Development of an Innovative Oxygen Scavenging Label: A journey from the Idea to the Product

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Zurich University
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- Institute of Biotechnology
- Institute of Chemistry and Biological Chemistry
- **Institute of Food and Beverage Innovation**
- Institute of Natural Resource Sciences
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Center for Food Processing and Packaging

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Prof. Dr. Selcuk Yildirim

Innovative and sustainable processes and packaging development for optimal food quality and safety

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Pius Meier

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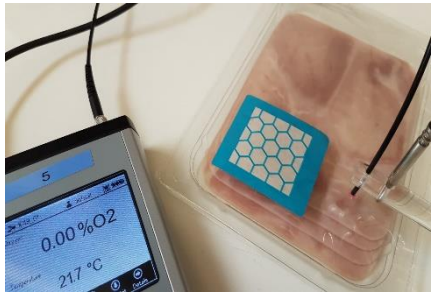
Research Fields

Innovative Packaging Materials

- Active Packaging
- Antimicrobial films
- Oxygen Scavengers
- Moisture Scavengers
- High barrier materials



Biopackaging

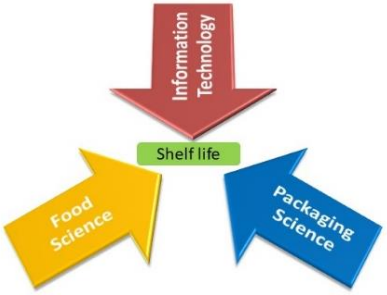
- Biobased materials
- Biodegradable materials
- Sustainable packaging development

Development and Optimization of Packaging Processes

- Modified atmosphere packaging
- Controlled atmosphere packaging
- Integration in food processing
- New packaging processes

Shelf life simulations

- Shelf life simulations
- Optimal packaging design
- Optimization of packaging
- Optimization of storage cond.



Content

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1. Active Packaging

2. Development of Palladium based Oxygen Scavenging Label
   - Idea
   - Development
   - Industrialisation
3. Applications

Content

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1. **Active Packaging**

2. Development of Palladium based Oxygen Scavenging Label
   - Idea
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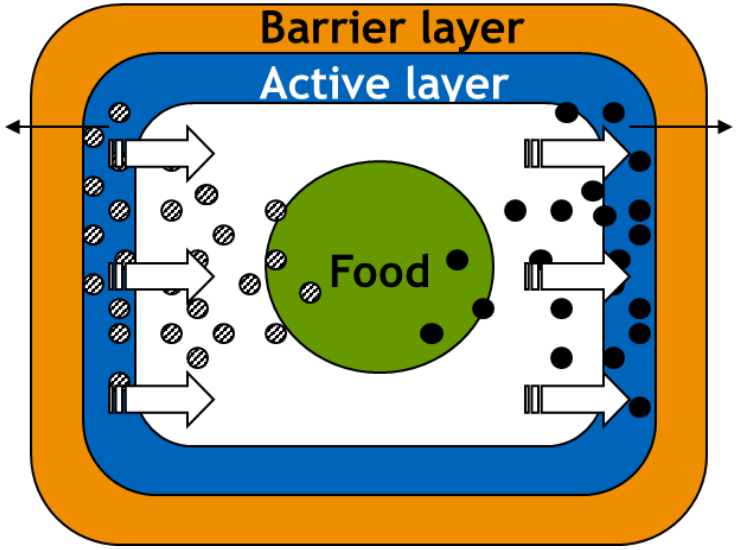
3. Applications

Active Packaging

Active Packaging: „..designed to deliberately incorporate components that would release or absorb substances into or from the packaged food or the environment surrounding the food“

Regulation (EC) No 1935/2004 A

*** Active Releasing Systems**
- Antimicrobial agent
- CO_2
- Antioxidant
- Flavours
- Ethylene



Active Scavenging Systems
- Oxygen
- CO_2
- Moisture
- Ethylene
- Odour

* Yildirim S. Active Packaging for Food Biopreservation, in Protective Cultures, Antimicrobial Metabolites and Bacteriophages for Food and Beverage Biopreservation, Lacroix C (ed). Woodhead Publishing: Cambridge, 2011; 460-489.

Comprehensive REVIEWS in Food Science and Food Safety

Active Packaging Applications for Food

Selçuk Yildirim, Bettina Röcker, Marit Kvalvåg Pettersen, Julie Nilsen-Nygaard, Zehra Ayhan, Ramune Rutkaite, Tanja Radusin, Patrycja Suminska, Begonya Marcos, and Véronique Coma

Abstract: The traditional role of food packaging is continuing to evolve in response to changing market needs. Current drivers such as consumer's demand for safer, "healthier," and higher-quality foods, ideally with a long shelf-life; the demand for convenient and transparent packaging, and the preference for more sustainable packaging materials, have led to the development of new packaging technologies, such as active packaging (AP). As defined in the European regulation (EC) No 450/2009, AP systems are designed to "*deliberately incorporate components that would release or absorb substances into or from the packaged food or the environment surrounding the food.*" Active packaging materials are thereby "*intended to extend the shelf-life or to maintain or improve the condition of packaged food.*" Although extensive research on AP technologies is being undertaken, many of these technologies have not yet been implemented successfully in commercial food packaging systems. Broad communication of their benefits in food product applications will facilitate the successful development and market introduction. In this review, an overview of AP technologies, such as antimicrobial, antioxidant or carbon dioxide-releasing systems, and systems absorbing oxygen, moisture or ethylene, is provided, and, in particular, scientific publications illustrating the benefits of such technologies for specific food products are reviewed. Furthermore, the challenges in applying such AP technologies to food systems and the anticipated direction of future developments are discussed. This review will provide food and packaging scientists with a thorough understanding of the benefits of AP technologies when applied to specific foods and hence can assist in accelerating commercial adoption.

Keywords: active packaging, antimicrobial packaging, antioxidant releaser, ethylene absorber, oxygen scavenger

Trends in Food Science & Technology 80 (2018) 212–222

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journal homepage: www.elsevier.com/locate/tifs

Review

A concise guide to active agents for active food packaging

Carla Vilela[a,**], Mia Kurek[b], Zvi Hayouka[c], Bettina Röcker[d], Selçuk Yildirim[d], Maria Dulce C. Antunes[e], Julie Nilsen-Nygaard[f], Marit Kvalvåg Pettersen[f], Carmen S.R. Freire[a,*]

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Yildirim S., Röcker B., Pettersen M.K., Nygaard Julie N., Ayhan Z., Rutkaite R., Radusin T., Suminska P., Marcos B., Coma V., Active Packaging for Food Applications, Comprehensive Reviews in Food Science and Food Safety, 2018, 17: 165–199.

Vilela C., Kurek M., Hayouka Z., Röcker B. Yildirim S., Antunes M. D. C. Nygaard J. N. Pettersen M. K., Freirea, C. S. R. A concise guide to active agents for functional food packaging, Trends in Food Science & Technology, 2018, 80, 212-222

Content

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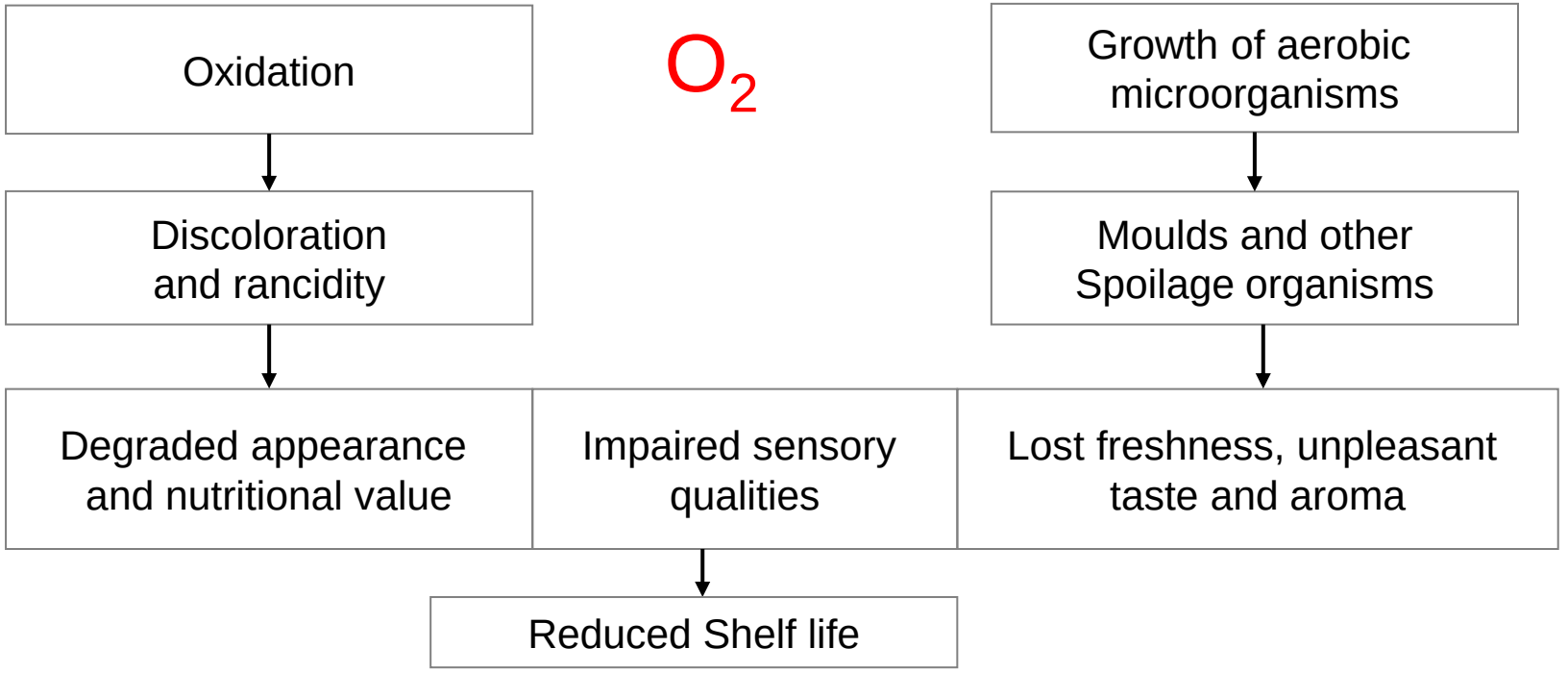
1. Active Packaging

2. **Development of Palladium based Oxygen Scavenging Label**
   - Idea
   - Development
   - Industrialisation

3. Applications

Oxidation of Food



Modified Atmosphere Packaging

- Gas Flushing
- Modified Atmosphere Packaging

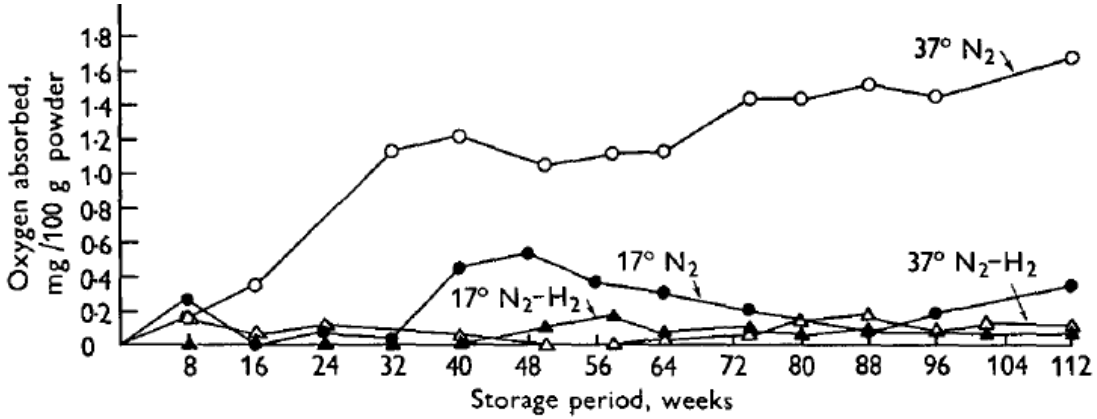
Up to 3-5% residual oxygen[11]

Oxygen Scavengers

J. Dairy Res. (1961), **28**, 285

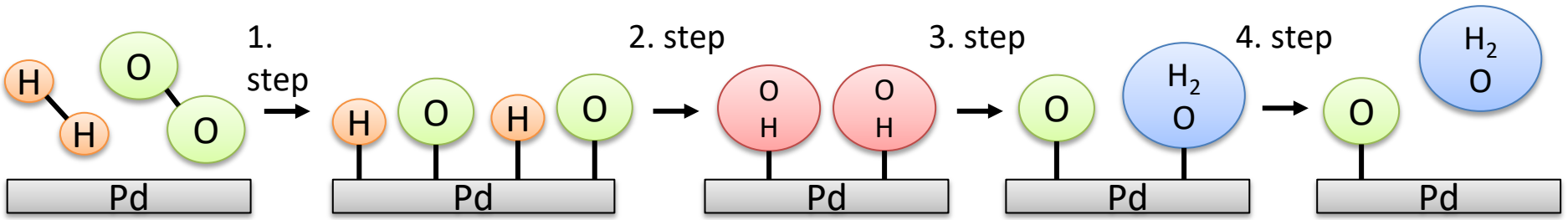
Gas packing milk powder with a mixture of nitrogen and hydrogen in the presence of palladium catalyst

By J. ABBOT and R. WAITE
The Hannah Dairy Research Institute, Ayr
AND
J. F. HEARNE
Ministry of Agriculture, Fisheries & Food, London



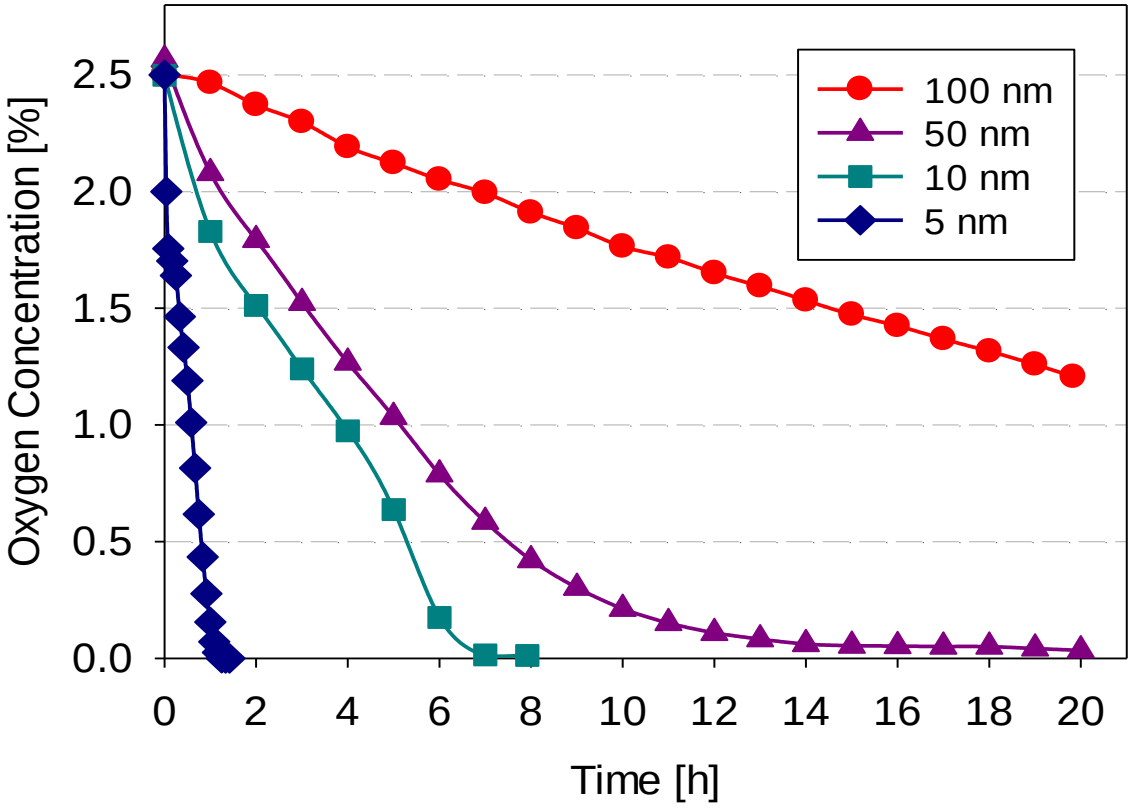
Palladium-based Oxygen Scavenger

$$H_2 + \tfrac{1}{2} O_2 \xrightarrow{Pd} H_2O$$



Nyberg C, Tengstål CG. Adsorption and reaction of water, oxygen, and hydrogen on Pd(100): Identification of adsorbed hydroxyl and implications for the catalytic H2–O2 reaction. The Journal of Chemical Physics 1984. 80(7): pp. 3463-3468, DOI: 10.1063/1.447102.

Pd Deposition Thickness



PET/Pd

Patent: EP2236284, 2010, S. Yildirim, J.C-Jammet, W. Lohwasser

Pd Coated Surface Analysis

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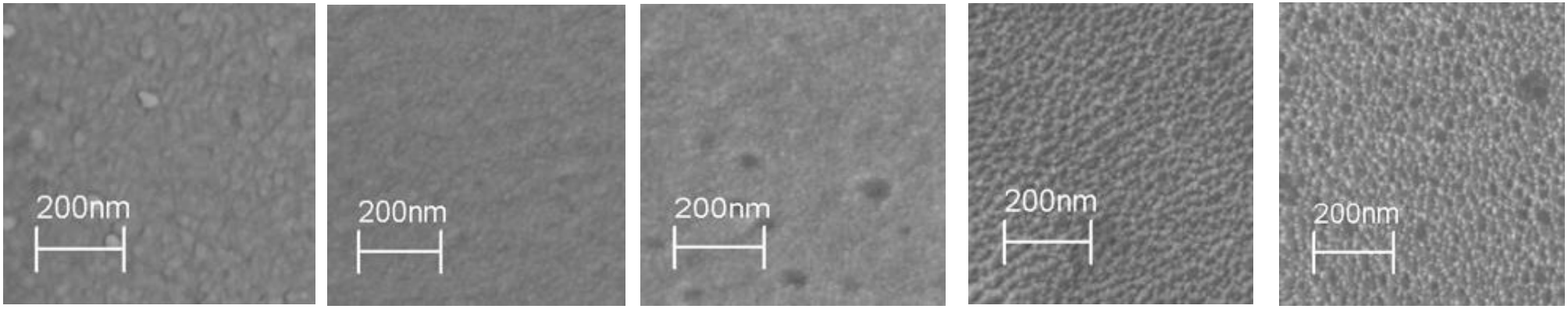
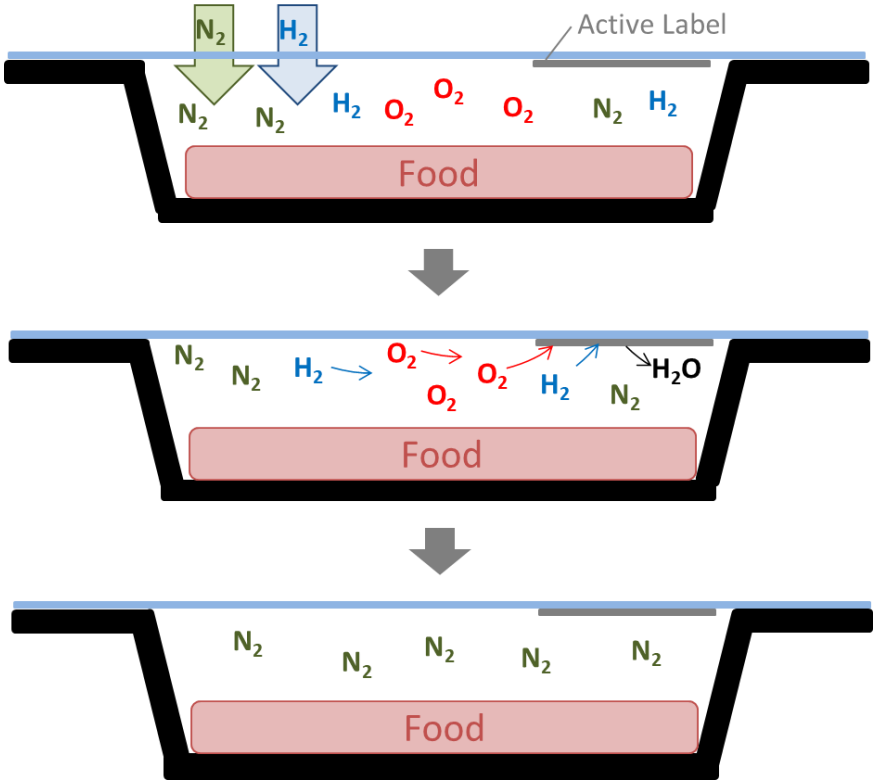
100 nm | 50 nm | 20 nm | 10 nm | 5 nm



- Pd coated surfaces were analyzed using scanning electron microscopy
- 100 nm to 20 nm surface is flat
- A sponge like structure in 10 and 5 nm sample
- 10 nm sample is more dense than 5 nm sample

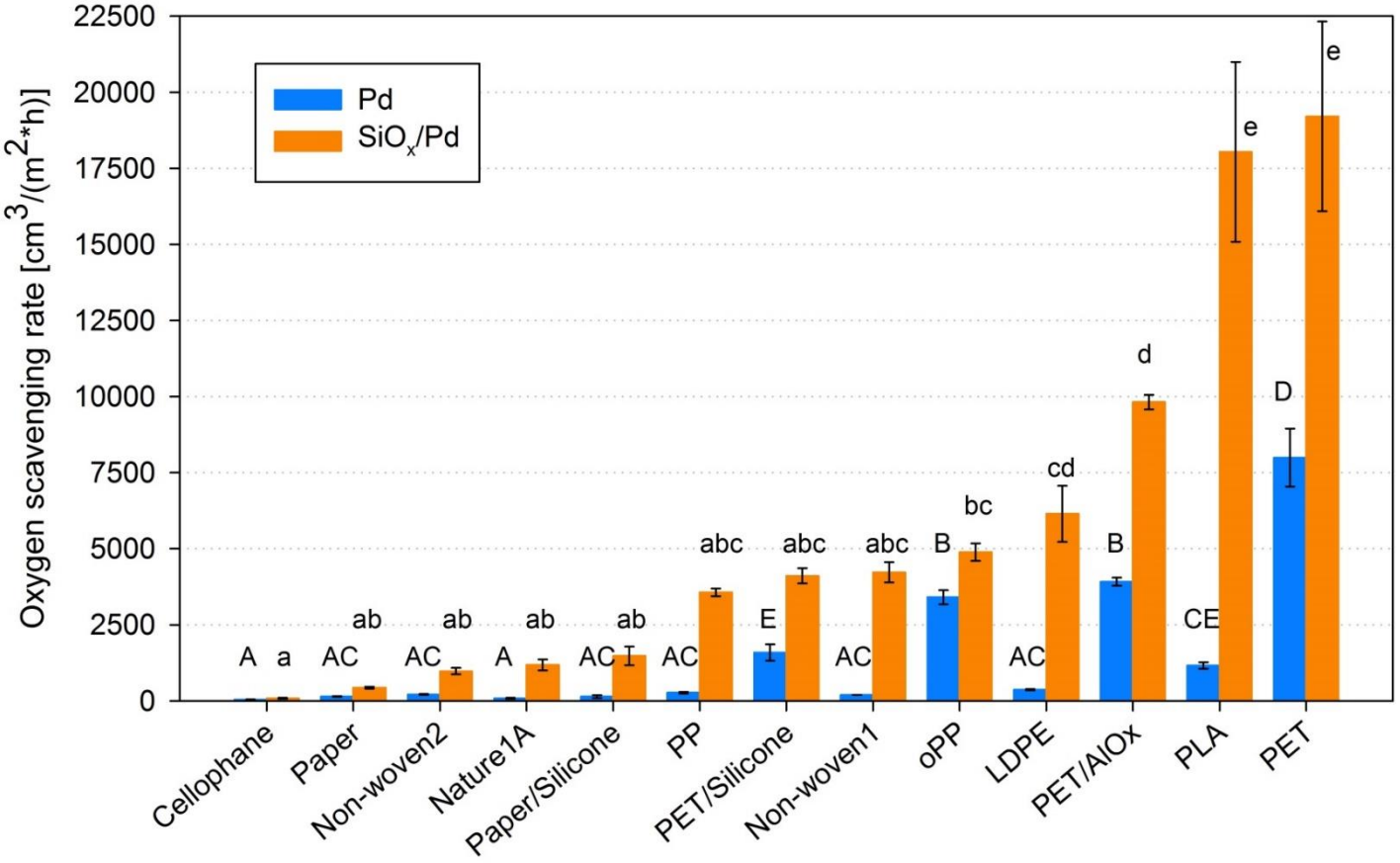
Palladium-based Oxygen Scavenging Label

$$H_2 + \tfrac{1}{2} O_2 \xrightarrow{Pd} H_2O$$

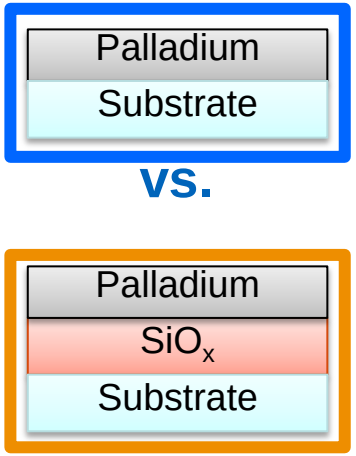


Yildirim S, Jammet JC, Lohwasser W. Multi-layer film. European Patent, 2236284, 6/10/2010.

Effect of Coating Substrate on the Oxygen Scavenging Activity

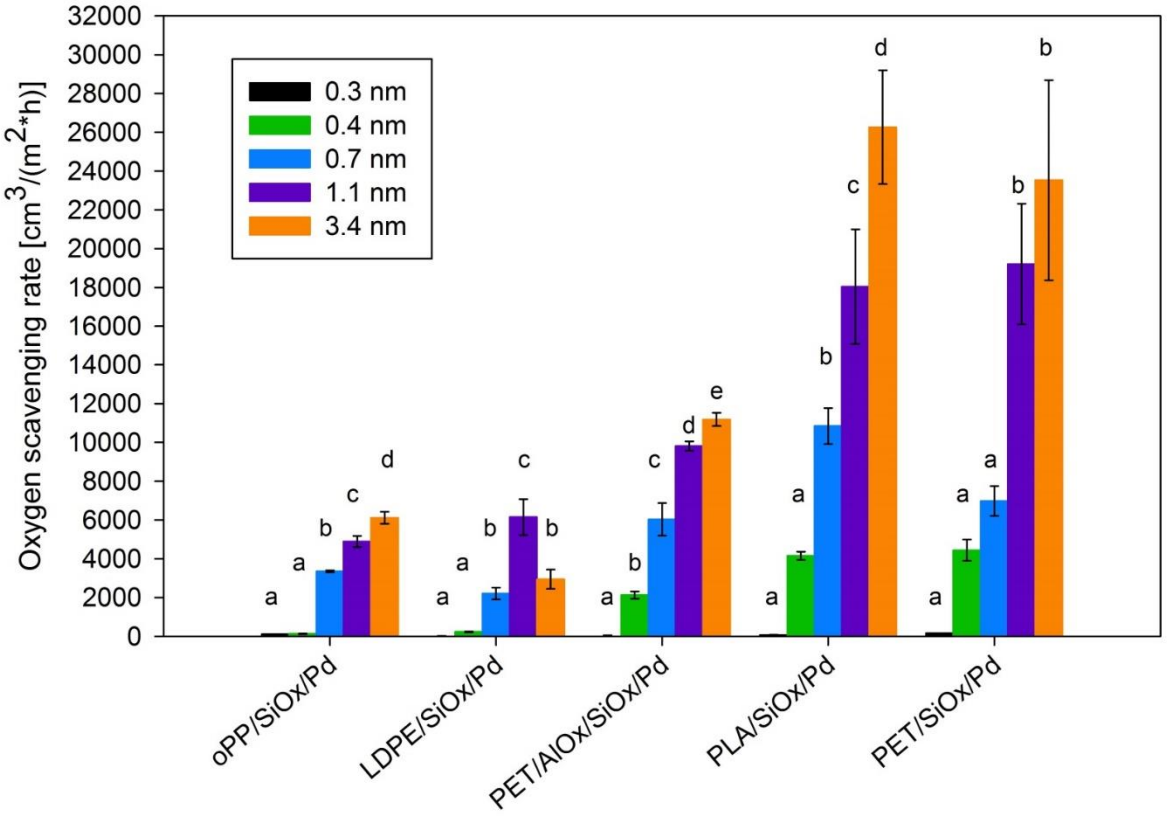


Oxygen Scavenger

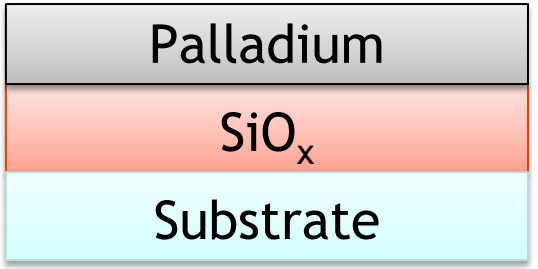


Yildirim S, Röcker B, Rüegg N, Lohwasser W. Development of Palladium-based Oxygen Scavenger: Optimization of Substrate and Palladium Layer Thickness. Packaging Technology and Science 2015. 28(8): pp. 710-718

Effect of Palladium Deposition Thickness on the Oxygen Scavenging Activity



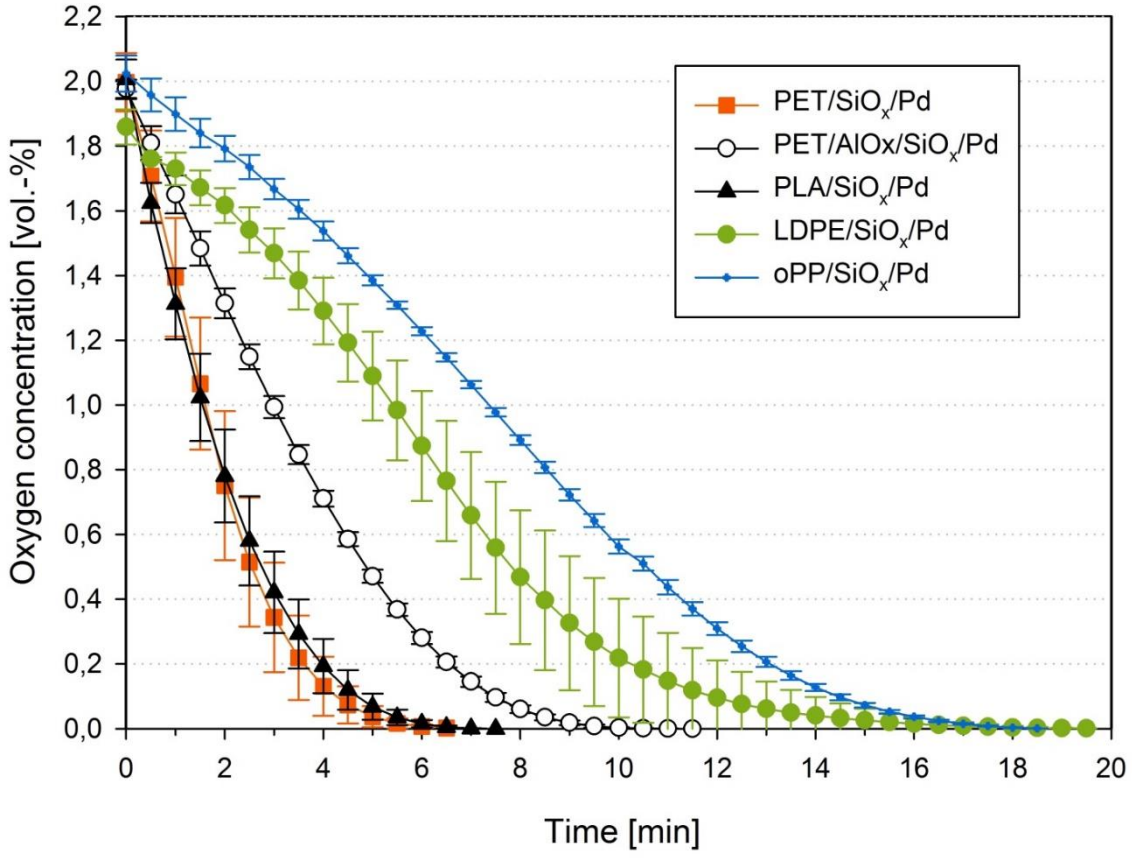
Oxygen Scavenger



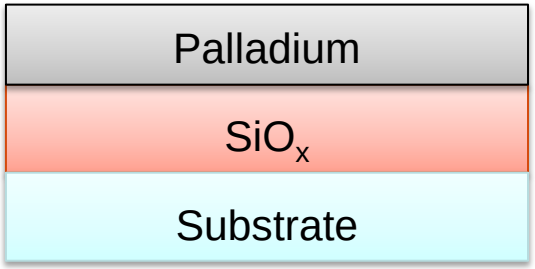
Best Substrates:

- PET
- PET/AlOx
- PLA
- LDPE
- oPP

Effect of Coating Substrate on the Oxygen Scavenging Activity



Oxygen Scavenger



Best Substrates:

- PET
- PET/AlOx
- PLA
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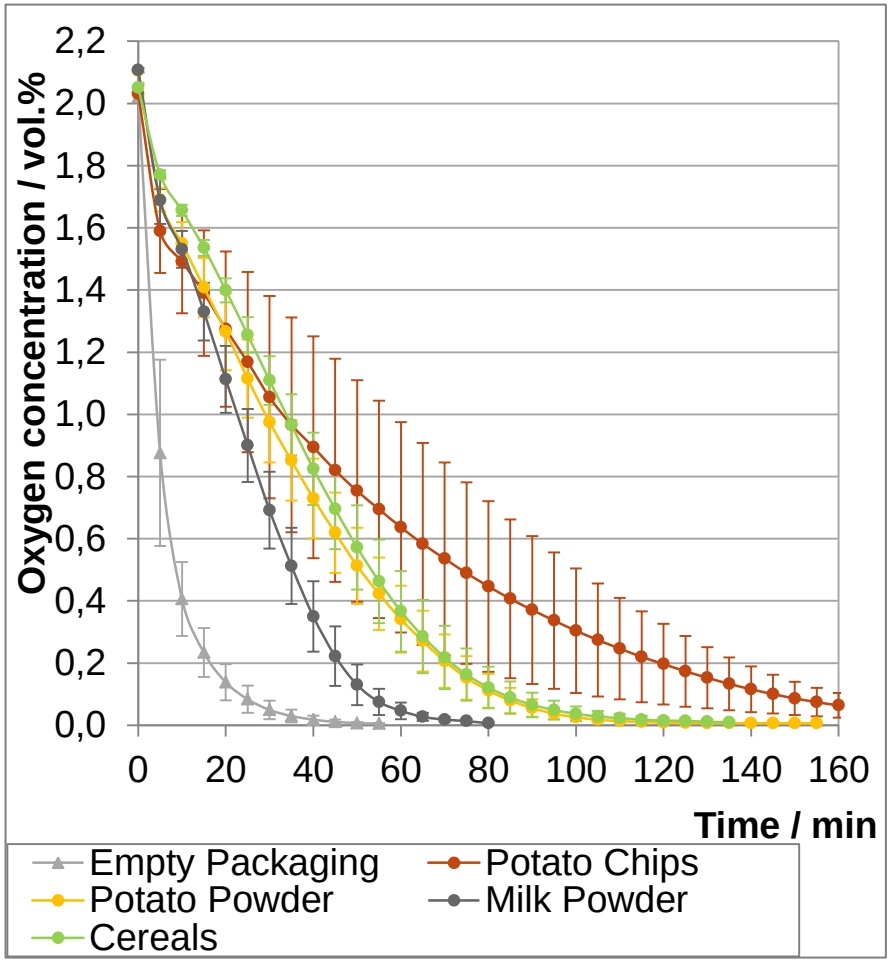
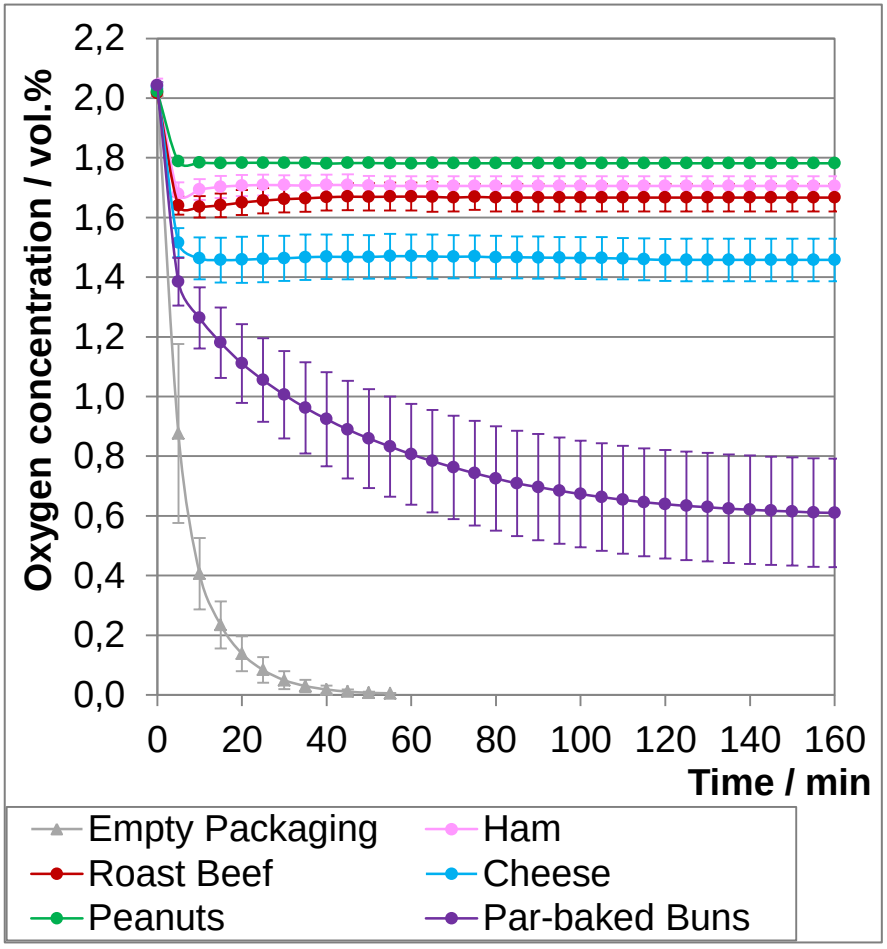
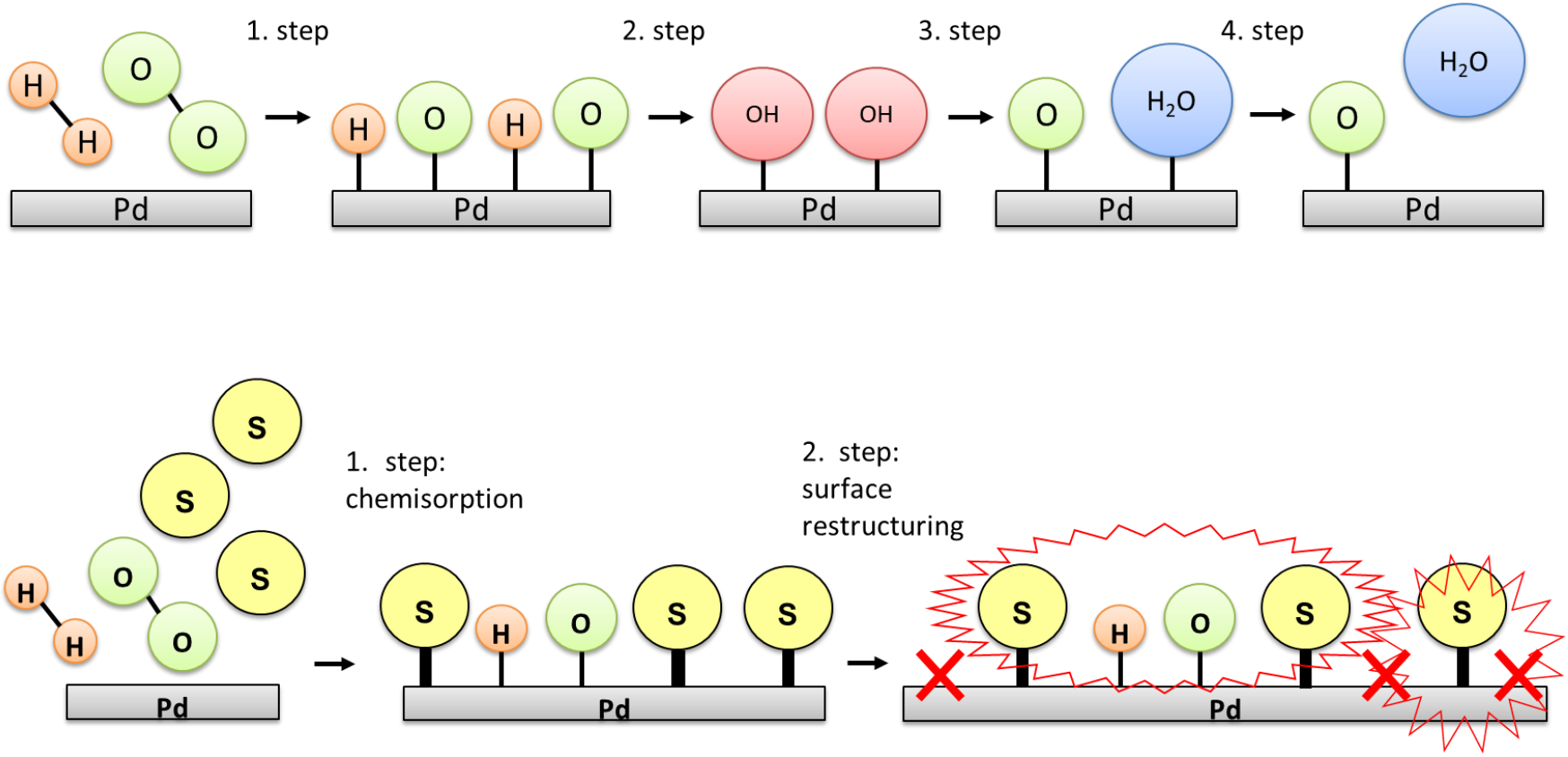
Oxygen Scavenging Activity in the Presence of Food





Röcker B., Rüegg N., Glöss A. N., Yeretzian C., Yildirim S., Inactivation of Palladium-based Oxygen Scavenger by Volatile Sulphur Compounds Present in the Headspace of Packaged Food, Packaging Technology and Science, 2017, 30, 8, 427-442

Catalyst Poisoning
by Volatile Sulphur compounds (VSCs)



Maxted EB. The Poisoning of Metallic Catalysts, in Advances in Catalysis, Frankenburg WG, Komarewsky VI, Rideal EK, Emmett PH, Taylor HS (ed). Academic Press, 1951

Bartholomew CH. Mechanisms of catalyst deactivation. Applied Catalysis A: General 2001.

Volatile Sulphur Compounds (VSCs) in Foods

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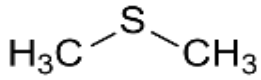
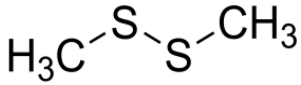
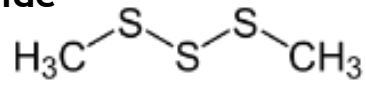
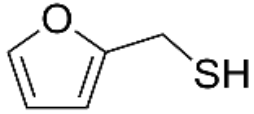
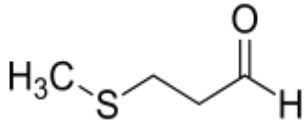
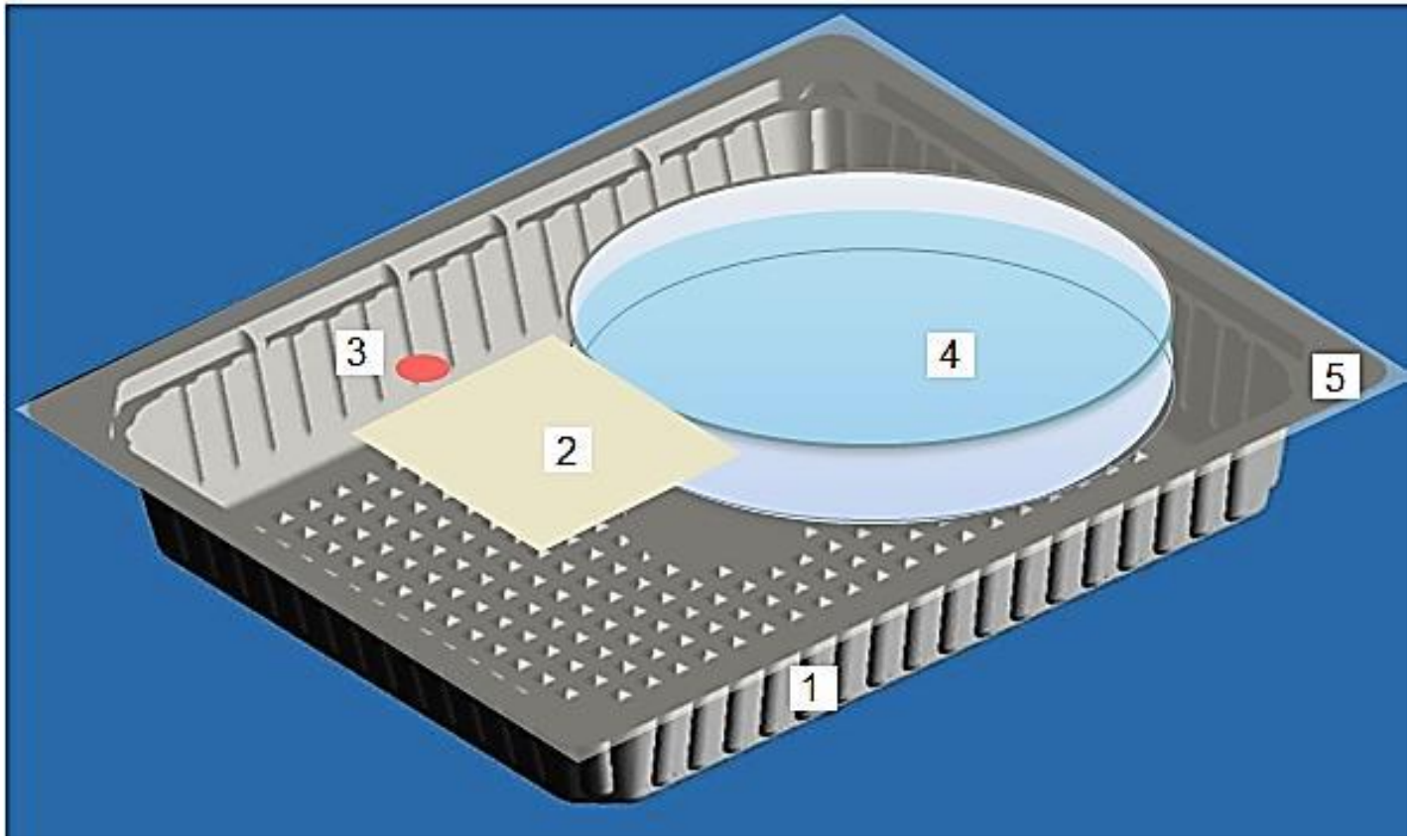
Volatile sulphur compounds (VSCs)	Beef (Roast Beef)	Pork (Ham)	Potato Chips	Roasted Peanuts	Cheese	Bread
Dimethyl sulphide (DMS) 	x		x	x	x	x
Dimethyl disulphide (DMDS) 	x	x	x	x	x	x
Dimethyl trisulphide (DMTS) 	x	x		x	x	x
Furfuryl thiol (FFT) 	x	x	x	x		
Methional (MET) 	x	x	x	x	x	x

Pd Scavenging Activity in the Presence of VSC



(1) Tray

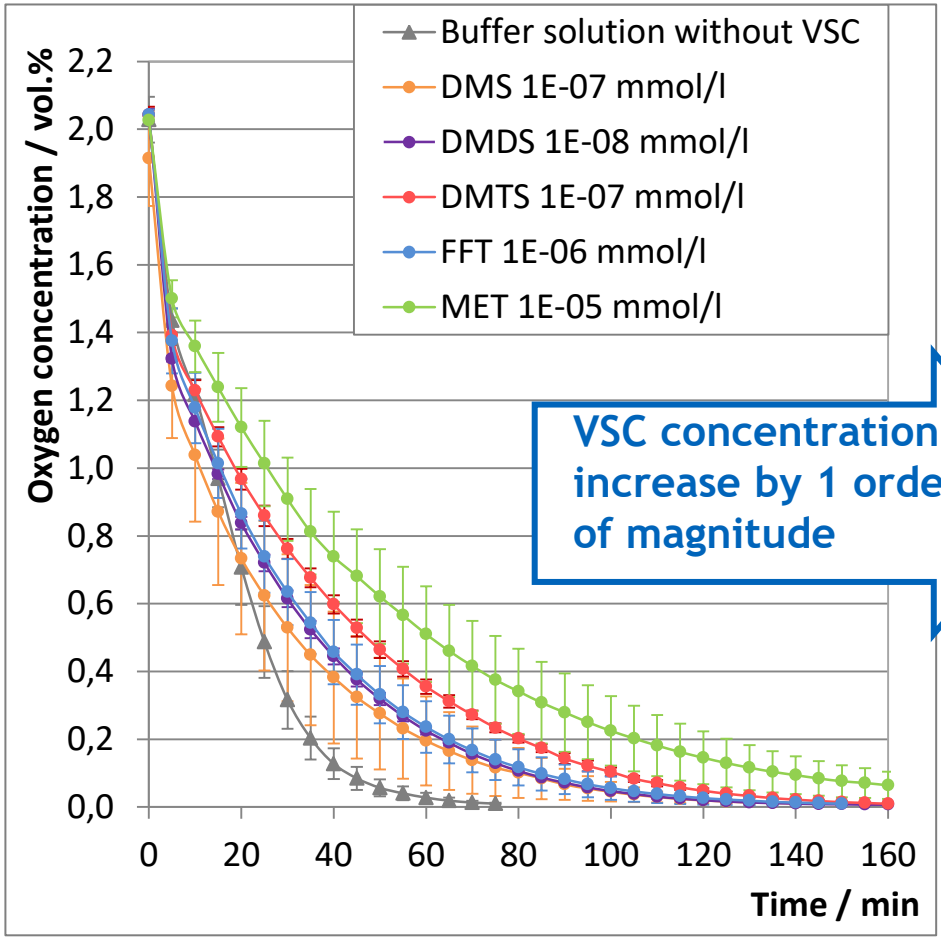
(2) Palladium-coated film

(3) Sensor spot

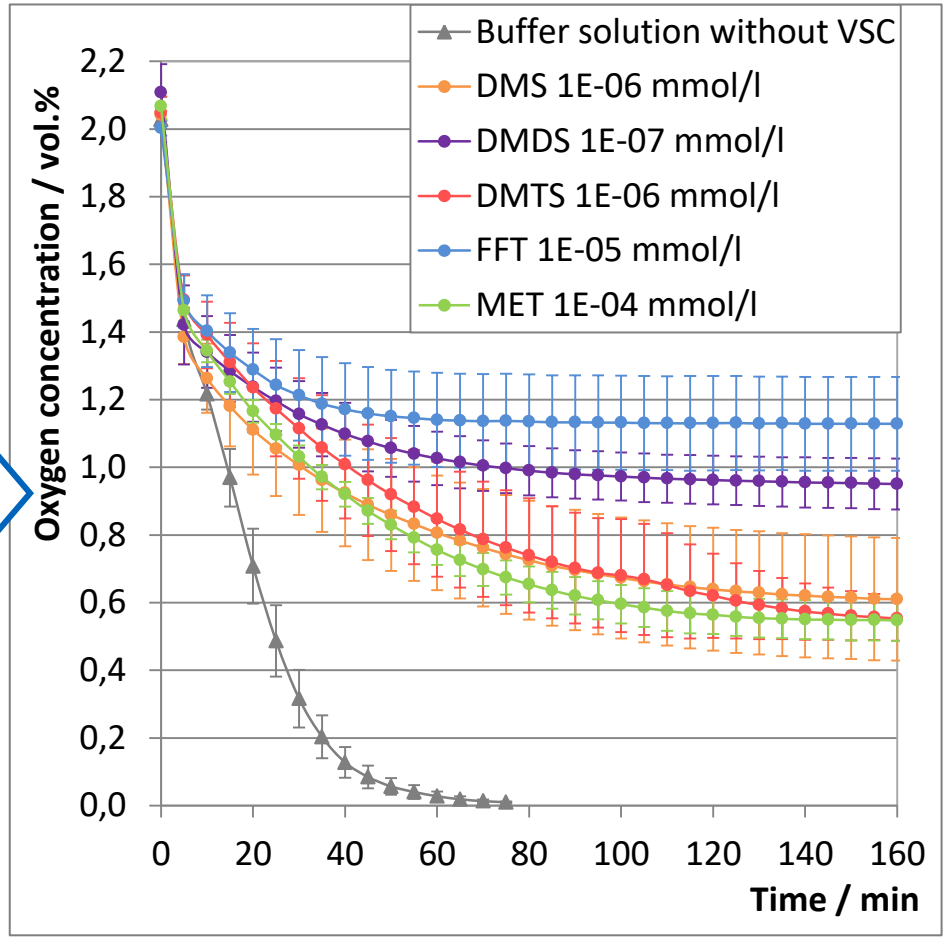
(4) Glass petri dish
+ VSC-Solution

(5) Lidding film

Pd Scavenging Activity in the Presence of VSC



VSC concentration increase by 1 order of magnitude



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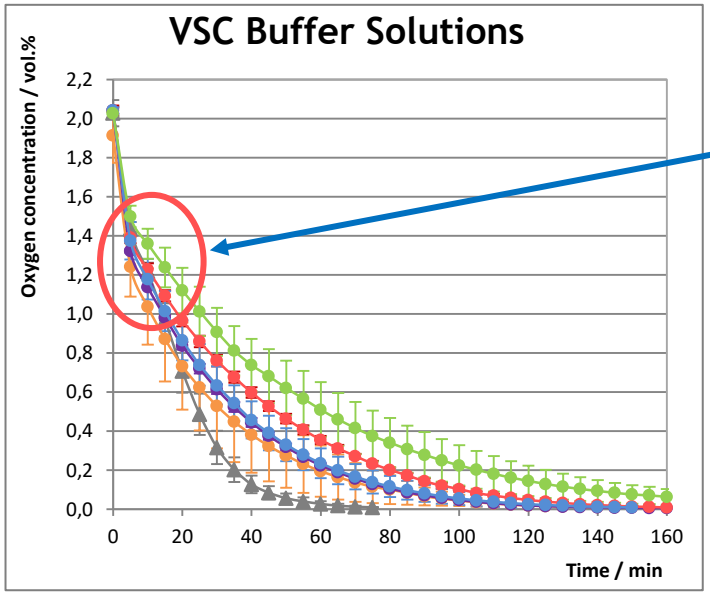
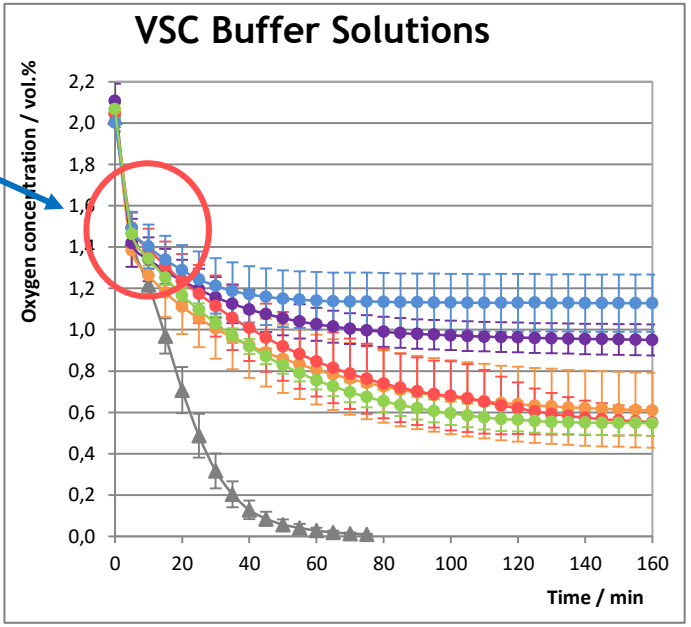
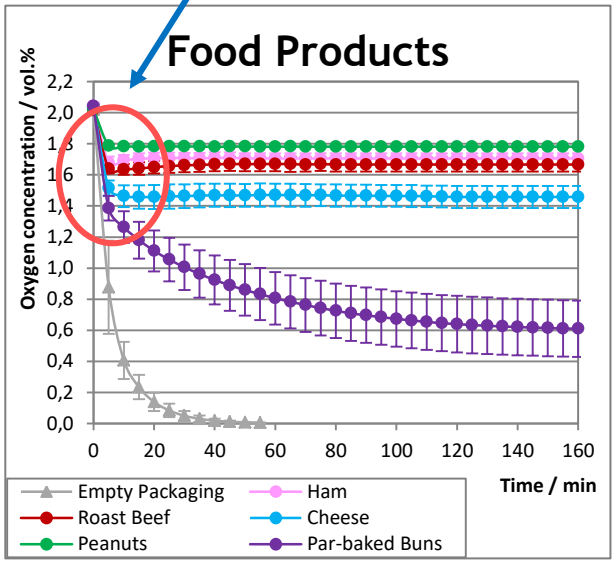
Determination of Minimum Inhibitory Concentrations Range of VOC

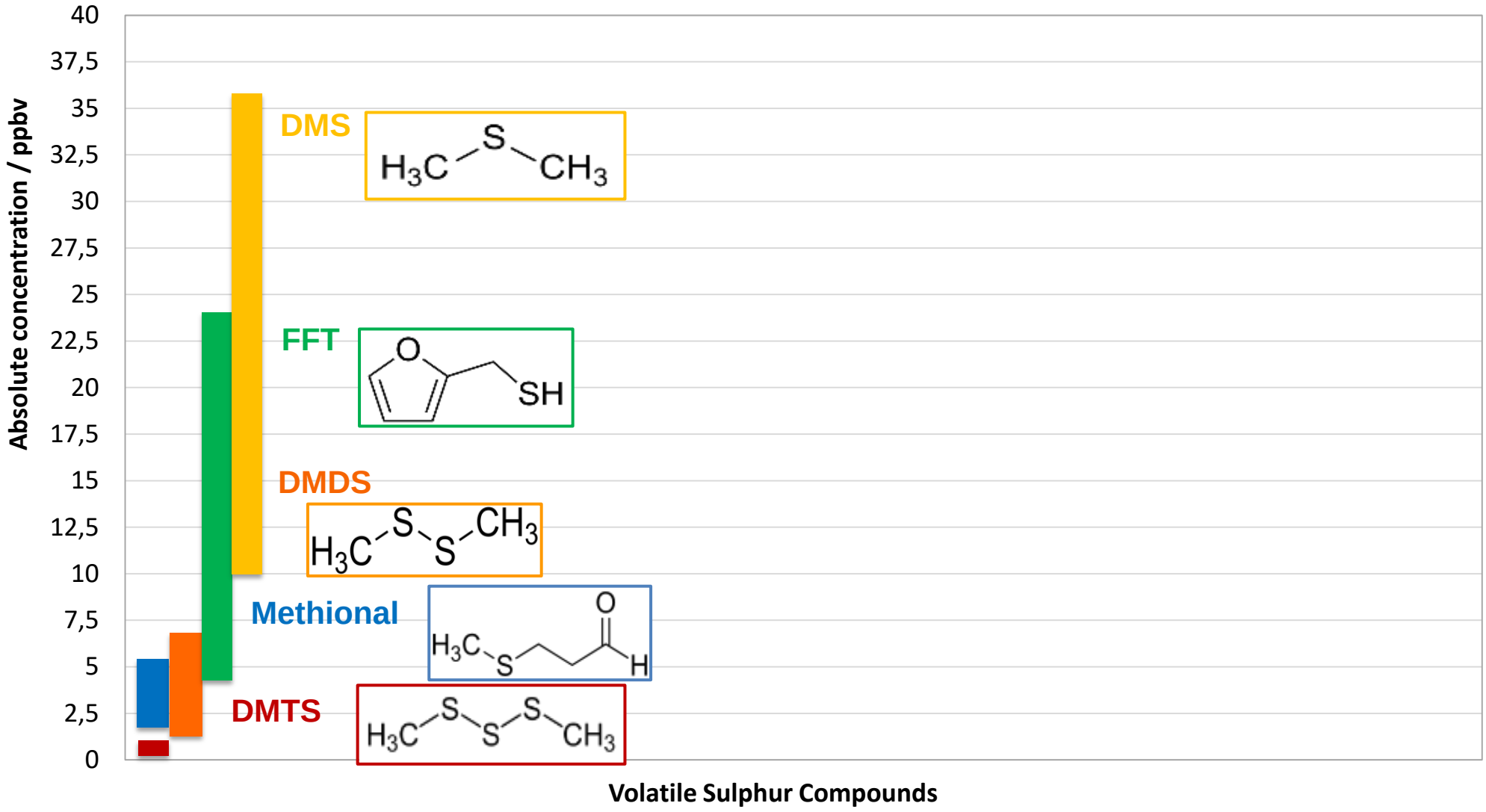


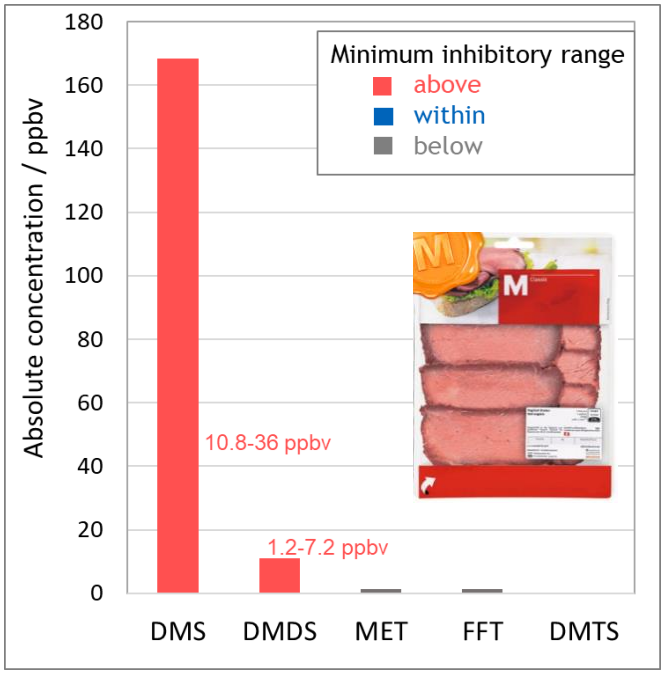
Head Space Analysis

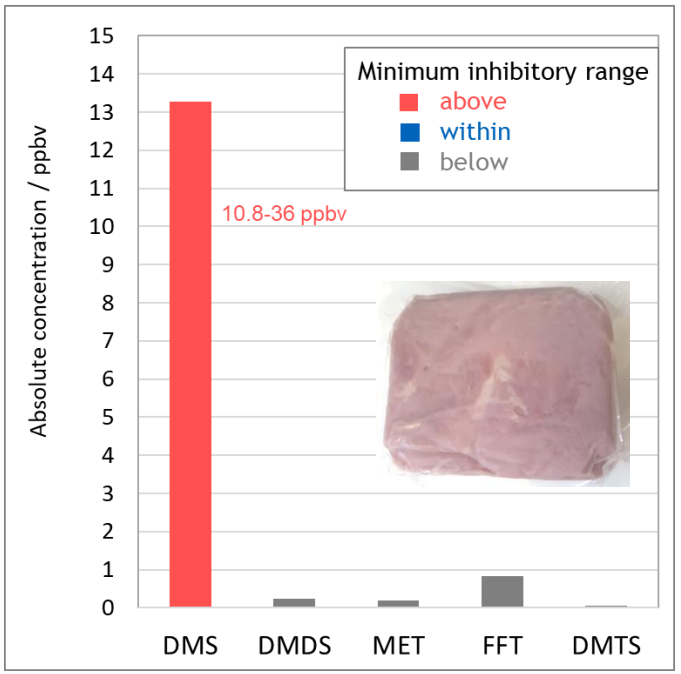


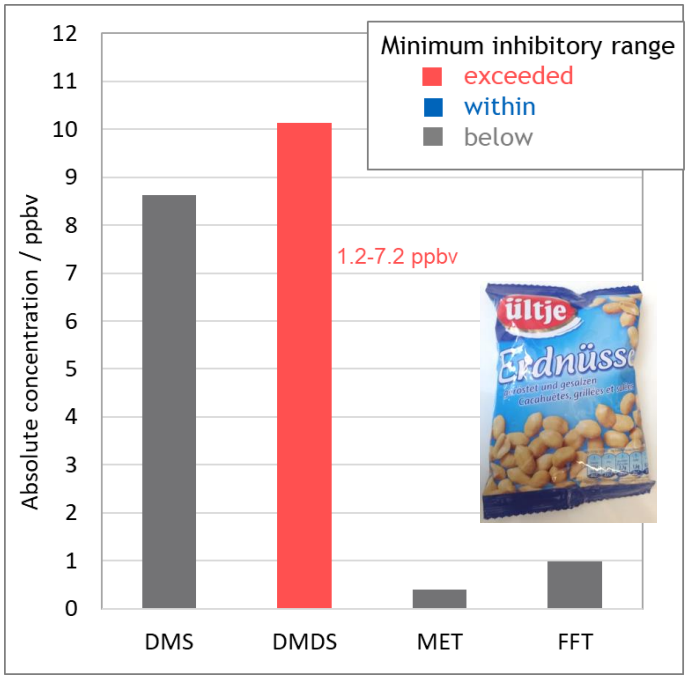


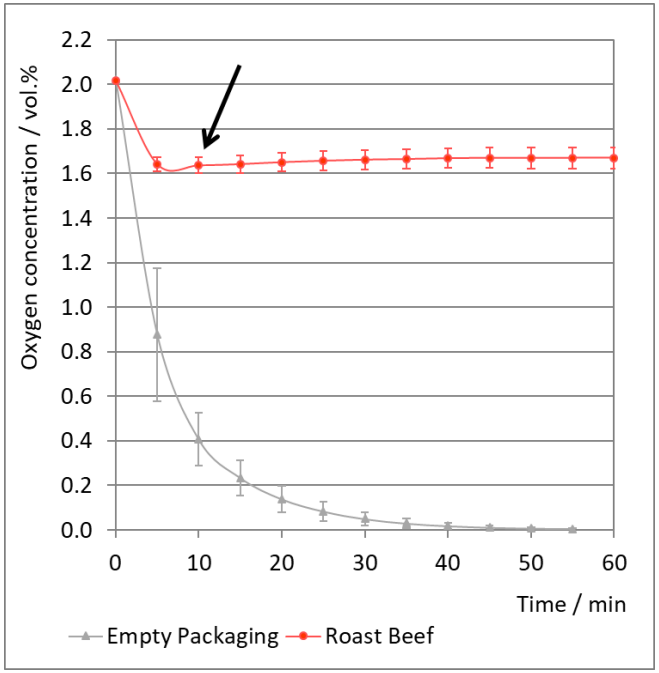
Minimum Inhibitory Concentration Range of VOC

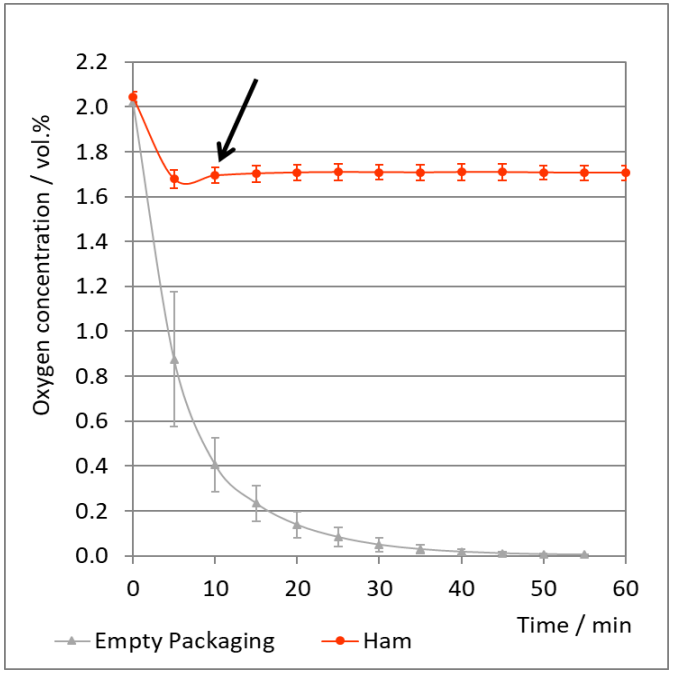


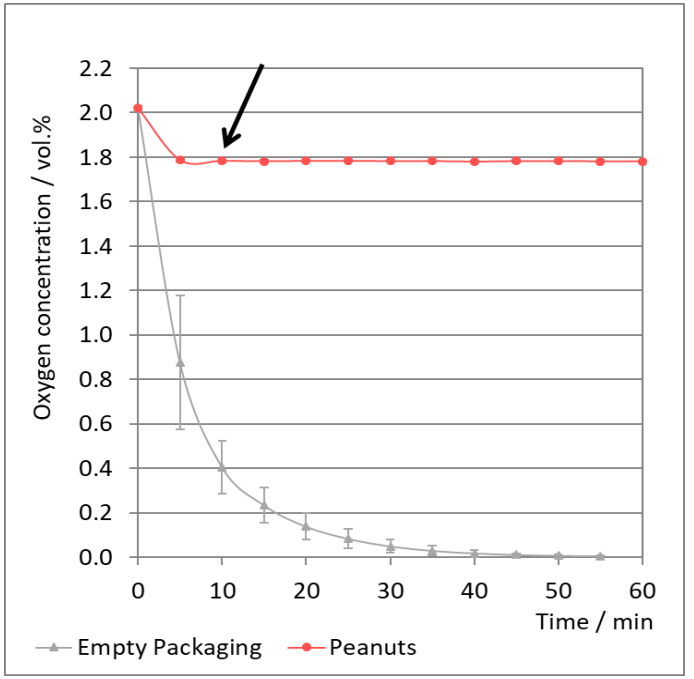

Absolute concentration / ppbv
180
160
140
120
100
80
60
40
20
0
Minimum inhibitory range
above
within
below
10.8-36 ppbv
1.2-7.2 ppbv
DMS
DMDS
MET
FFT
DMTS


Absolute concentration / ppbv
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
Minimum inhibitory range
above
within
below
10.8-36 ppbv
DMS
DMDS
MET
FFT
DMTS


Absolute concentration / ppbv
12
11
10
9
8
7
6
5
4
3
2
1
0
Minimum inhibitory range
exceeded
within
below
1.2-7.2 ppbv
DMS
DMDS
MET
FFT


Oxygen concentration / vol.%
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
10
20
30
40
50
60
Time / min
Empty Packaging
Roast Beef


Oxygen concentration / vol.%
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
10
20
30
40
50
60
Time / min
Empty Packaging
Ham


Oxygen concentration / vol.%
2.2
2.0
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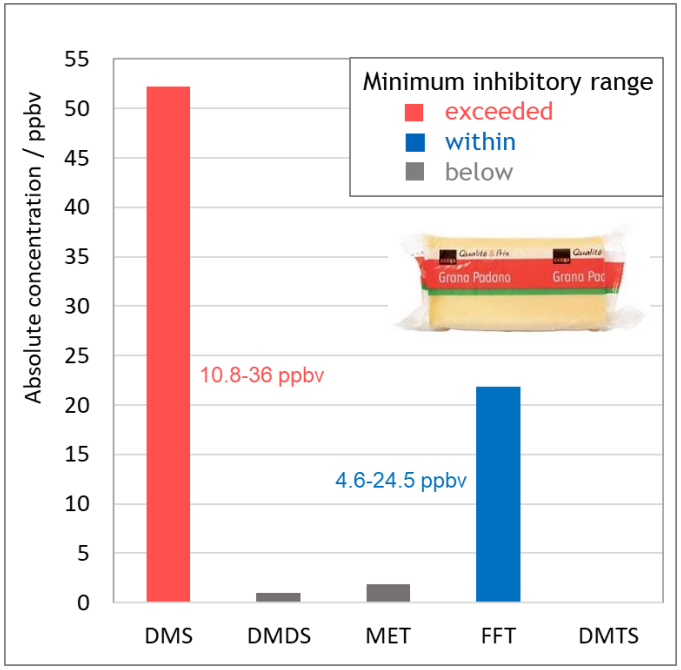
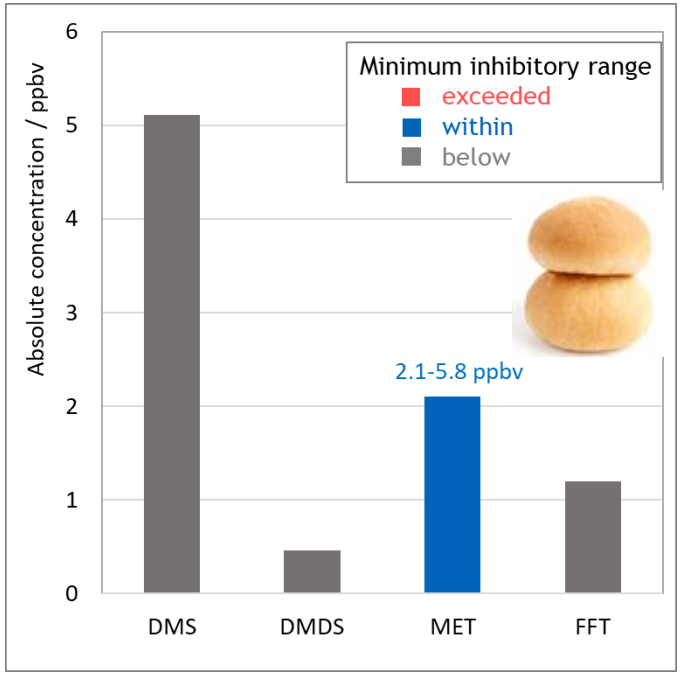
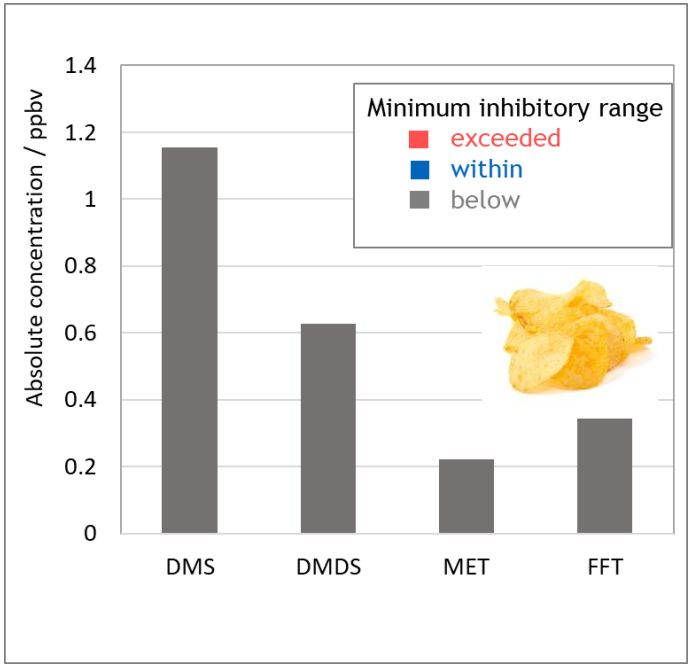
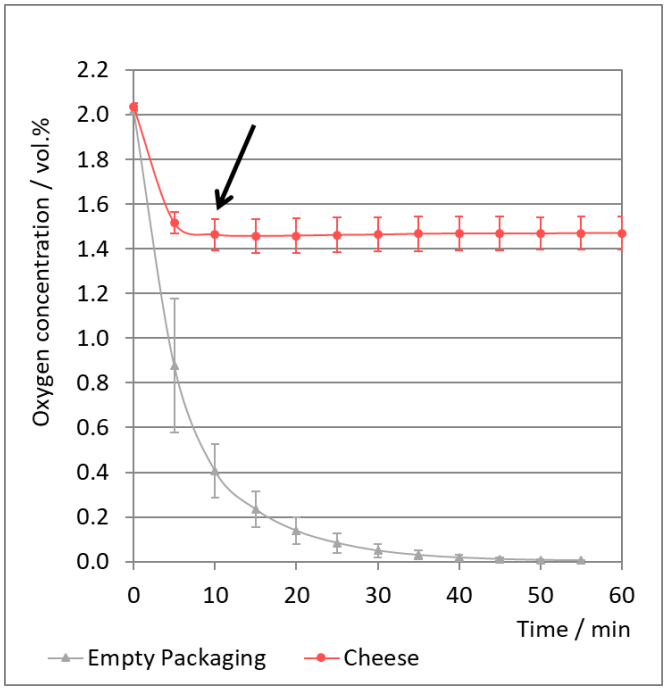
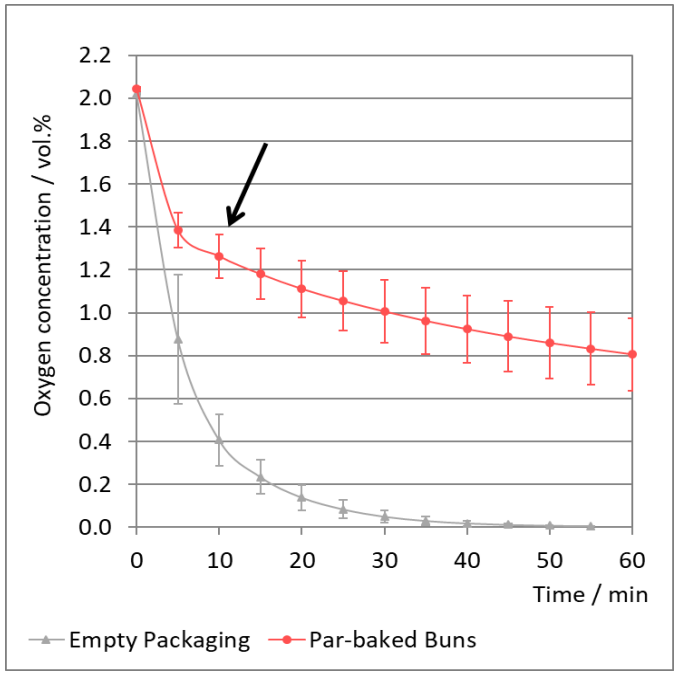
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
10
20
30
40
50
60
Time / min
Empty Packaging
Peanuts

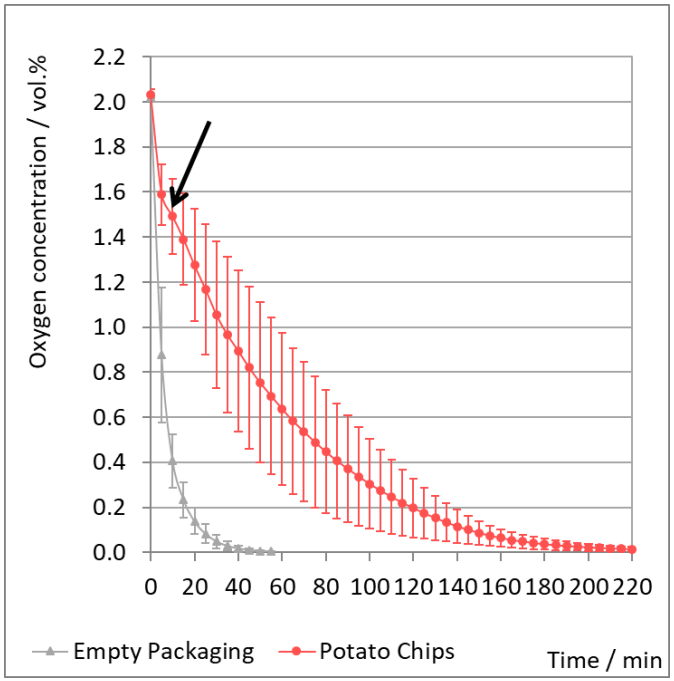

Absolute concentration / ppbv
Minimum inhibitory range
exceeded
within
below
10.8-36 ppbv
4.6-24.5 ppbv
DMS
DMDS
MET
FFT
DMTS


Absolute concentration / ppbv
Minimum inhibitory range
exceeded
within
below
2.1-5.8 ppbv
DMS
DMDS
MET
FFT


Absolute concentration / ppbv
Minimum inhibitory range
exceeded
within
below
DMS
DMDS
MET
FFT


Oxygen concentration / vol.%
Time / min
Empty Packaging
Cheese


Oxygen concentration / vol.%
Time / min
Empty Packaging
Par-baked Buns


Oxygen concentration / vol.%
Time / min
Empty Packaging
Potato Chips

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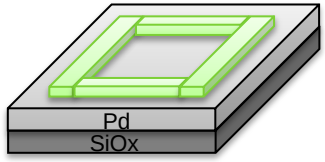
Further VSC

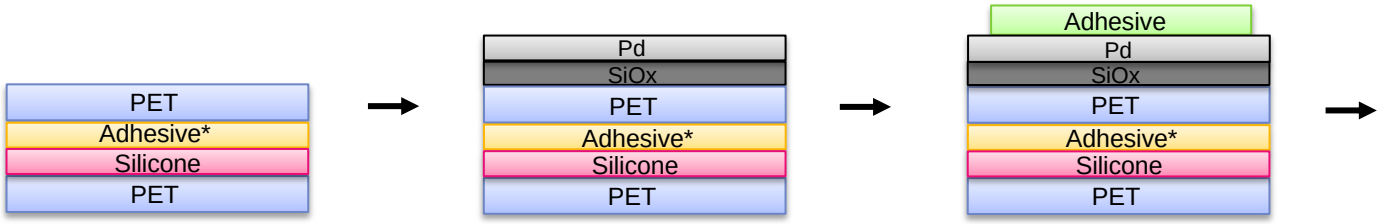
VSC [ppbv]	Roast beef		Ham		Cheese		Peanuts		Par-baked buns		Potato Chips	
	identified	Literature	identified	Literature	identified	Literature	identified	Literature	identified	Literature	identified	Literature
Hydrogen sulphide	1.4	✓	14.8	✓	0.8	✓	0.7		0.1		<LOQ	
Methane thiol	1.6	✓	49.2	✓	13.8	✓	92.9	✓	1.8	✓	0.5	✓
Methyl ethyl sulphide	5.4		3.5		1.2		0.4		0.3		<LOQ	
Thiophene	0.1		0.07		0.1		0.9		0.4		0.05	
Thiazole	0.05	✓					0.2		<LOQ	✓		
2-Methyl thio acetaldehyde	0.3					✓	0.1					✓
Butane thiol	3.5		7.7		5.7	✓	0.3		4.4		0.1	
2-Methyl thiophene	0.2	✓	0.2	✓	0.3		1.2		0.6		0.08	
4-Methyl thiazole	0.1	✓		✓					0.08			
Methionol	7.8		0.3		6.0	✓			4.2	✓	0.4	
3-Mercapto-2-pentanon	0.8	✓		✓								
Methyl propyl disulphide	0.1		0.1		0.4				0.2			✓
Methyl benzene thiol	0.1		0.08		<LOQ	✓					2.1	
2-Acetyl thiophene	0.4		0.09		0.07			✓	0.2	✓		
2-Acetyl thiazole	0.1	✓		✓				✓		✓		
2,4,5-Trimethyl thiazole	0.1	✓		✓					<LOQ			
Methyl furfuryl thiol	0.1		0.07						0.1			
Tetramethyl thiourea	0.3				0.4	✓			0.6			
Benzo thiazole	0.1	✓	0.1	✓	<LOQ	✓			0.1			
Ethyl 3-(methyl thio) propanoate	0.4				0.2	✓			<LOQ			
2-Methyl benzo thiazole	0.1				<LOQ	✓			<LOQ			
Propyl disulphide	0.3		0.1		<LOQ		0.1	✓	0.1			
Bis-(2-methyl-3-furyl) disulphide	<LOQ	✓										

Label Development

1. Step:
SiOx/Pd-Coating

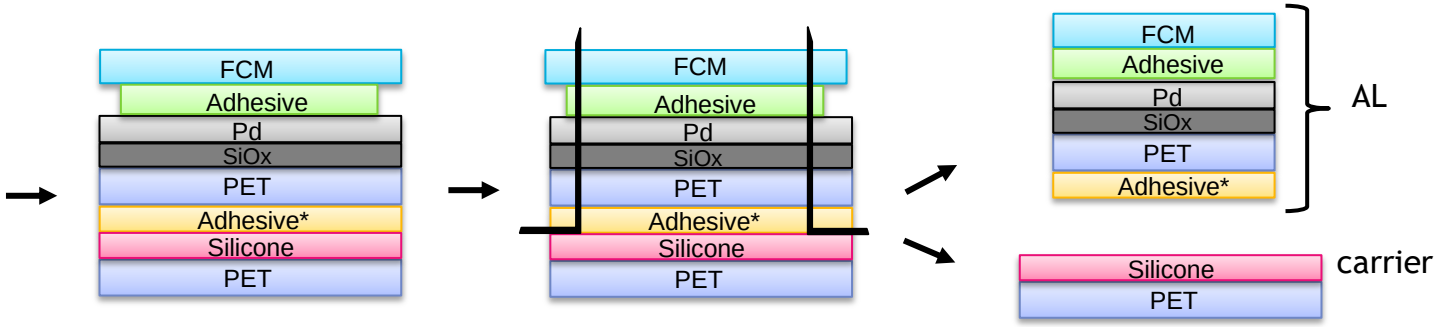
2. Step:
Partial application of
Adhesive





3. Step:
Application of FCM

4. Step:
Punching



Content

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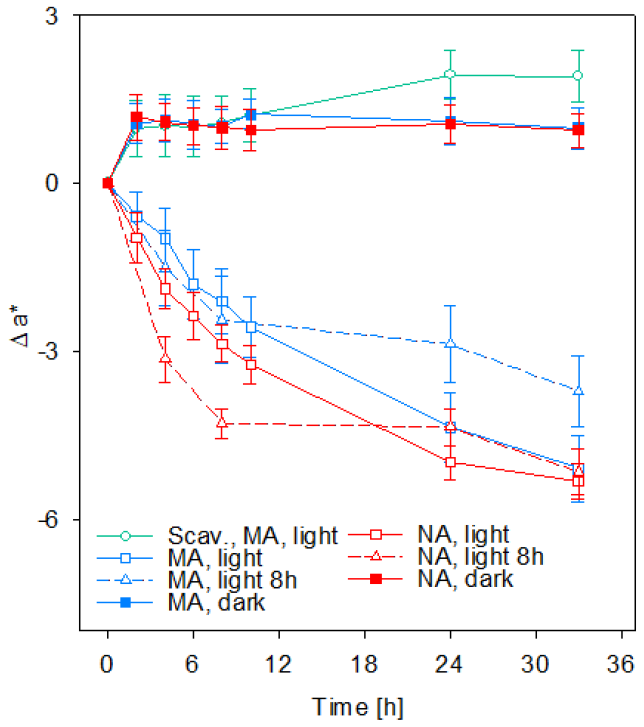
1. Research Group Food Packaging @ZHAW

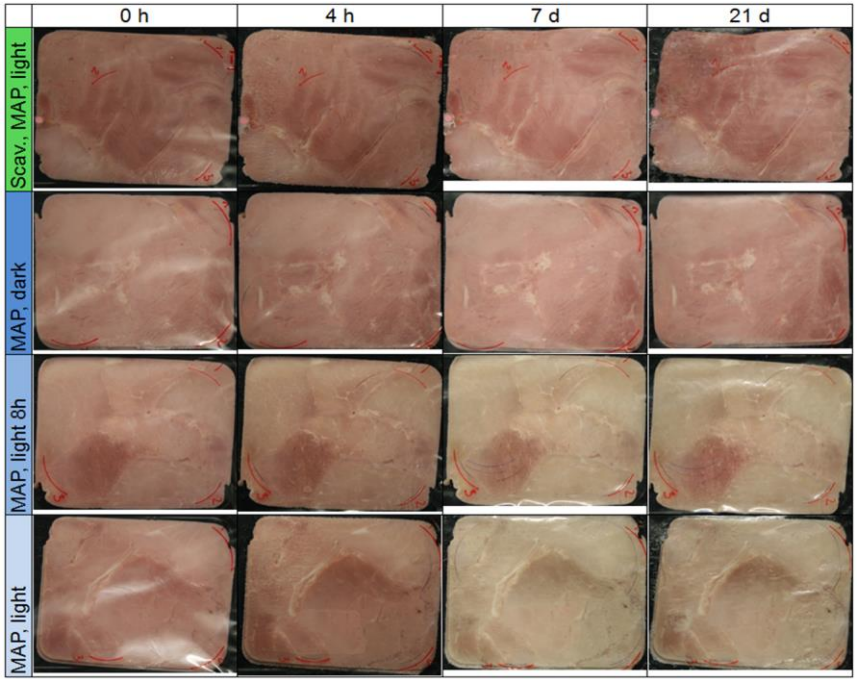
2. Active Packaging

3. Development of Palladium based Oxygen Scavenging Label
   - Idea
   - Development
   - Industrialisation

4. Applications

Use of palladium based oxygen scavenger to prevent discoloration of ham





Hutter S., Rüegg N., Yildirim S., Use of palladium based oxygen scavenger to prevent discoloration of ham, Food Packaging and Shelf Life, 2016, 8, 56-62

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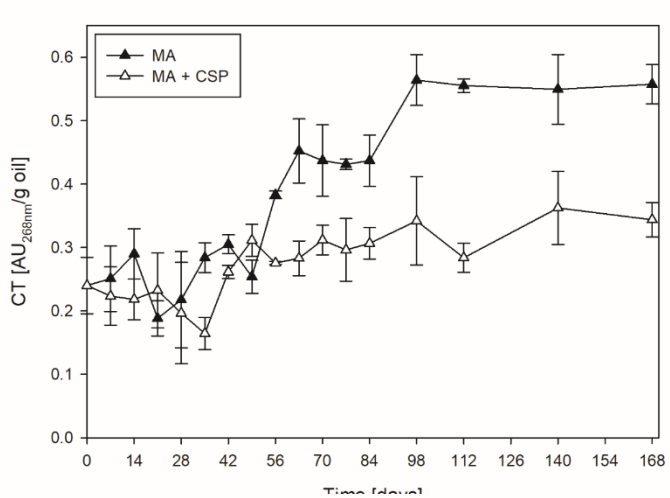
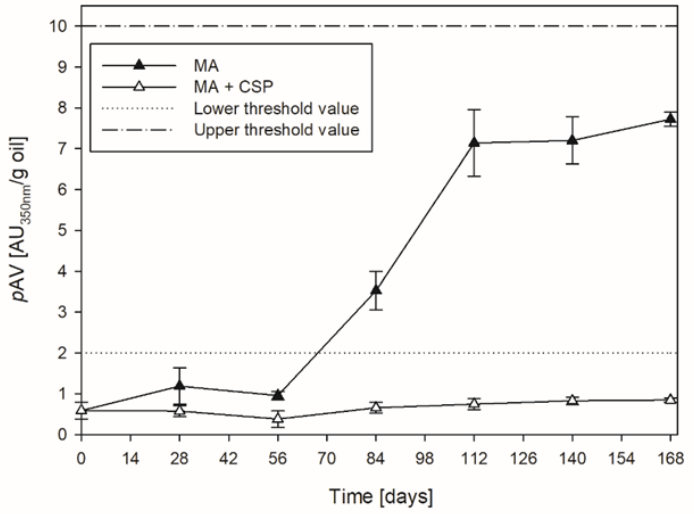
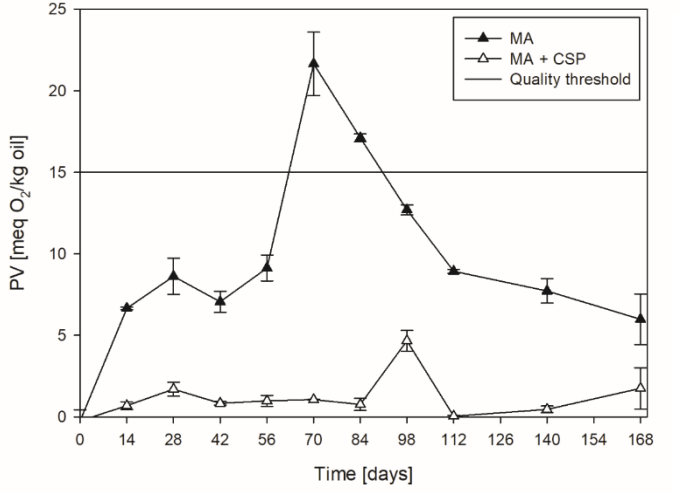
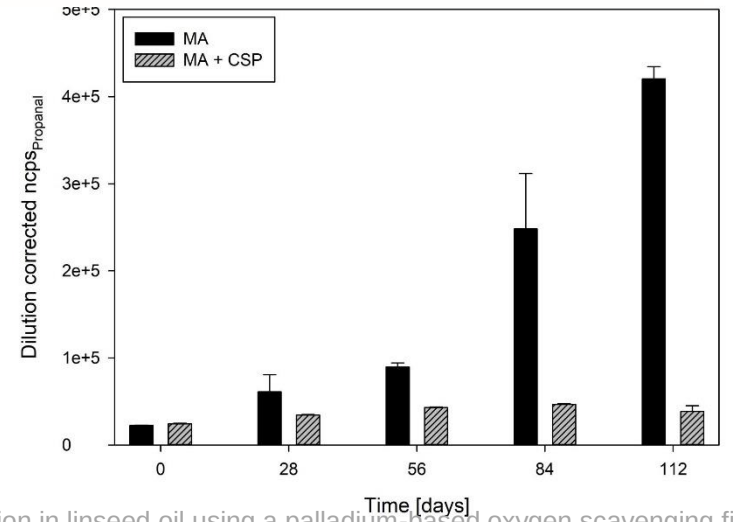
Use of Palladium based Oxygen Scavenger to Prevent Oxidation in Linseed Oil



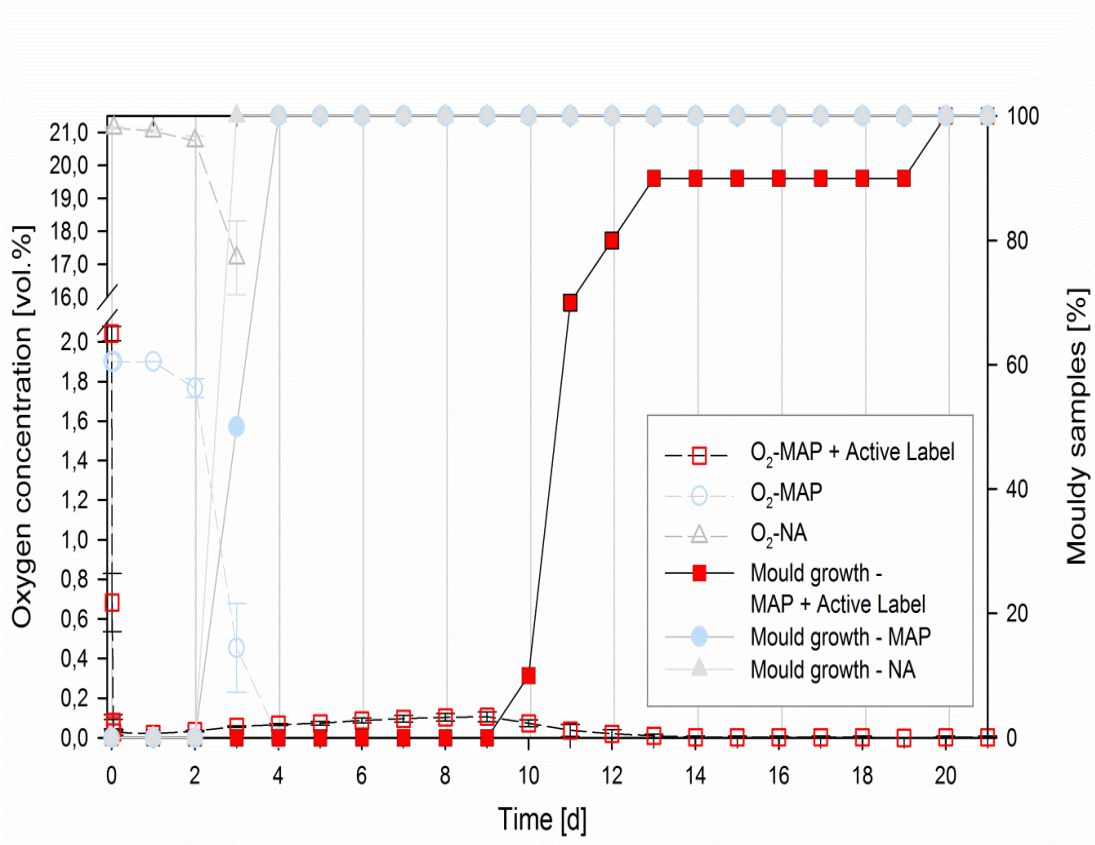






Faas N., Röcker B., Smrke S., Yeretzian C.,Yildirim S. Prevention of lipid oxidation in linseed oil using a palladium-based oxygen scavenging film, Food Pacakging and Shelf Life, to be submitted

Use of Palladium based Oxygen Scavenger to Prevent Mould Growth of Bakery Products



Rüegg N, Röcker B. Yildirim S. Use of palladium based oxygen scavenger to prevent mould growth of bakery product. Manuscript in preperation

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Swiss Confederation

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Thank you very much for your attention