values for TOC (Optional)		No photocatalyst	Dark experiment	Dark experiment	Day 1	Day 1	Day 2	Day 2	Day 3	Day 3
Informative	**Material:**	No	NIST SRM 1898	Cristal	NIST SRM 1898	Cristal	NIST SRM 1898	Cristal	NIST SRM 1898	Cristal
Informative	**pHi=**									
Start irradiation	**C_A (mg/L)=**									
	TOC_A (mg/L)=									
		Start irradiation	**No irradiation**	**No irradiation**	**Start irradiation**	**Start irradiation**	**Start irradiation**	**Start irradiation**	**Start irradiation**	**Start irradiation**
	Time (min)	**C_{phenol} (mg/L)**	**C_{phenol} (mg/L)**	**C_{phenol} (mg/L)**	**C_{phenol} (mg/L)**	**C_{phenol} (mg/L)**	**C_{phenol} (mg/L)**	**C_{phenol} (mg/L)**	**C_{phenol} (mg/L)**	**C_{phenol} (mg/L)**
Irradiation times are indicative (you can change), but use the same irradiation times in all test series.	10									
	20									
	40									
	60									
	120									
	180									
	240									
	300									
	360									
	420									
	pH_f=									
	Time (min)	**TOC (mg/L)**	**TOC (mg/L)**	**TOC (mg/L)**	**TOC (mg/L)**	**TOC (mg/L)**	**TOC (mg/L)**	**TOC (mg/L)**	**TOC (mg/L)**	**TOC (mg/L)**
	10									
	20									

- Two materials tested (NIST SRM 1898 and Cristal Activ PC 500)
- Three replicates in three different days for each material (within-lab reproducibility)
- Dark experiments and experiment with no catalyst

Results : NIST SRM 1898

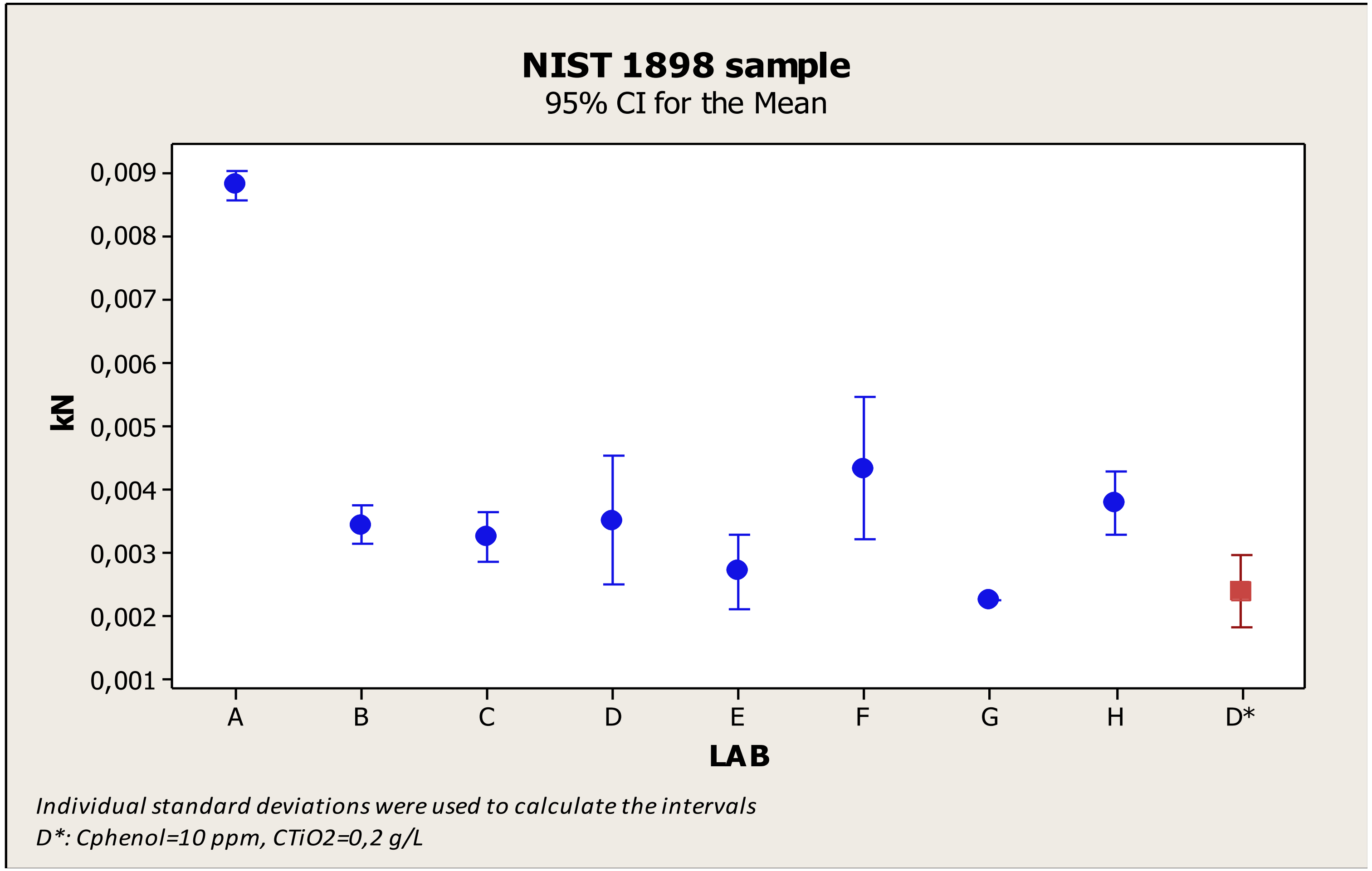

Table 1: Observed rate constants for the NIST 1898 sample (units: min^{-1})

Day	Lab A	Lab B	Lab C	Lab D	Lab E	Lab F*	Lab G*	Lab H	Lab D*
1	0,00886	0,00340	0,00307	0,00305	0,00271	0,00451	ND	0,0038	0,00214
2	0,00871	0,00333	0,00330	0,00380	0,00294	0,00468	0.00423	0,004	0,00252
3	0,00887	0,00357	0,00338	0,00370	0,00246	0,00382	ND	0,0036	0,00255
Mean k_N	**0,00881**	**0,00343**	**0,00325**	**0,00352**	**0,00270**	**0,00434**	**0.00423**	**0,00380**	**0,00240**
RSD%	**1,0**	**3,6**	**5,0**	**11,0**	**8,8**	**10,6**	**ND**	**5,3**	**9,6**

Results: Cristal Aktiv PC500

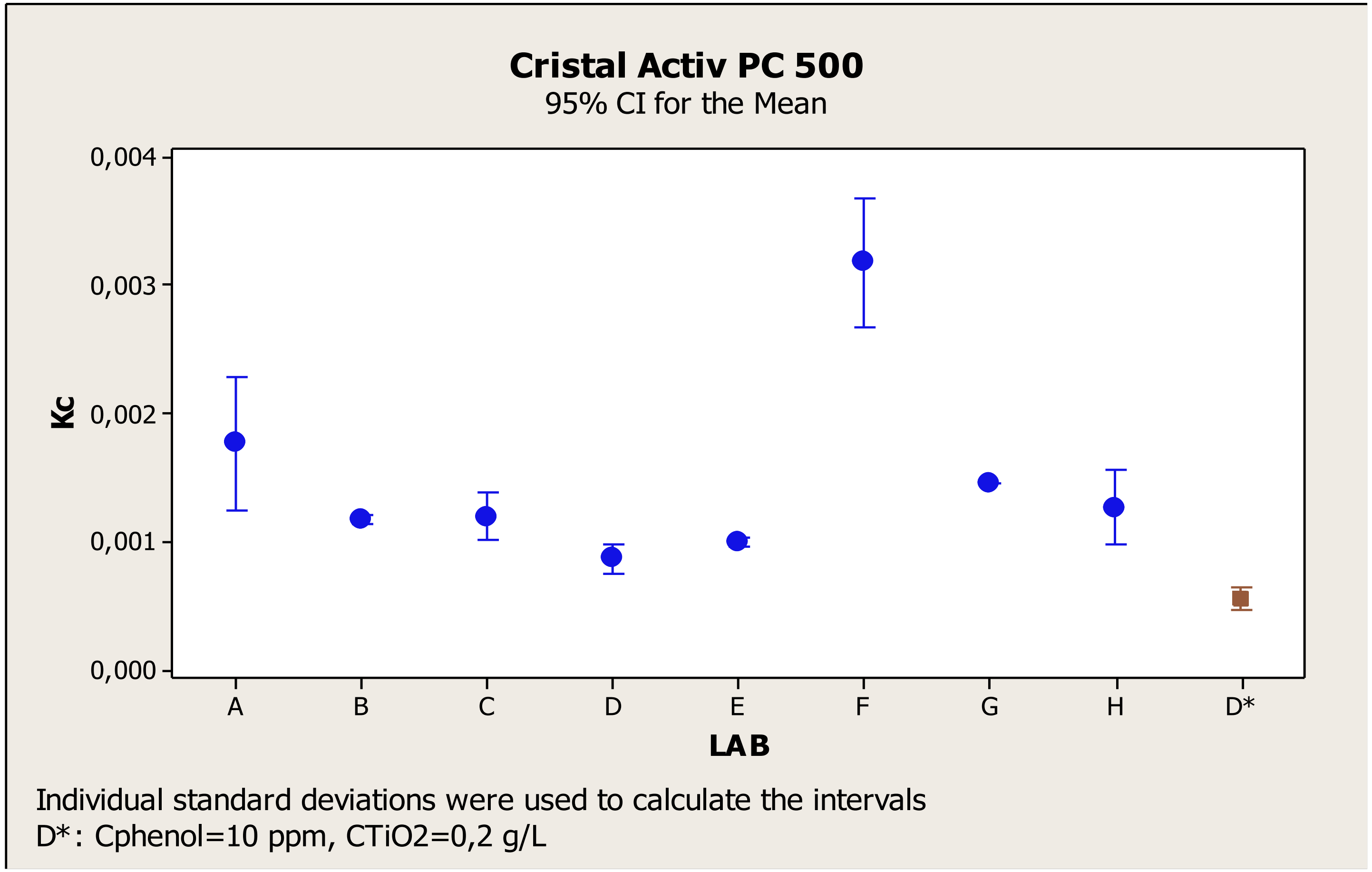

Table 2: Observed rate constants for the Cristal Activ PC 500 sample (units: min^{-1})

Day	Lab A	Lab B	Lab C	Lab D	Lab E	Lab F*	Lab G*	Lab H	Lab D*
1	0,00184	0,00118	0,00127	0,00090	0,00098	0,00299	ND	0,00120	0,0005397
2	0,00193	0,00116	0,00112	0,00081	0,00100	0,00314	0,00145	0,00120	0,0005235
3	0,00153	0,00119	0,00119	0,00088	0,00098	0,00340	ND	0,00140	0,0005925
Mean k_c	**0,00177**	**0,00118**	**0,00119**	**0,00086**	**0,00099**	**0,00318**	**0,00145**	**0,00127**	**0,00055**
RSD%	**11,8**	**1,1**	**6,3**	**5,3**	**1,4**	**6,4**	**ND**	**9,1**	**6,5**

Results : k_C/k_N

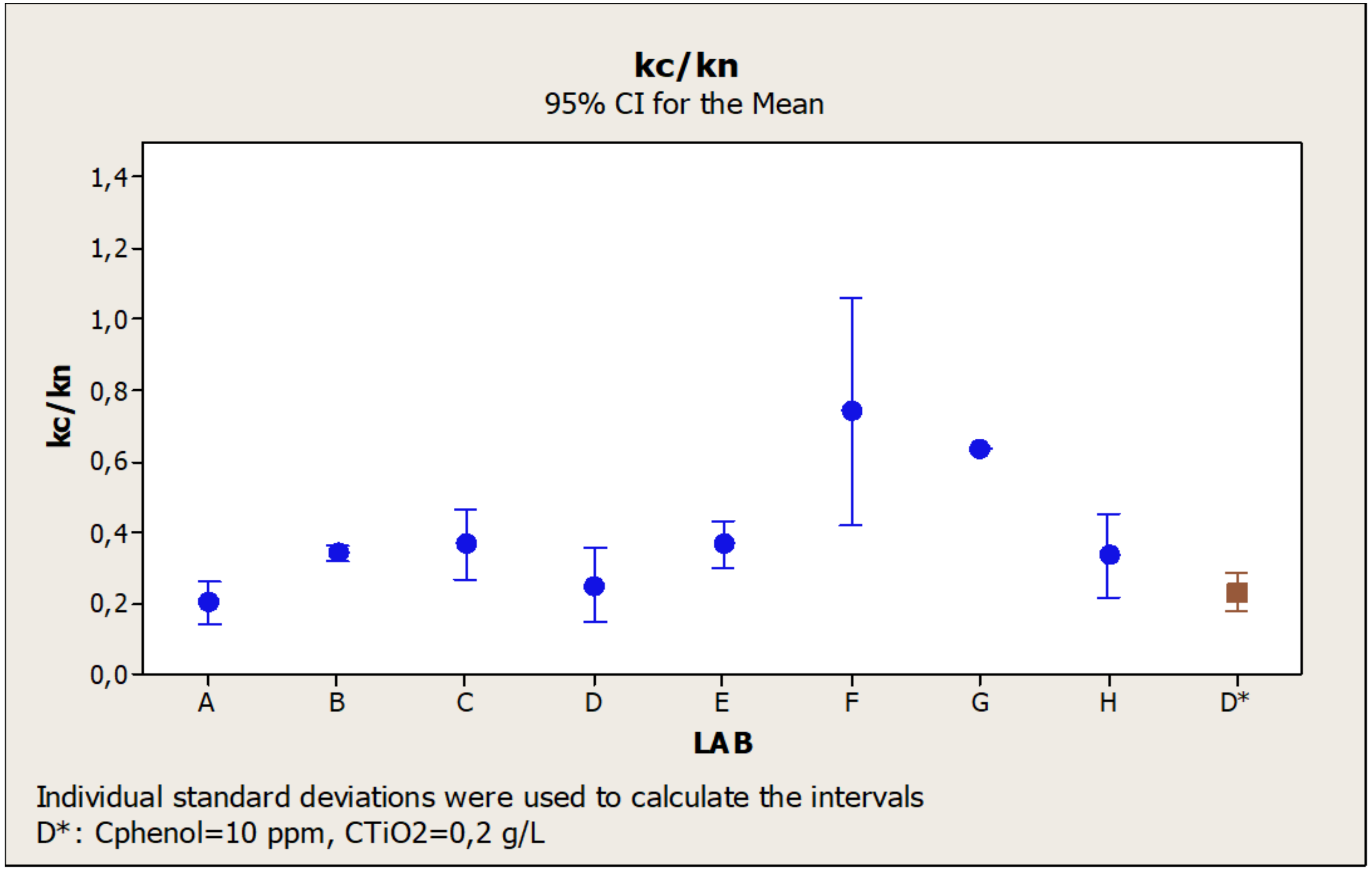

Table 3: Rate constants ratios (k_C/k_N)									
Day	Lab A	Lab B	Lab C	Lab D	Lab E	Lab F*	Lab G*	Lab H	Lab D*
1	0,208	0,347	0,413	0,296	0,362	0,664	ND	0,316	0,253
2	0,222	0,349	0,338	0,214	0,341	0,671	0,342	0,300	0,208
3	0,173	0,332	0,353	0,237	0,396	0,890	ND	0,389	0,233
Mean k_C/k_N	**0,201**	**0,343**	**0,368**	**0,249**	**0,366**	**0,742**	**0,342**	**0,335**	**0,231**
RSD%	**12,5**	**2,6**	**10,8**	**17,0**	**7,5**	**17,3**	**ND**	**14,2**	**9,7**

Conclusions

- All blank tests (with no photocatalyst or with no irradiation) gave no significant degradation meaning that the method doesn't give false positive results, e.g. due to direct photolysis or thermal reactions of phenol.
- All degradation tests (44 tests by 8 laboratories) with the two photocatalytic materials gave observable degradation rates with $k > 0$, i.e. the method did not produce any false negative results.
- In all degradation tests (44 tests by 8 laboratories) ratios $k_C/k_N < 1$ were determined. The method systematically showed that the one sample (NIST 1898) had higher photocatalytic performance than the other (Cristal PC500), indicating its potential for evaluation of photocatalytic materials.
- Within each laboratory the method produced reproducible results (RSD <20%). Between participating laboratories the range of reported k values was wider, indicating differences in experimental setup as a possible cause.
- The ratios k_C/k_N seem to have a normalizing effect on those differences, as shown from the good agreement of results of all labs. This means that the ratios k_C/k_N (c: Cristal; sample and N: NIST; reference) can be the most appropriate measure for the evaluation of photocatalytic materials

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 17120

February 2019

ICS 25.220.20

English Version

Photocatalysis - Water purification - Performance of photocatalytic materials by measurement of phenol degradation

Photocatalyse – Purification de l'eau - Évaluation des performances des matériaux photocatalytiques par mesurage de la dégradation du phénol

Photokatalyse - Wasserreinigung - Leistungsbewertung von photokatalytischen Werkstoffen durch Messung des Phenolabbaus

This European Standard was approved by CEN on 19 November 2018.

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This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the CEN–CENELEC Management Centre has the same status as the official versions.

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1 Scope

This document describes a test method to evaluate the performance of photocatalytic materials in water purification by measuring phenol degradation. This test method is applicable to photocatalytic materials in form of powders (suspensions in water, slurries) under UV irradiation. The photocatalytic performance of the tested material is assessed by the observed rate of phenol degradation at specified experimental conditions as determined by HPLC.

Material for study

The European Committee for Standardization (CEN) published standard entitled: *"EN 17120:2019. Photocatalysis - Water purification - Performance of photocatalytic materials by measurement of phenol degradation"*.

Development of EN 17120:2019 standard was carried out by CEN TC 386 "Photocatalysis", Working Group 3 "Water treatment", convened by Dr. Anastasia Hiskia with collaboration of Dr. Triantafyllos Kaloudis and Dr. Theodoros Triantis of INN-NCSR Demokritos.

Thank you for your attendance!!!