

AUTOPROTECT WEBINAR SERIES

*Get your surfaces  
self-protected!*



*Closing webinar #6*



## **Wrap-Up AutoProtect – 8.12.2022**

Webinar Serie of the AutoProtect Project

Hosted by  **plasmatreat**

# Past Webinars



AUTOPROTECT WEBINAR SERIES

impact of  
**SURFACE HYGIENE**  
on transmission of infections



*Webinar #1*



AUTOPROTECT WEBINAR SERIES

**REGULATORY  
REQUIREMENTS**  
for antimicrobial surfaces



*Webinar #2*



AUTOPROTECT WEBINAR SERIES

**ANTIMICROBIAL  
COATINGS**  
new technical approaches



*Webinar #3*



AUTOPROTECT WEBINAR SERIES

Innovative Solutions for  
Hygiene and Cleanliness



*Webinar #4*



AUTOPROTECT WEBINAR SERIES

Characterization and  
validation of **cleanliness**



*Webinar #5*





## Introduction & Tips regarding GoToWebinar

Hosted by  **plasmatreat**



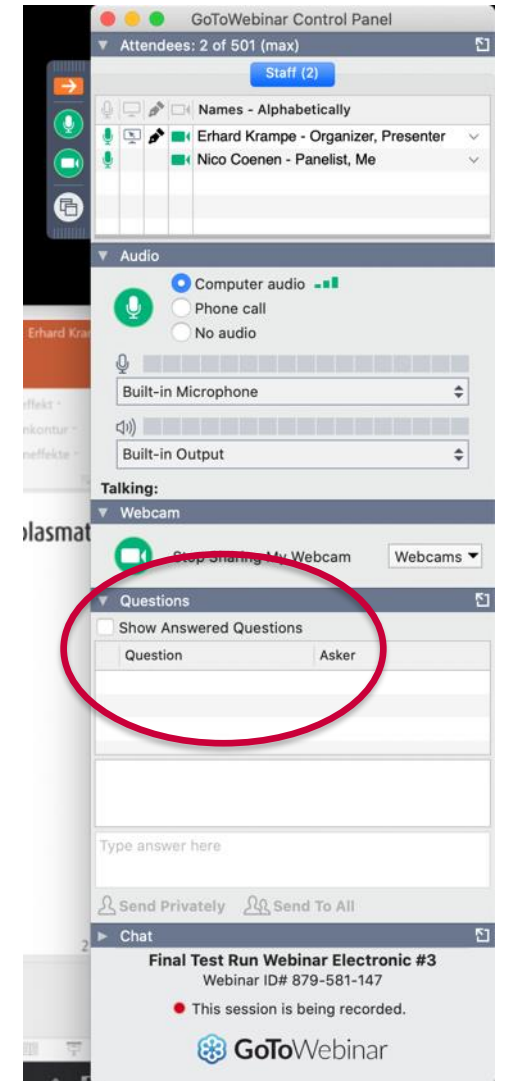
# Webinar Procedure

## General information

- Duration approx. 150 minutes incl. Q&A
- PDF of presentations will be available

## How to ask your questions

- Your questions during the lecture: Please use the "Questions" module of GoToWebinar
- Questions will be recorded & are only visible to the moderator
- Questions are answered anonymously





# Webinar - Organisation



**Dr. Markus Wehrl**  
Head of Department Hygiene  
and Microbiology

**DGKH e.V, wfk**  
Moderator & Presenter



**Paul Simons**  
Manager Innovation &  
Technology

**TSG Group**  
Moderator



**Erhard Krampe**  
BDM medical technology &  
Head of Plasmatrix Academy

**Plasmatrix GmbH**  
Host & Moderator

Please keep informed about future activities:

<https://auto-protect.org>



### AutoProtect - Interreg V A

AutoProtect is an Interreg V A cross-border project between Dutch and German partners in which new surface coatings are developed that provide sustainable self-protective properties with regard to microbial and chemical cleanliness. The Partners work closely together to join forces in R&D to develop catalytically active multi-stimulus-systems that inactivate microorganisms and that break down chemical contaminations on coated surfaces using the combined effectiveness of photo-, piezo- and pyro-catalytically active materials that can be activated and/or reactivated by various sources of excitation energy. Another R&D focus is on the development of highly sensitive detection methods to monitor surfaces for the absence of microorganisms and chemical contaminations urgently needed by medtech and pharma companies.

# Get your Surface self-protected! – Agenda Wrap-Up Webinar



Dr. Markus Wehrl – Introduction to AutoProtect

Dr. habil Ludger Schnieder, *SMP GmbH, DE* - Quantitative and qualitative detection of soilings

Dr. Stefan van den Eijnde, *Innobus, NL* - Functional surfaces are non-superficial

Guus Ploeger, *Militex, NL* - Solutions & Surface

Dr. Dhia Ben Salem, *Plasmatreat GmbH, DE* - Atmospheric pressure plasma treatment and thin film deposition for antimicrobial application

- Technical break -

Robert Beckers, *Vero Metal Holding B.V., NL* - MSS-Coatings: Features and Applications

Dr. Joachim Meeßen, *wfk-Cleaning Technology Institute e.V.* - Deep into MSS-Coatings: Mechanisms and efficacy

Dr. Cyriel Mentink, *CHILL, NL* - Towards light responsive coatings against biofilm formation

- Panel Discussion -



# Webinar Presenter



Quantitative and qualitative  
detection of soilings  
Dr. Ludger Schnieder  
SMP GmbH (Germany)

# Quantitative and qualitative detection of soilings

by Vacuum Induced Desorption Mass Spectrometry

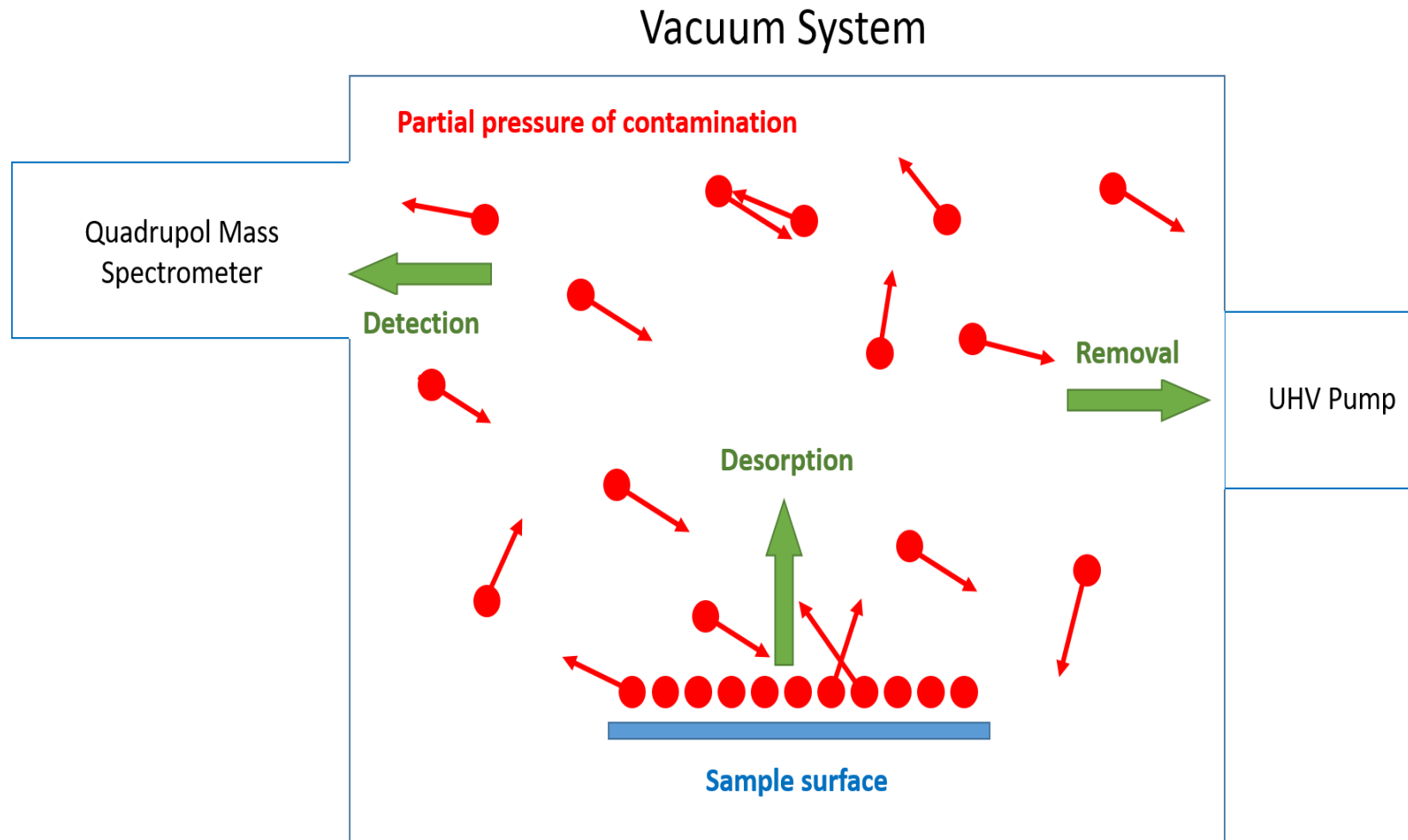
Dr. Ludger Schnieder

SMP GmbH Prüfen Validieren Forschen; 72072 Tübingen; Germany

Funded by:  
No. 144131

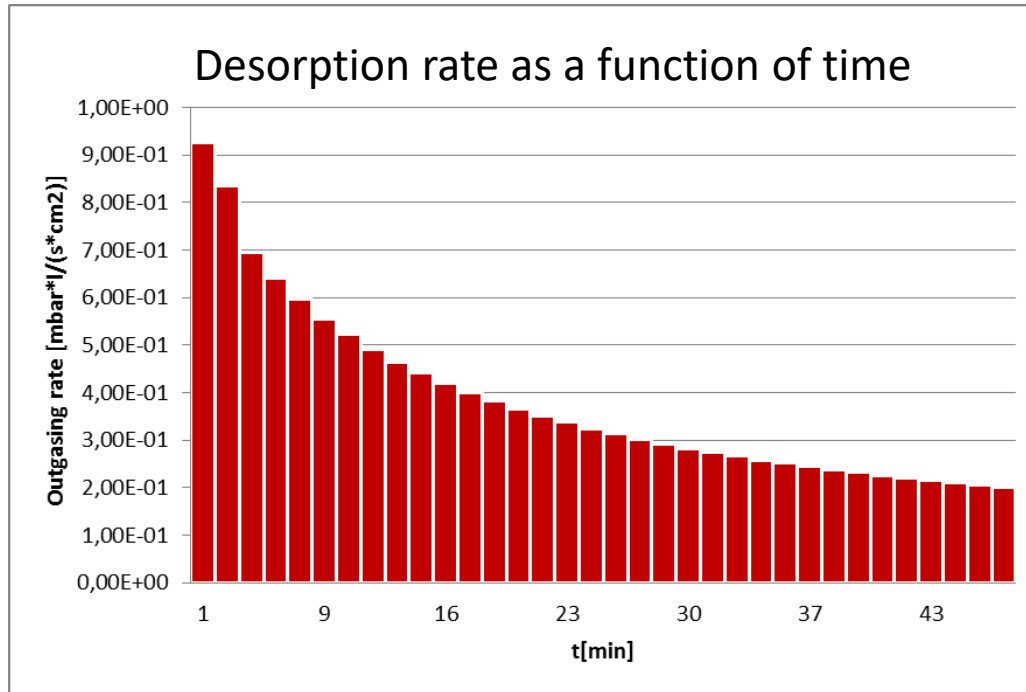


# Detection of Soilings – Vacuum-induced-Desorption Analysis





# Interpretation / Evaluation



## Desorption rate $Q(t)$

Residual contamination on the surface =  $\int Q(t)dt$

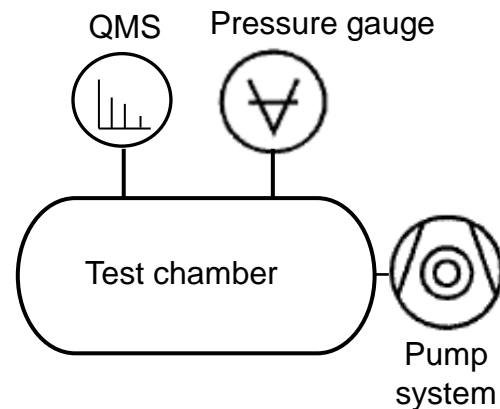
Each column shown represents the result of a complete mass spectrum ( $m/z = 1-200$ )

- Allows for non-destructive evaluation without prior preparation of the samples
- Allows for evaluation of any geometry of single samples as well as complete modules or production lots

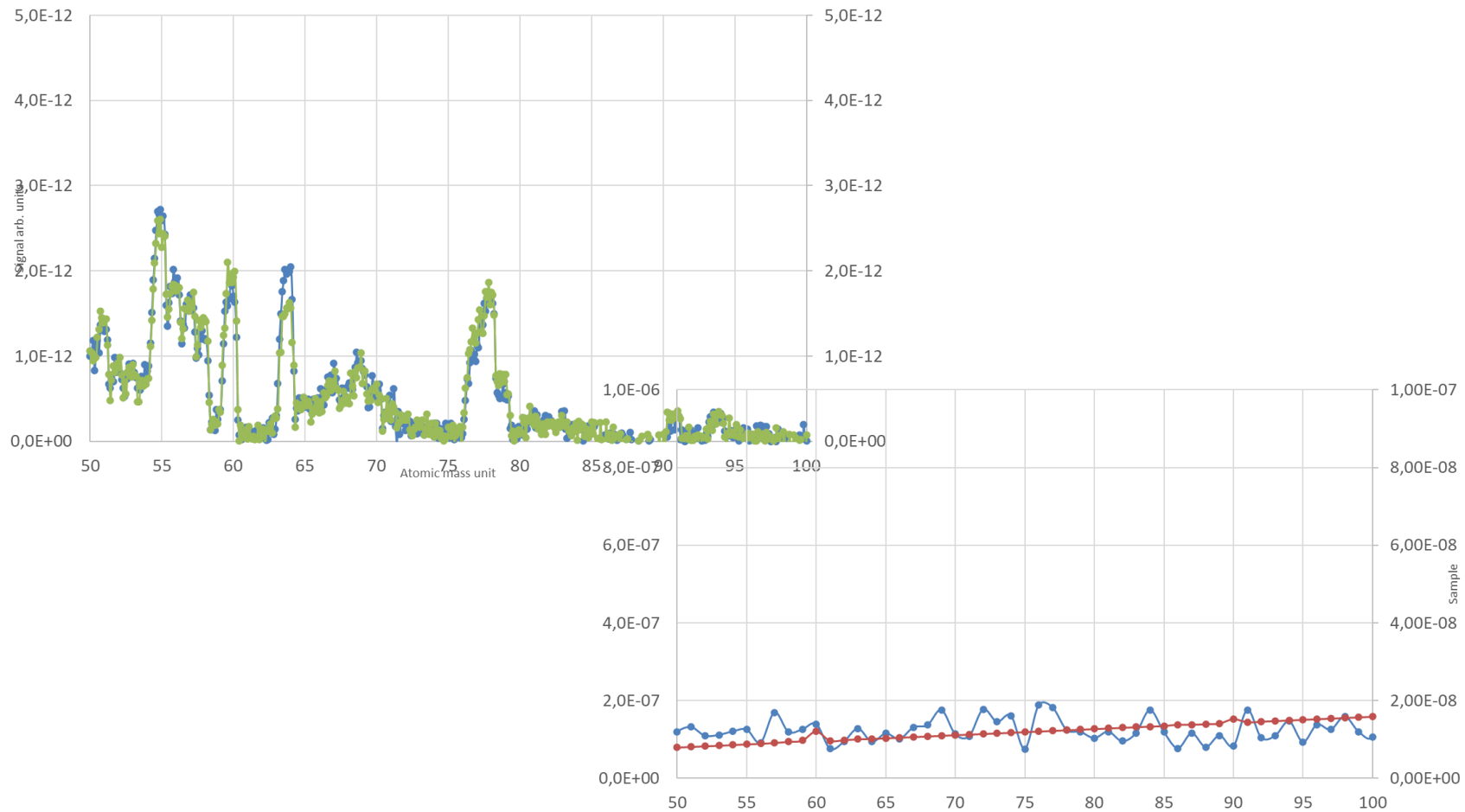
VIDAM



- VIDAM = Vacuum-induced desorption-analysis measurement system  
= Vacuum-induced mass-spectrometry
- Developed by VACOM Systems

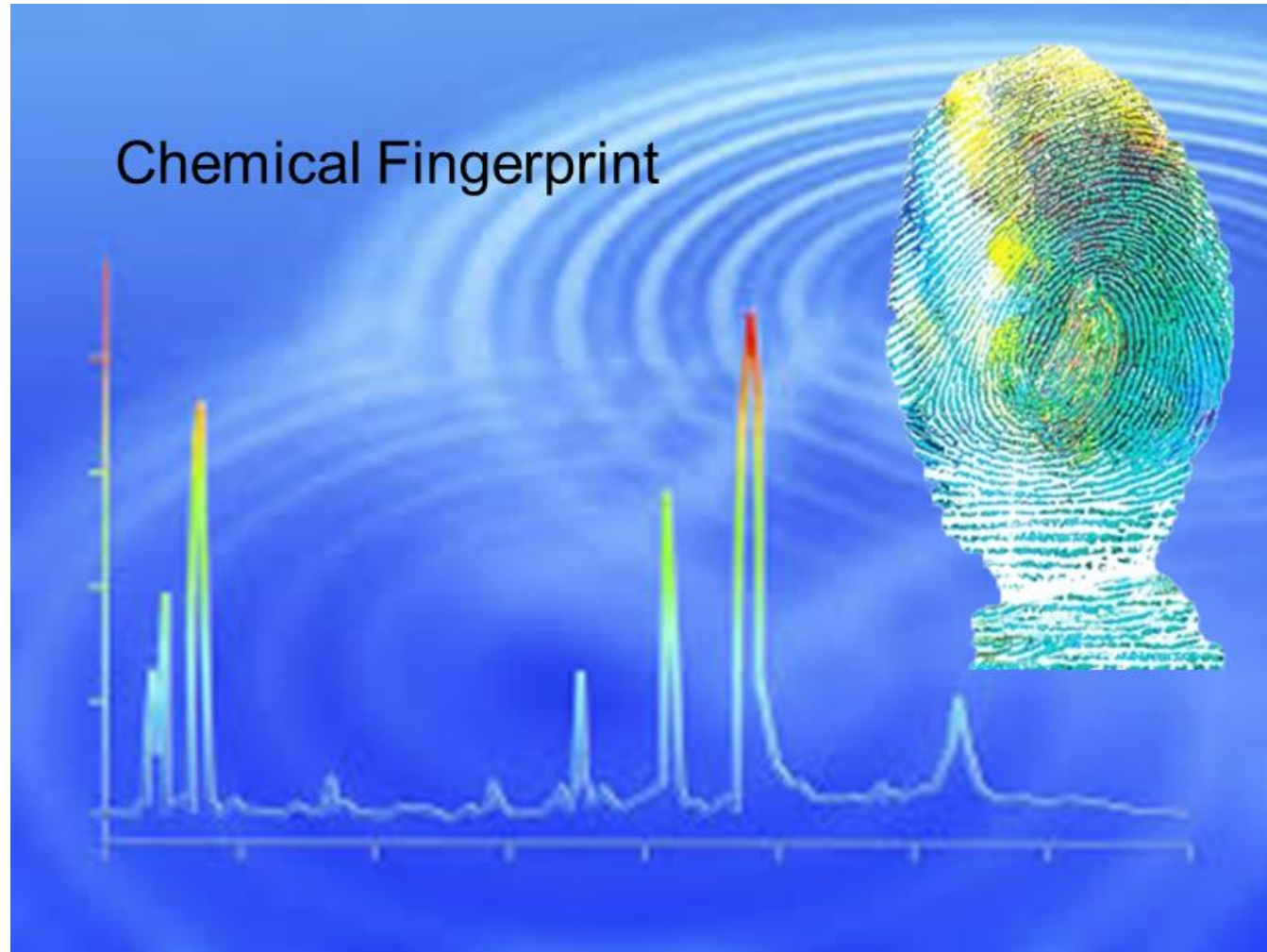


# Compensation for Background

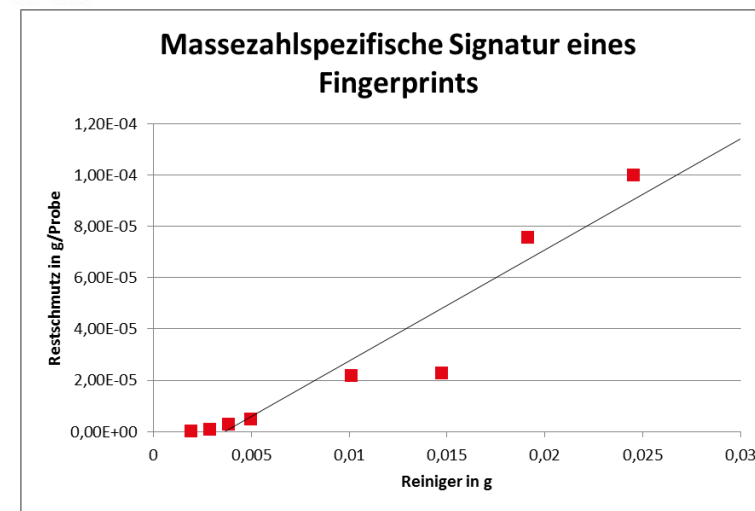
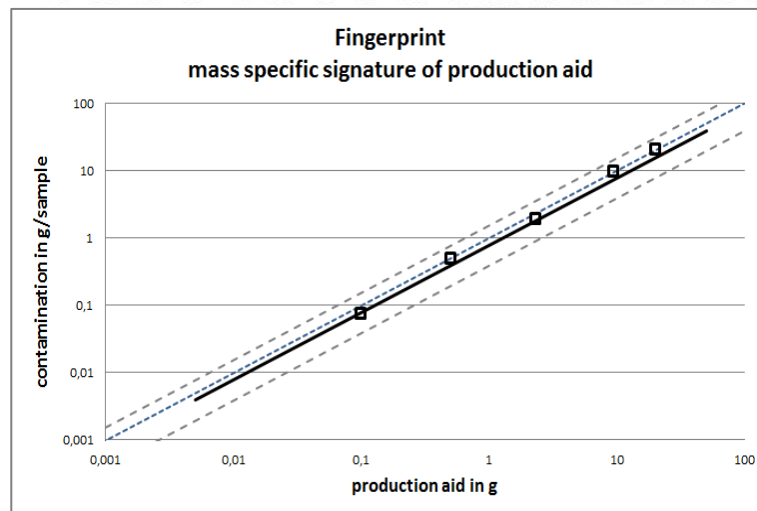
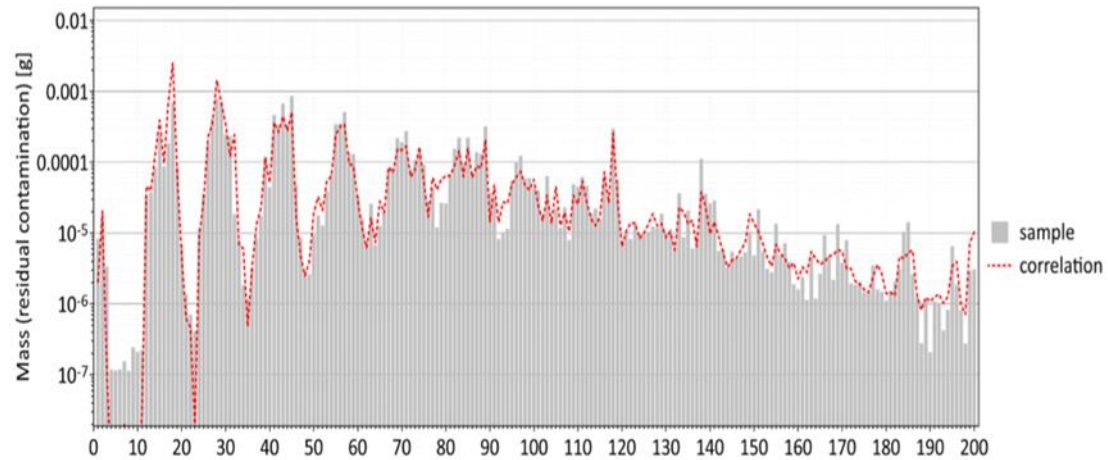




# Identification of unknown substances



# Quantitative Detection of Soiling



# Reprocessing of Implants

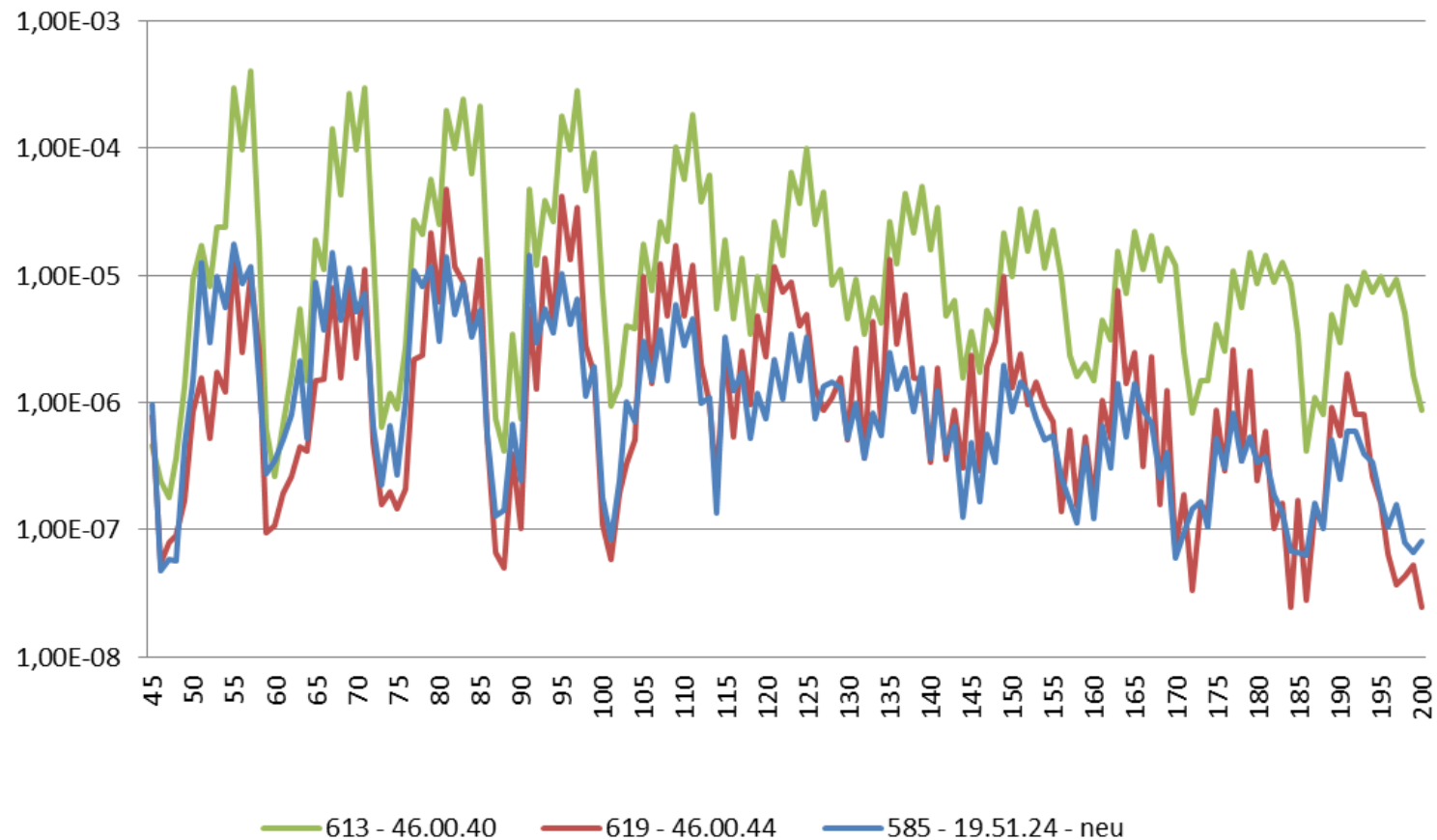


Timepoint	Titanium ( $\mu\text{g}$ )	Stainless Steel ( $\mu\text{g}$ )
Post Manufacturing	4.1	744
Simulated Passivation	N/A	48
1 Processing Cycle	3.7	3.8
50 Reprocessing Cycles	1.9	1.1
Acceptance Criteria	500	500

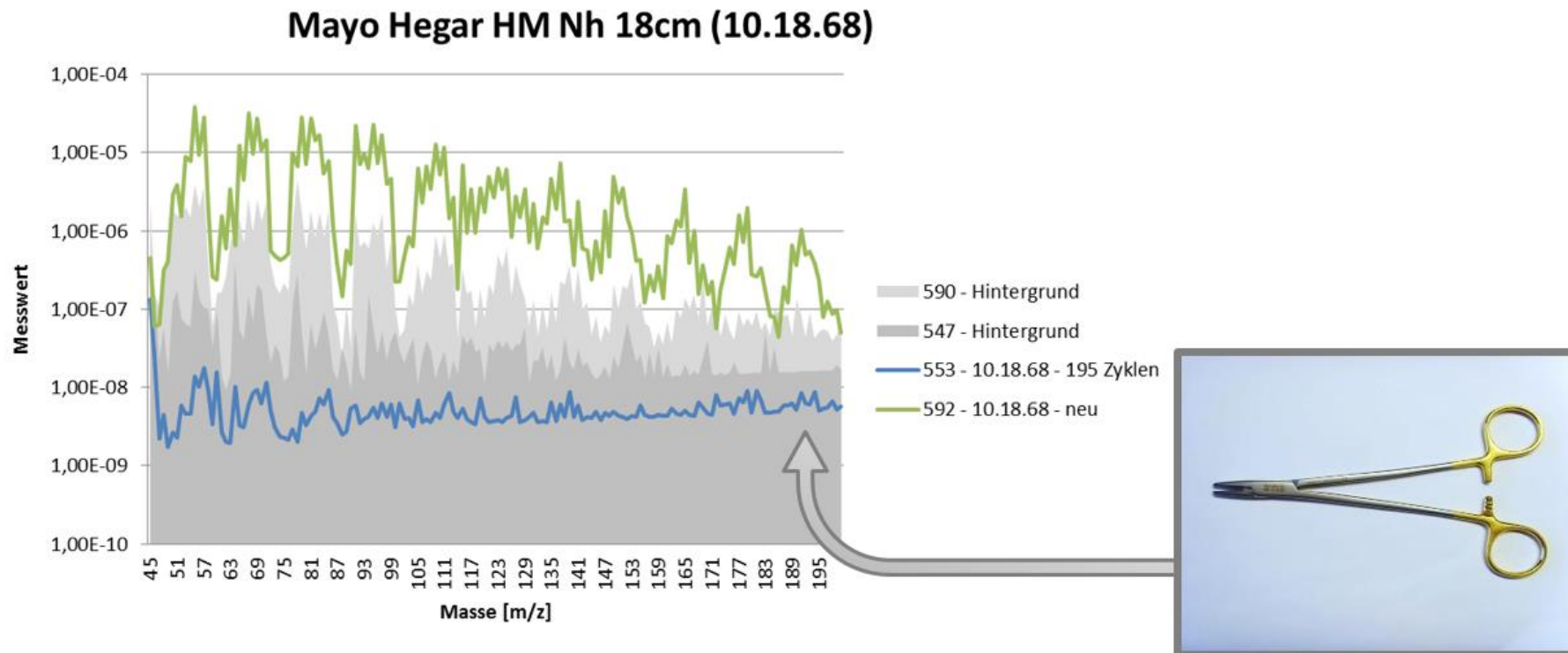
# Reprocessing of surgical devices

## 200 cycles of reprocessing

References: green and red

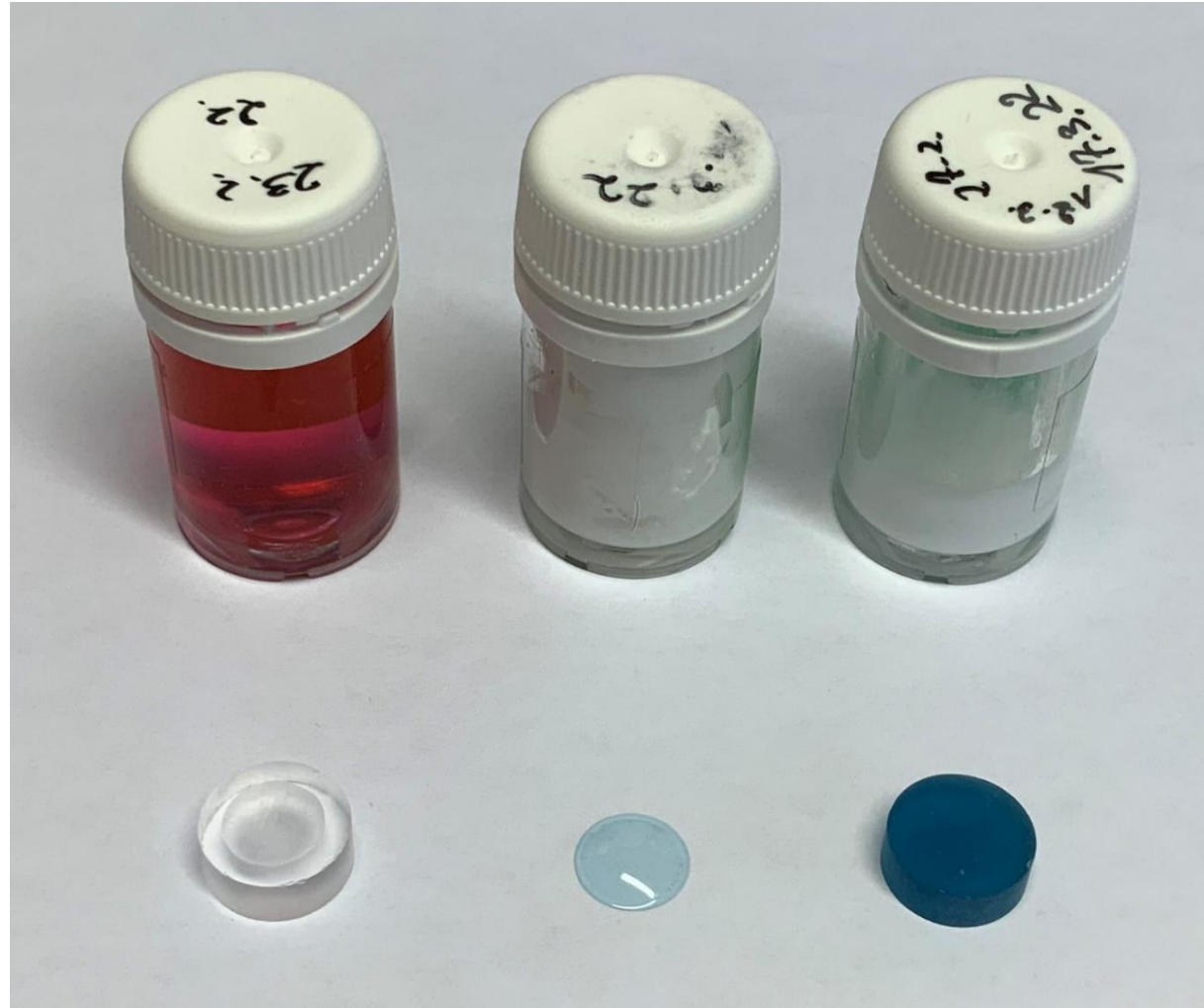


# Reprocessing of surgical devices



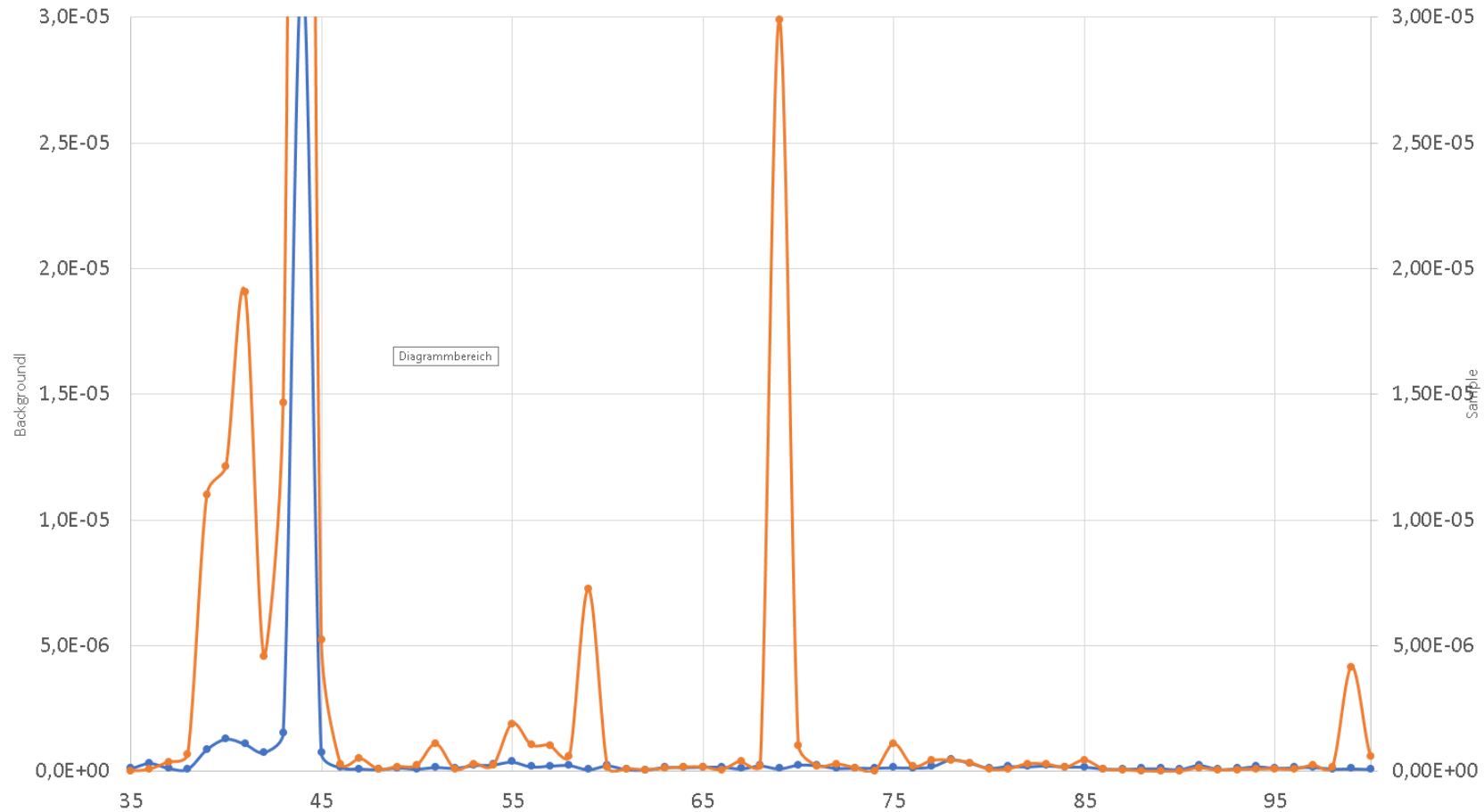


# Manufacturing of Contact Lenses

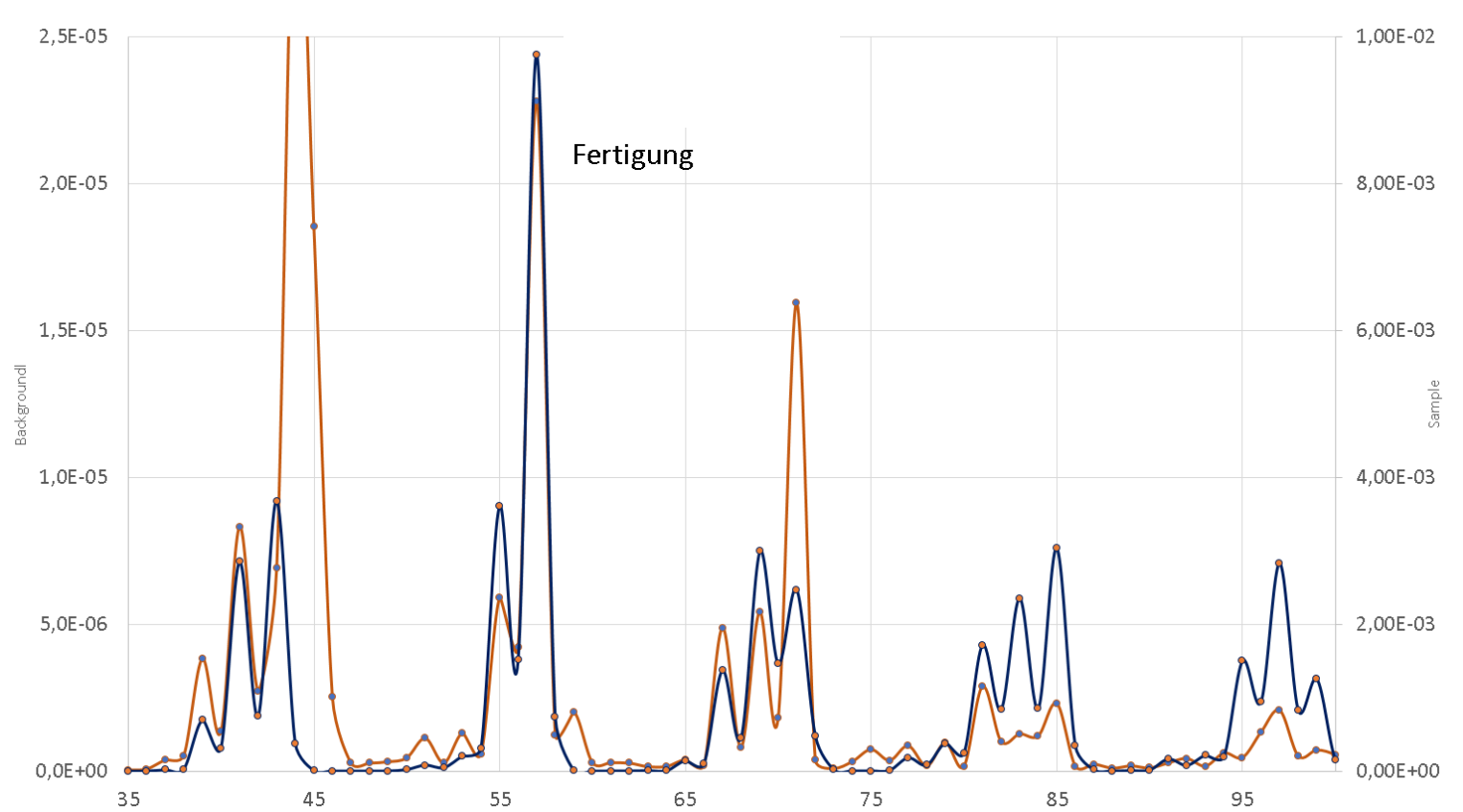




# Base material (orange) + background (blue)

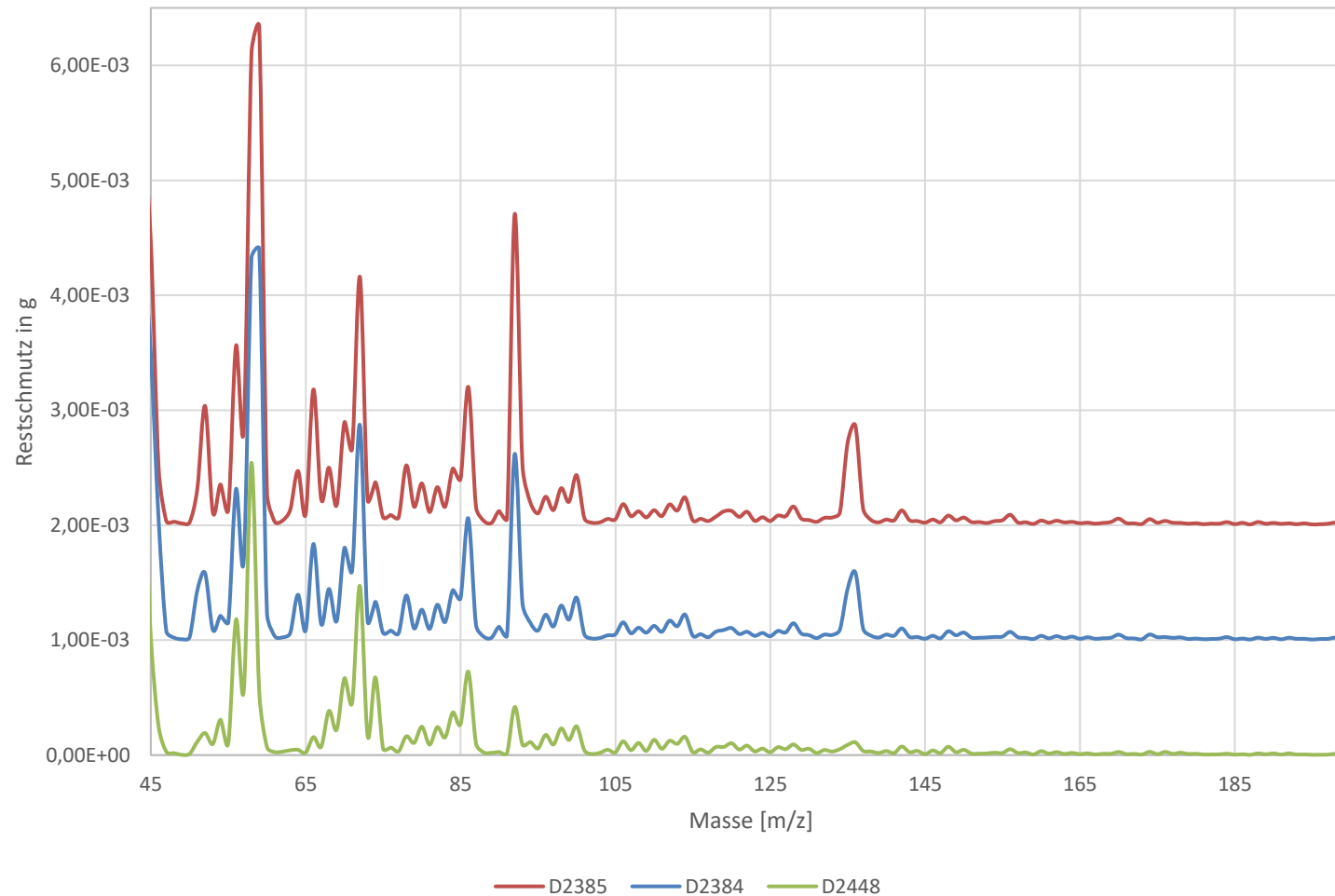


20 Lenses after final cleaning → orange  
Polishing paste → blue



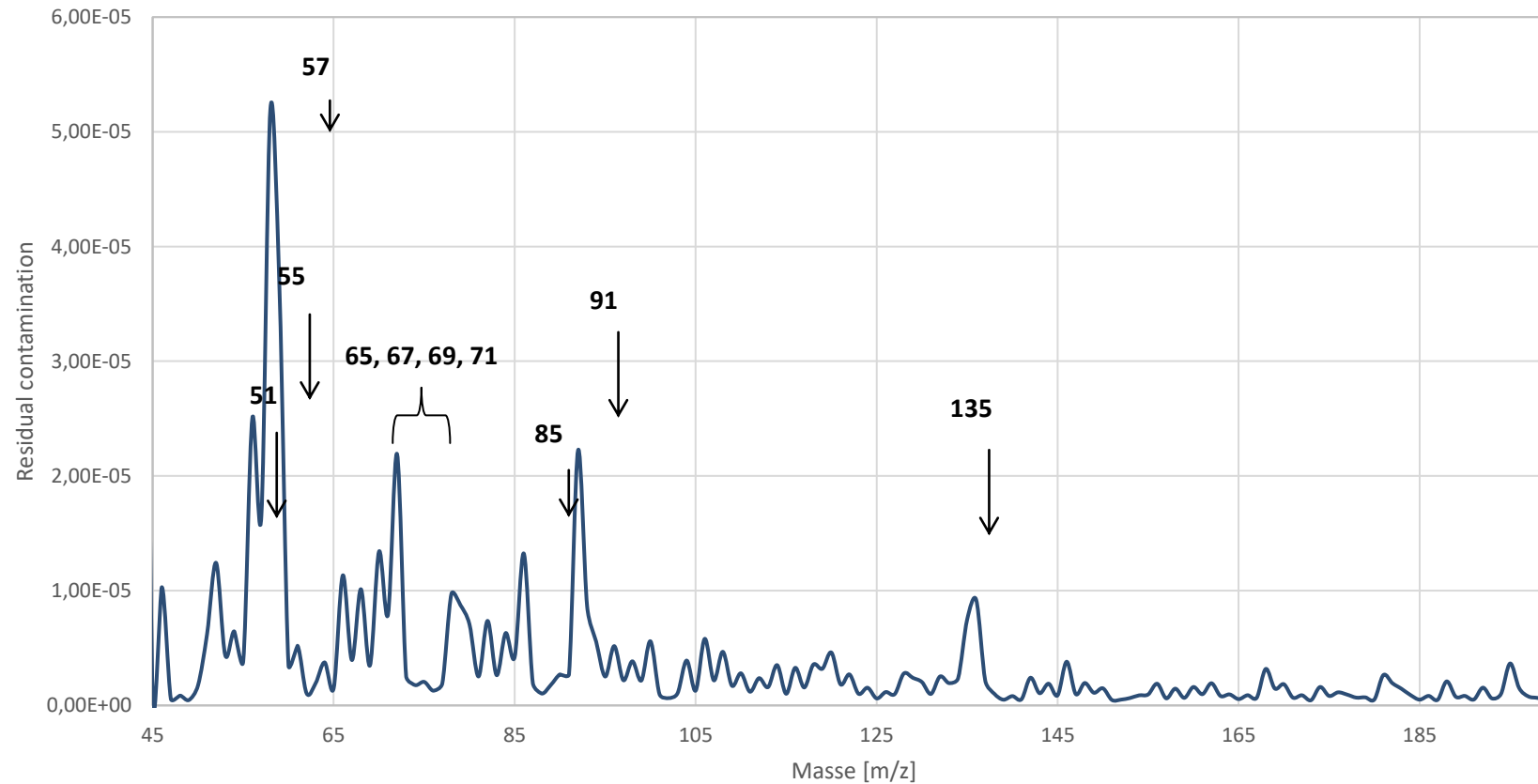
# Endoscopes with problems

3 Endoscopes



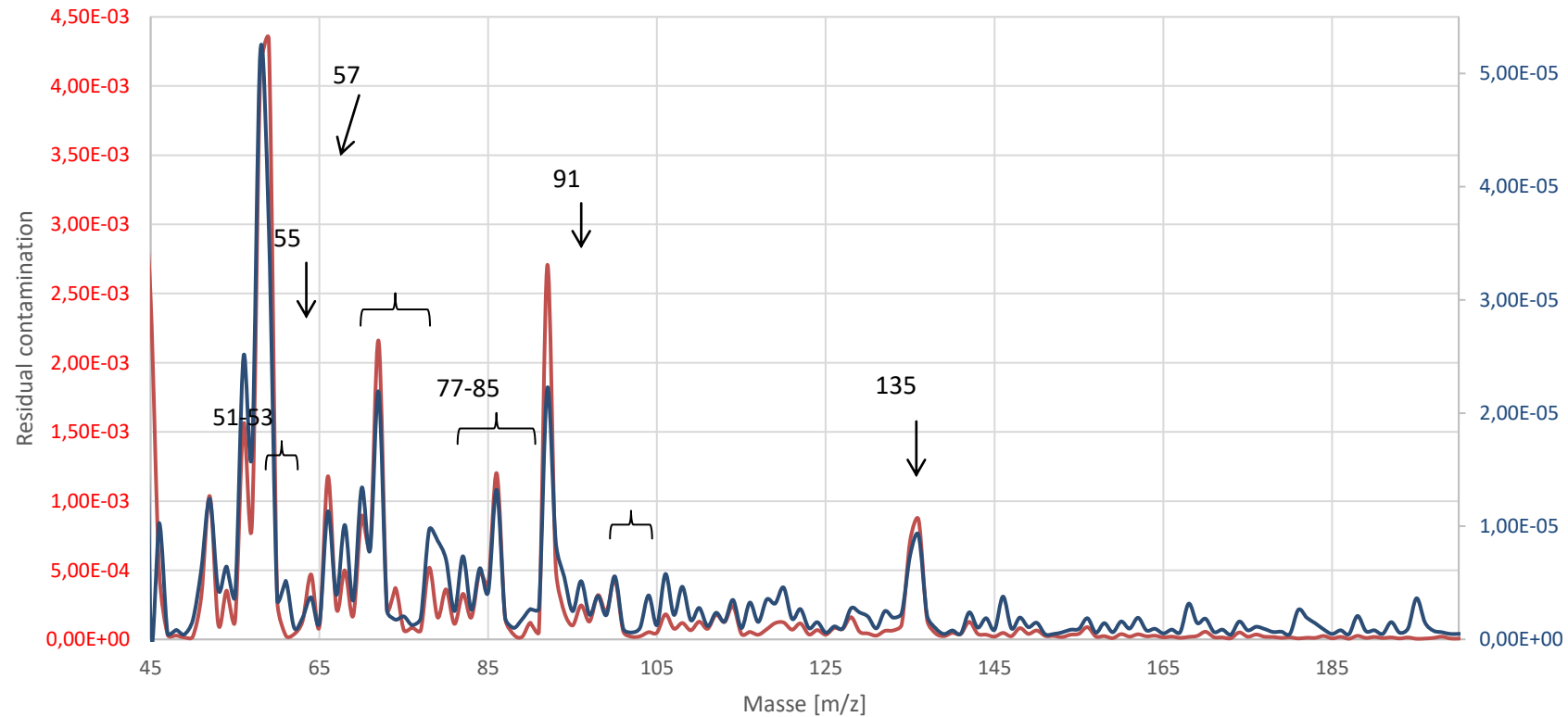
# Packaging of Endoscopes

PUR-Foam from the packaging



Endoscope → red  
Pur-Foam → black

Endoscope in contact with PUR-foam



- Thank you for your Attention



# Webinar Presenter



Functional surfaces are non-  
superficial

Dr. Stefan van den Eijnde  
Innobus (Netherlands)



InnoBUS  
Innovation into Business

**Functional Surfaces are Non Superficial**

Dr. Stefan van den Eijnde

**militeX**  
Surfaces and Solutions

Guus Ploeger

Wrap up meeting

**AutoProtect - Interreg V A**

<https://auto-protect.org/nl>

December 8 2022



# InnoBus and Militex

- InnoBus (Maastricht, anno 2011)
  - Innovation into Business
  - Collaborative research and product development
- Militex (IJmuiden, anno 1948)
  - In company R&D up to fill and finish of detergents
  - Pioneer in biotechnological detergents
  - Sustainability and product safety are in Militex' DNA
  - Militex is a family company



**militex**

**InnoBus**  
Innovation into Business

Militex is developing a special cleaning agent compatible

- Lessons learned
  - Product definition
  - Concept development
  - Initial results

- Next steps

These antimicrobial MSS-coatings are developed by consortium partner VeroMetal in cooperation with many other partners of the project.



**militex**

**InnoBUS**  
Innovation into Business


# Product definition

- Self protective surfaces
  - Microbial and chemical cleanliness
- Hygiene (Hygieia)
  - Proper cleaning is the condition achieved after removal of dirt
    - Perception, look and feel
    - Prevention exposure to unwanted agents
    - Extending lifespan of objects
    - Preserving the functionality of objects
  - Health, safety and wellbeing





**militeX**



 [Redacted name] • 12:25  
very interesting!  
For curiosity - what is 'proper cleaning'?  
And how could a company be sure that they have done enough to not need to disinfect?  
Thanks!

31 OKT.

 **Stefan van den Eijnde** • 09:33  
Short answer: disinfection is about killing germs (typically 1 on [100.000](#) or less may survive). Cleaning is getting rid of (visible) dirt (to extend lifespan of machines/infra, and a suitable/pleasant environment fitting normal fysiologie). Advice is to prevent desinfection where possible (ecology/antimic resistance), and use it where really needed (food production, severely weakened people....). Cleaning and Desinfection also have diff. Regulatory aspect.  
Best regards,  
Stefan

 [Redacted name] • 12:29  
Wow I'm glad I asked - a very interesting answer. Thank you for taking the time to explain! Have a lovely day!

16 NOV.





# Product definition

- Cleanliness depends on the application area
  - Food industry is not equal to a farm
  - Hospital is not equal to a school
  - Microbial cleanliness differs from chemical (and other types of) soiling
  - Disinfection is not equal to cleaning



**militex**

**InnoBus**  
Innovation into Business



# Product definition

- The innovative surface has to
  - Fit real world expectations, rules, and regulations
  - Be environmentally friendly
  - Be robust and verifiable
- Fit of change the circle of Sinner



**militeX**

**InnoBUS**  
Innovation into Business

# Concept development

- Plasma modification of cleaning solutions
- Preservation of InnoCoating coated surfaces
- Cleaners compatible with novel antimicrobial coatings

Compliant

yes  
Initial results

yes

yes

- Plasma activated cleaners are an interesting avenue to modify functionality of cleaning agents/detergent

yes

yes

- Detergents can impact binding of coating to their surface, as well as the esthethical characteristics

Compliant

no

- Detergents can destroy, and maybe also enhance the self cleaning properties of surface coatings

yes

yes

no

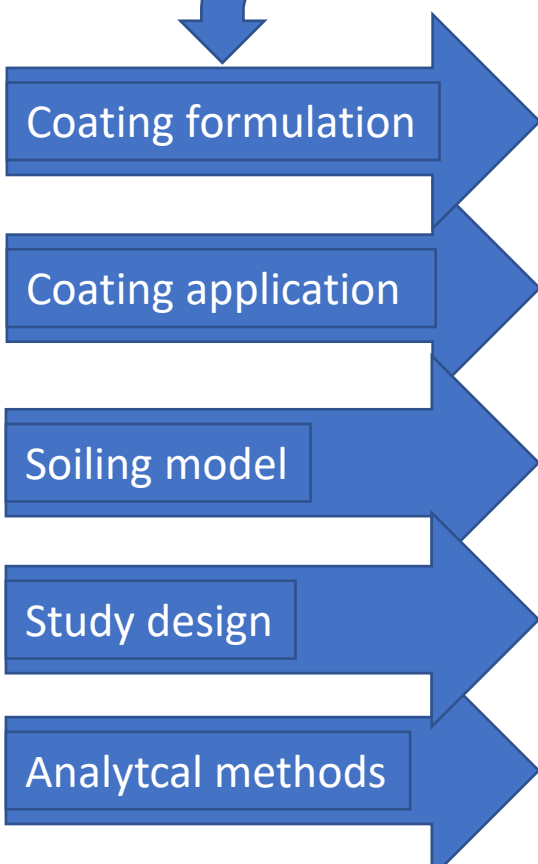
yes



**militek**

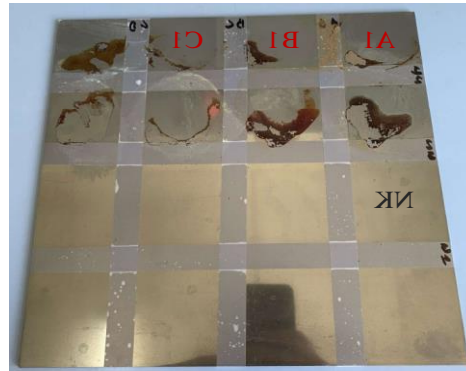
**InnoBUS**  
Innovation into Business

# Why Autoprotect Matters? Collaboration!

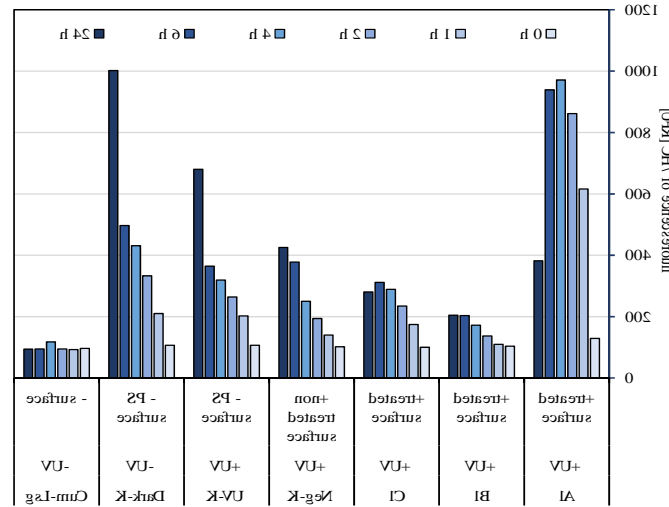


Effect of Cleaning Procedures on the Multi-Catalytic Surfaces

Assessing the degradation of cumarin on cleaned catalytic surfaces



troublesome effects for no obvious reason. various extend. Dark control also shows seem to degrade cumarin as well as VHC to acting effects of UV irradiation and surface difficult interpretation since the counter-



Verometal®

militex wfk

InnoBus  
Innovation into Business

# Surface coatings are not superficial

*pH*

*Solid*

*Foam*

2.6

2.2

170

- Product definition

4.0

190

- Regulatory and professional/branche specific requirements

190

- Have to survive real world use over long(er) time periods

180

- Cleaners and coatings in many cases are part of one concept

180

- Un-approved detergents pose a risk to coating performance

effect on the pH of the products.  
 the pH of the product is lower.  
 difference between the cleaners is very



**militeX**

**InnoBUS**  
 Innovation into Business

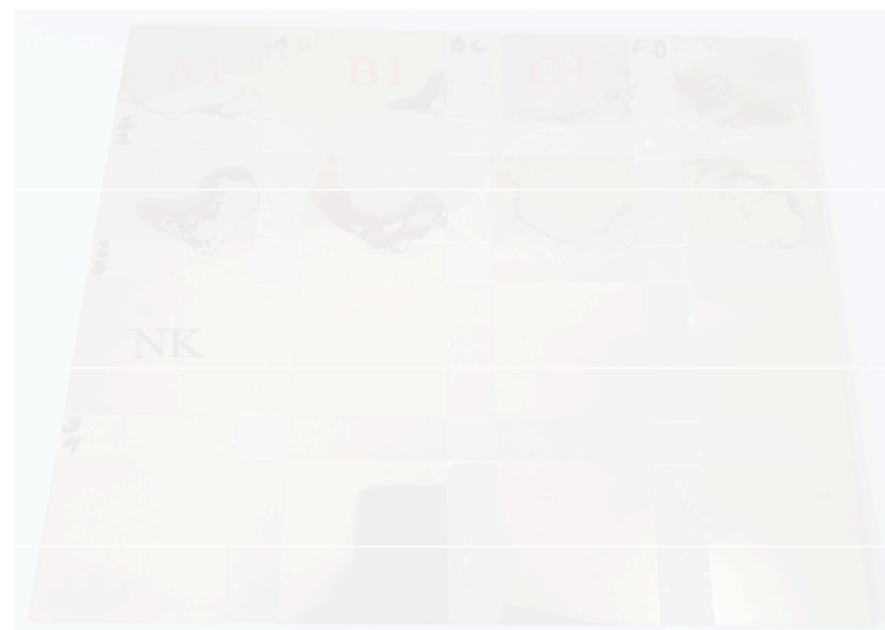
# Next steps

Assessing the degradation of cumarin on cleaned catalytic surfaces

- Innovation takes lots of time



- Product definition
- Product development
- Concept
- Regulatory
- Market adaptation



Difficult interpretation since the counteracting effects of UV irradiation and surface seem to degrade cumarin as well as 7HC to various extent. Dark control also shows troublesome effects for no obvious reason.



Thank you

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wfk

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VeroMetal<sup>®</sup>

INNOCOATING EUROPE BV

 plasmacreat



**TOTAL SUPPORT**  
*innoteq*

- Whole consortium for the scientific discussions and exchange of views opinions and expertise



**militeX**

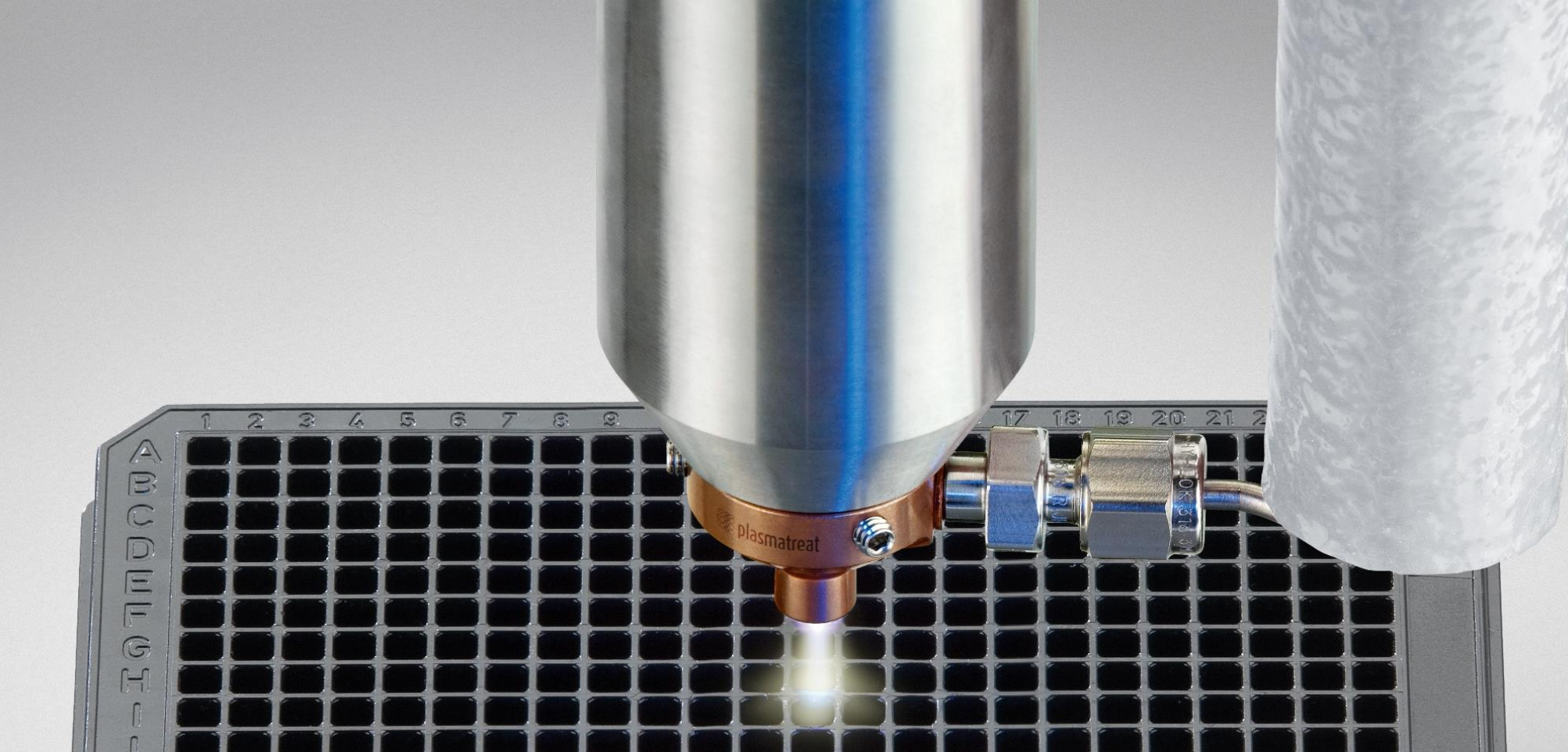
**InnoBUS**  
Innovation into Business

# Webinar Presenter



Atmospheric pressure plasma  
treatment and thin film  
deposition for antimicrobial  
application

Dr. Dhia Ben Salem,  
Plasmatreat GmbH,  
(Germany)



Europäische Union  
Europese Unie



## AutoProtect Webinar-Series # 6

# Atmospheric pressure Plasma treatment and thin film deposition for antimicrobial coatings



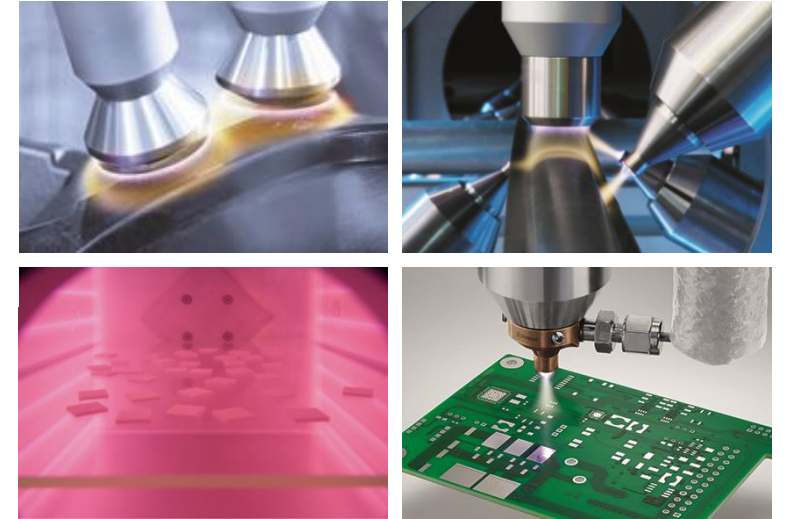


# Company presentation



We are surface specialists and leading supplier for atmospheric Plasma technology as well as experts for low pressure Plasma processes

- HQ in Germany
- Production sites in Germany, China & USA
- 19 subsidiaries & Technology Centers in 12 Countries
- 15+ agents in ROW



## Family Owned Business

- Founded in 1995
- 250 employees worldwide
- Consolidated turnover: €45 Million



## Milestones

- 1995: Invention of Openair-Plasma®
- 2007: PlasmaPlus® coating
- 2019: Opening of the HQ Technology Center
- 2020: Plasmamatreat Academy

# What is Plasma?

Plasma is formed when additional energy is supplied to the gas by electrical discharge. Plasma is an ionized gas with electrical conductivity which is electrically neutral. It is also called 4<sup>th</sup> state of matter.

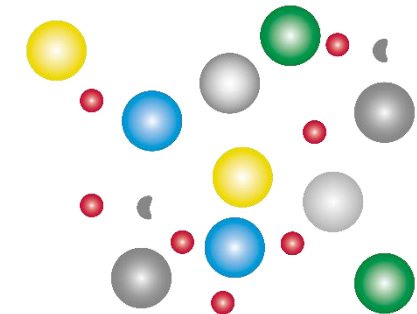
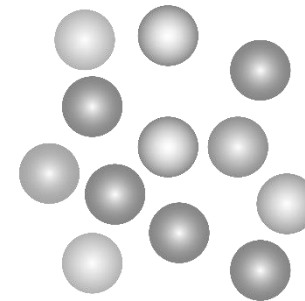
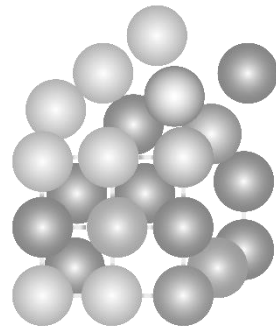
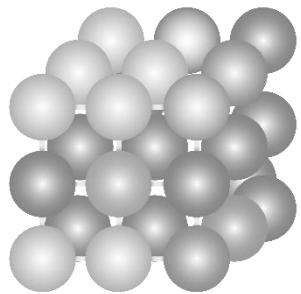


SOLID

LIQUID

GAS

PLASMA



● Molecule

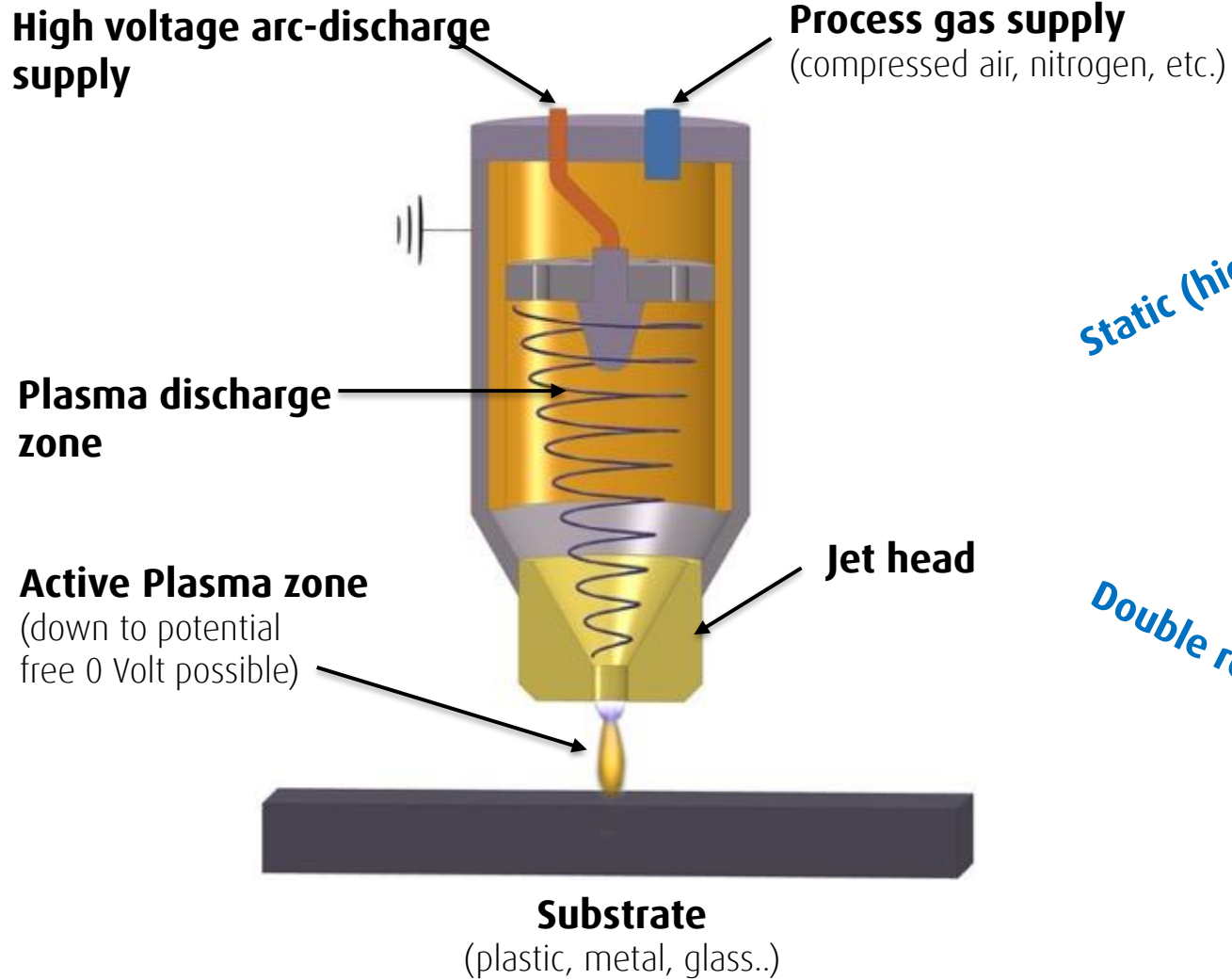
● Excited Gas-Molecule

● Ion's

● Free Electron's

● Excited Molecule-Fragment's

# Operating principle Openair-Plasma®



*Static (higher speed) →*



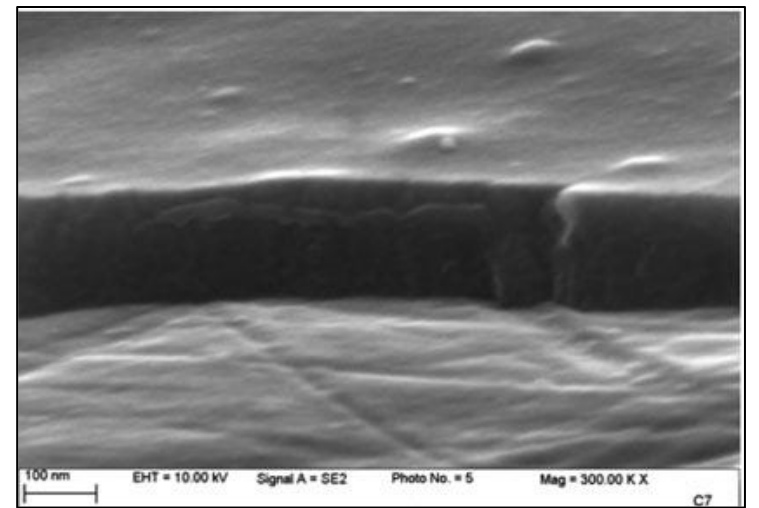
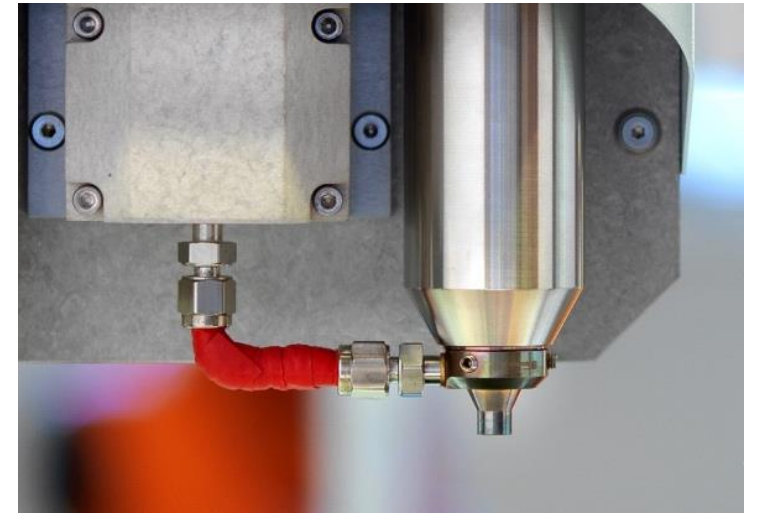
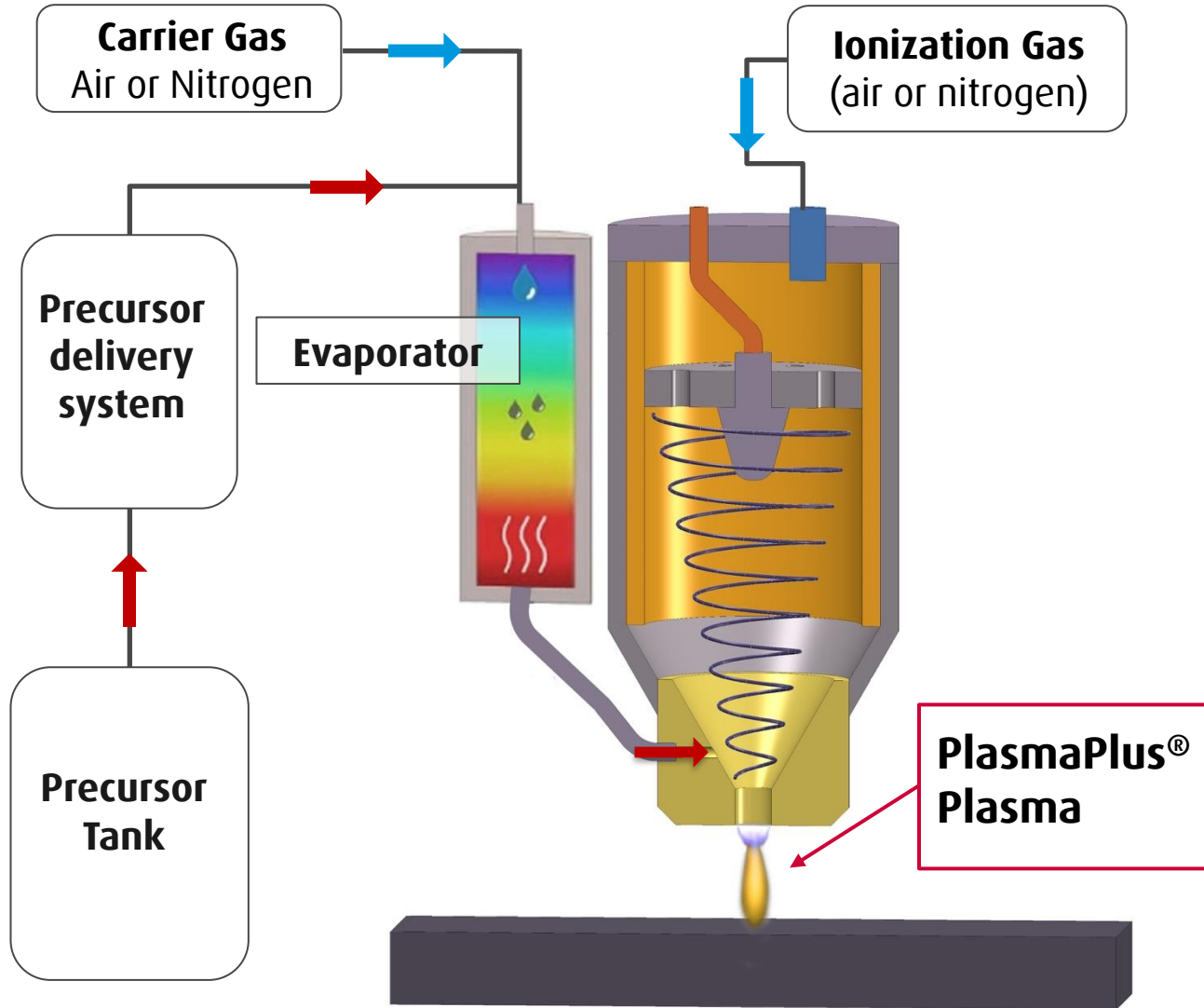
*Rotating (larger width) →*



*Double rotating (largest width) →*



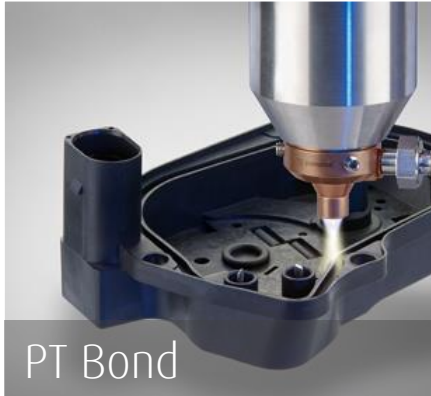
# Operating principle PlasmaPlus®



*SiO<sub>x</sub> films grown on stainless steel substrates*  
Thickness deposited : 150 nm  
Deposition rate: 920 nm/s



# Openair-Plasma® and PlasmaPlus® processes combination



PT Bond

PT Bond is a Plasma coating designed to promote the adhesion of adhesives and sealants.



AntiCorr®

The PT AntiCorr® coating is a high-performance barrier coating which provides an inline and active corrosion protection.



PT Print

PT Print enables a one-step digital printing process which significantly improves the adhesion and moisture resistance of UV inks on hard materials.



... and other functionalities. Be it coatings that implement Anti-Ice®, insulation, adhesion promoters for 3D printing, long-term hydrophilic functionality on fuel cells and more

## toward Plasma-based antimicrobial coatings...

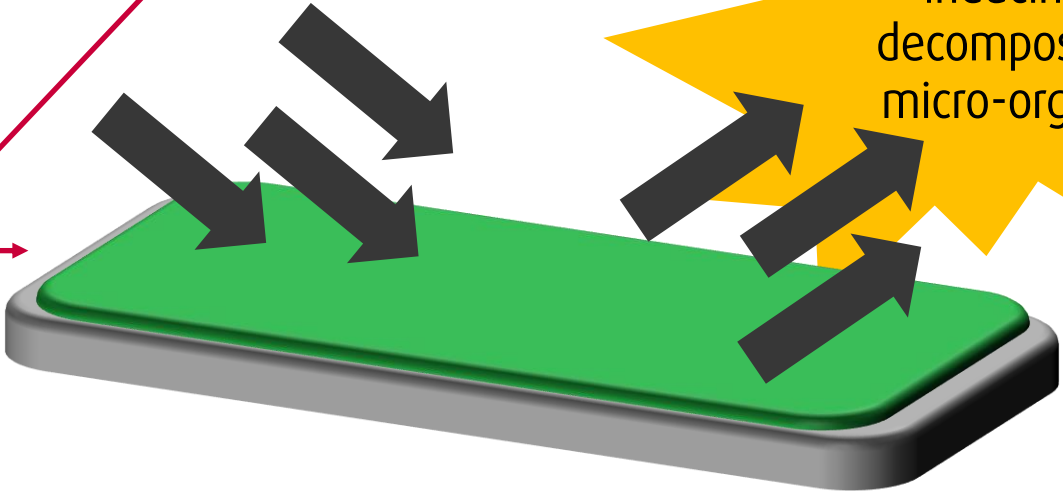
# Goal definition

**Piezo-electric excitation**  
Pressure of <math><0,01\text{ MPa}</math>  
Contact pressure, wind, water

**Pyro-electric excitation**  
 $\Delta 2-5\text{ K}$   
Heating, Cooling

**Photo-catalytic excitation**  
Light excitation 200-550 nm  
Day light, artificial illumination

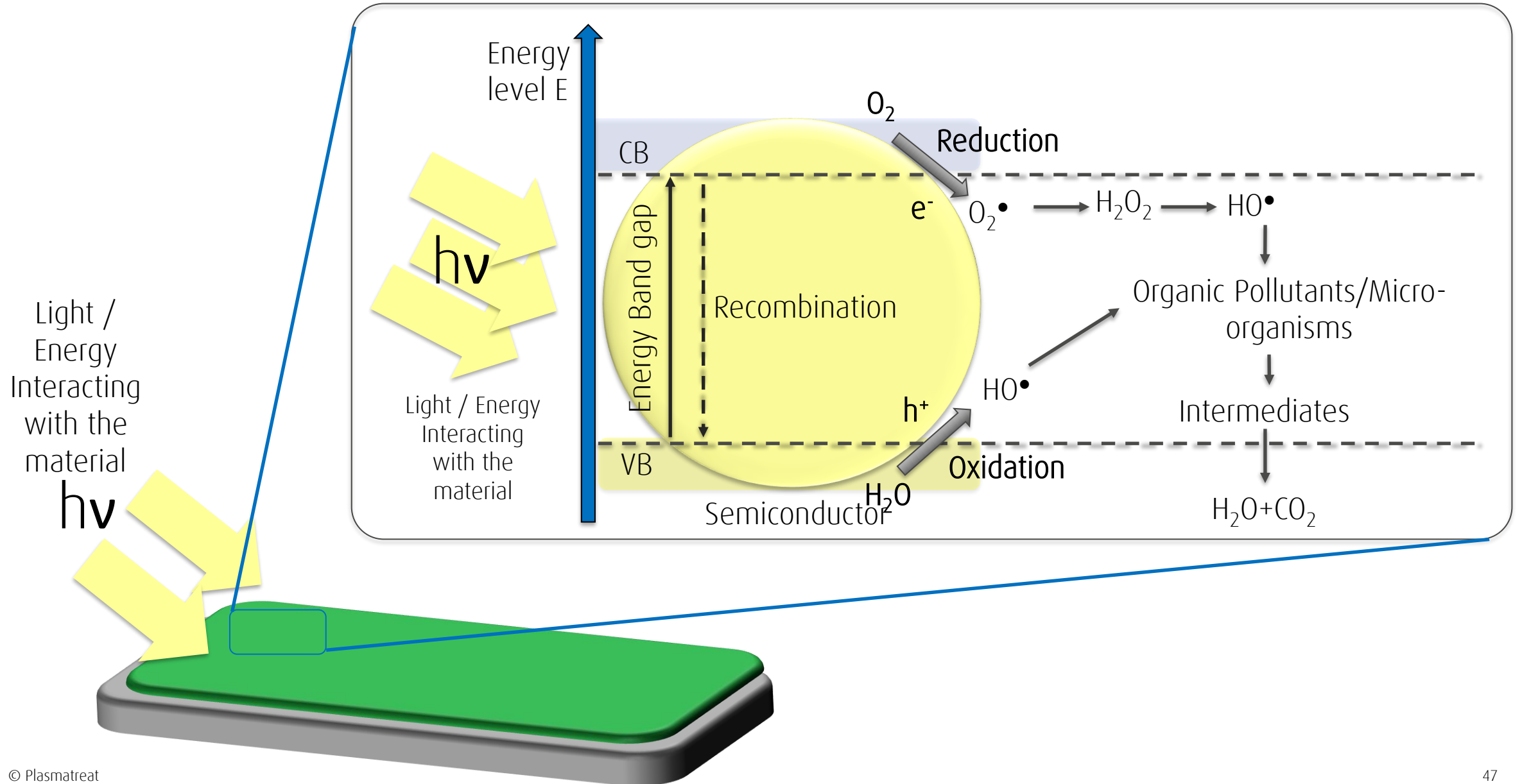
Plasma deposited coatings



Hydroxyl radicals generation inducing the decomposition of micro-organisms

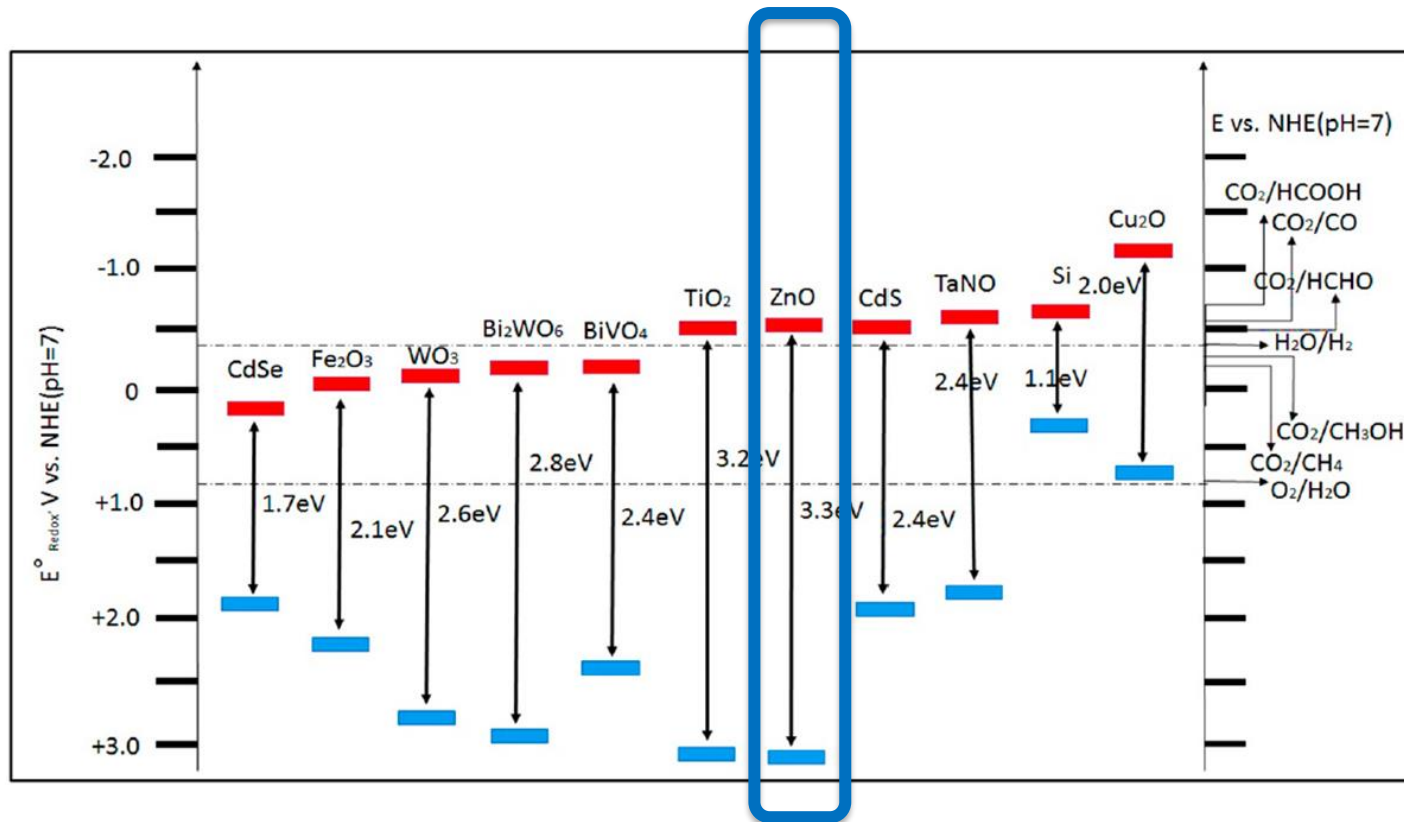
Substrate: Glass, Metal, Polymer, Ceramic...

# Photocatalytic principle and coating definition



# Photocatalytic principle and coating definition

PlasmaPlus® towards innovative coatings

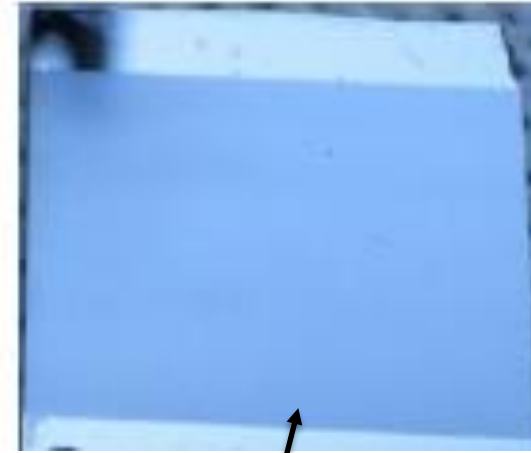


Photocatalyst	Band gap (eV)	Spectral region
ZnS	3.8	UV (326 nm)
SnO <sub>2</sub>	3.8	UV (326 nm)
TiO <sub>2</sub> (anatase)	3.24	UV (383 nm)
SrTiO <sub>2</sub>	3.2	UV (387 nm)
ZnO	3.2	UV (387 nm)
Degussa P25	3.14	UV (395 nm)
TiO <sub>2</sub> (rutile)	3.02	Visible (411 nm)
WO <sub>3</sub>	2.8	Visible (443 nm)
CdS	2.4	Visible (517 nm)
Fe <sub>2</sub> O <sub>3</sub>	2.3	Visible (539 nm)
Cu <sub>2</sub> O	2.2	Visible (564 nm)
MoS <sub>2</sub>	1.8	Visible (689 nm)
CdSe	1.7	Visible (729 nm)

This presentation will be focused on presenting the latest results obtained depositing ZnO/SiO mixed oxide films by Plasma

# Results and characterization

## PlasmaPlus® process Optimization



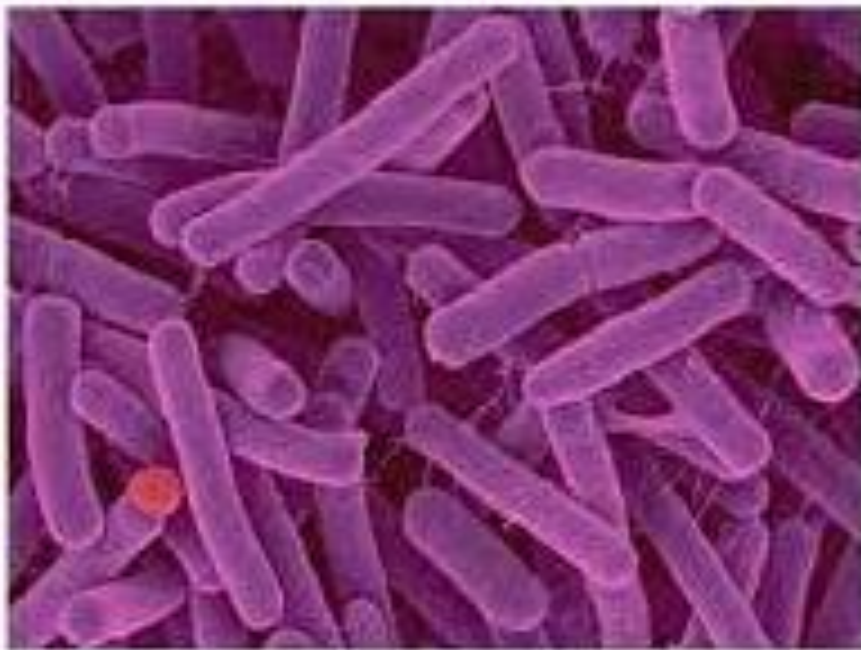
Homogeneous coating  
observed during  
deposition on Si Wafer

More homogeneous coating obtained using the external  
precursor introduction – Validation of the deposition process

# Results and characterization

## Methodology used for Antibacterial surface property evaluation:

- Test germ: *Bacillus atrophaeus* 2277 in LB Solution
- Incubation: 20°C, rf. ca 90%, 2h
- Samples: Polycarbonate samples 1x1 cm  
5 samples per coating parameter



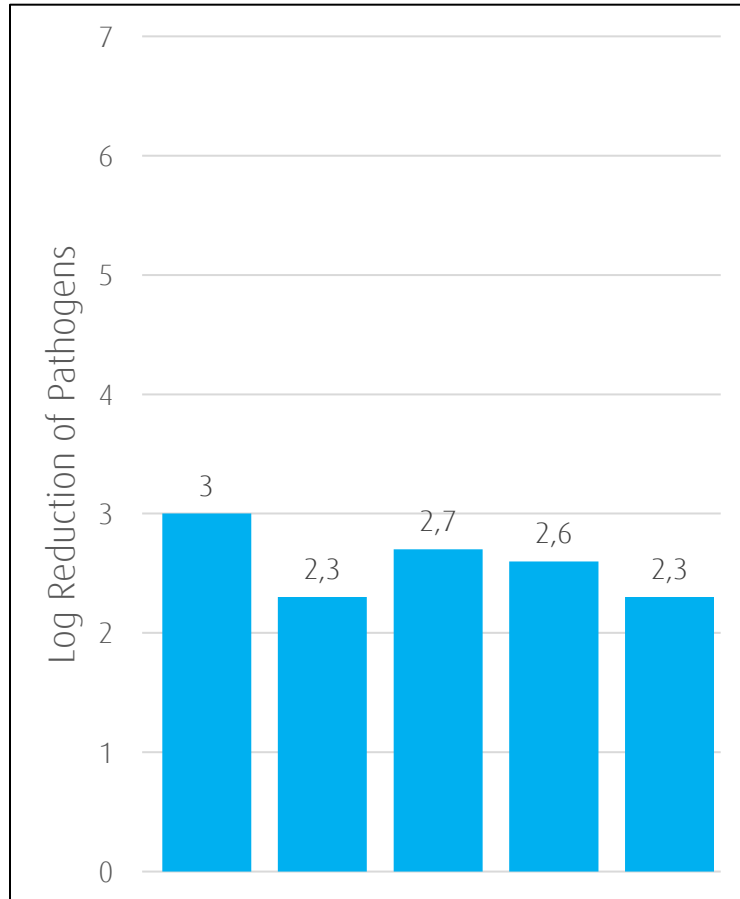
Source : <https://www.sciencephoto.com/media/798576/view/bacillus-atrophaeus-bioindicator-bacterium-sem>





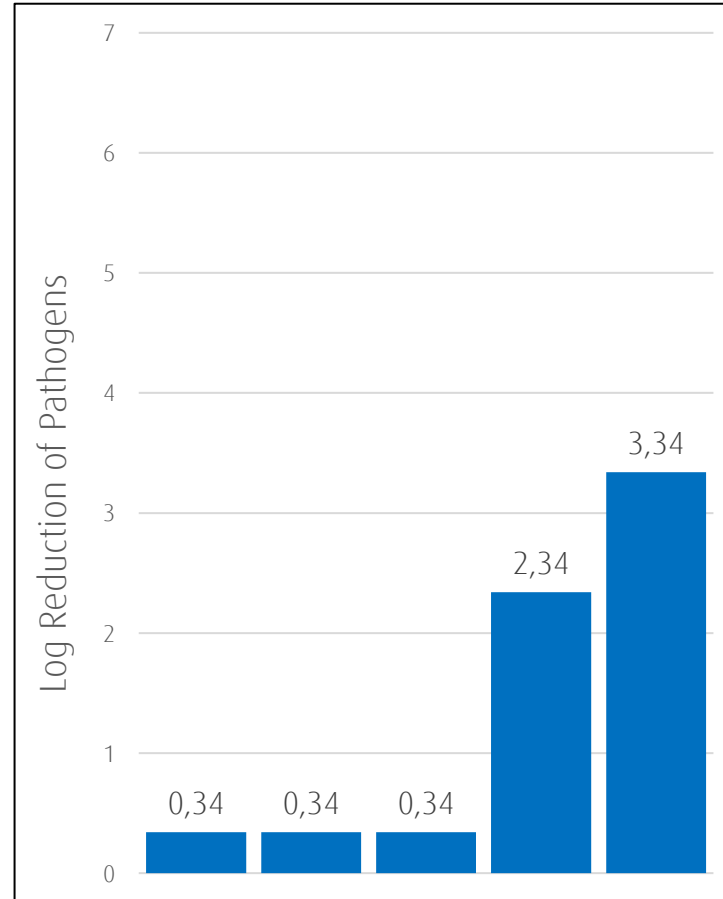
# Results and characterization

## Influence of film composition



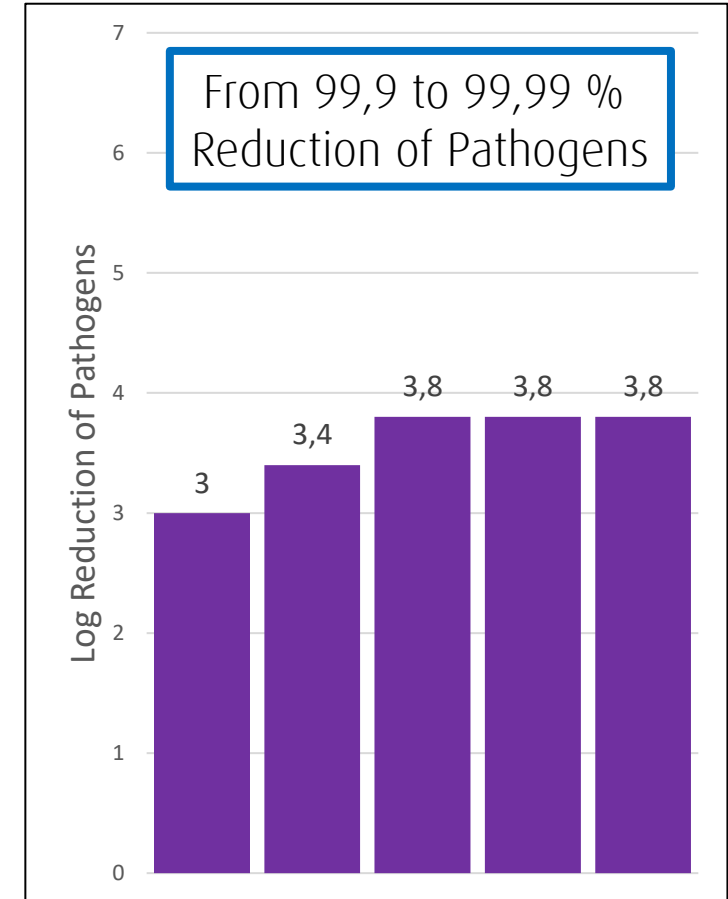
ZnO coatings Air-Plasma

Good antimicrobial properties of ZnO based coating



SiO<sub>x</sub>/ZnO Air-Plasma

Improvement of the antimicrobial properties observed for SiO/ZnO based coating  
However additional efforts required to improve **the mechanical stability**



SiO<sub>x</sub>/ZnO Nitrogen-Plasma

# Results and characterization

Through changes in deposition parameters mechanically stable coatings could be achieved

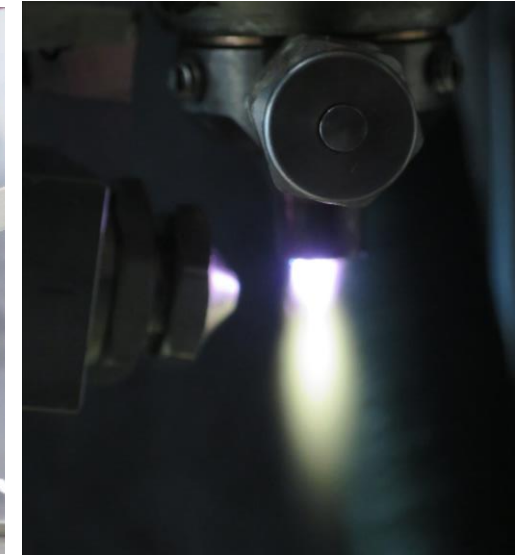
## Stability on Substrates:

Tested by tape-test in reference to Din EN ISO 2409

As Well as crosscut test as described in Din EN ISO 2409

## Optimized Spray configuration

Substrate	Tape test	Crosscut -Test
Si Wafer	No detachment	Value 0 - OK
Aluminium	No detachment	Value 0 - OK
Polycarbonate	No detachment	Value 0 - OK

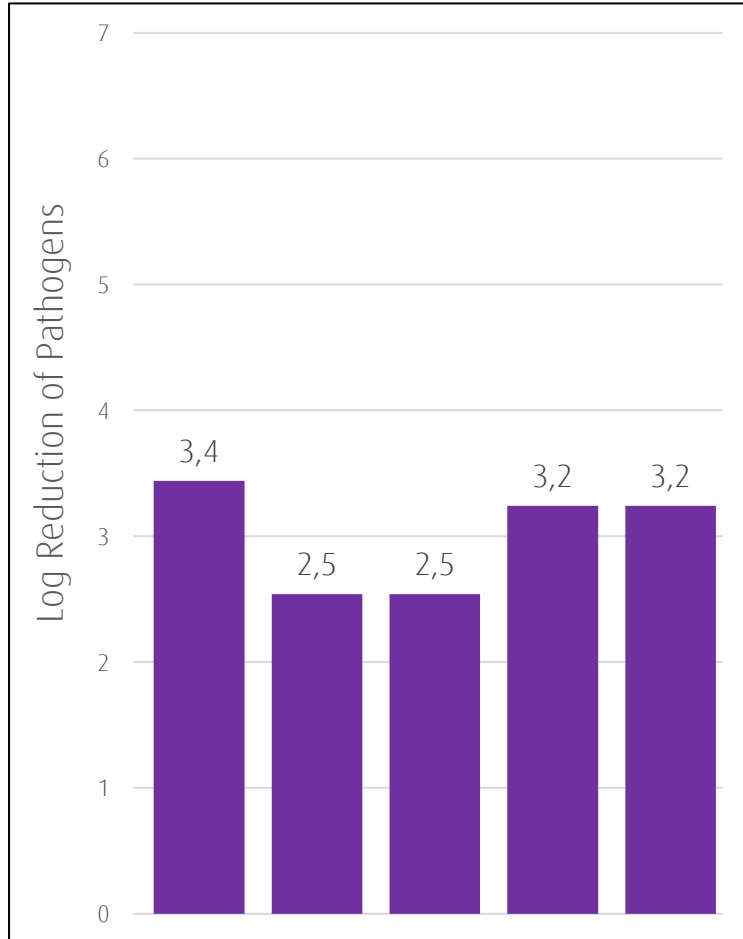


Optimization in deposition parameters :

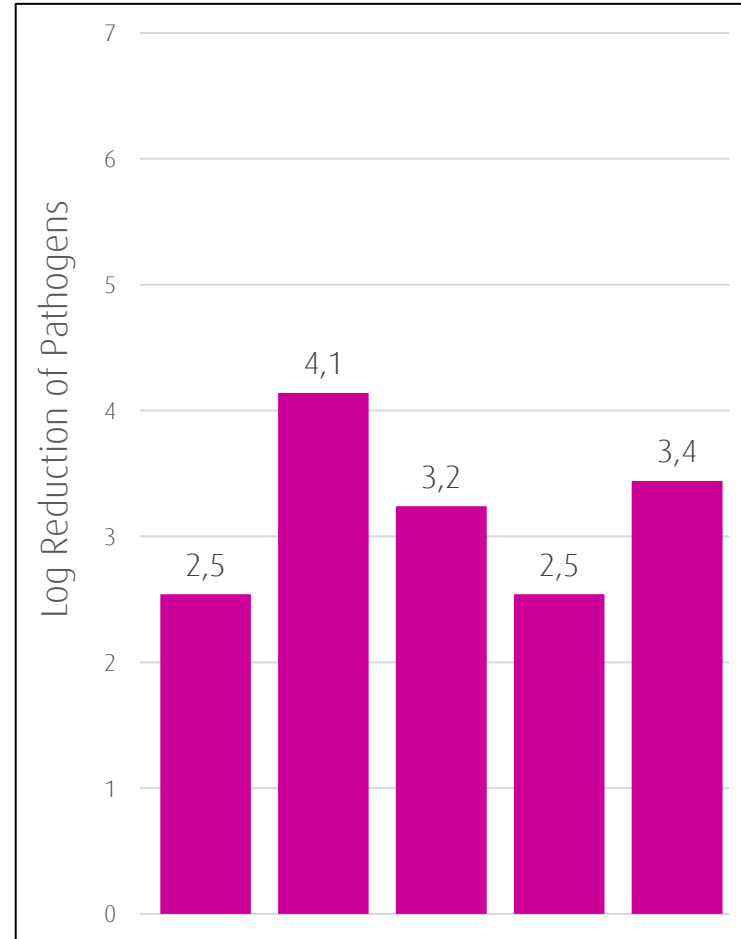
- Spray fixtures
- Spray parameters
- Angle of injection

# Results and characterization

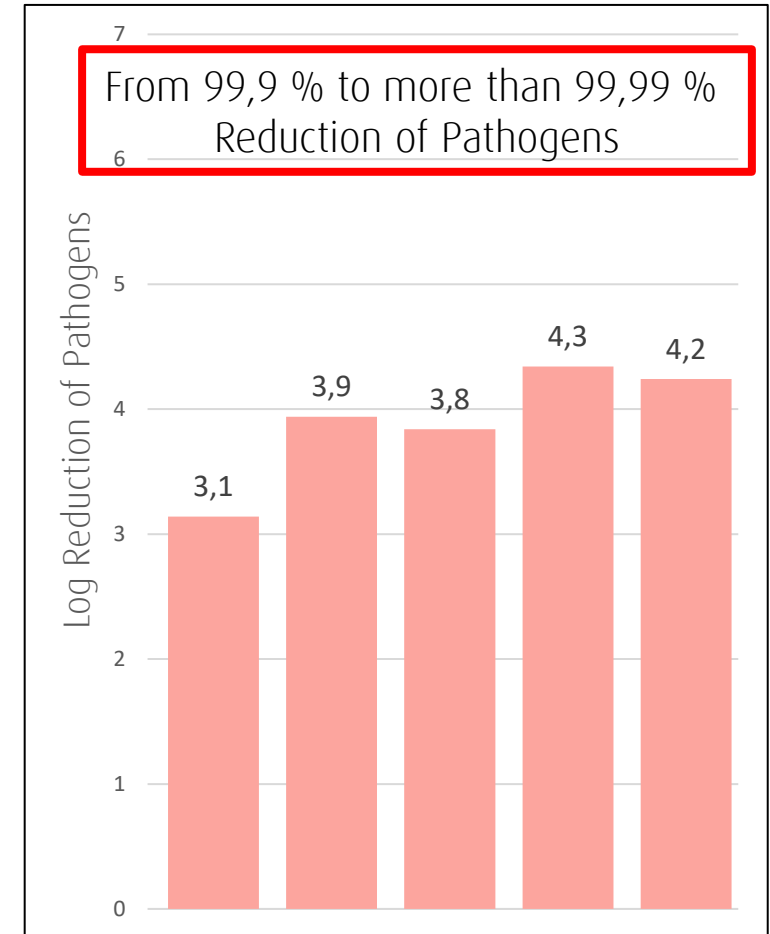
Influence of the Plasma power using Nitrogen as ionization gas



SiO/ZnO coatings Nitrogen Plasma High Power



SiO/ZnO coatings Nitrogen Plasma Medium Power

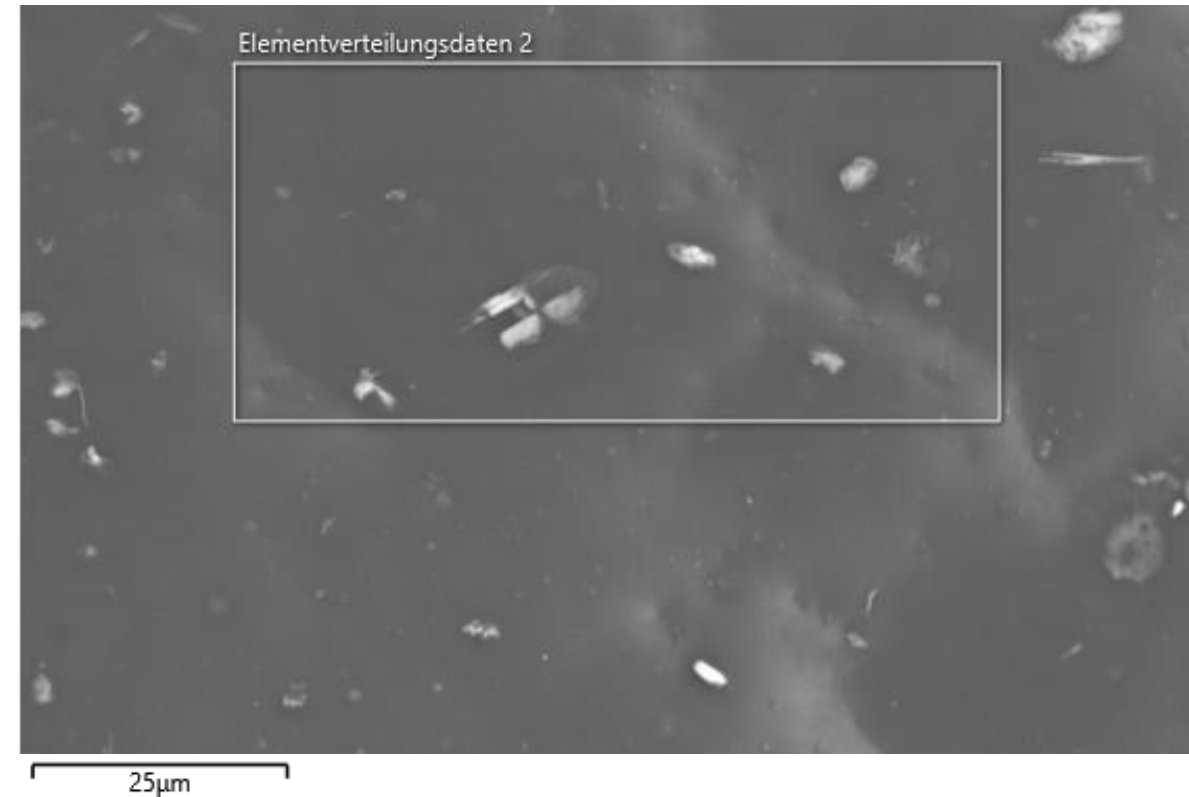
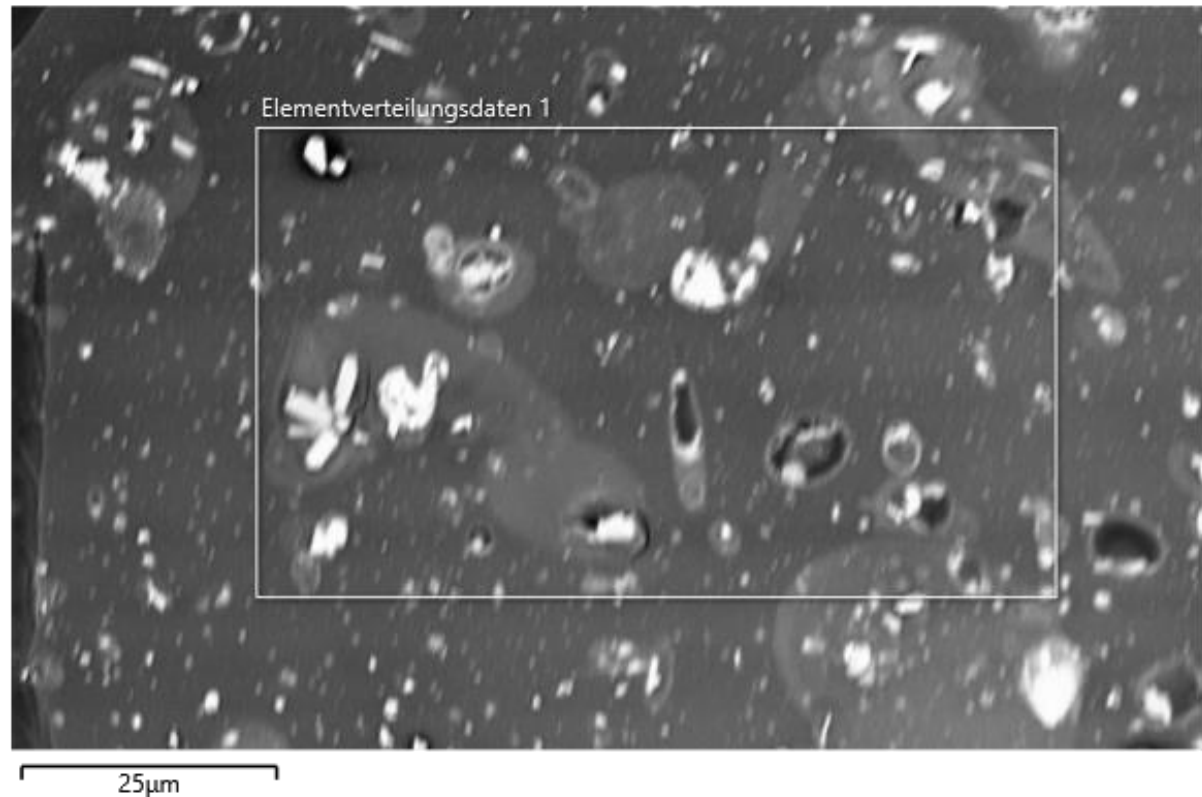


SiO/ZnO coatings Nitrogen Plasma Low Power

Plasma Power shows little influence on antibacterial properties, but slightly increased mechanical stability.

# Results and characterization

Scanning Electron Microscopy observations before and after cleaning

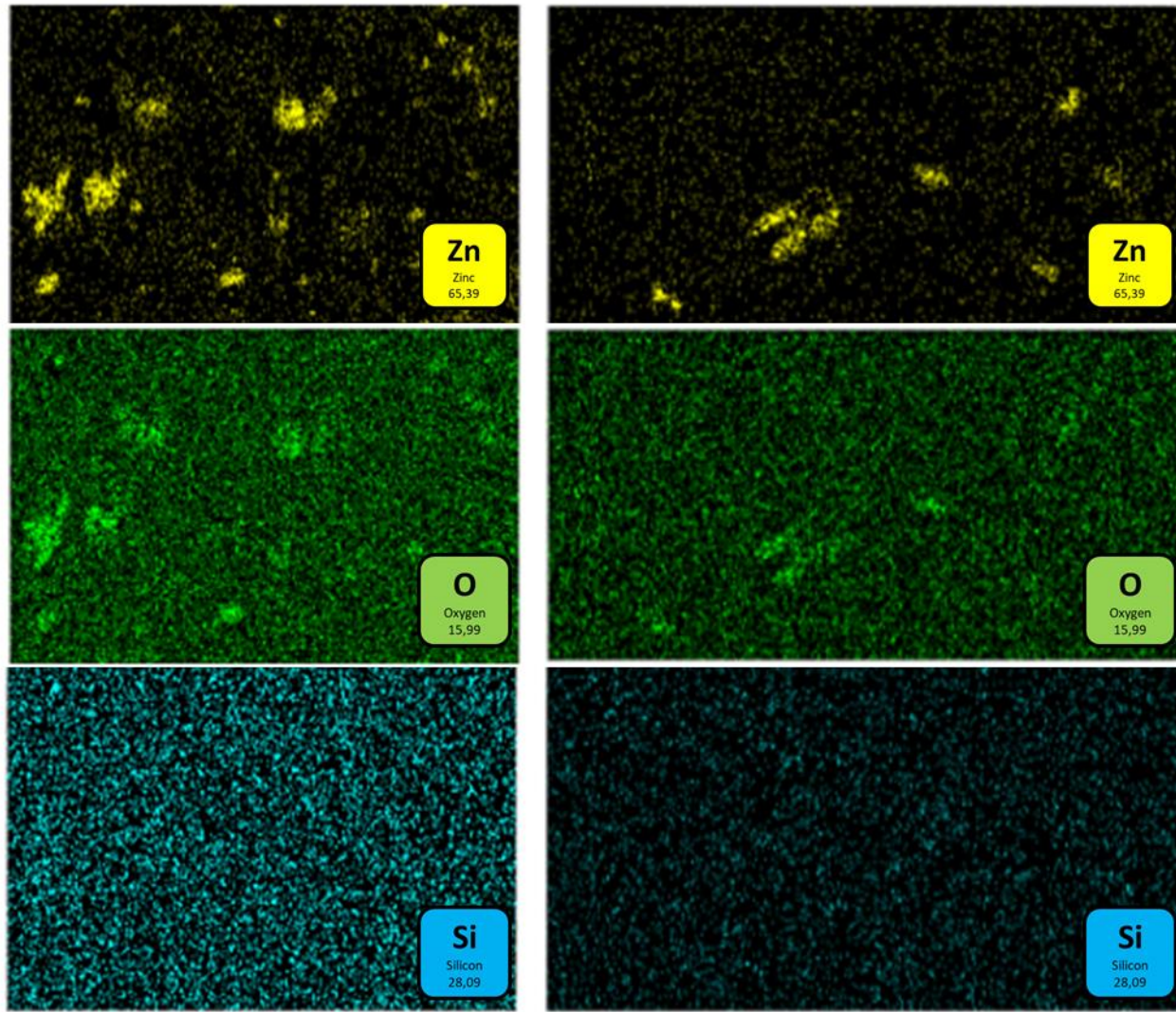


Electron micrographs at 1000 times magnification of the SiO<sub>x</sub> ZnO coatings on polycarbonate before a) and after 5 cleaning cycles b). The frame shown represents the area of element analysis examined in the EDX.



# Results and characterization

Scanning Electron Microscopy observations before and after cleaning - EDX



EDX – Elemental analysis highlighting Zn, Si and Oxygen elements before a) and after 5 cleaning cycles b)

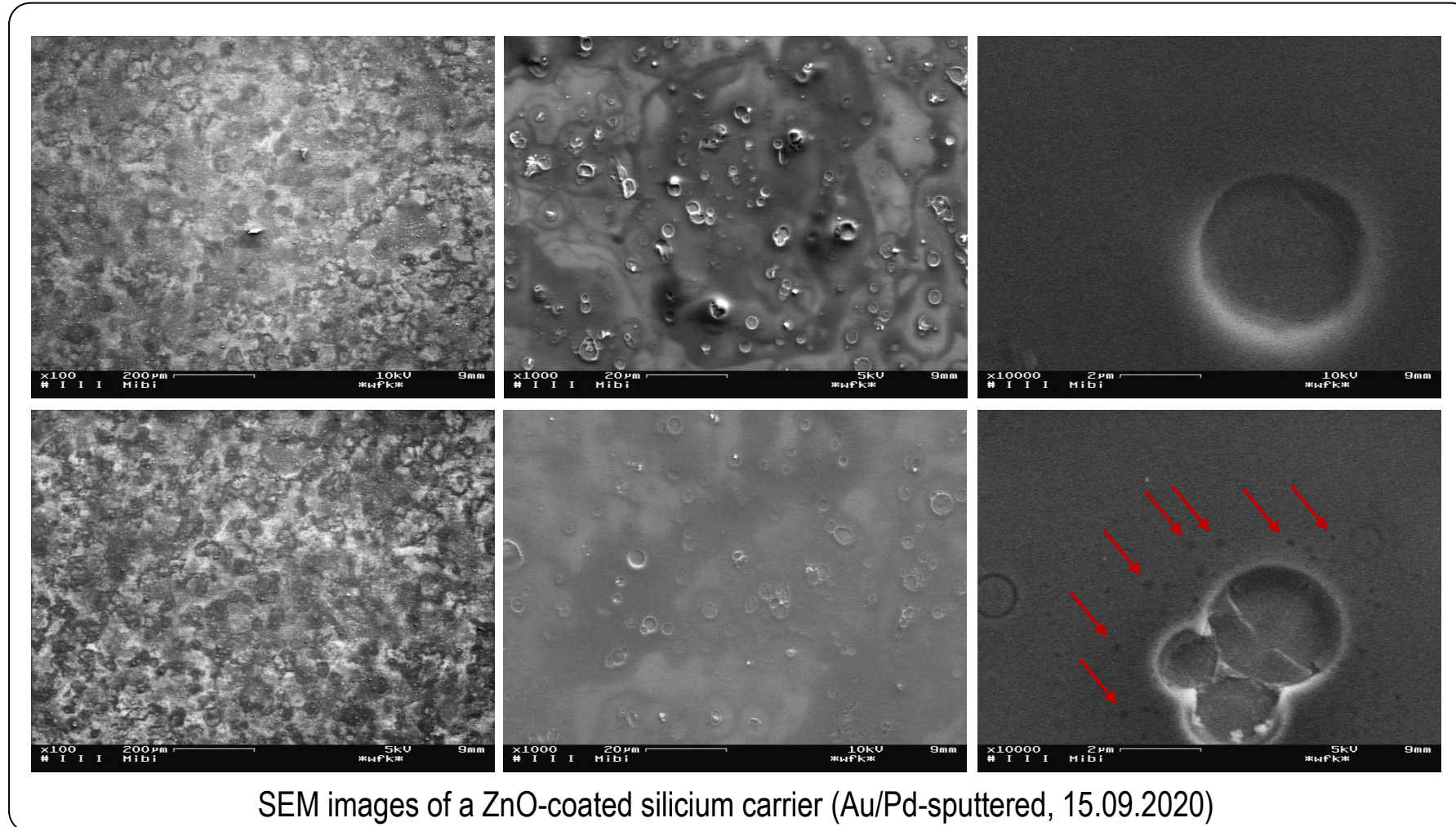


Following the coating, Zn / Si / O are clearly present on the surface however following the cleaning it can be observed that Zn particles are removed from the surface but also Oxygen content.

For the Si content, it seems that the Si is stable and no visual modification following the cleaning step on the concentration of the particles (only loss in the intensity)

# Results and characterization

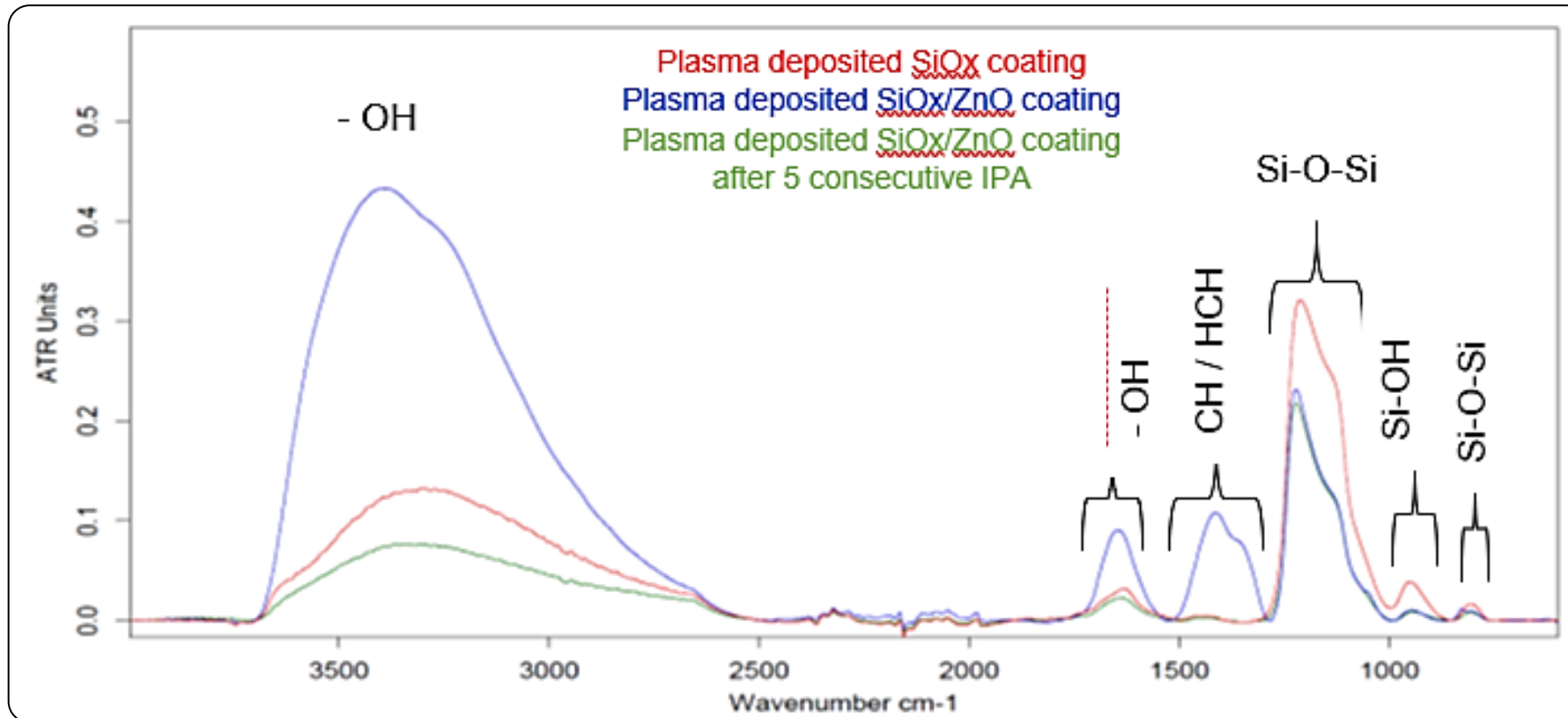
## Scanning Electron Microscopy characterization





# Results and characterization

FTIR characterization in ATR Mode

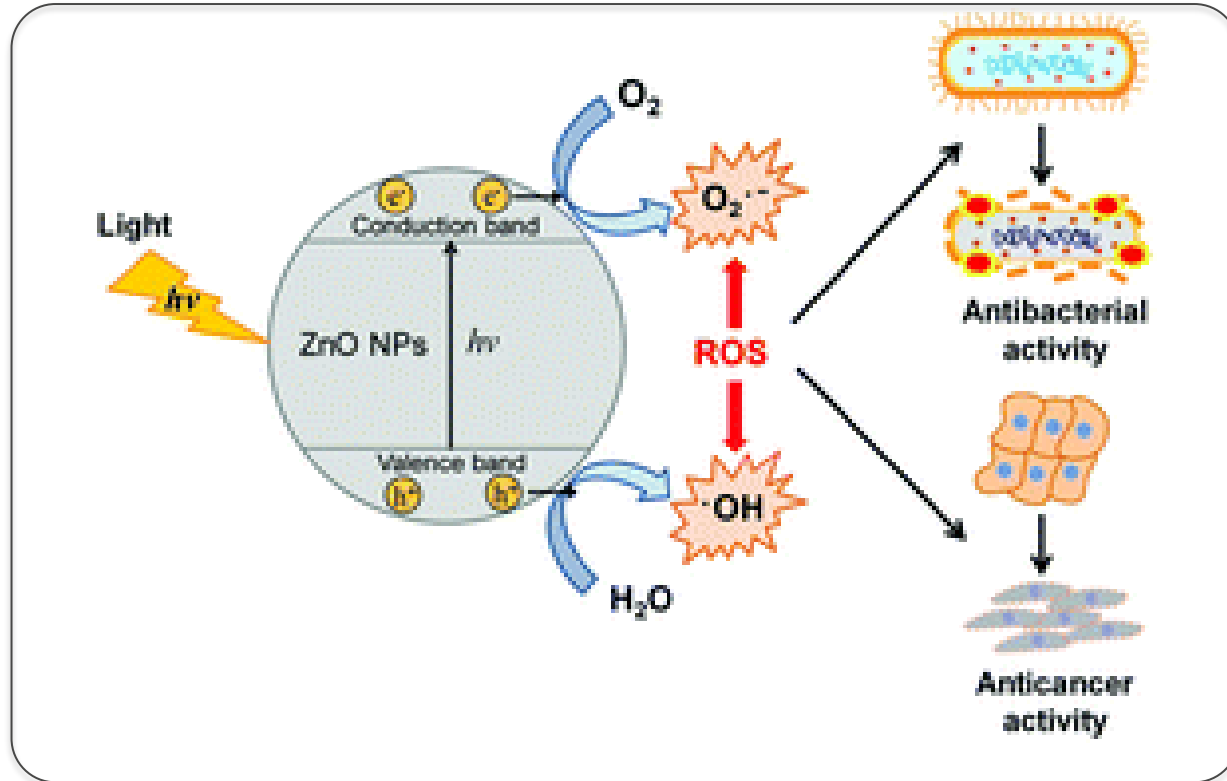


Chemical composition of the SiO<sub>x</sub>/ZnO Plasma deposited coating films :

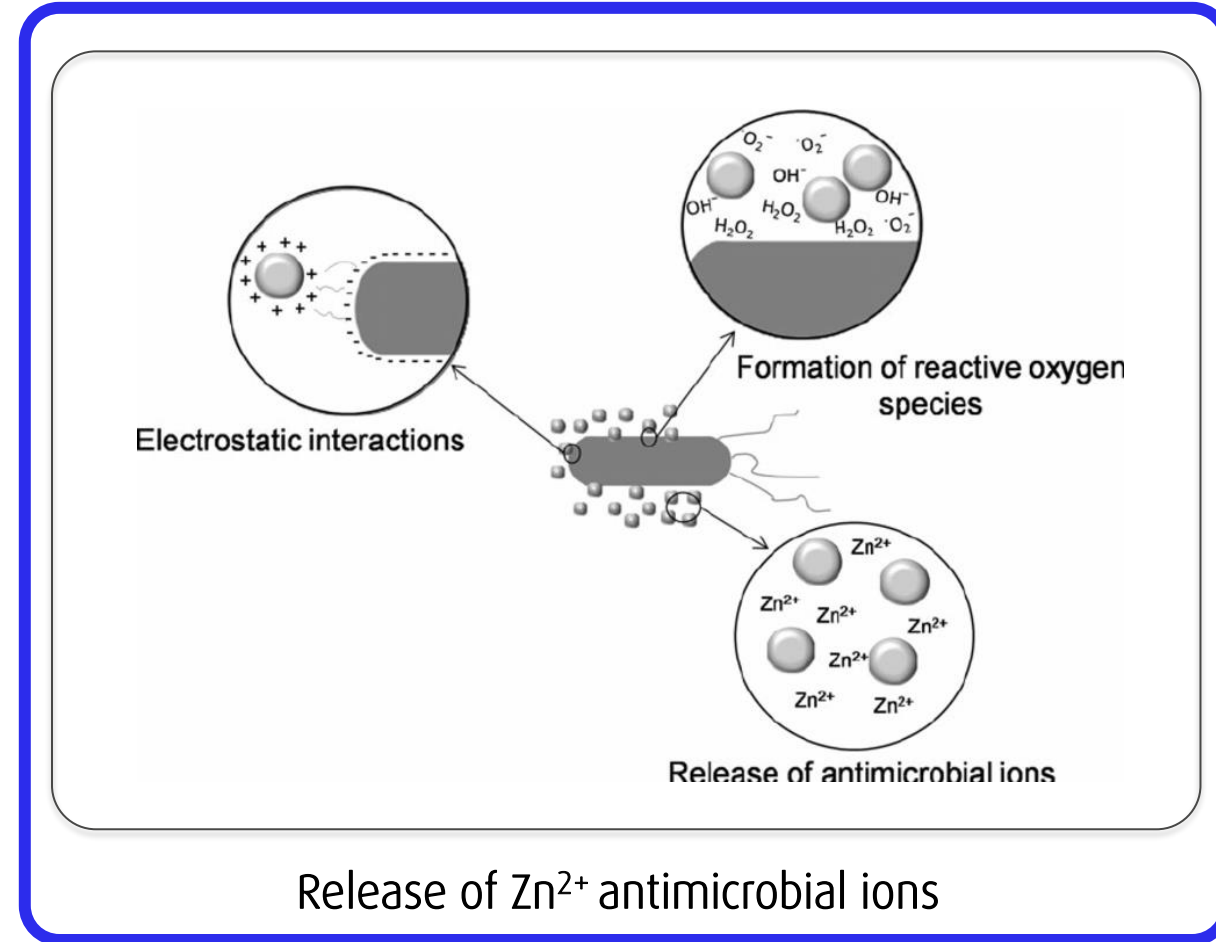
- SiO<sub>x</sub> Plasma deposited Coating
- SiO<sub>x</sub>/ZnO Plasma deposited coating composition similar to the composition of SiO<sub>x</sub>/ZnO even following 5 cleaning cycles (IPA)

The loss in absorbance may be attributed to a thinner coating.

# Proposed mechanisms for antibacterial activity



Release of ROS (Reactive Oxygen Species) under light excitation

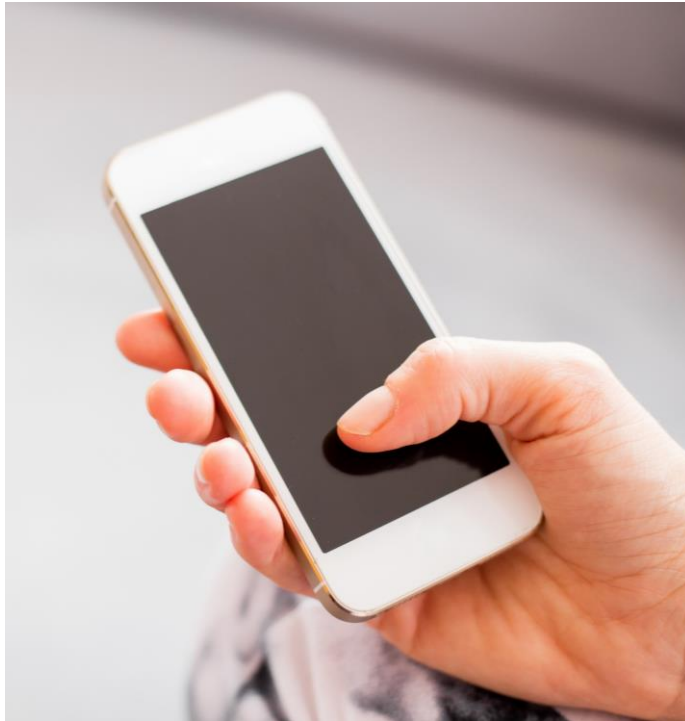


Release of Zn<sup>2+</sup> antimicrobial ions

Sivakumar et al., Photo-triggered antibacterial and anticancer activities of zinc oxide nanoparticles, *J. Mater. Chem. B*, 2018,6, 4852-4871 (2018) <https://doi.org/10.1039/C8TB00948A>

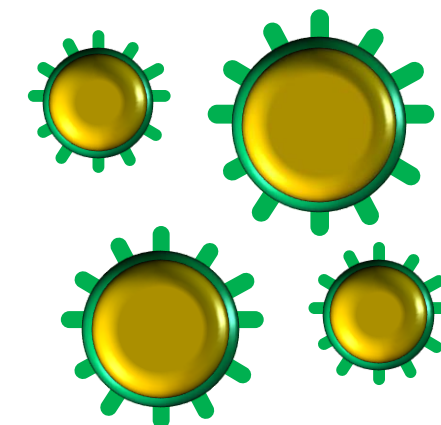
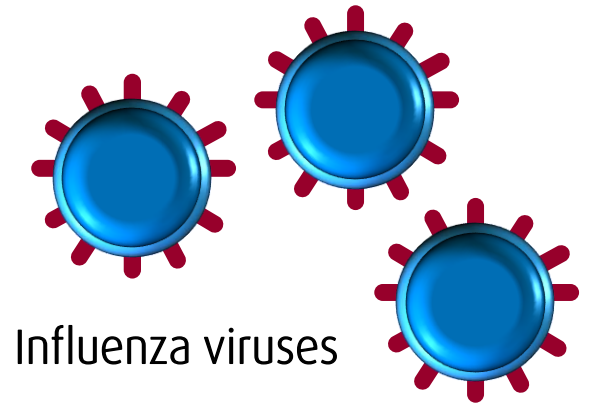
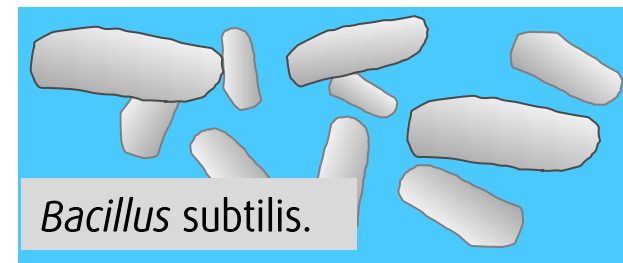
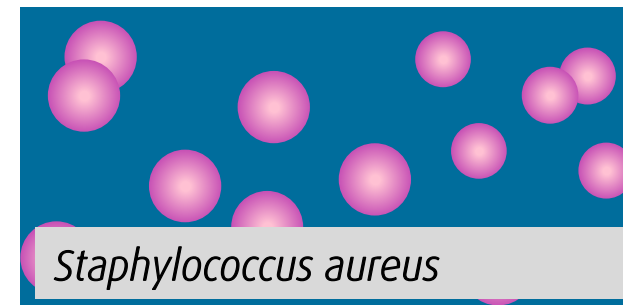
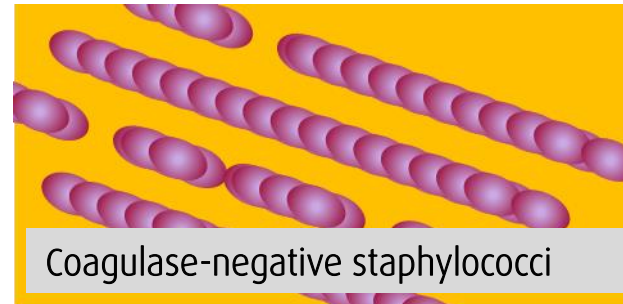
Espitia et al. Zinc Oxide Nanoparticles: Synthesis, Antimicrobial Activity and Food Packaging Applications. *Food Bioprocess Technol* 5, 1447-1464 (2012). <https://doi.org/10.1007/s11947-012-0797-6>

# Atmospheric pressure Plasma treatment for surface decontamination



© Kaspars Grinvalds - Fotolia

Phones are contaminated with a lot of **bacteria and viruses!**



Important Cause of nosocomial infections especially in Healthcare (hospital, clinics...)

# Atmospheric pressure Plasma treatment for surface decontamination



Contaminated phone

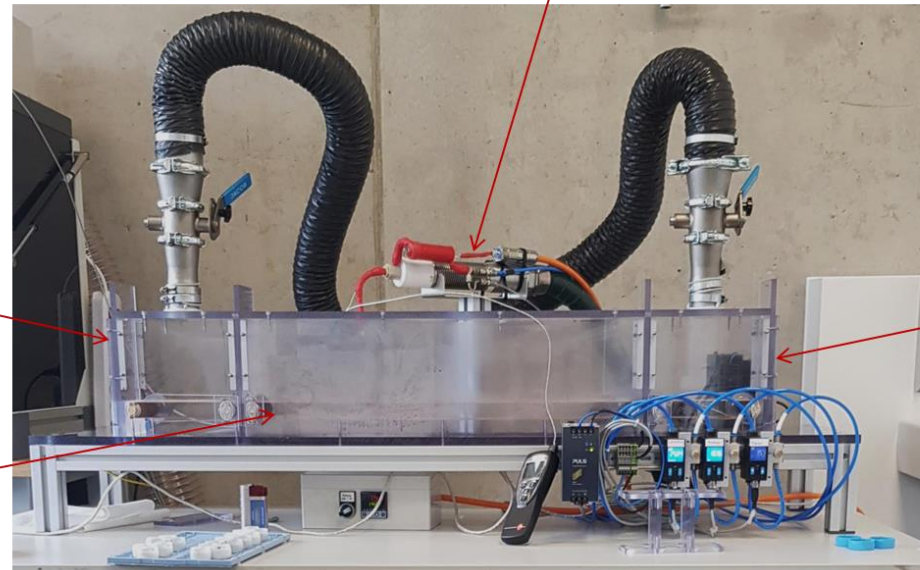
## Atmospheric pressure Plasma treatment

CD40 Jet with vaporizer



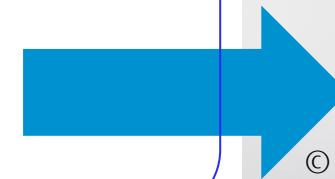
Entrance Gate with suction

Middle chamber Treatment area



Exit Gate with suction

- Moving Belt in each chamber
- Process Gas is injected in the middle chamber



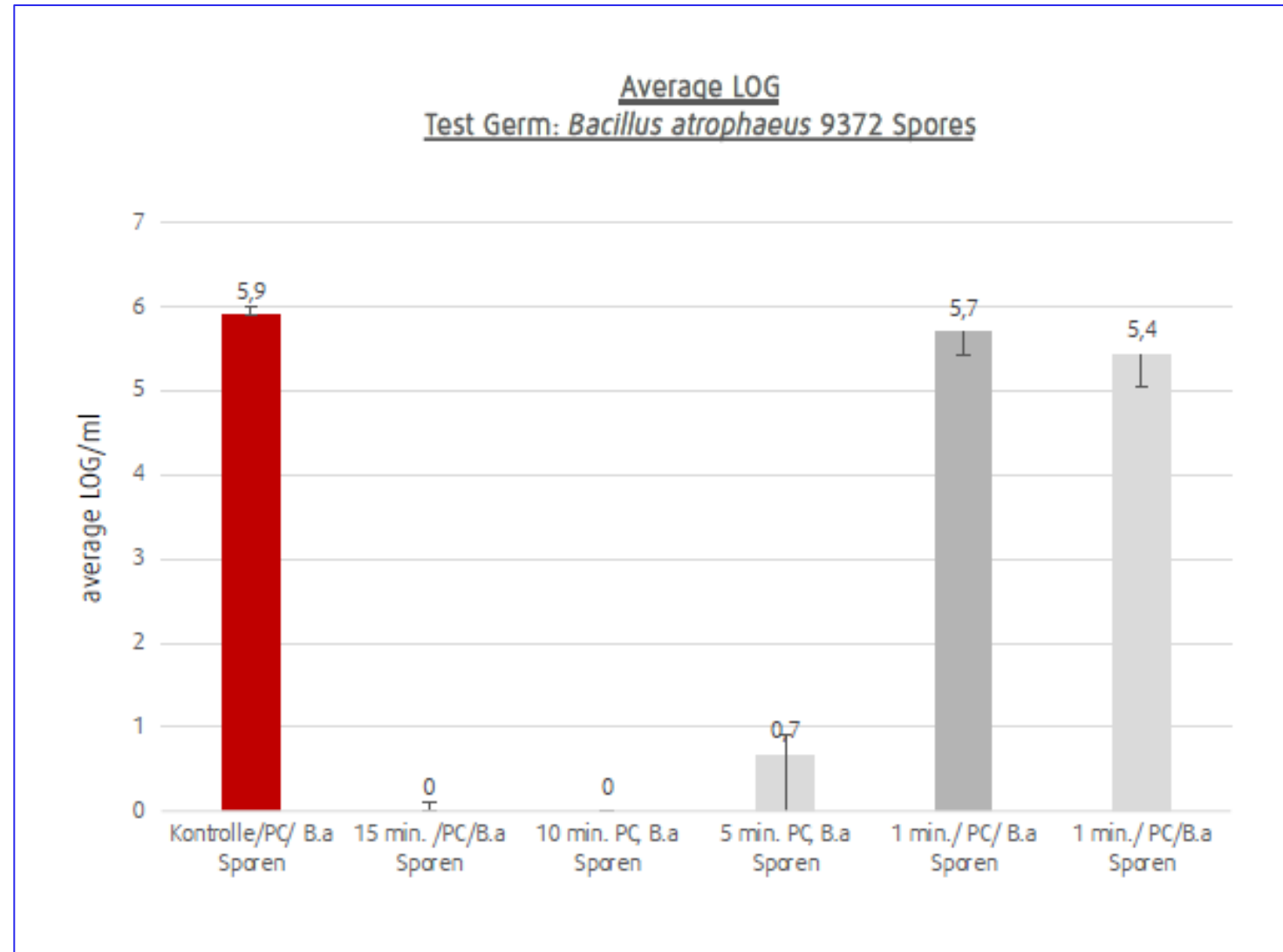
© Kaspars Grinvalds - Fotolia

Decontaminated phone

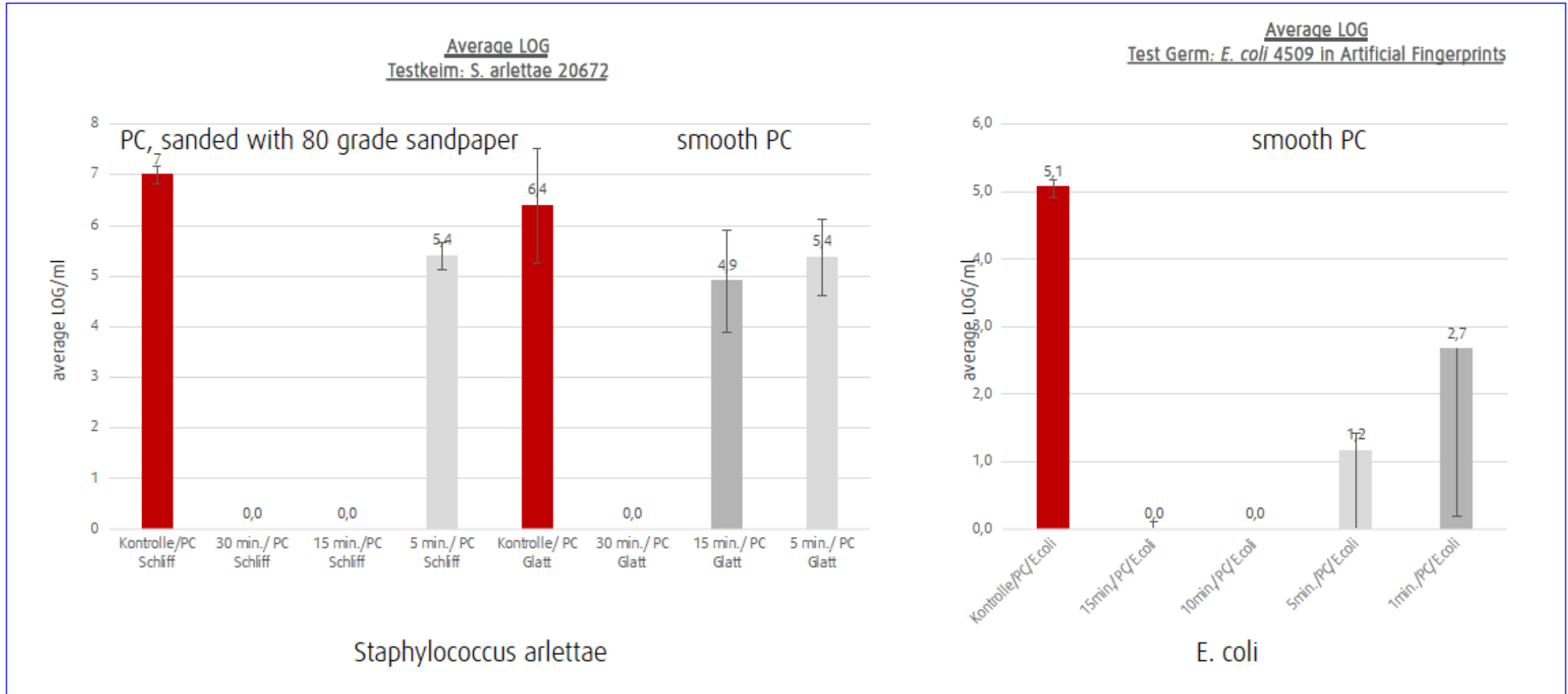
# Atmospheric pressure Plasma treatment for surface decontamination



Polycarbonate contaminated surface with Artificial fingerprints developed by WFK

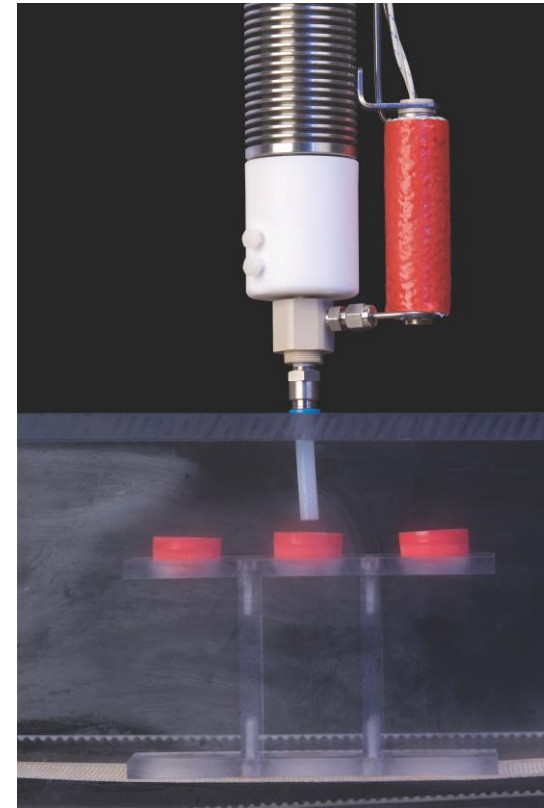
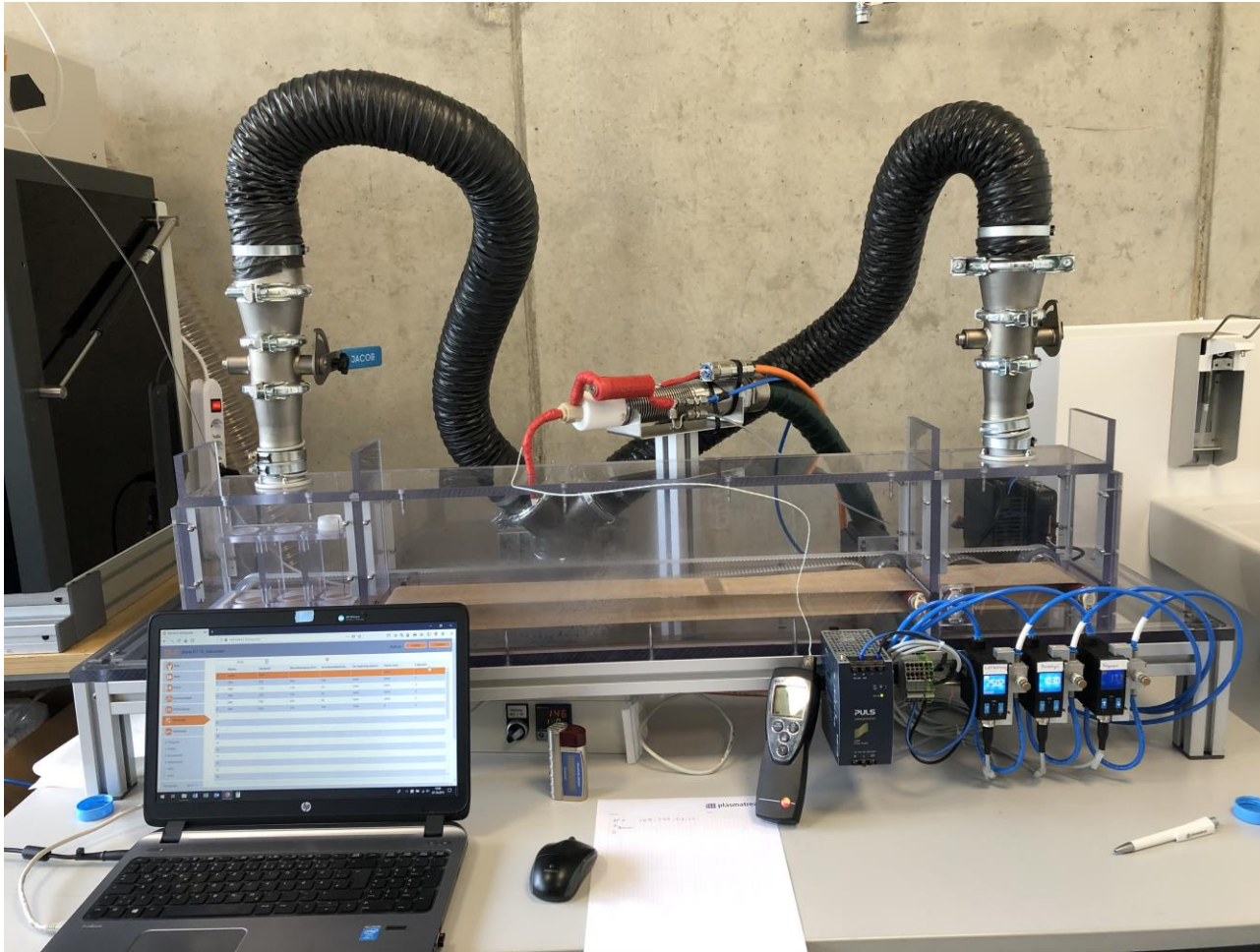


# Atmospheric pressure Plasma treatment for surface decontamination

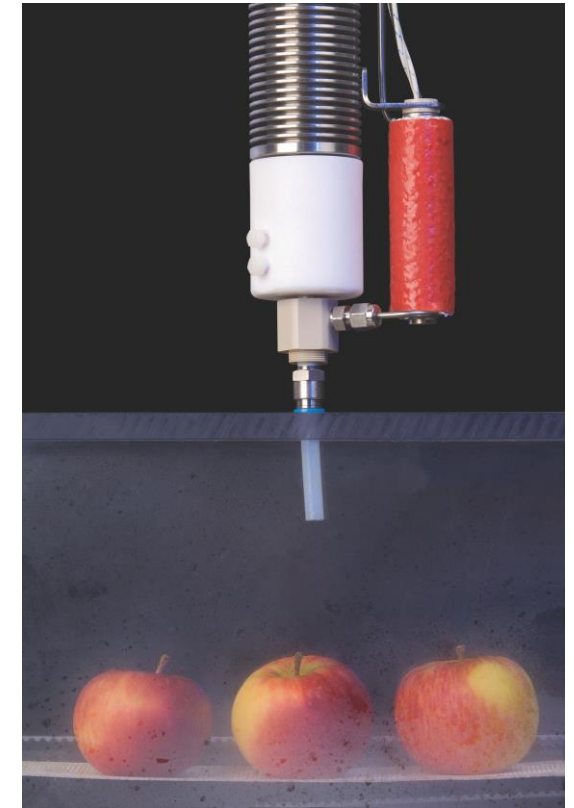




# Atmospheric pressure Plasma treatment for surface decontamination



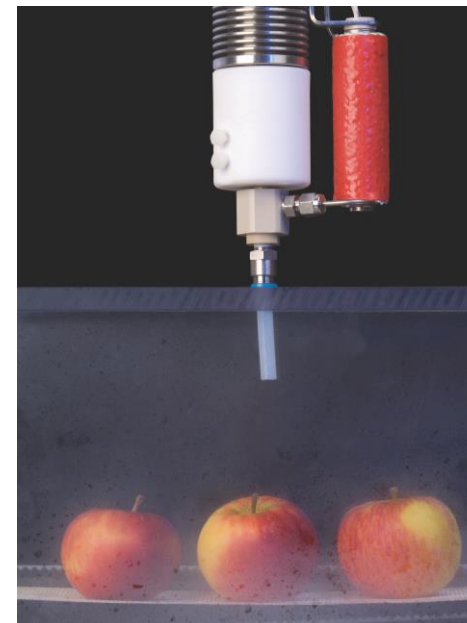
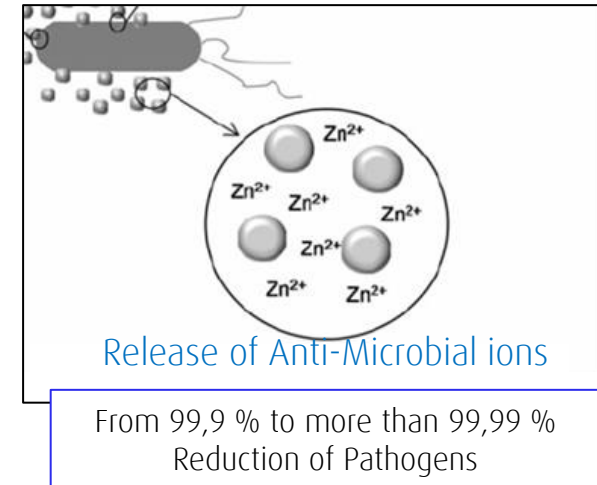
Decontamination of 3D polymer surfaces



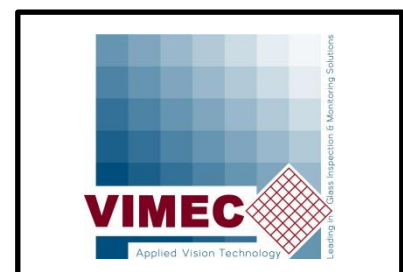
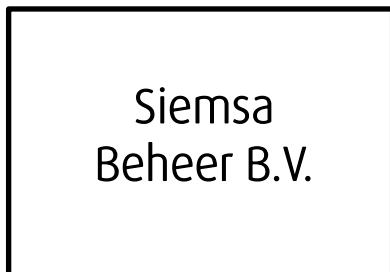
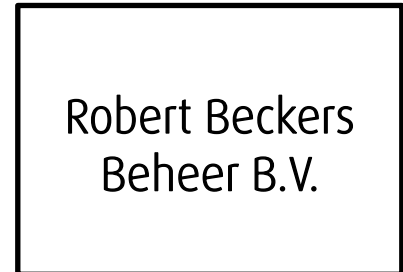
Decontamination of fruits or food

# Conclusion

- It was possible to deposit an **antibacterial coating** using ZnO/SiO based precursor.
- Identification of the mechanism associated to the **antibacterial activity** due to the **release of Zn<sup>2+</sup> ions**.
- Further work will be focused on improving the « **photocatalytic** » **properties** of the ZnO/SiO coatings and consider thermal post treatment procedure.
- It was possible to use Plasma processes for **decontamination of polymer surfaces**.
- Further work will be focused on **optimizing the process** with an improvement of the decontamination efficiency.

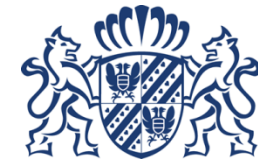


# AutoProtect – Project partners





Niedersächsische  
Staatskanzlei



provincie  
groningen



provincie limburg



Europäische Union  
Europese Unie

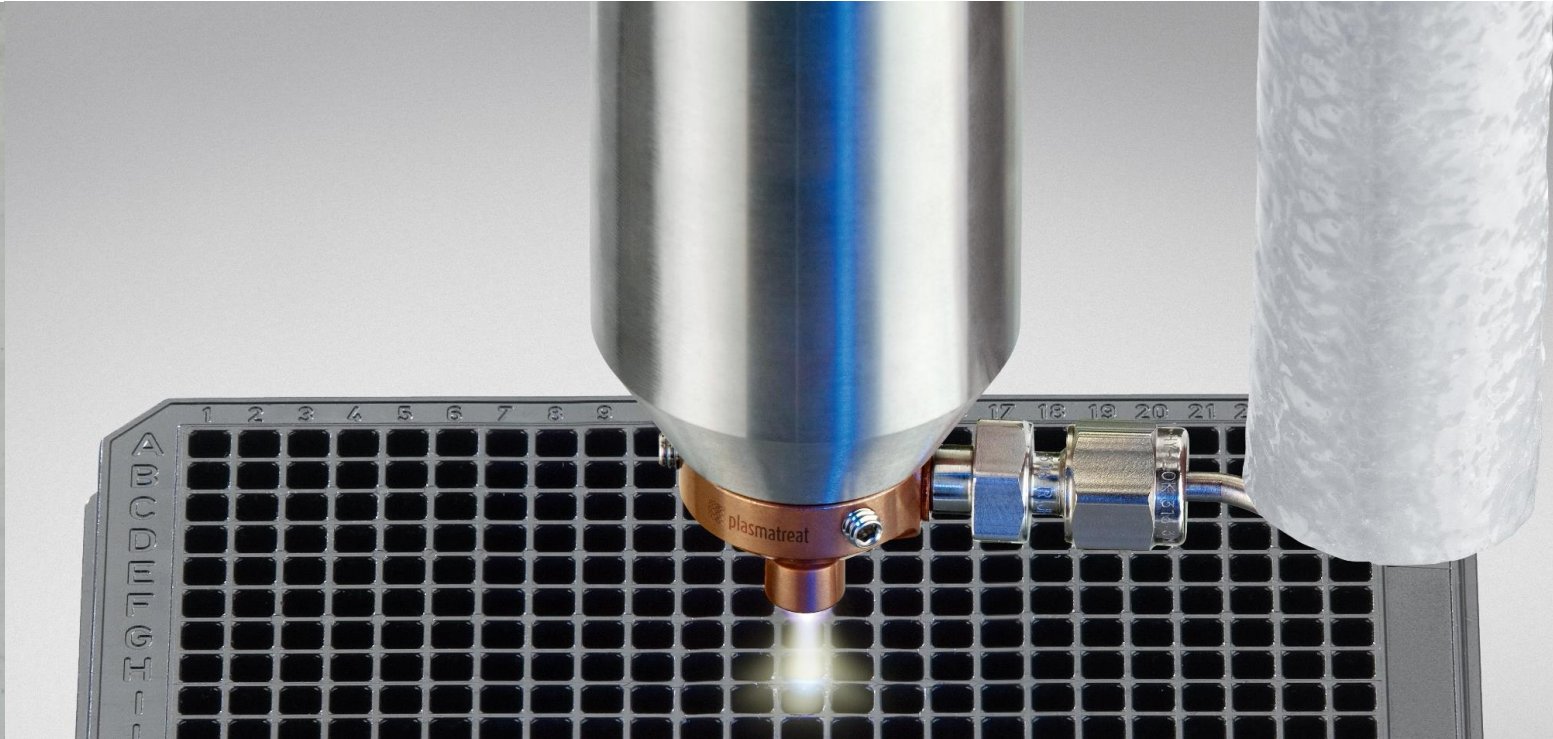
Ministerium für Wirtschaft, Innovation,  
Digitalisierung und Energie  
des Landes Nordrhein-Westfalen



Ministerie van Economische Zaken  
en Klimaat



Thank you very much for your attention



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Dhia.bensalem@plasmatreat.de



[www.plasmatreat.com](http://www.plasmatreat.com)

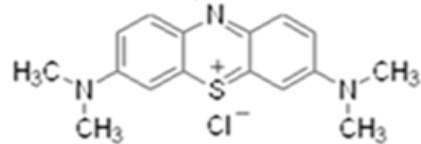




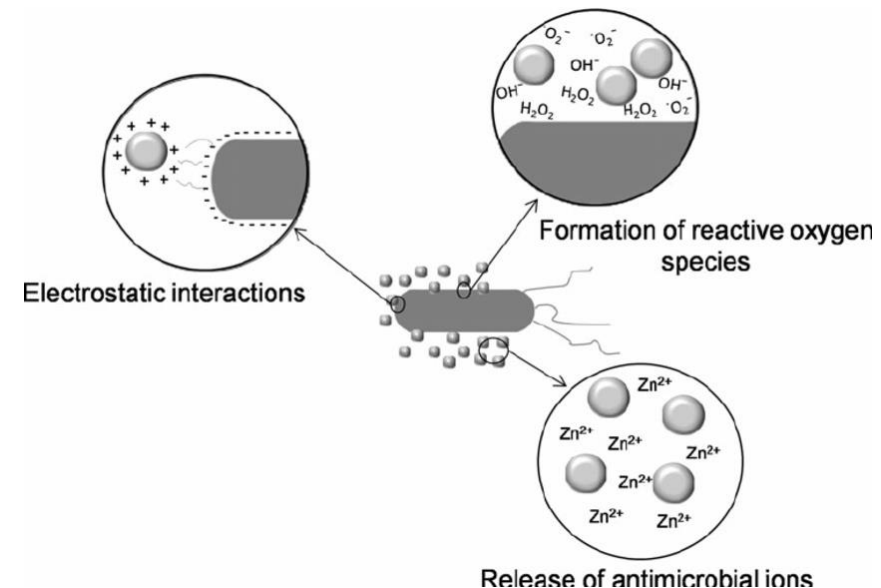
## Additional Information

Evaluation through MB degradation and optimization in UV/Vis region

Photocatalytic evaluation according to German Standard DIN 52980 with the degradation of methylene blue solution



The plasma deposited ZnO/SiO coating presented **no photocatalytic activity** following plasma deposition that indicates that the mechanism of antibacterial activity is associated to the release of Zn<sup>2+</sup> ions in the medium.

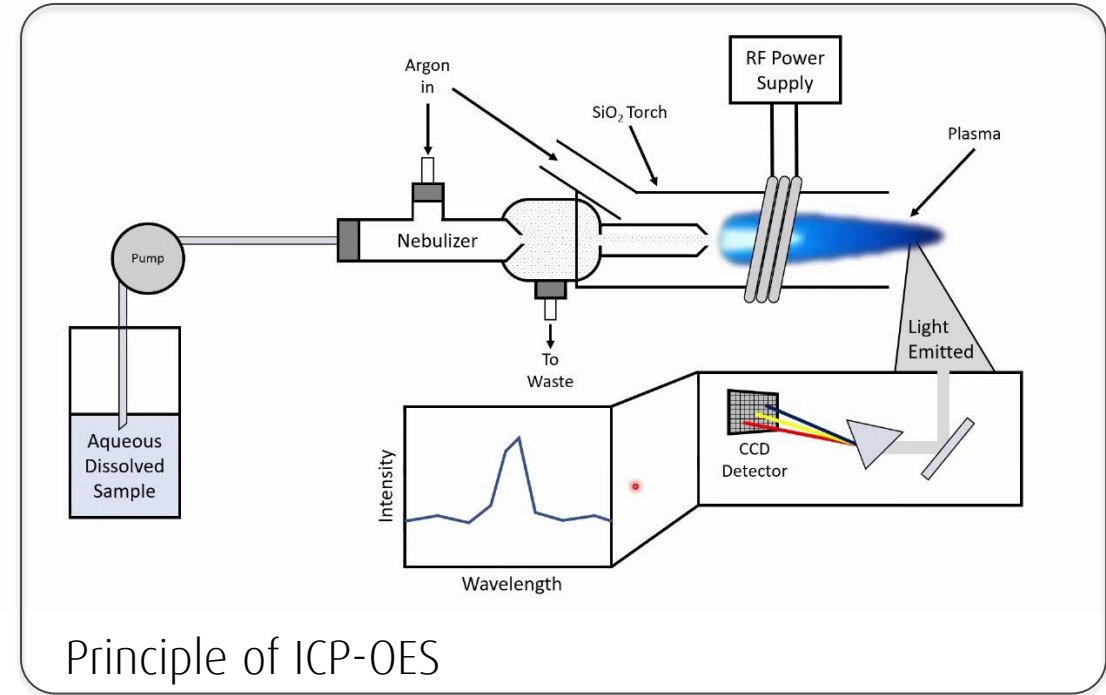


Source : <https://www.mrc-systems.de/en/products/photo-activation>

# Additional Information

## Methodology used for ICP/OES:

- Plasma coated polycarbonate samples on approximately - 200 cm<sup>2</sup> are immersed in 100 mL of pure HPLC Water
- Samples are prepared for 12 / 24 and 48 h to maximize the release of ions in the solution
- Zinc ion concentration are then evaluated in comparison with Zn calibration done prior measurement



Time [h]	12	24	48
Calculated concentration [mg / l]	7.3	4.52	5.62

**ICP-OES measurement results of the coatings produced based on a 200 cm<sup>2</sup> coating area per 100 ml of solution.**

## Additional Information

Regarding Decontamination and current situation



Plasmatreat Sterilization Cabinet (PTSC580)

## Additional Information

Regarding Decontamination and current situation - Case study: Ventilation Tube Sterilization





It's time for a short break now....



the WEBINAR will continue in 5 minutes





# Webinar Presenter



## MSS-Coatings: Features and Applications

Robert Beckers, Vero Metal Holding B.V. (Netherlands)

VeroMetal<sup>®</sup>  
*Technical Finishes*



VeroMetal<sup>®</sup>  
**Robert Beckers**

## VeroMetal develops and produces cold spray metal coatings



- Esthetical



## VeroMetal develops and produces cold spray metal coatings

- Functional



## VeroMetal and Antibacterial coatings

**First anti microbial coating in 2007 based on pure Copper**

Clinical trials Birmingham Hospital





## VeroMetal and Antibacterial coatings

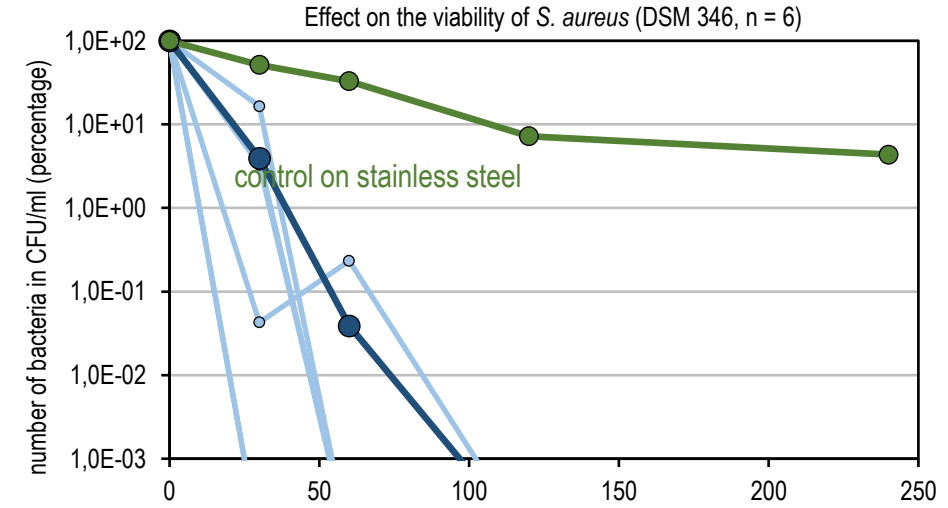
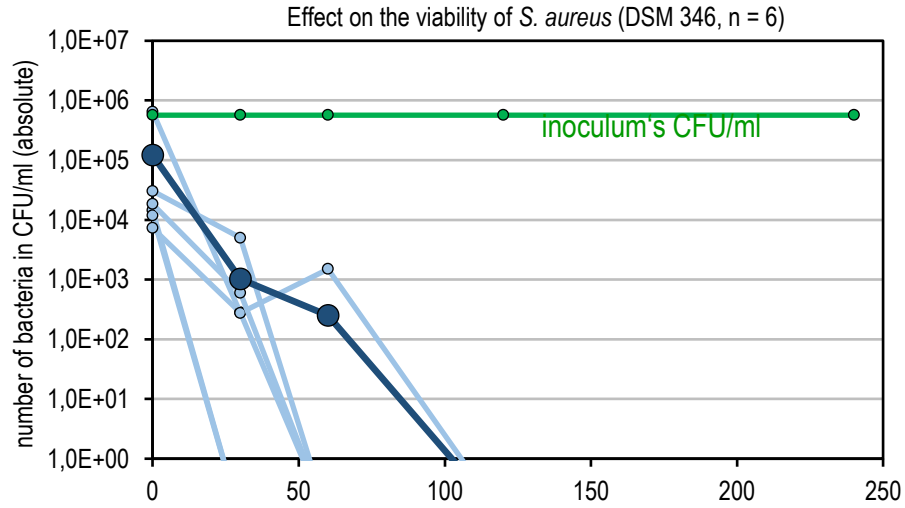
**First anti microbial coating in 2007 based on pure Copper**

Clinical trails Birmingham Hospital

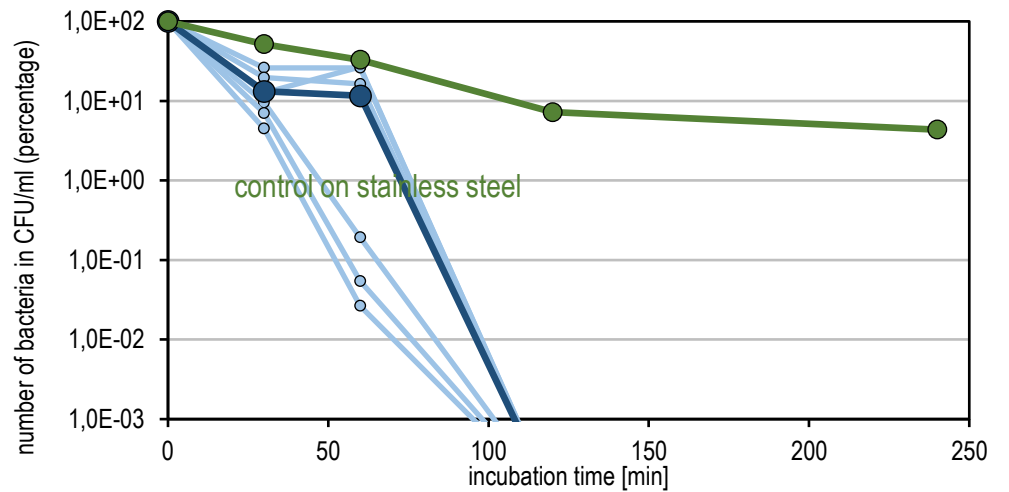
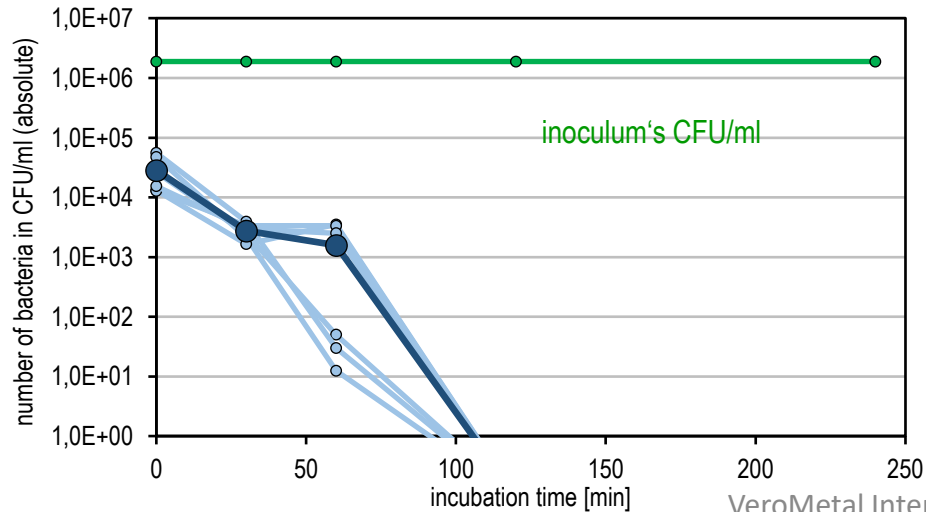


## Generation One

„Copper“



„Bronze“



## Practical Use

This relief from Herculaneum shows Achilles scraping rust from his bronze spear onto the wound of Telephus



Humanity knows for ages that copper has anti microbial and antifouling properties

## Practical Use



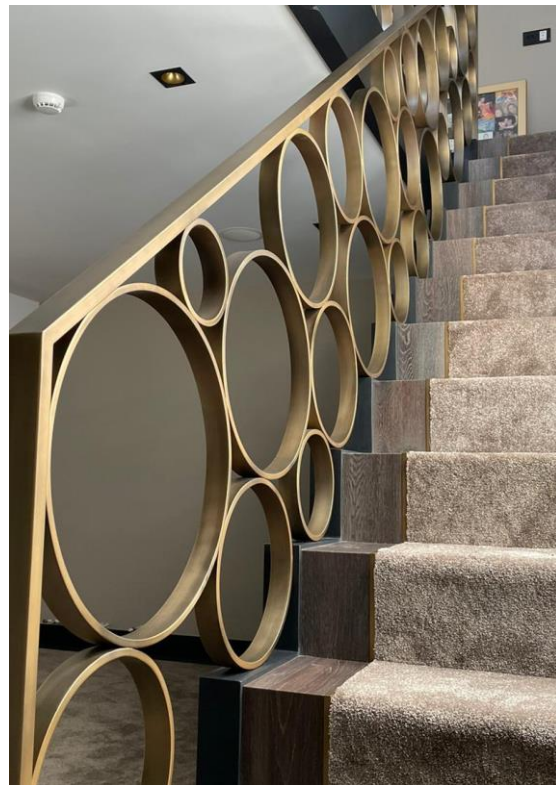


# VeroMetal<sup>®</sup>

*Technical Finishes*



## Nowaday's applications





## Property's Generation 1.0

### Functional quality

- Functional in light and dark environment

### Durable

- Very robust and durable due to the metal in the layer
- Polymer stability > 10 years

### Ease of use

- Easily check of physical presence of the **Copper** layer

### Design freedom

- Suitable for almost any surfaces and base materials
- For indoor and outdoor use
- Suitable for almost all forms
- Variable layer thickness between 50 - 200 micron
- Long lasting aesthetically pleasing surface



## First anti microbial coating based on pure Copper had to compare with TiO2

### Functionality

#### Copper

- Durable +++
- Visible +++
- Works within 1 hour +++
- Works in the Dark +++
- Application ++ -
- No Stains + --
- Cleaning ++-
- TCO ++

#### TiO2

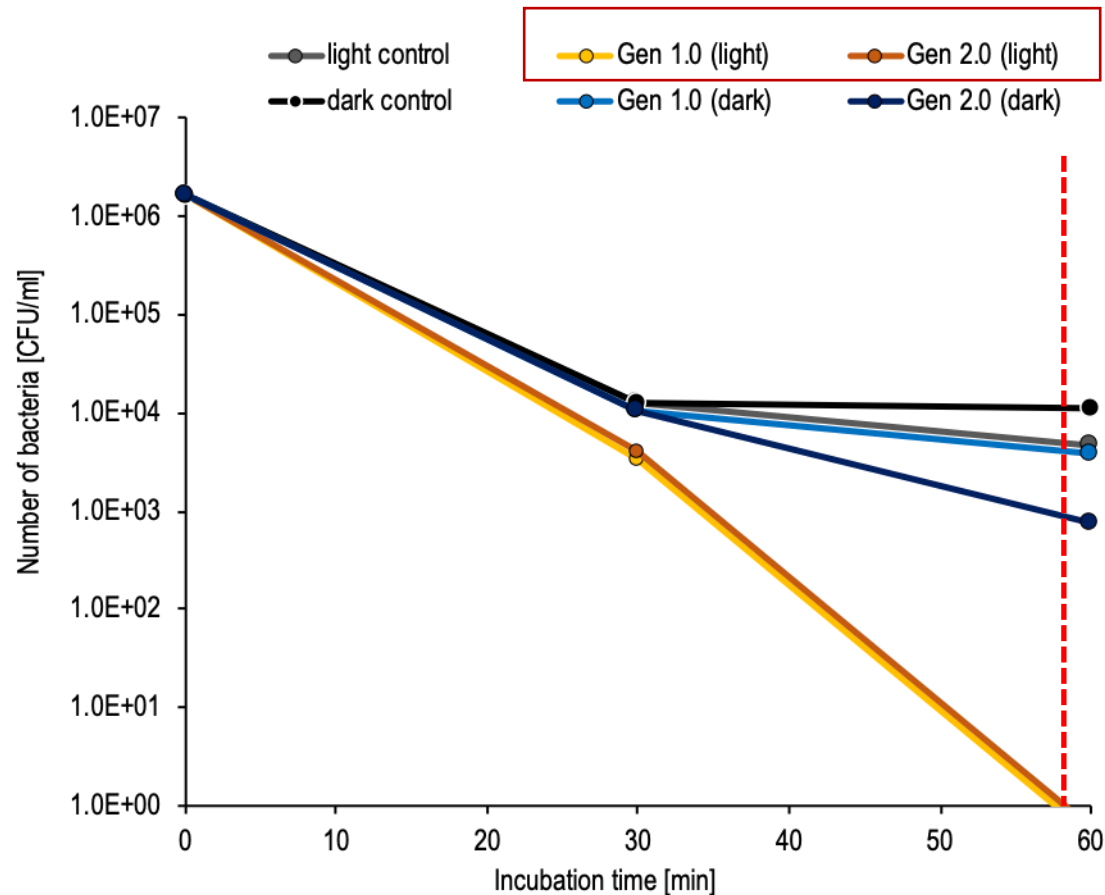
- Durable +
- Visible +--
- Works after 1 Hours ---
- Works in the Dark ---
- Application ++-
- No stains ++-
- Cleaning +--
- TCO +--

## VeroMetal Second Generation Anti Microbial Coating

- Durable +++
- Visible +++
- Kills Microbes within 1 hour +++
- Kills Microbes in the Dark +++
- No Stains +++
- Application ++-
- Cleaning +++
- TCO +++



## Inactivation of bacteria (*E. coli*) under artificial daylight



Setup acc. to ISO 22169:2011  
*Escherichia coli* as test bacterium

Excitation: Daylight fluorescents  
lamp

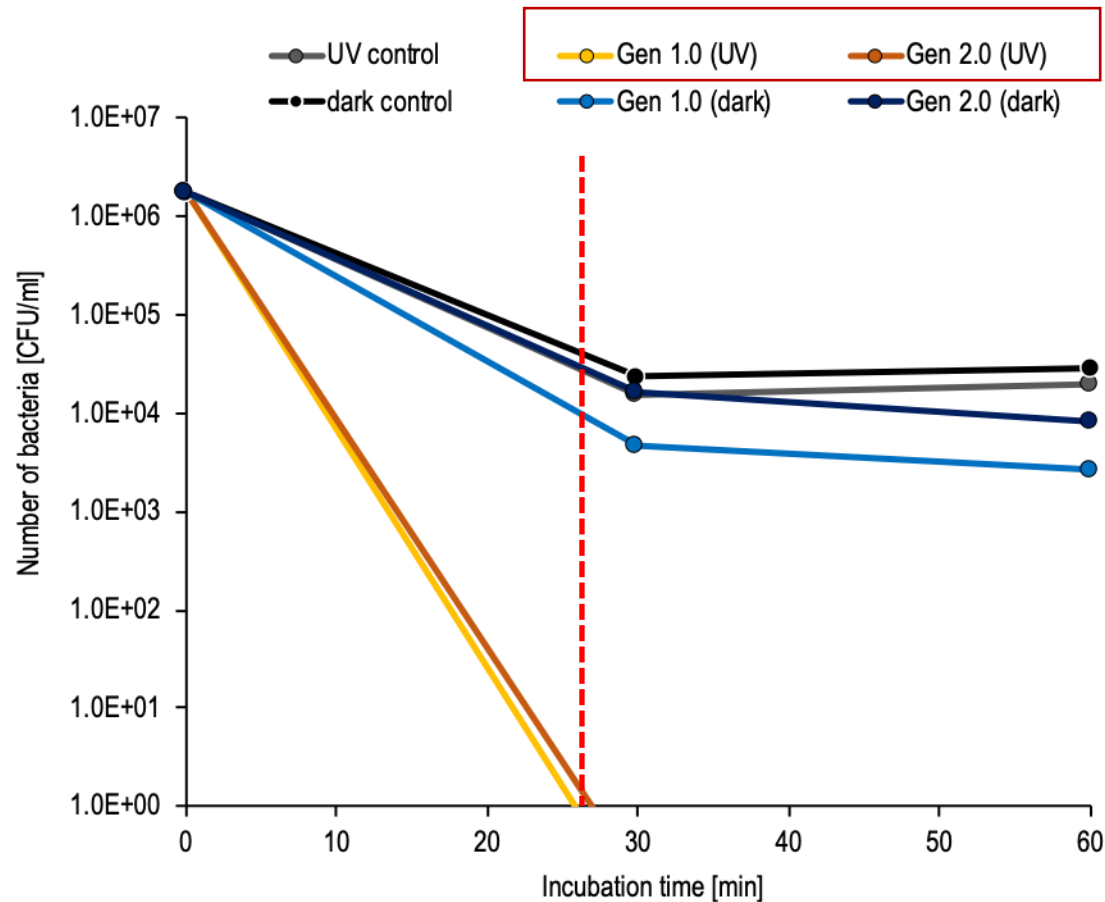
Intensity: **129  $\mu\text{W}/\text{cm}^2$ , equal  
to the illumination of  
offices (~950 lux)**

Both VAM coatings are equally capable of inactivating the test organism *E. coli* under ambient-like conditions.

Total inactivation of *E. coli* under UV irradiation after 60 min, and thus some self-disinfecting properties.

**Very strong antimicrobial effect under ambient conditions**

## Inactivation of bacteria (*E. coli*) under UV irradiation



Setup acc. to ISO 22169:2011  
*Escherichia coli* as test bacterium

- Excitation: 365 nm
- Intensity: 500  $\mu\text{W}/\text{cm}^2$

•Total inactivation of *E. coli* under UV irradiation after 30 min.

→ Very strong and rapid antimicrobial effect



## Property's Generation 2, Generation 3 and Generation 4

### Functional quality

- Functional in light and dark environment
- The effectiveness accelerates with artificial Light
- The effectiveness accelerates in the sun
- The effectiveness increases extremely by the influence of UV light
- The effectiveness is improved by heat/cold-changes or pressure

### Durable

- Very robust and durable due to the metal in the layer
- Polymer stability > 10 years

### Ease of use

- Easily check of physical presence of the VAM layer

### Design freedom

- Suitable for almost any surfaces and base materials
- For indoor and outdoor use
- Suitable for almost all forms
- Variable layer thickness between 50 - 200 micron
- Long lasting aesthetically pleasing surface



## Practical Use



## Practical Use



# Thanks for Attention



# Webinar Presenter



Deep into MSS-Coatings:  
Mechanisms and efficacy  
Dr. Joachim Meeßen, wfk-  
Cleaning Technology Institute  
e.V. (Germany)



wfk – Cleaning Technology Institute e. V.

wfk

# Highlights of 5 Years AutoProtect



## **wfk – Cleaning Technology Institute e.V.**

Private Research Institute, founded 1949

R&D projects with the aim to develop new technological solutions, companies can benefit from

Industrial research

Focus: cleaning, renewability, hygiene, surfaces, clean rooms, Personal protective equipment, industrial plants, health care sector, medical devices, new processes for disinfection and sterilisation

National guidelines

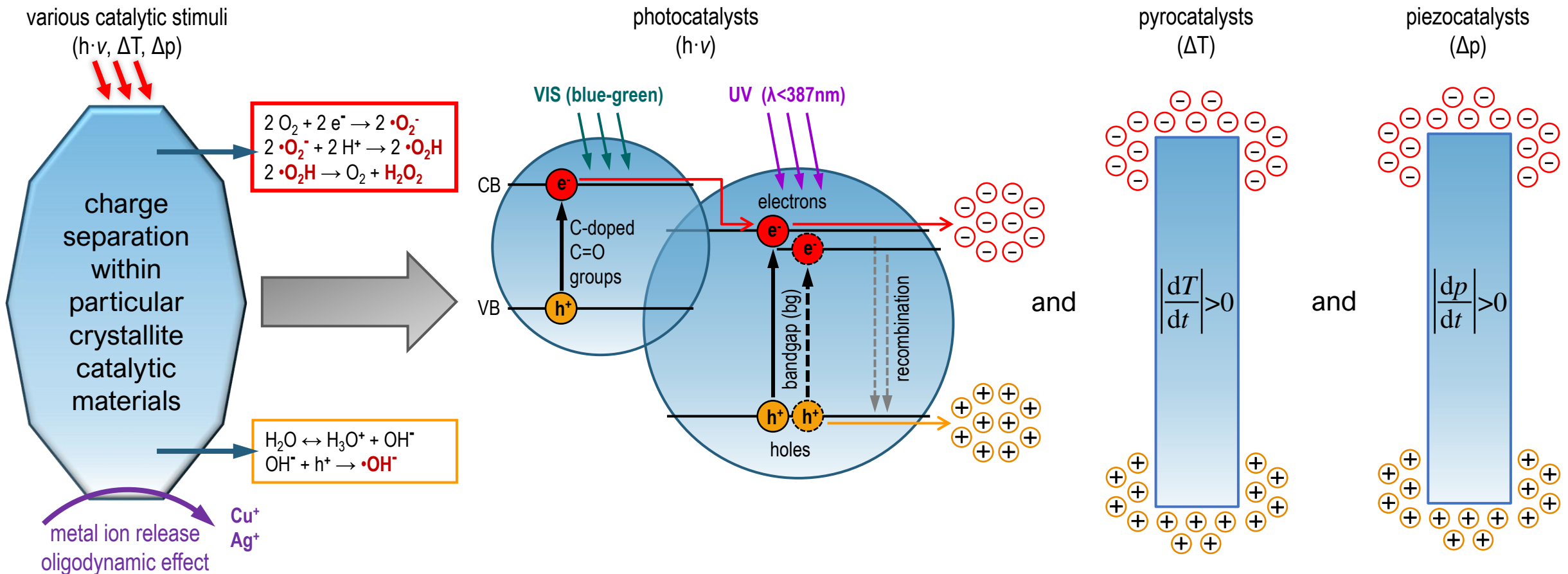
Standardization work: DIN / EN / ISO

[www.wfk.de](http://www.wfk.de)

# The physics behind the proposed catalytic Multi-Stimulus Systems (MSS) for new coatings



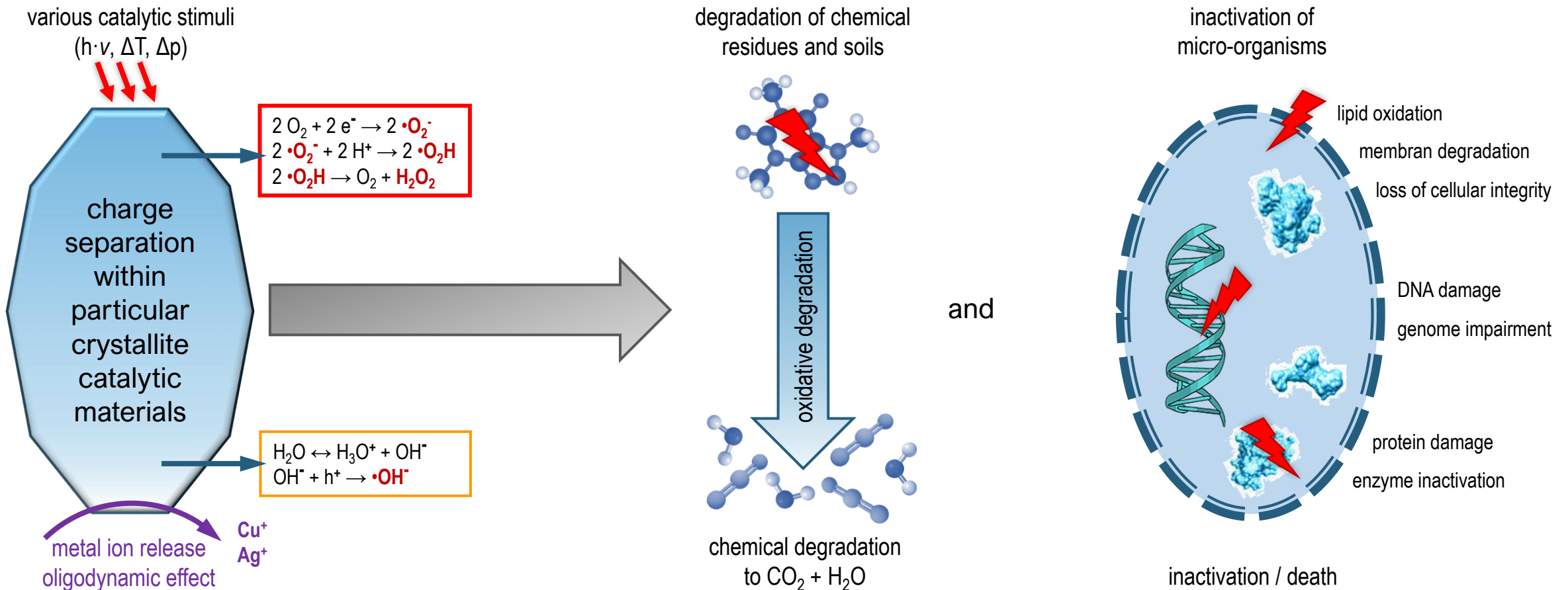
- Aims:**
- develop catalytically active surface coatings based on Multi-Stimulus-Systems (MSS)
  - using a range of crystalline photo-, pyro-, and piezocatalysts
  - utilizing the generation of reactive oxygen species (and the release of transition metals)



# The physics behind the proposed catalytic multi-stimulus systems for new coatings



- Aims:**
- develop catalytically active surface coatings based on multi-stimulus-systems (MSS)
  - using a range of crystallite photo-, pyro-, and piezocatalysts
  - utilizing the generation of reactive oxygen species (and the release of transition metals)



assessing the anti-microbial activity of coatings

assessing the degradational activity of coatings

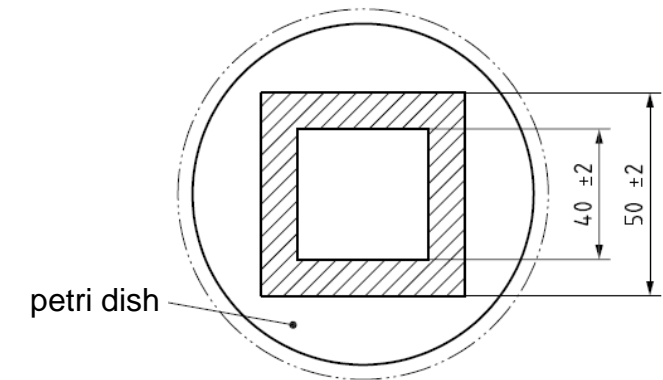
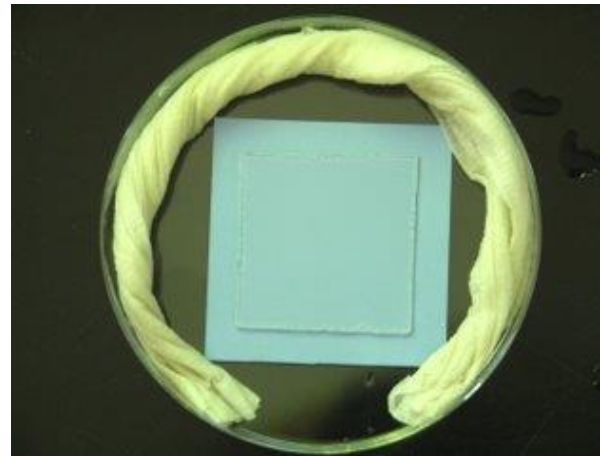
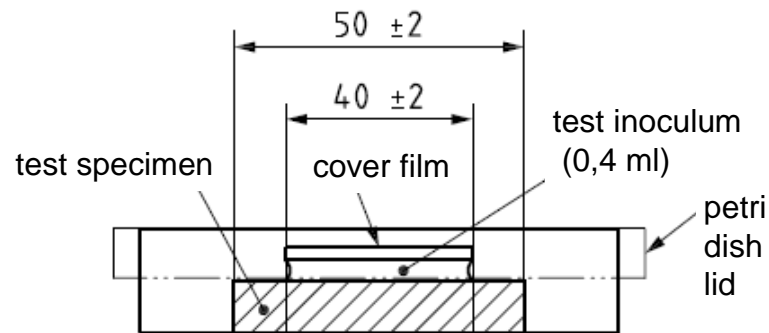
ISO 22196: Antimicrobial products – Test for antimicrobial activity and efficacy\*

application with bacteria

adaptation for viruses

*E. coli* / *S. aureus* / *P. aeruginosa* / *E. faecium* / *E. hirae*

Phi 6 resembling SARS-CoV-2 (lipid envelope, ssRNA, 75nm)



Testing with various stimuli: a) UVB<sub>365nm</sub>, c) UVB<sub>351nm</sub> (QUV), b) daylight, c) near infrared (NIR) cycling

Testing various surfaces: a) metal, b) alloy, c) with metal particles, d) with photocats, e) with metal particles and photocats, f) with metal particles, photo-, and pyrocats



## assessing the anti-microbial activity of coatings

## assessing the degradational activity of coatings

### fluorophor / dye degradation

### protein degradation

### DNA degradation

#### coumarine assay

#### methylene blue assay

#### protein breakdown

#### enzyme activity

#### DNA break-down

#### RAPD-PCR

Measuring degradation of chemical compounds by the stimulus-induced radical formation at the catalyst's surface.

Measuring degradation of chemical compounds by the stimulus-induced radical formation at the catalyst's surface.

Measuring protein concentration. Breakdown into smaller peptides results in more groups accessible.

Enzyme activity as a measure of protein damage and / or protein degradation.

DNA integrity is used as a measure of degrading catalytic effects in gelelectrophoresis.

DNA integrity is measured by a special PCR technique using randomly binding primers



radical formation increases fluorescence

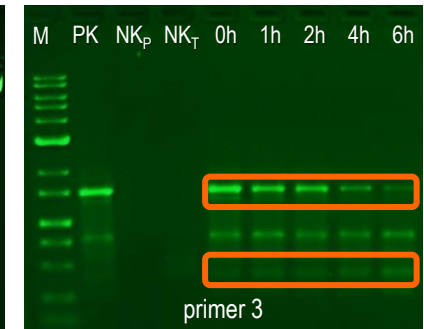
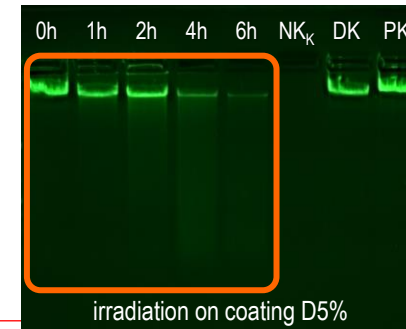
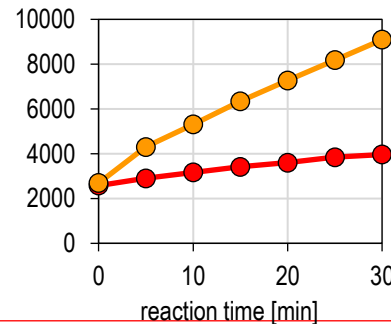
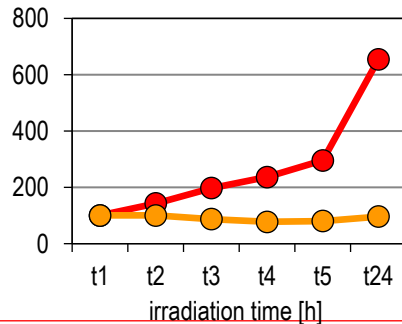
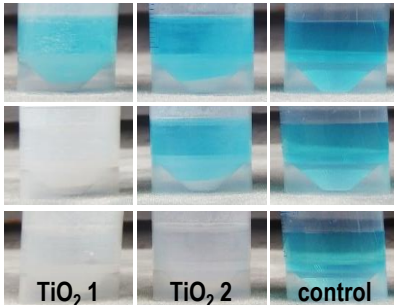
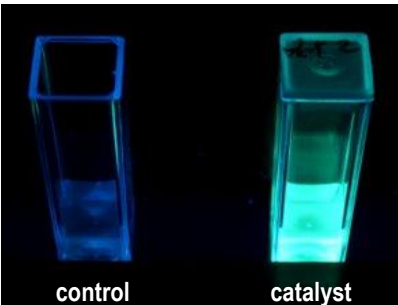
radical formation decreases colouring

decomposition increases measured results

declining activity indicates degradation

impaired integrity is represented by a smear

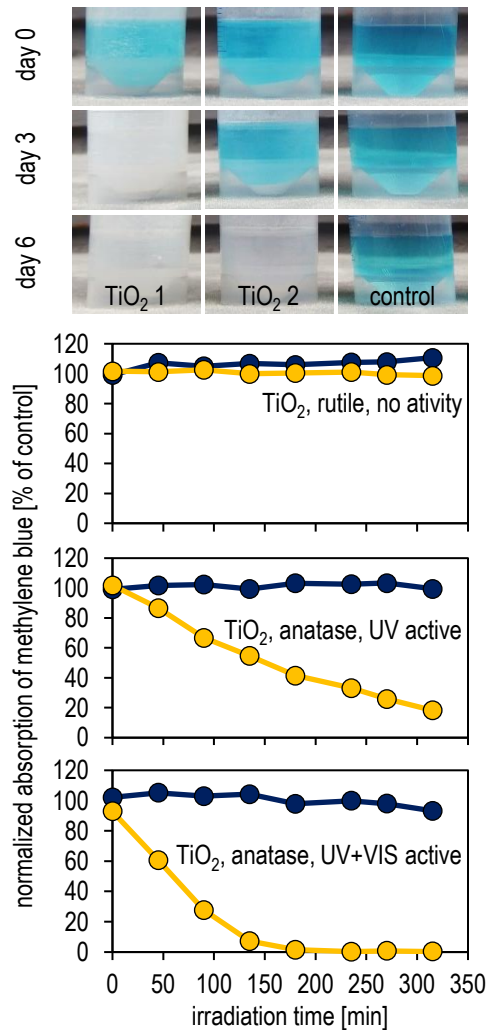
PCR pattern shift indicates DNA damage



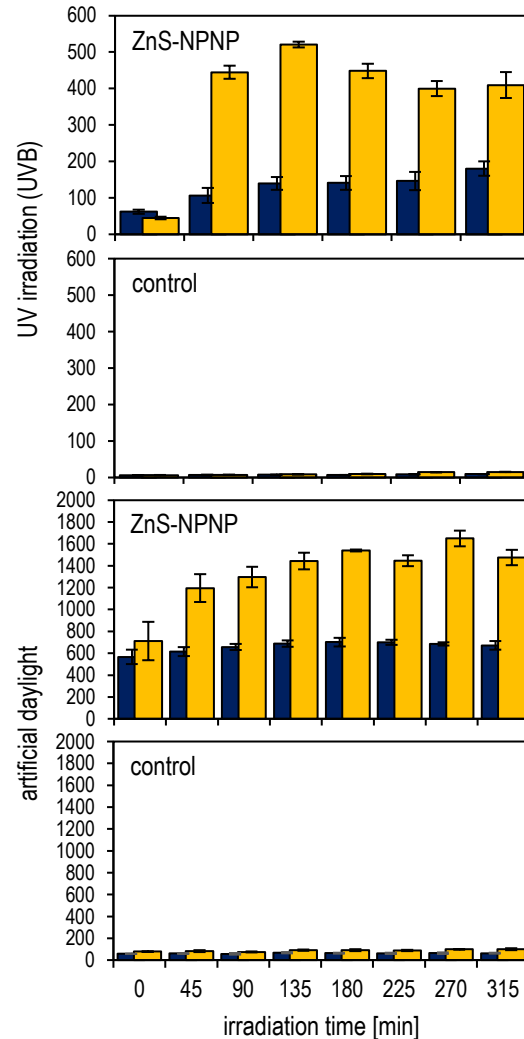
# WP2/3 Coatings with Photocatalytic Activity



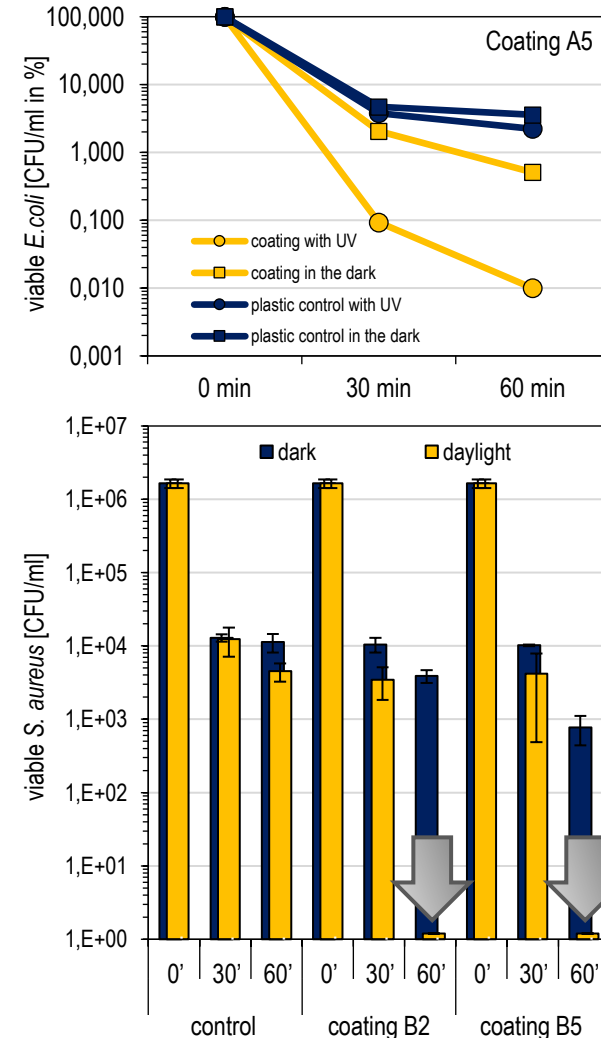
## methylene blue



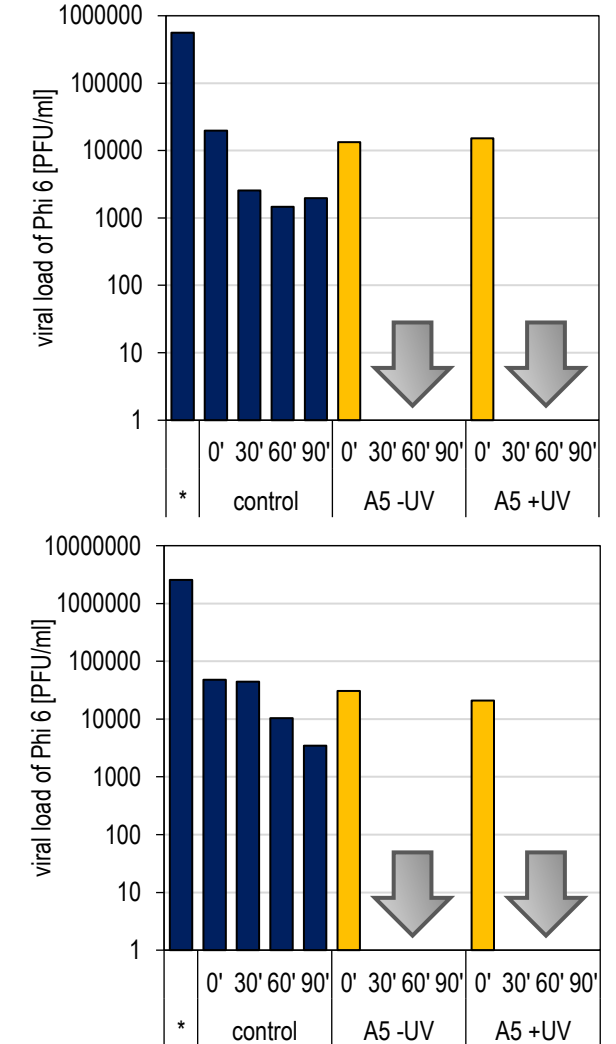
## coumarin



## bacteria (ISO 22196)



## viruses





methylene blue

coumarin

bacteria (ISO 22196)

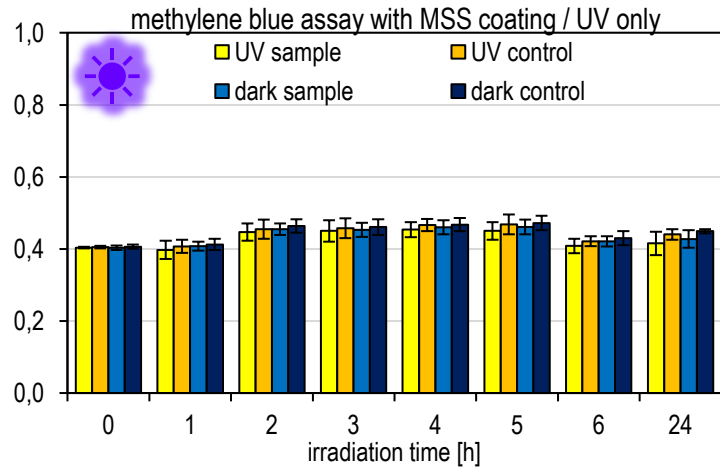
viruses

### Research on Photocatalytic Activity

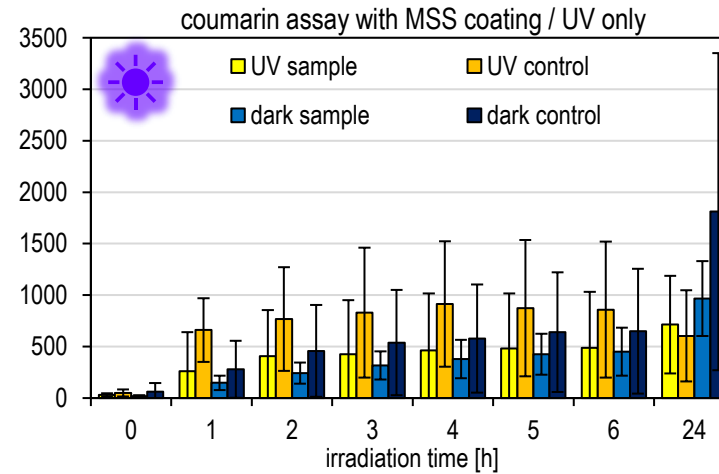
- 10 TiO<sub>2</sub> types by 4 providers tested
- 4 other photocatalysts tested
- in-house synthesis of ZnS-NPNPs
- low to high activity in suspension assay
  
- picking best candidates for further research
- 9 surfaces / coating formulations with TiO<sub>2</sub> and ZnS
- moderate to high activity in coatings
- within coatings:
  - good capacity of radical formation
  - high capacity to inactivate bacteria
  - good capacity to inactivate viruses (Phi 6)



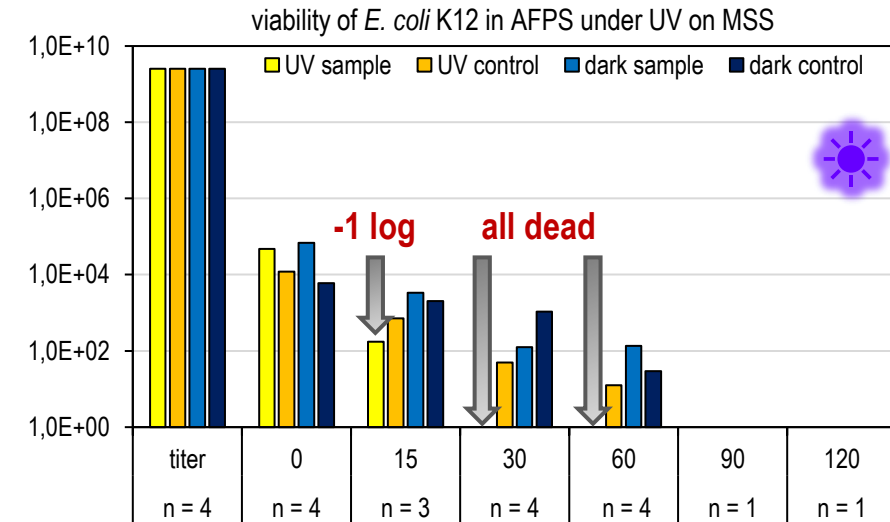
## methylene blue



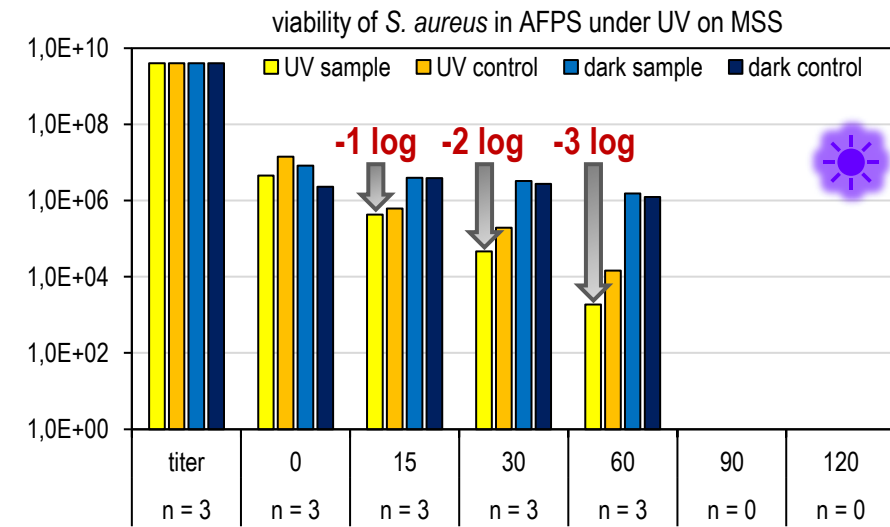
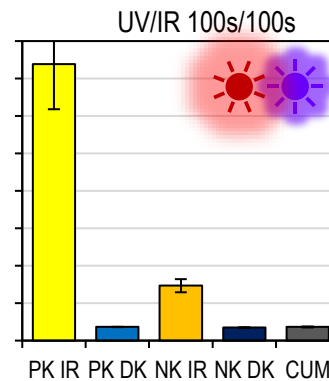
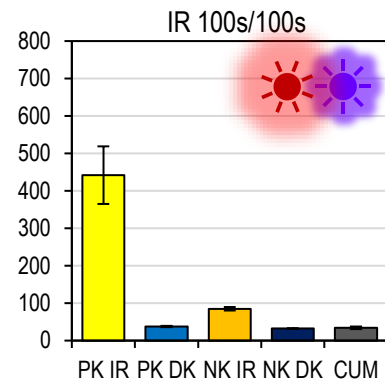
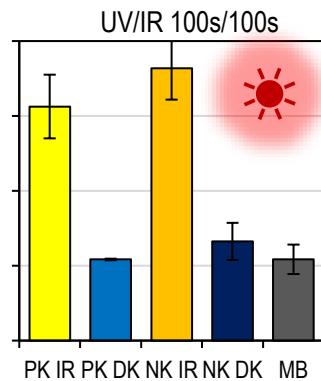
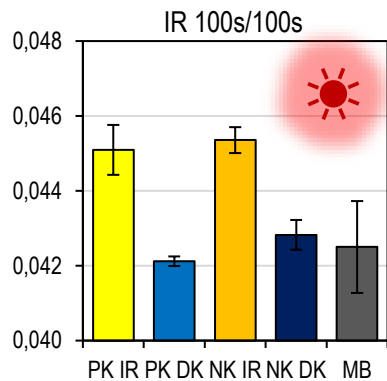
## coumarin



## bacteria (ISO 22196)

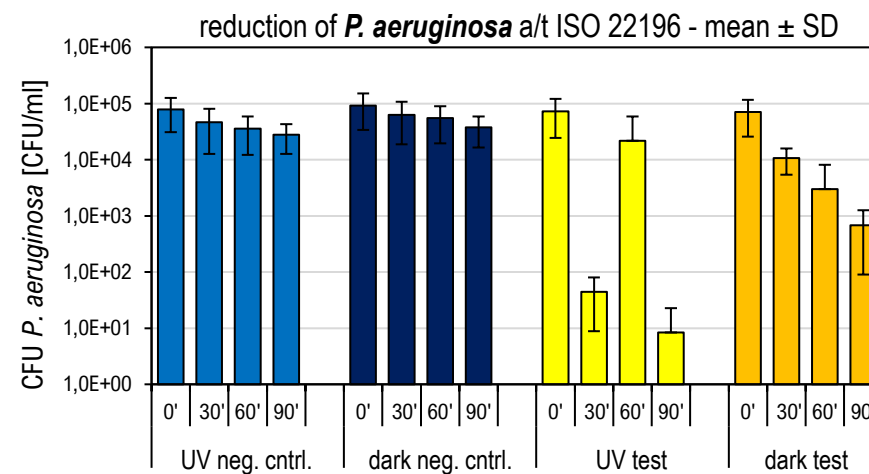
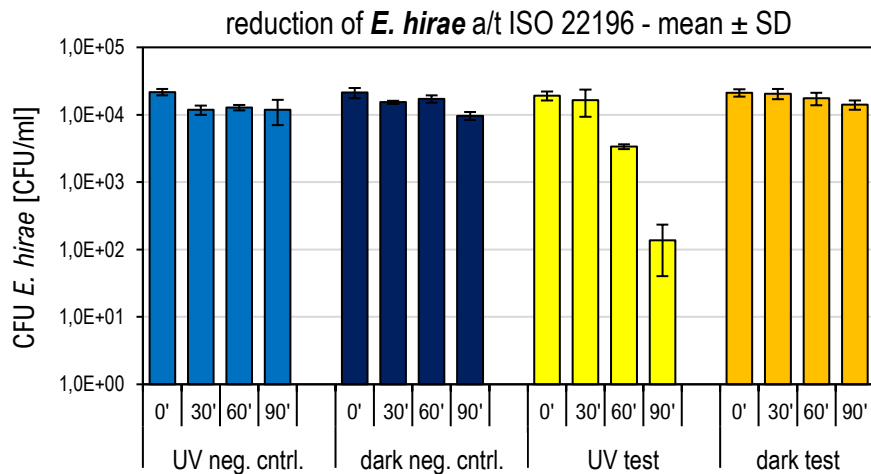
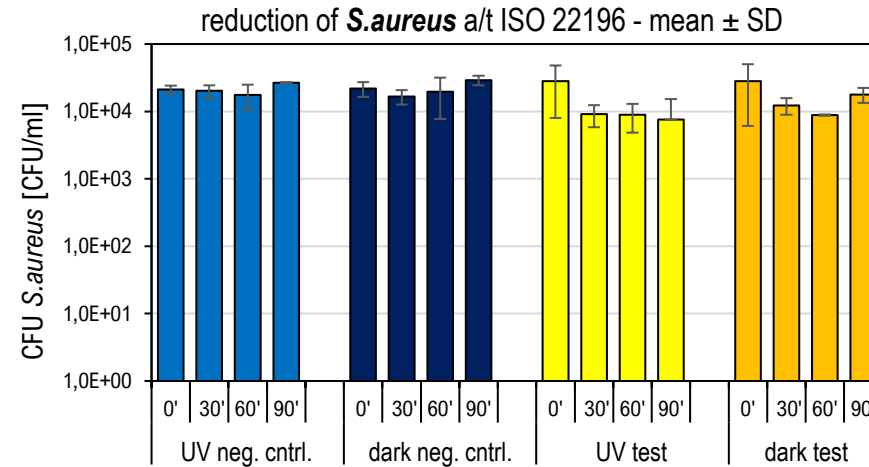
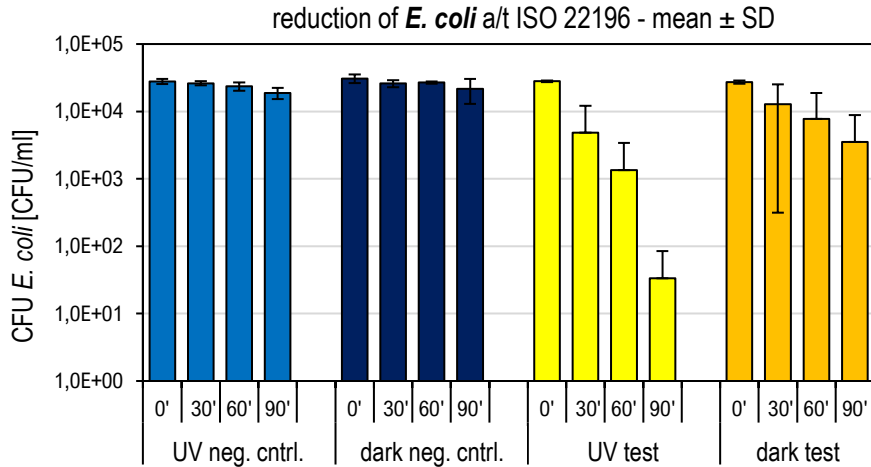


Inconclusive results with UV-irradiation only (above), but some effects with IR cycling and IR/UV cycling (each with 50 x 100/100s)!





Bacteria (ISO 22196) → broadening the range of bacterial species tested on the MSS-Coating (under UV only)



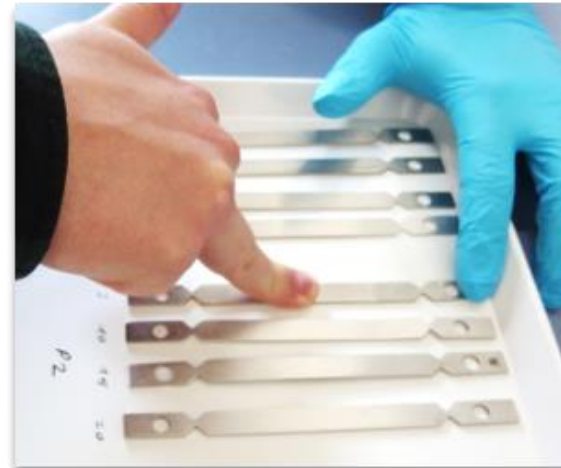
- 3 out of 4 species tested show strong reduction of viability after testing on the MSS-Coating
- *S. aureus* shows no reduction, despite the anti-microbial effect being demonstrated in previous experiments (see previous slide)



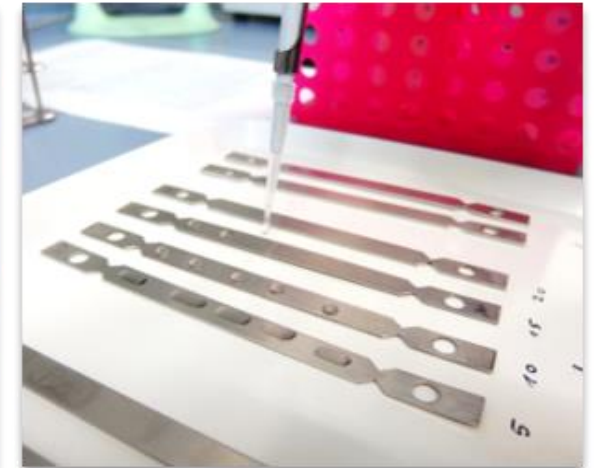
Developing test methods for chemical and microbial cleanliness of surfaces

- ↳ Continuous catalytic activity and longevity of coatings to be periodically tested
- ↳ Standard test methods have shortcomings or don't fit all purposes (ISO 22196, ATP tests)
- ↳ Developing alternative test methods is strongly indicated
- ↳ **Artificial Fingerprint Soiling (AFS)** to mimic realistic surface contamination

- frequently touched surfaces accumulate micro-organisms and residues (soiling)
- highly problematic in medical facilities
- fingermark matrices may:
  - contain residual water and organic compounds to promote microbial survival and growth
  - interfere with testing methods
  - protect micro-organisms from detrimental stressors as desiccation, UV, and disinfectants



real fingerprint soiling



artificial fingerprint soiling

# Action Modes for Catalytic Multi-Stimulus Coatings



Developing test methods for chemical and microbial cleanliness of surfaces

- ↳ Continuous catalytic activity and longevity of coatings to be periodically tested
- ↳ Standard test methods have shortcomings or don't fit all purposes (ISO 22196, ATP tests)
- ↳ Developing alternative test methods is strongly indicated
- ↳ **Artificial Fingerprint Soiling (AFS)** to mimic realistic surface contamination

**Task 1:** characterize the microbial burden on frequently touched surfaces

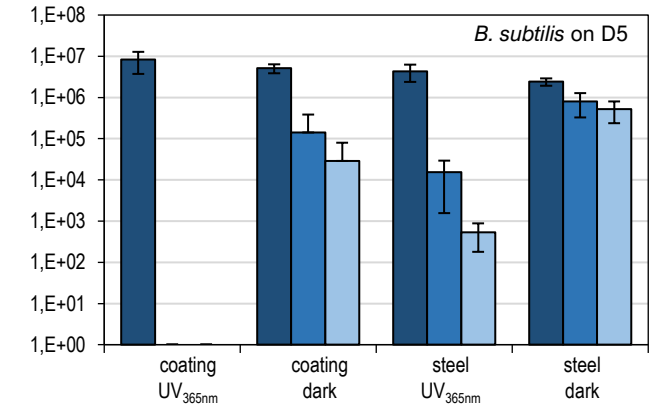
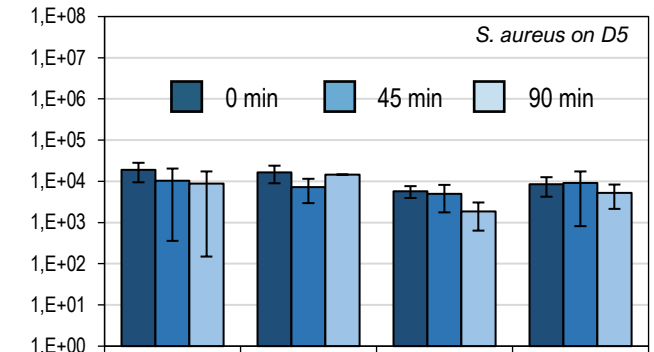
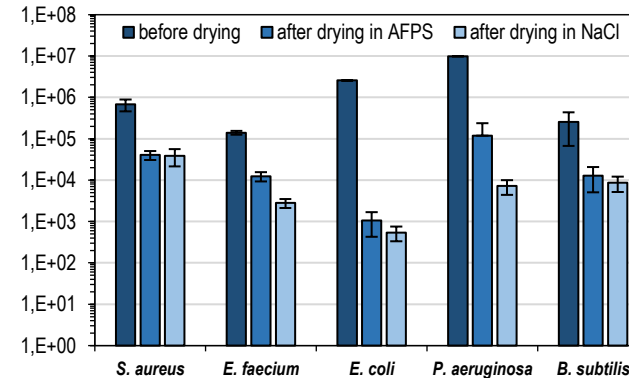
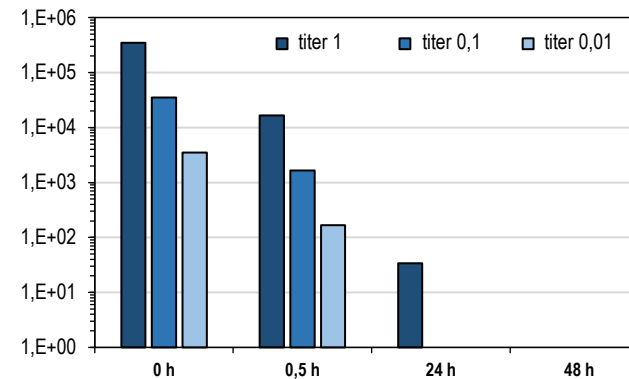
- phones: 32-1440 CFU per screen
- indoor floors: 7-498 CFU/dm<sup>2</sup>
- workplace surfaces: 8-922 CFU/dm<sup>2</sup>
- public surfaces: 8-4210 CFU/dm<sup>2</sup>  
(38% identified isolates are BSL 2)

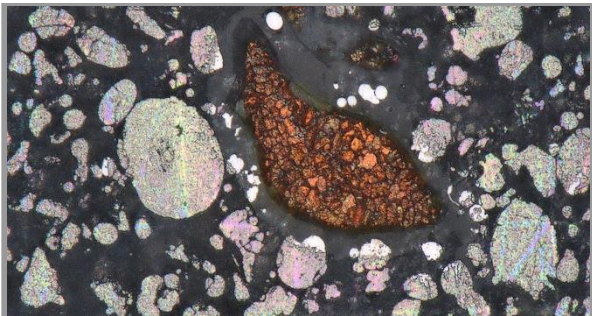
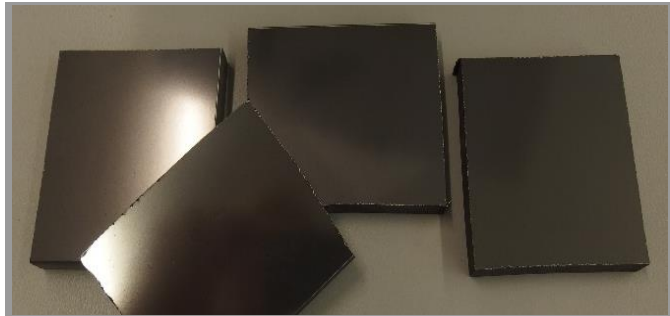
**Task 2:** develop a reproducible, artificial fingerprint (fp) matrix

- 3 µg/fp of protein
- 10 µg/fp of lipids
- 2 µg/fp of salts
- 10 µl for 1 fp soiling
- application in 10% IPA solution

**Task 3:** develop realistic application and transfer procedures

- methods for even distribution
- developing a reproducible transfers
- polyurethane stamps best suited
- determining reduction factors of transfer and desiccation





- Photo- / pyro- and piezo-catalysts identified
- Coating matrix identified, durability proofed
- Inactivation of bacteria (Gram +/-) and enveloped viruses proofed
- Monitor systems for checking of coating performance developed
- New methods for detection of radical formation developed
- New methods for testing antimicrobial activity of coatings developed
- New methods for quantification of vital bacteria developed

# Acknowledgements



Thank you for your interest....

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Siemsa Beheer B.V.



# Webinar Presenter

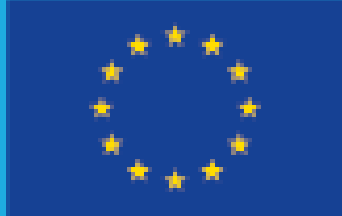


Towards light responsive  
coatings against biofilm  
formation

Cyriel Mentink, PhD.  
CHILL (Netherlands)



INTERREG  
Deutschland  
Nederland



Europäische Union  
Europese Unie

108

# Towards light responsive coatings against biofilm formation

Cyriel Mentink





## Introduction

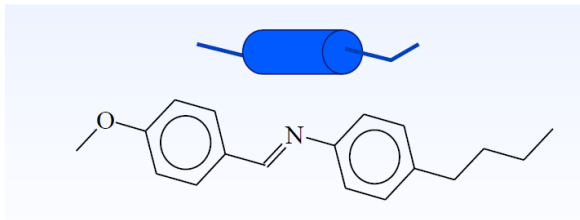
- Biocidal Products Regulation is becoming more strict
- Alternative to 'active substance'
- Morphological shifting surface due to stimulans

**Stimuli responsive dynamic coatings to prevent formation of biofilm  
based on Liquid Crystal Polymer Networks (LCN)**

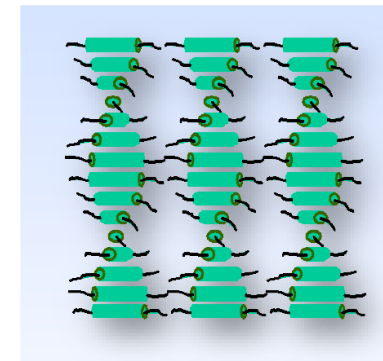
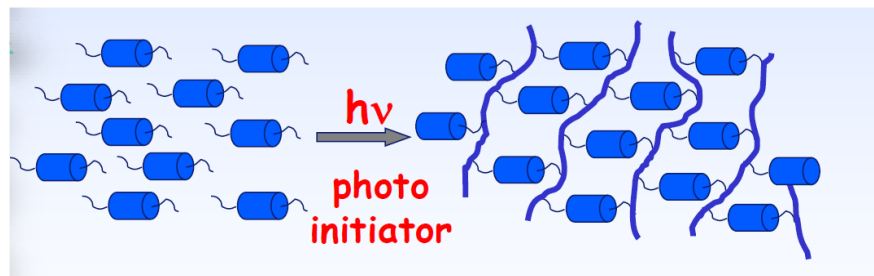


# Liquid Crystal Polymer Networks (LCN)

- Liquid Crystals



## LCN

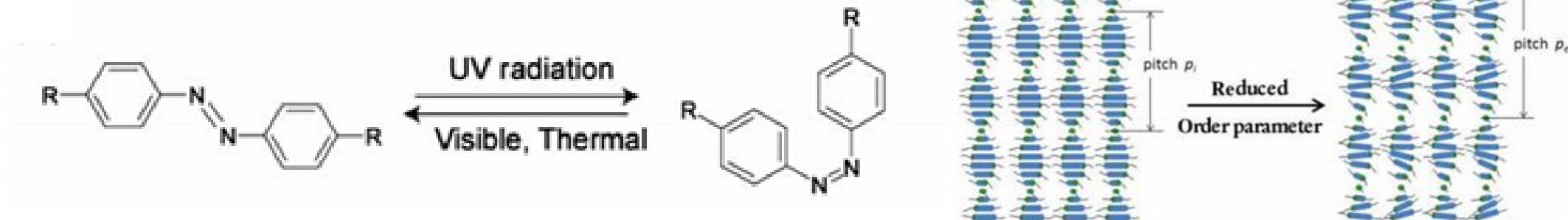


- To create dynamic surface topographies, a film is confined by adhering it firmly to a rigid substrate which prohibits lateral displacement.
- Polymerization: Light induced
  - Molecular alignment of the monomers are captured
  - Pattern added with photomask
  - Inspired by Technical university Eindhoven (Schenning)

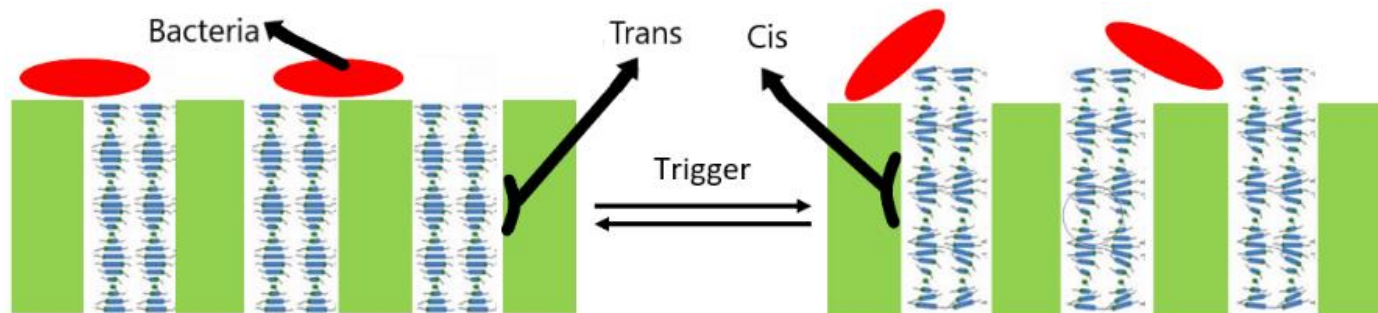


# Light responsive (Photochromic)

- Azo benzene-functionality



- Polymerisation with photomask leads to dynamic surfaces



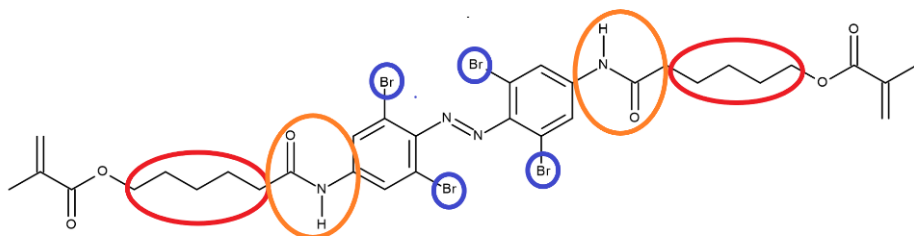
INTERREG  
Deutschland  
Nederland



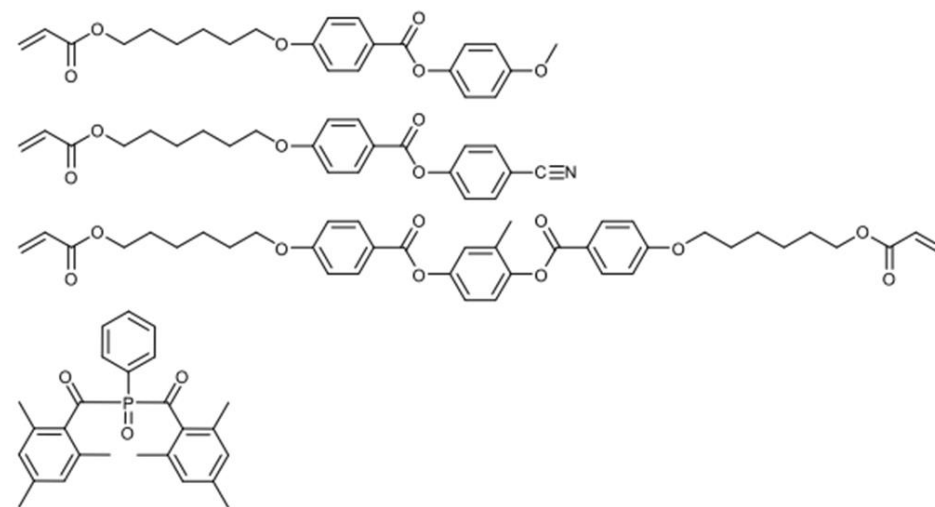
Europäische Union  
Europese Unie

# Building blocks for dynamic networks

Influence of substituents on the wavelength of the switchable monomers



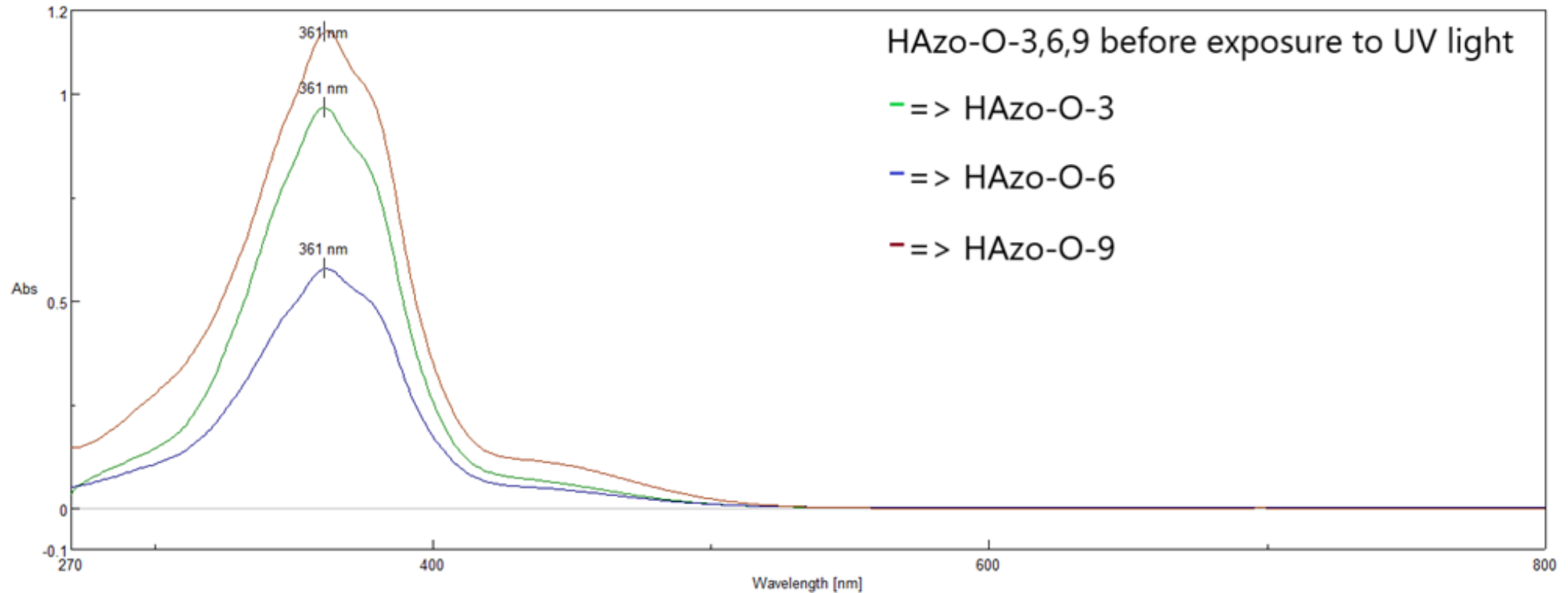
3 monomers & photo-initiator







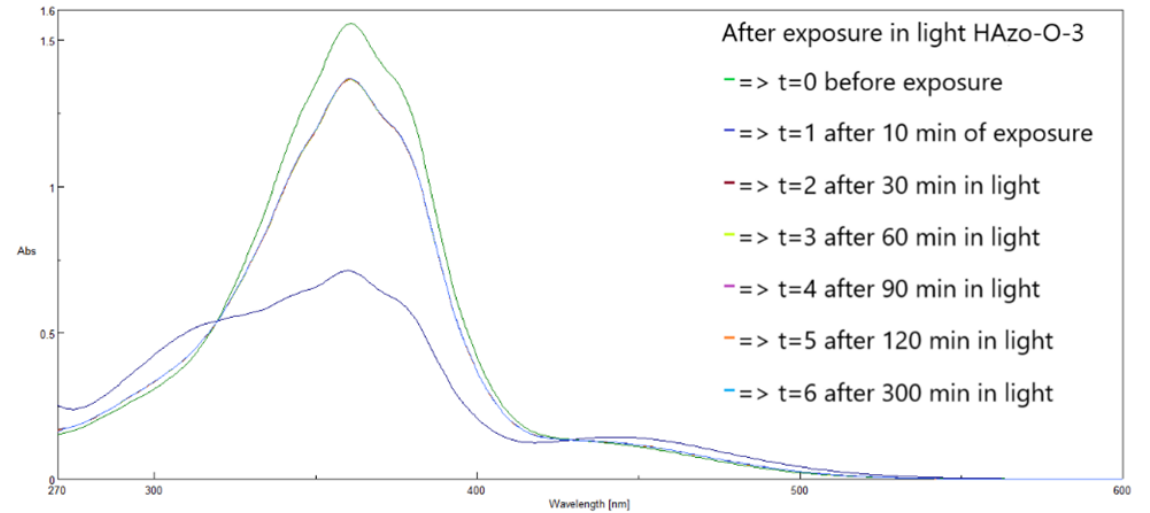
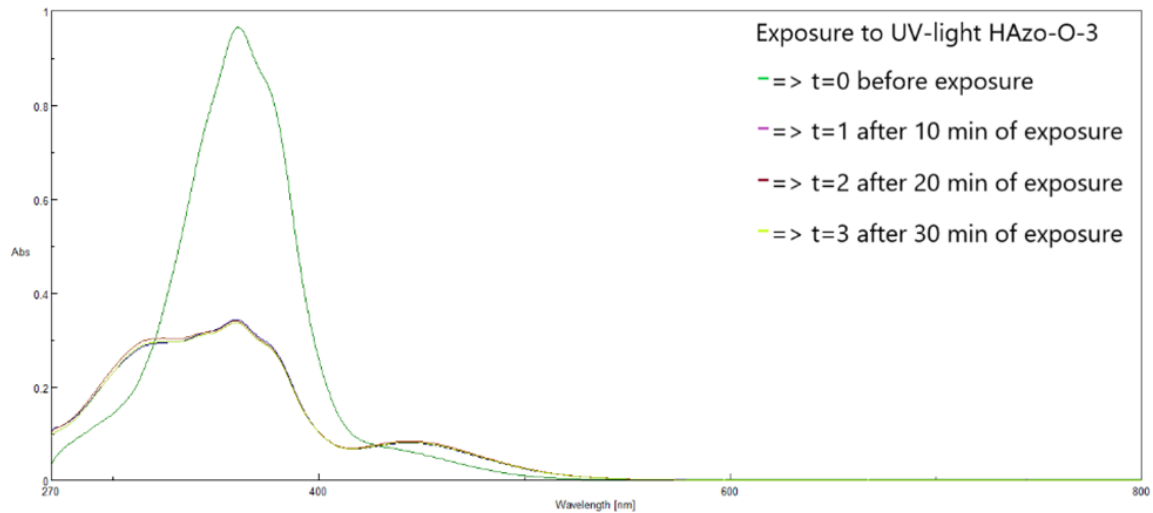
# UV-VIS Experiments



- $\lambda_{\max} = 361 \text{ nm} \rightarrow$  not depended on tail length

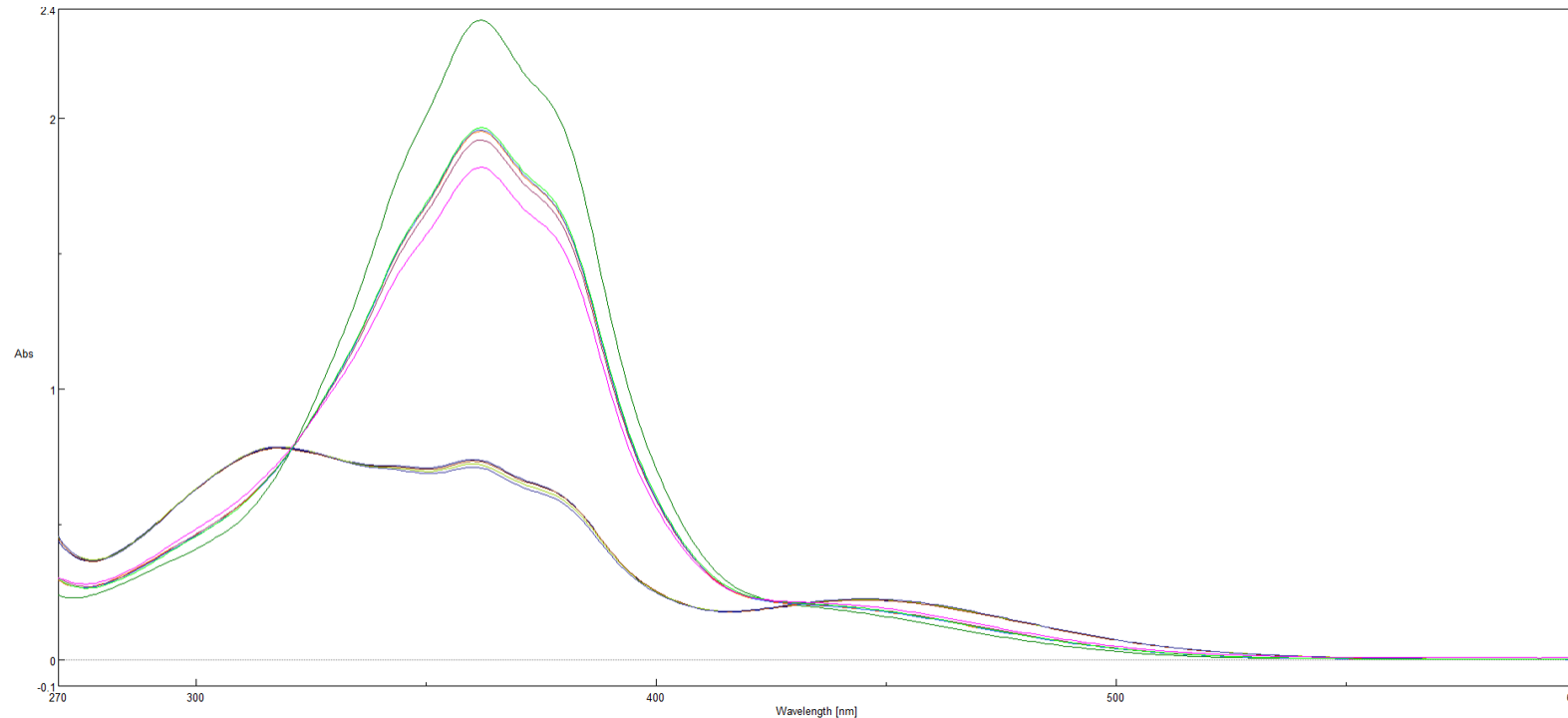


# UV-VIS: irradiation with UV & relaxation



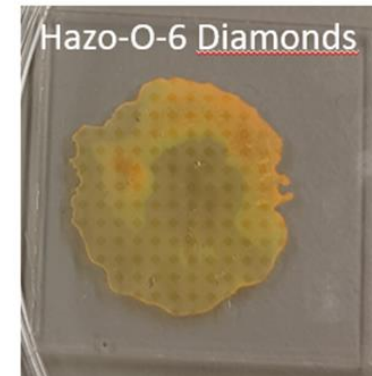
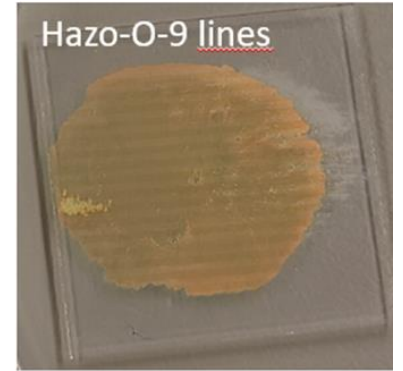
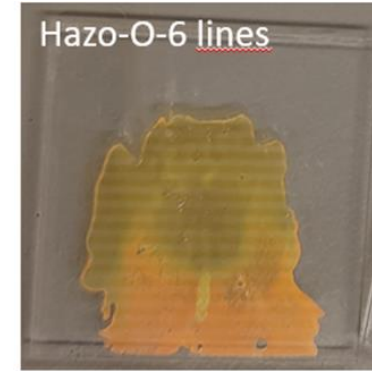
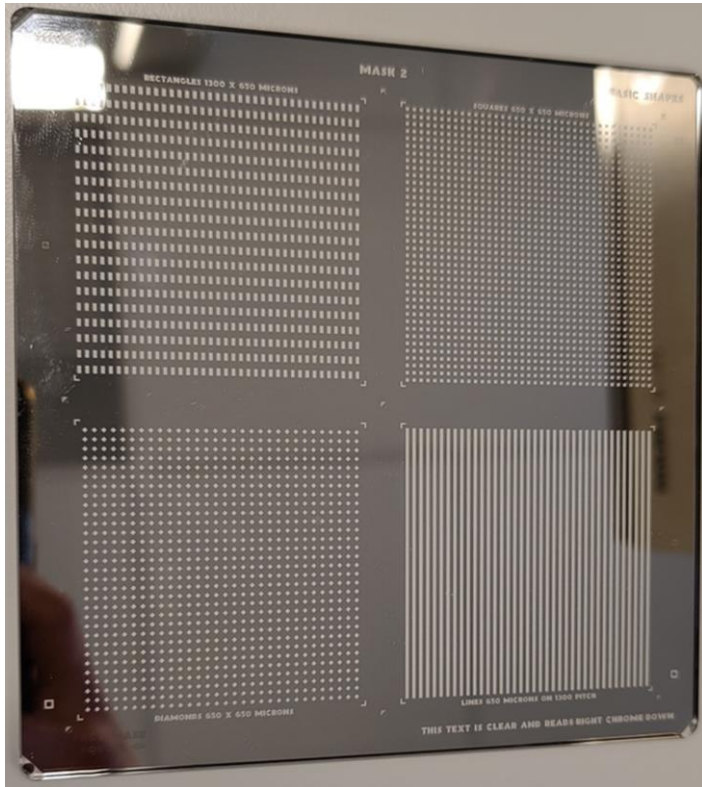
- After 10 min maximum conversion has been reached
- After 30 min in the light maximum relaxation has been reached → minimal change afterwards
- Similar results for **HAzo-O-6** and **HAzo-O-9**

## UV-VIS: Irradiation with UV & relaxation: Multiple Cycles



- After 1<sup>st</sup> relaxation azobenzene does not completely return to its initial configuration
- Next relaxation cycles show no difference in configuration

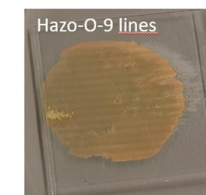
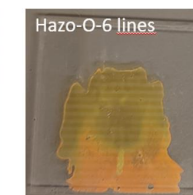
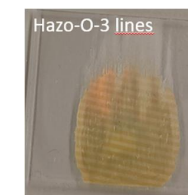
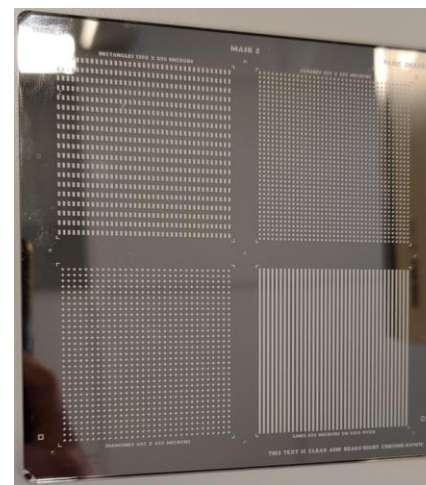
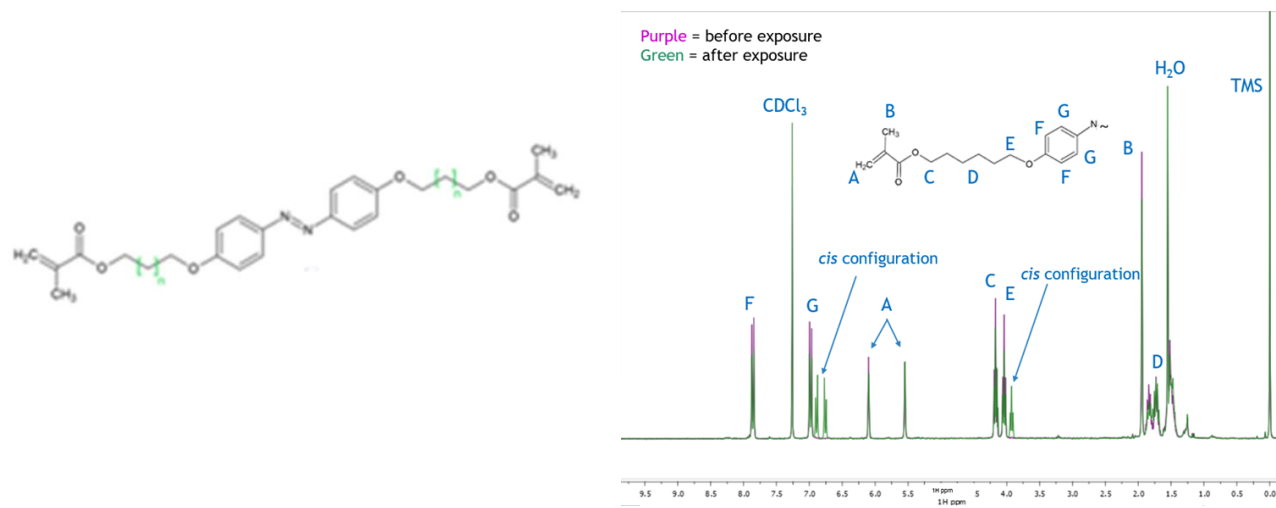
# Coatings



- Clear patterns observed

# Conclusions

- Several azobenenes have been synthesized
- Switching behaviour has been investigated
  - Maximum switch within 10 min of exposure
  - Maximum relaxation is reached within 30 min in the light and 34 min under heat (calculated)
  - Relaxation in the dark and at lower temperatures is slower than in the light
  - 1<sup>st</sup> relaxation decrease in configuration, subsequent cycles show no difference
- Coatings have been reproducibly produced







## Challenges

- Test under real-life conditions
- Upscaling of the synthesis of the building blocks
- Upscaling production of coatings
- Stability dynamic coatings

Questions?



Please feel invited to join the AutoProtect-Webinar series.....



<https://auto-protect.org>

.... get excited and experience new coating solutions and functionalities!

Thank you....



...for your attention



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