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A study of the barrier properties of ethylene vinyl alcohol copolymers using gas chromatography

2021 Member Conference
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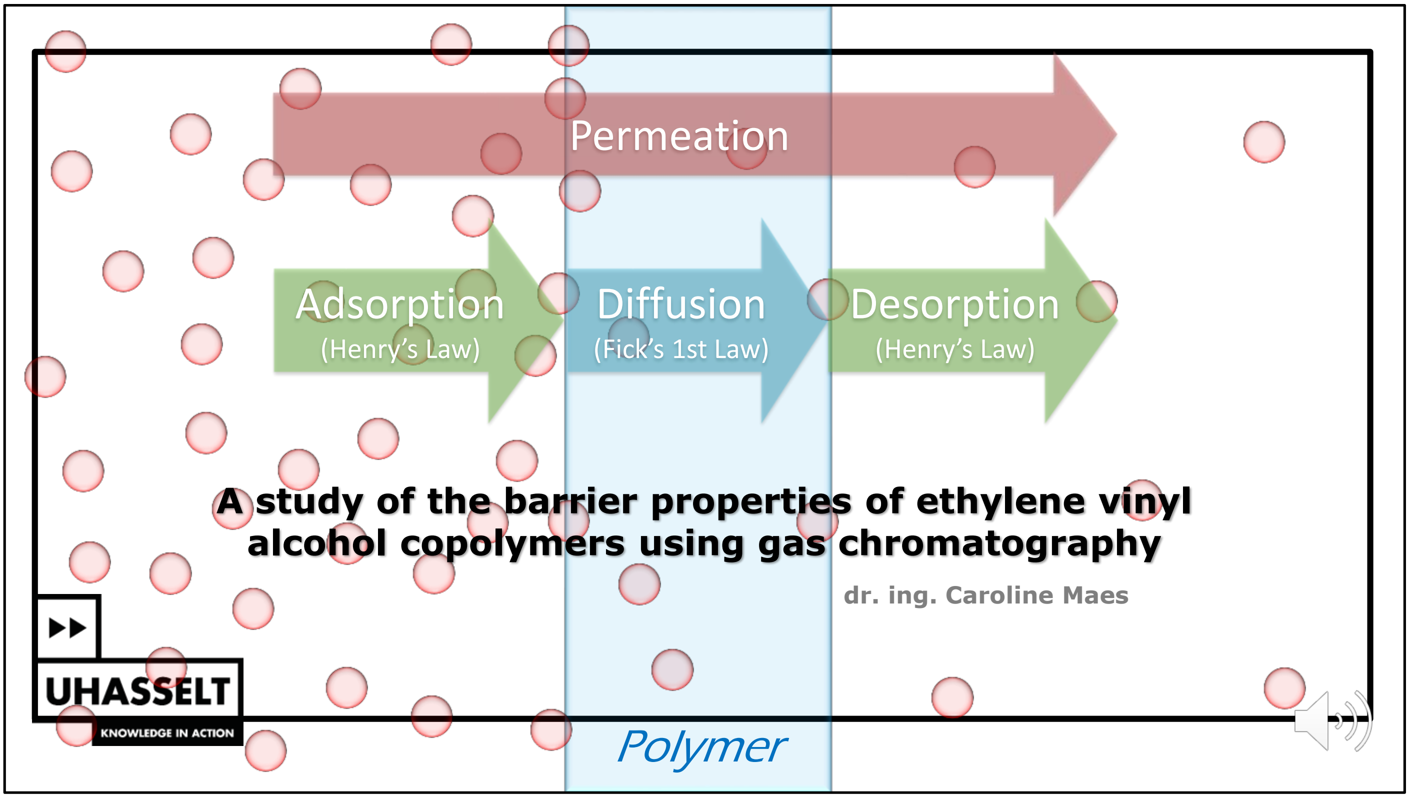
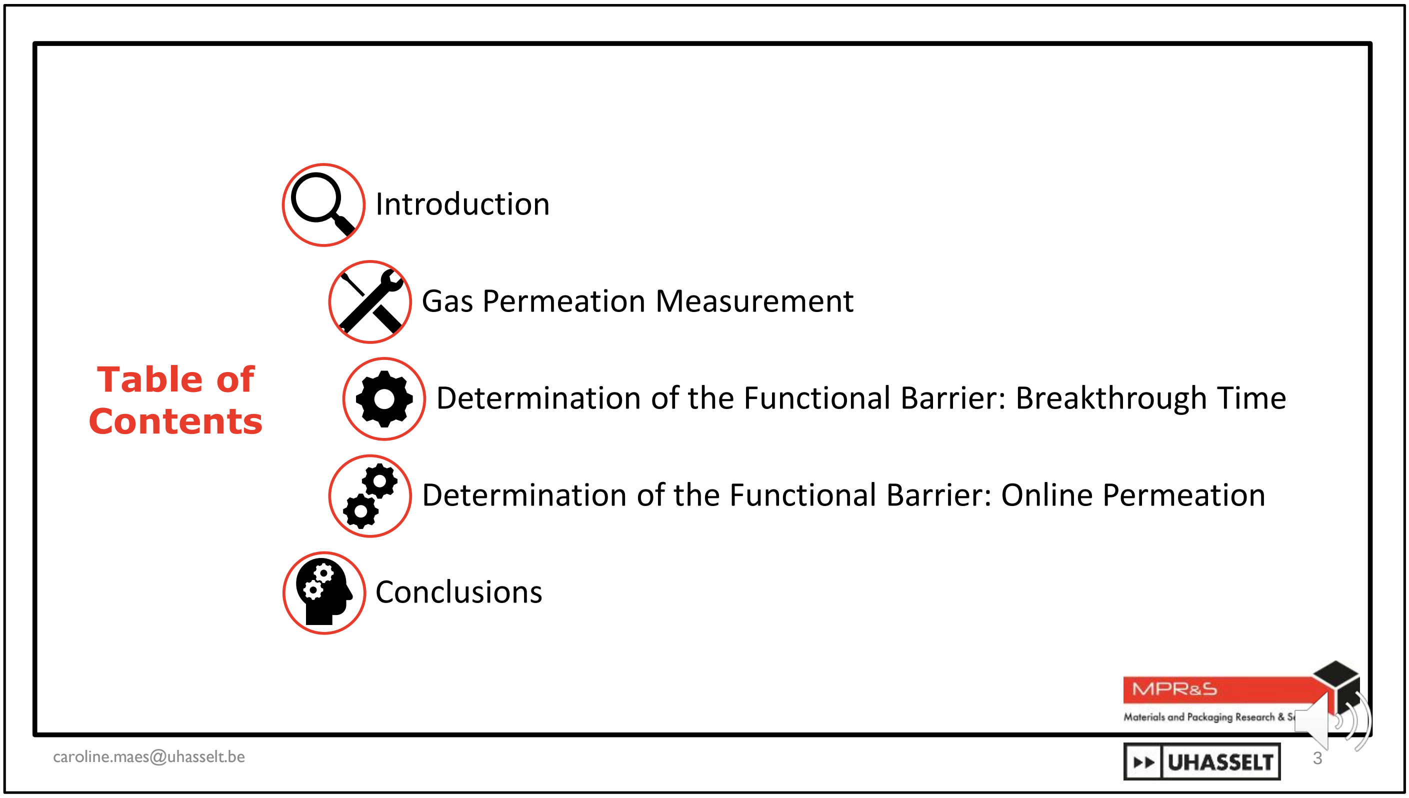
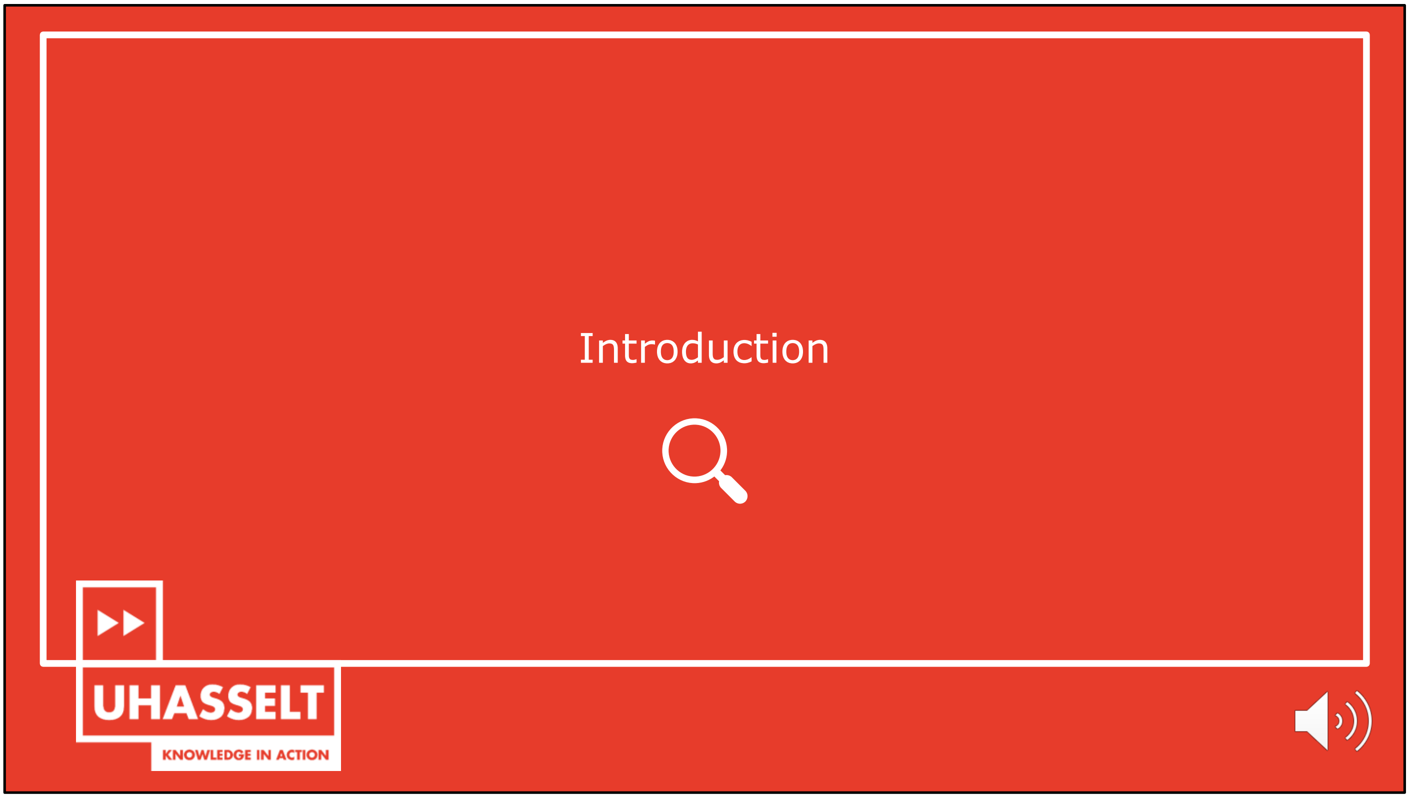


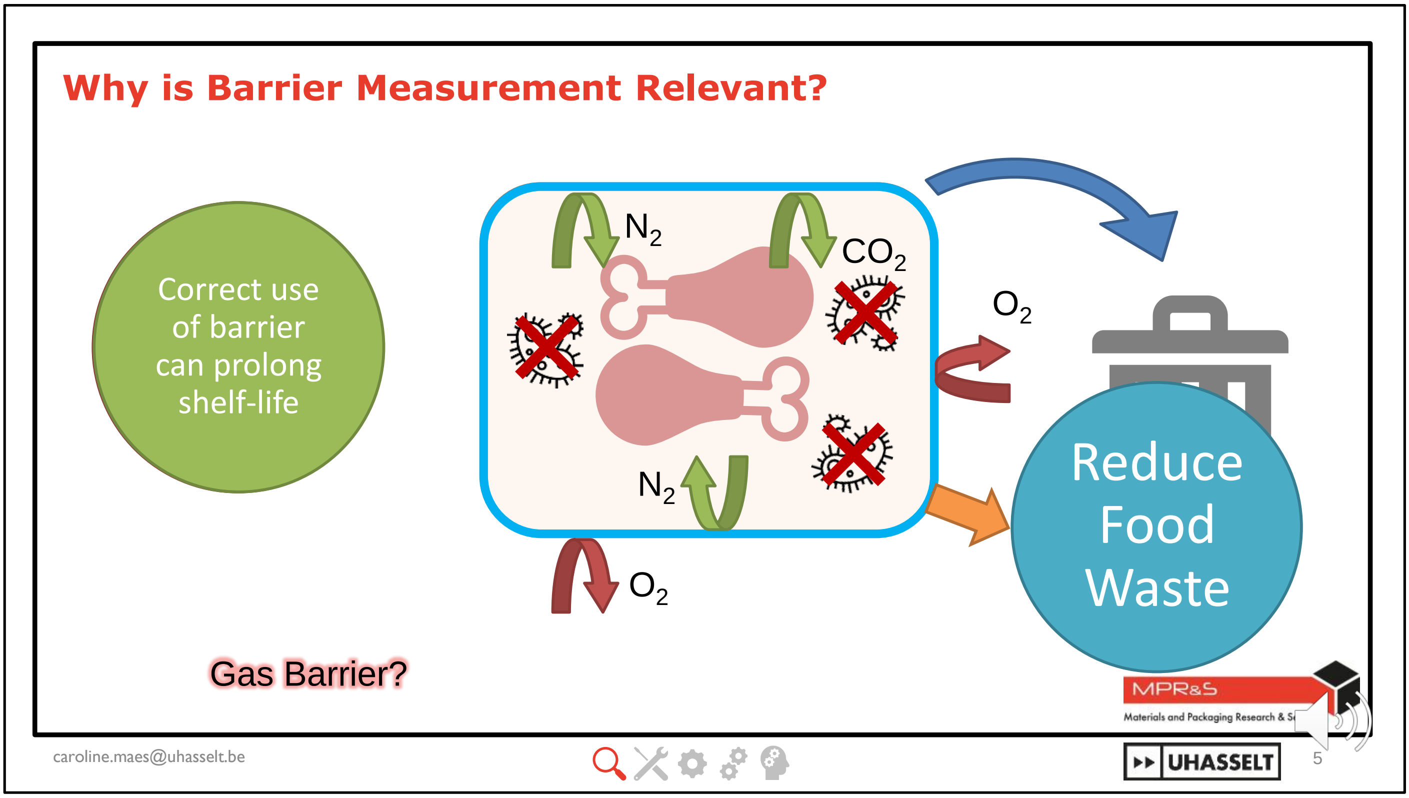
Good afternoon, my name is Caroline. I would like to show you how we measured the barrier properties of Ethylene vinyl alcohol by using gas chromatography. This research was a part of my PhD research at Hasselt University.



I will start with an introduction in which I will briefly explain why we did this research. Then I have divided the research in three parts. First I will start with the gas permeation measurement. For the determination of the functional barrier we used two different approaches: the breakthrough time on one hand and online permeation on the other.
And finally the conclusions of this research.



Let’s start with the introduction.

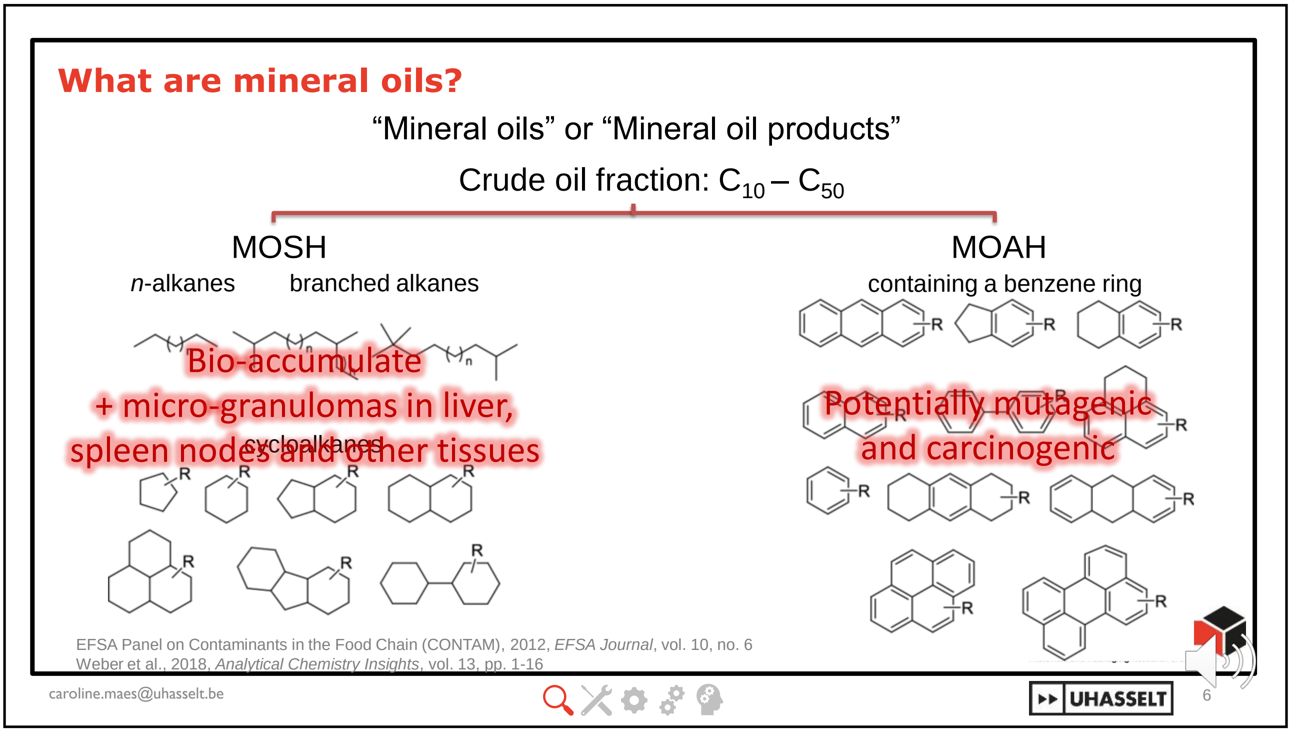


The first question I would like to answer: Why is barrier measurement relevant?

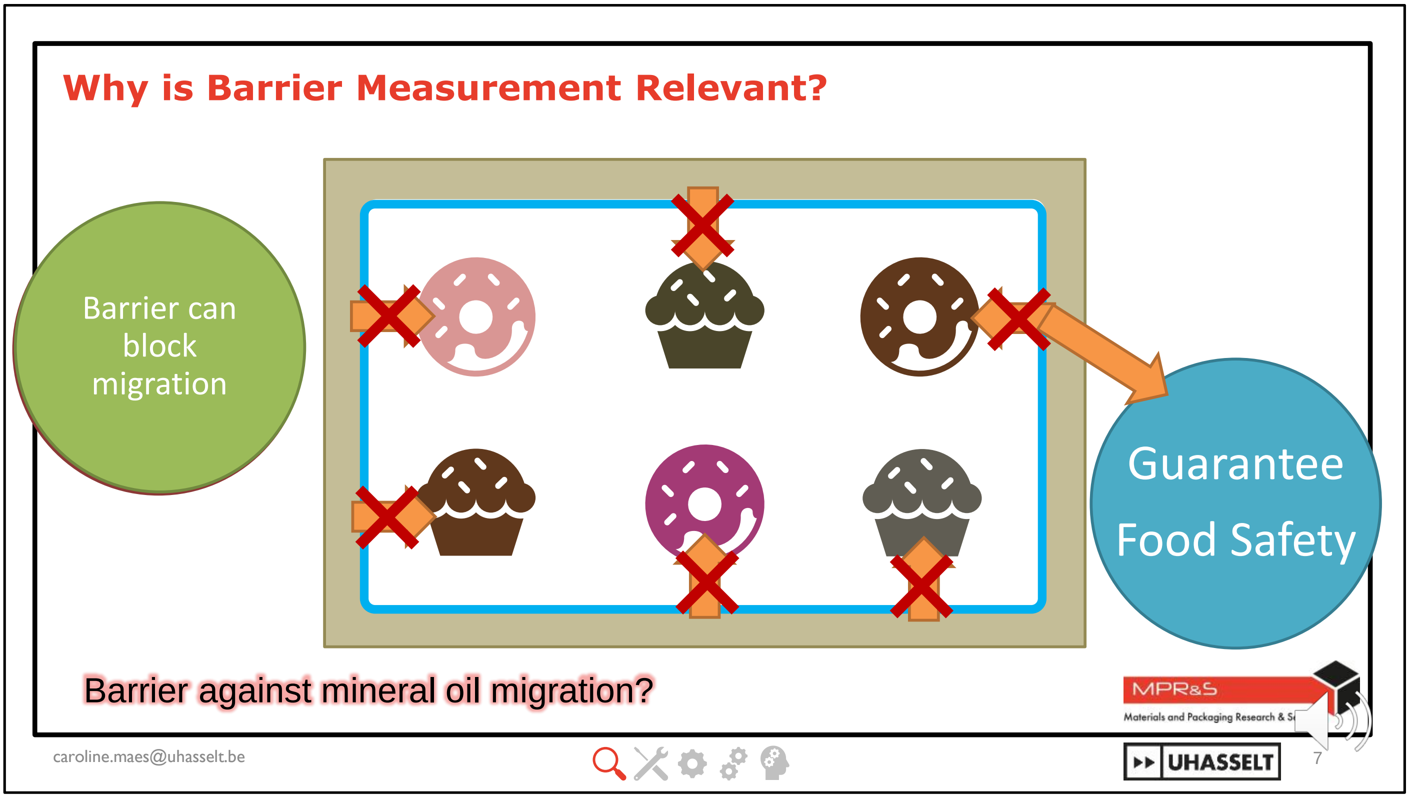
Gas permeation finds its use in many applications, one of the most common is food packaging.

Each year we throw about 30% food away before consumption because it has gone bad inside the package!

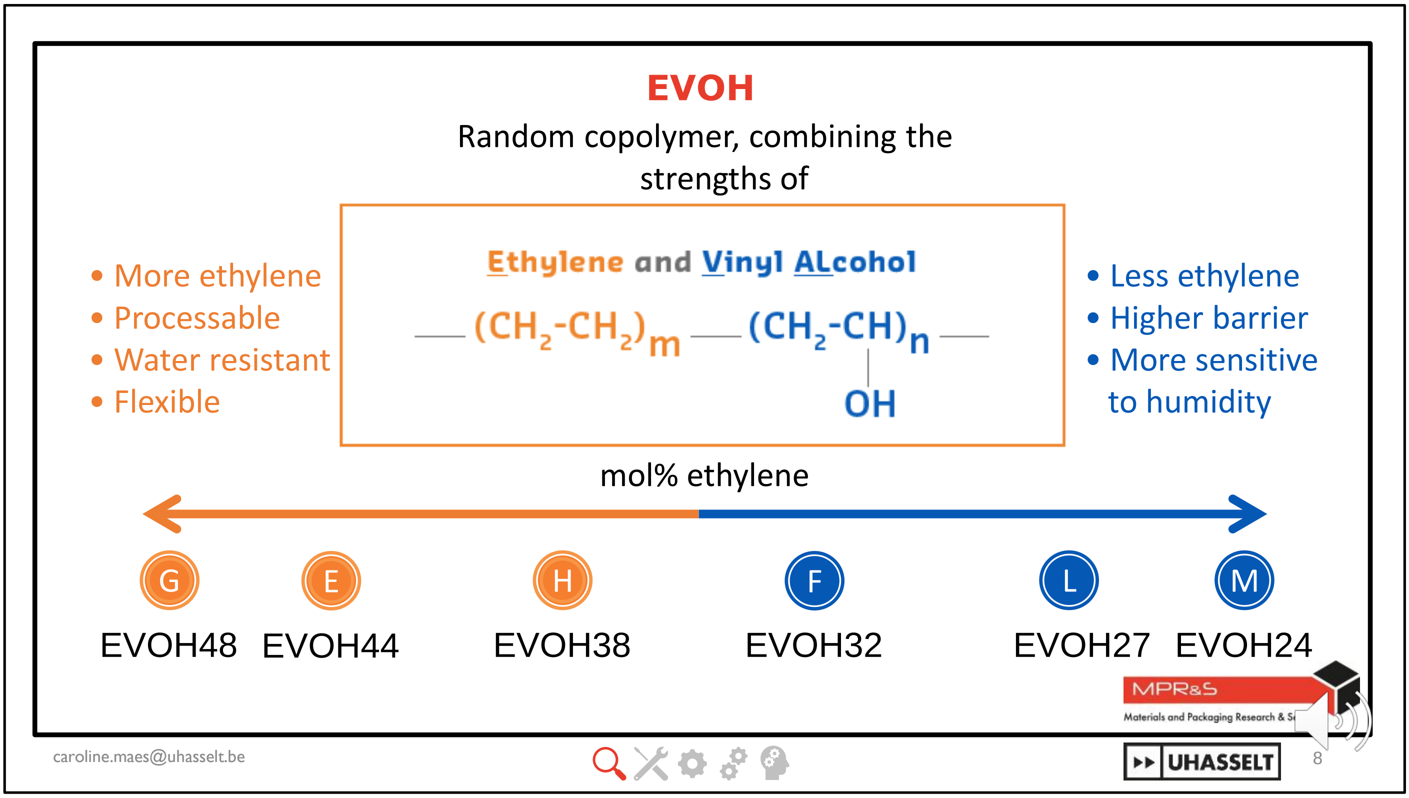
With the right barrier, we can maintain the atmosphere of nitrogen and carbon dioxide inside the package, while we keep out oxygen. Effectively preventing microbial growth and spoilage. And thus also reducing the food waste. So we need to know the barrier properties of the material against these gases.



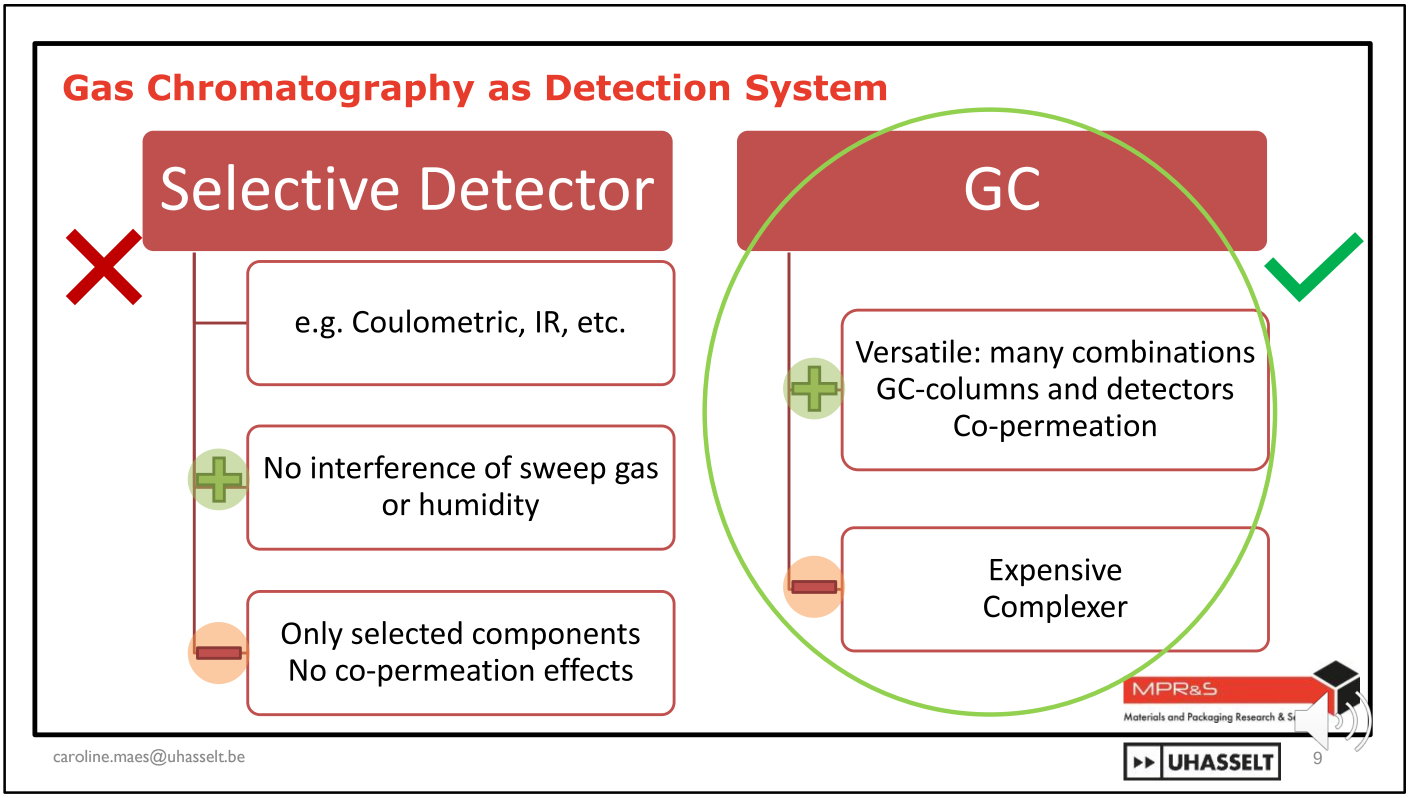
I would like to focus for a moment on mineral oil, which has been a trending topics for several years now.
According to the scientific opinion written by the EFSA in 2012 “mineral oils” or “mineral oil products” are complex mixtures of hydrocarbons classified by a carbon number ranging from about 10 to 50. The crude oil fraction is by far the most important source of mineral oils.
When talking about mineral oil contamination in food, usually two main groups are distinguished: MOSH on one side and MOAH on the other side.
The MOSH fraction or saturated mineral oil hydrocarbons consists of single bonded carbon chains or rings, such as n-alkanes, branched alkanes and cycloalkanes.
These components are known to bio-accumulate and form micro-granulomas in different organs such as the liver, spleen nodes and other tissues.
The MOAH fraction or aromatic mineral oil hydrocarbons contain a benzene ring. An example is naphthalene.
Toxicological studies showed that these components are potentially mutagenic and carcinogenic and therefor a reason for concern.



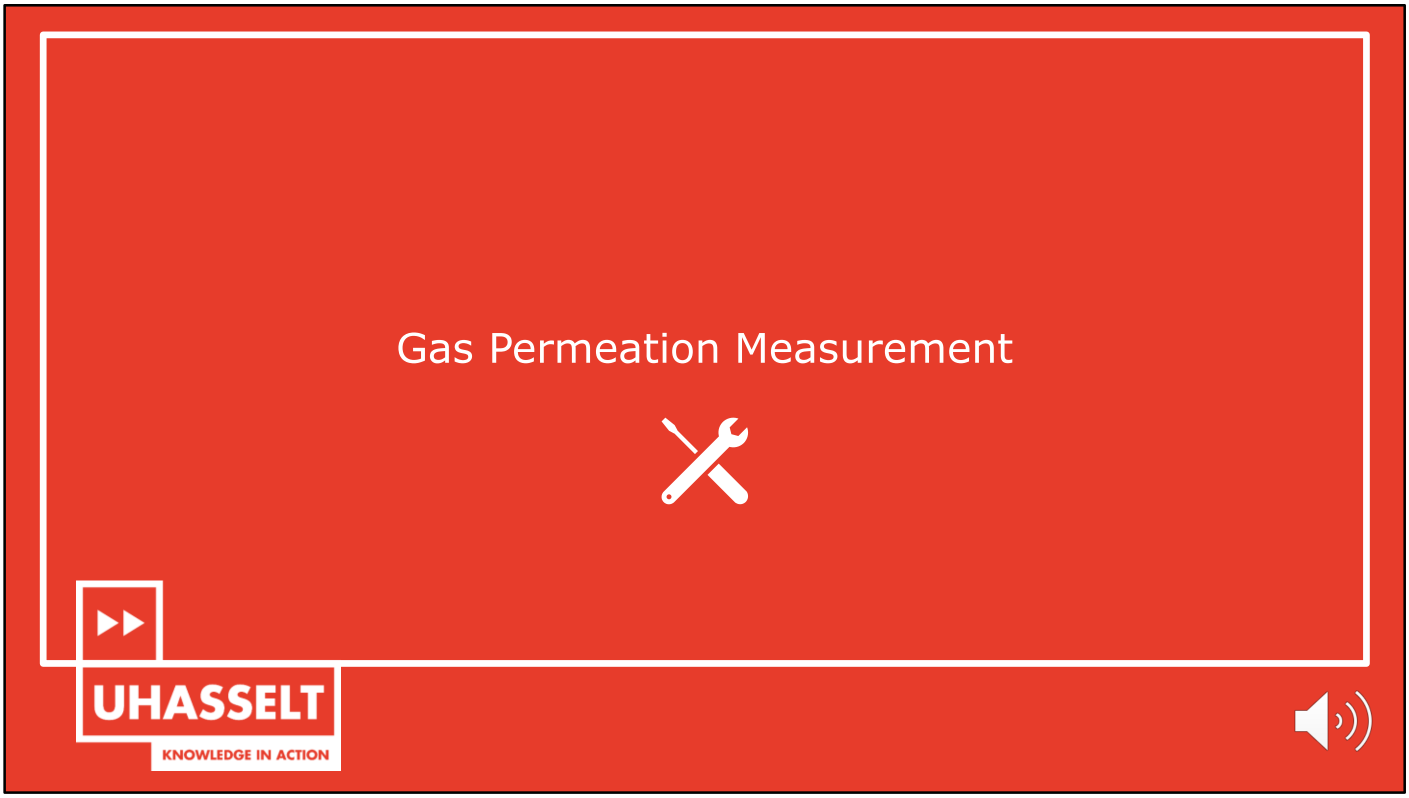
Paperboard used in packaging can contain these MOSH and MOAH components amongst other contaminants, which are released into the packaged food. Even when the paperboard is not in direct contact, this migration can occur. It was found that even when nearby sources contain these contaminants, they might end up migrating into the food.
This process is undesirable and should therefore be prevented.
Again this can be done by using an adequate barrier material.



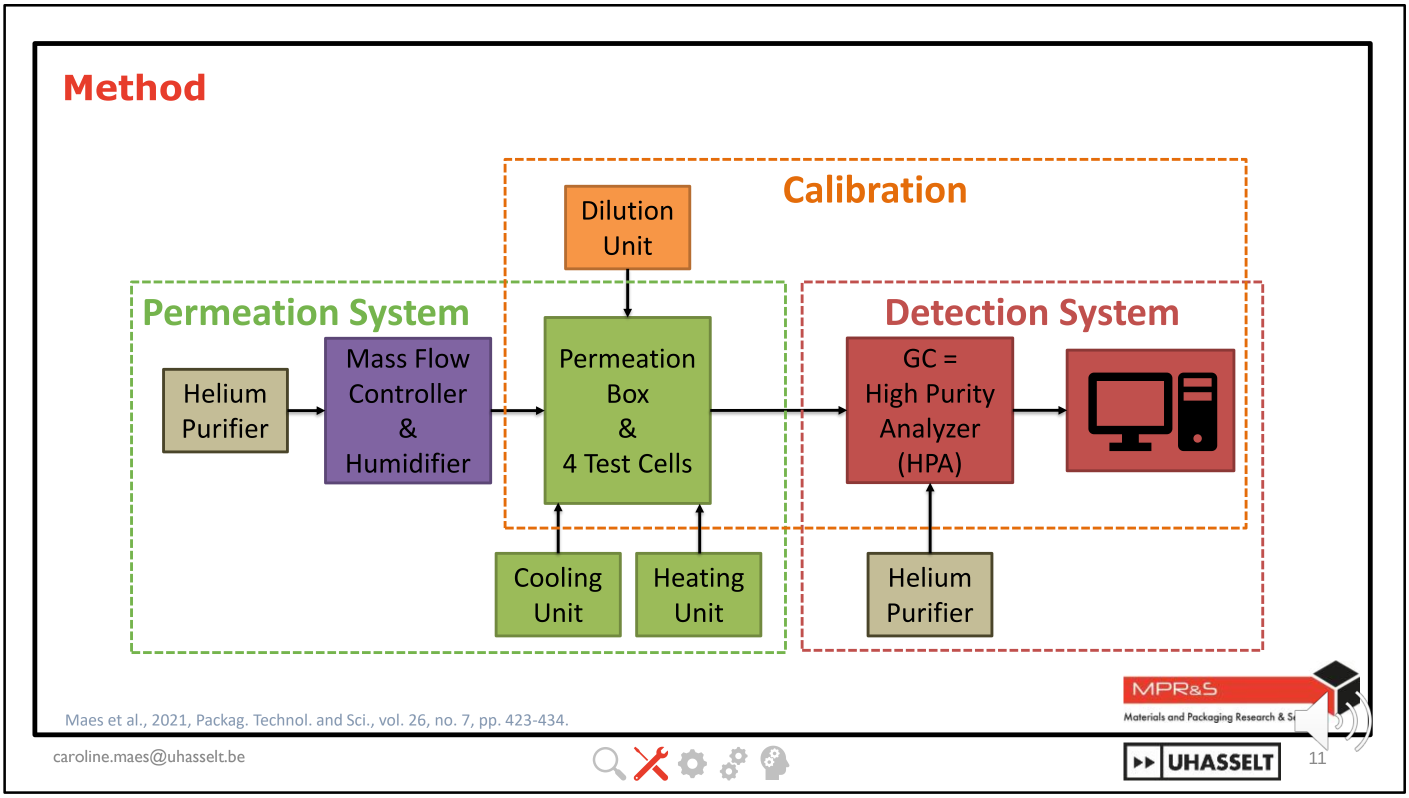
The key material of interest is EVOH or ethylene vinyl alcohol copolymer consisting of 2 units.
The properties of this material depend on how much of each of these units is present. For instance, EVOH with more ethylene units, will result in a material that is easier to process, water resistant and flexible.
Whereas more vinyl alcohol units give EVOH higher barrier properties, but also make it more sensitive to humidity.



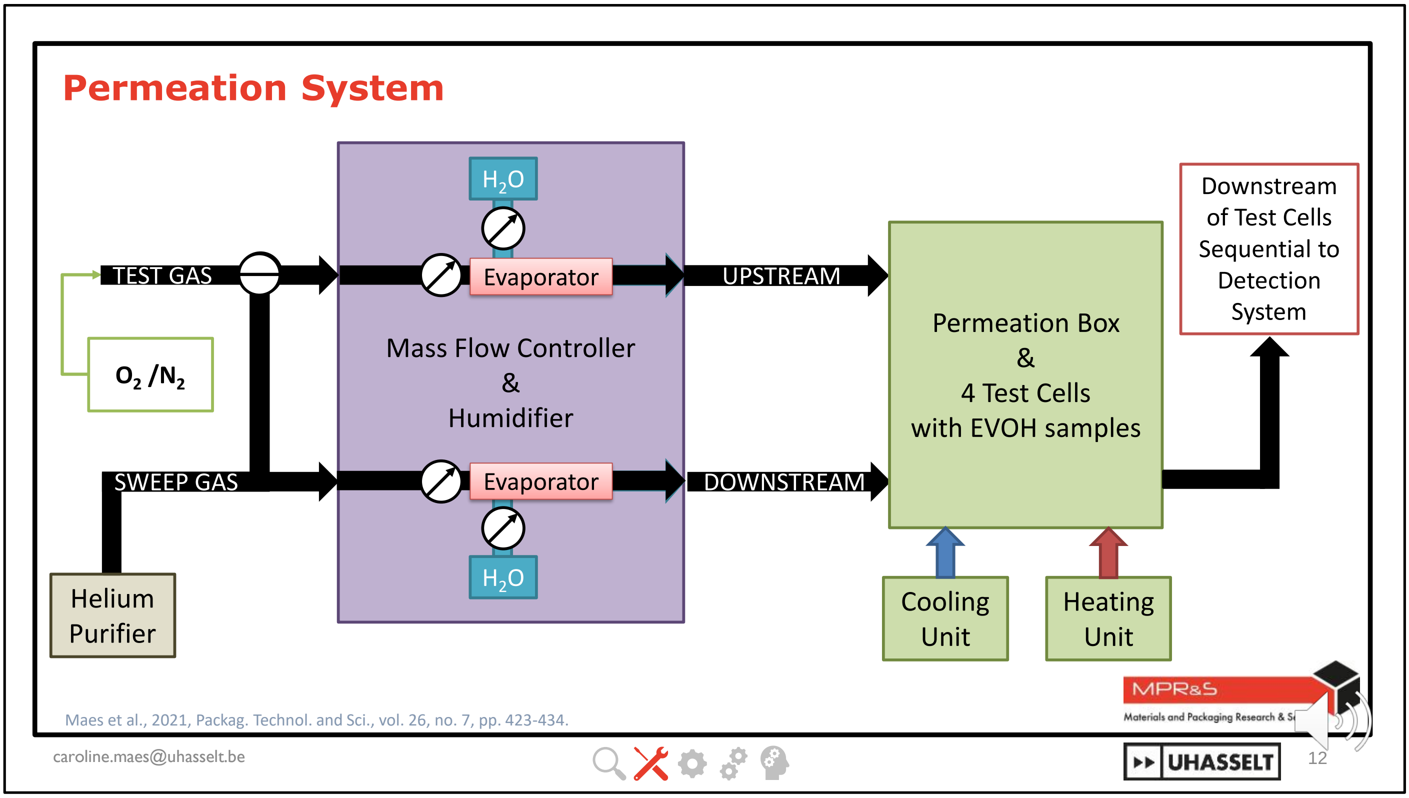
Most permeation methods use a selective detector like a coulometric detector in the MOCON modules as there is not interference of the sweep gas or humidity. However, these detectors only measure selected components.
Gas Chromatography on the other hand, is a versatile method and applicable for many different components.
We used GC analysis for both gas permeation measurement and the determination of the functional barrier.



First we have the gas permeation measurement.



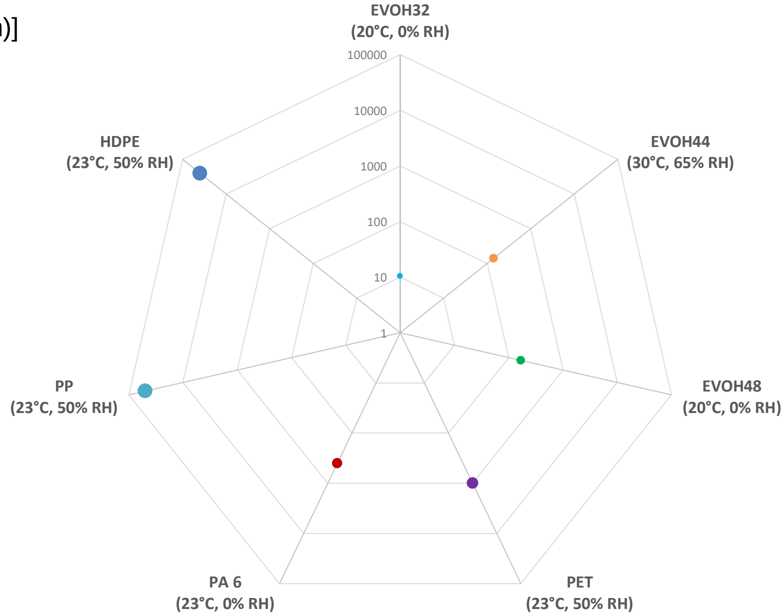
The used method was developed in cooperation with Interscience and consists a permeation system connected to a GC-based detection system.
The permeation system contains of two main parts: the mass flow controllers and humidifiers on one side, which regulate and humidifiy both up- and downstream flows.
And the permeation box on the other side, which contains the test cells.
There are also some minor parts like the gas purifier, cooling and heating unit, which support the main systems functions.
Secondly, we have the detection system, which is a special kind of gas chromatograph called High Purity Analyzer or HPA, hence the name PEBaMeT-HPA was given to this system.
Calibration can be performed by connecting a calibration gas to a dilution unit, which allows to make standards at different concentrations.



Let's first zoom in on the permeation system:
We use high purity helium as a sweep gas, which we additionally purify, so there is no interference with the detector.
In the mass flow controller and humidifier, we regulate the flow and add an amount of water which is vapourized to generate a certain humidity.
A similar process is applied for the test gas flow.
There is a two-way valve that allows us to switch the test gas to helium as well to perform an individual zero measurement similar to the MOCON.
When we start the actual permeation measurement this valve is switched on to allow test gas to pass.
In this case we used either oxygen or nitrogen.
The resulting up- and downstream flows go toward the permeation box which is set at a certain temperature thanks to the cooling and heating unit.
The downstream coming from the test cells goes in sequential order to the detection system.

Oxygen Permeability coefficient

[cm³·µm/(m²·day·atm)]



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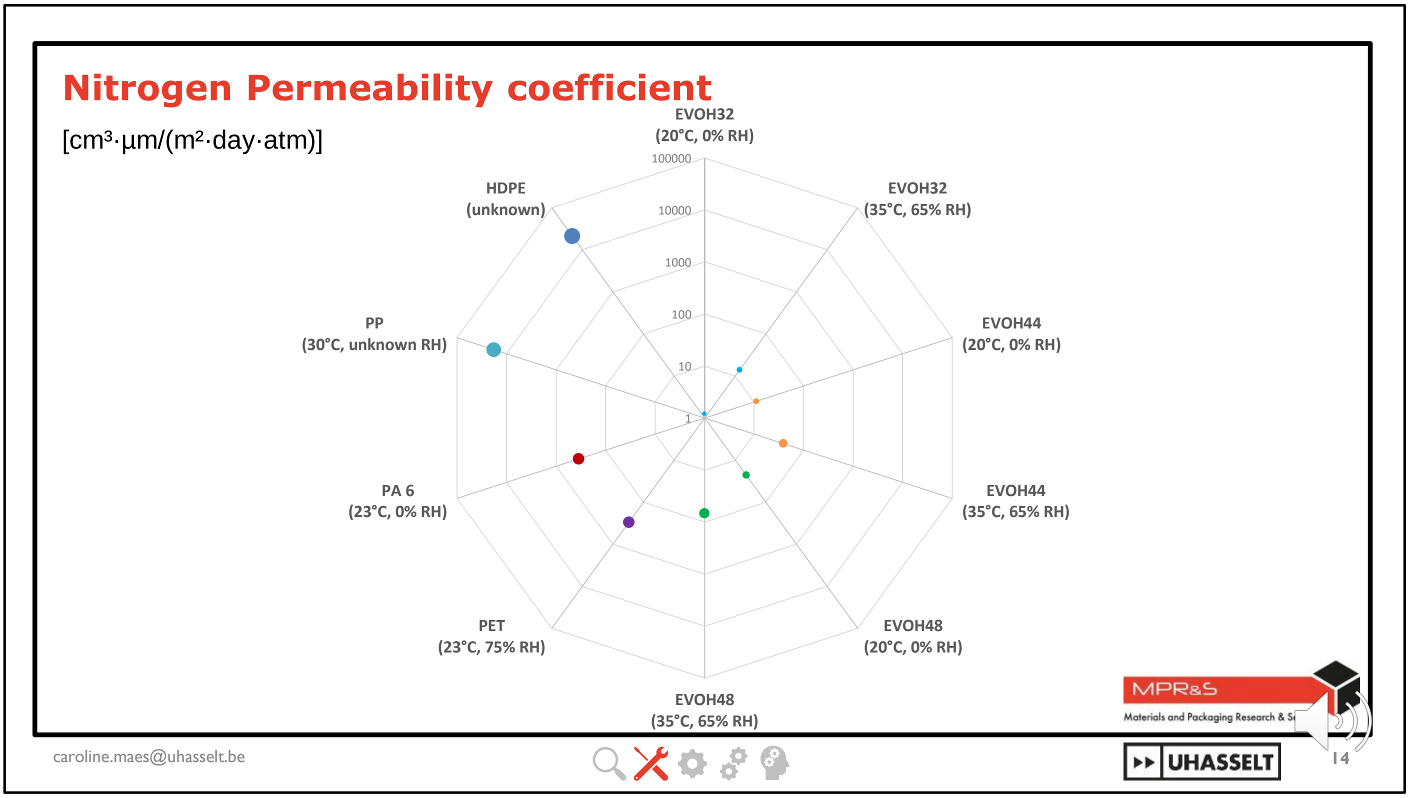
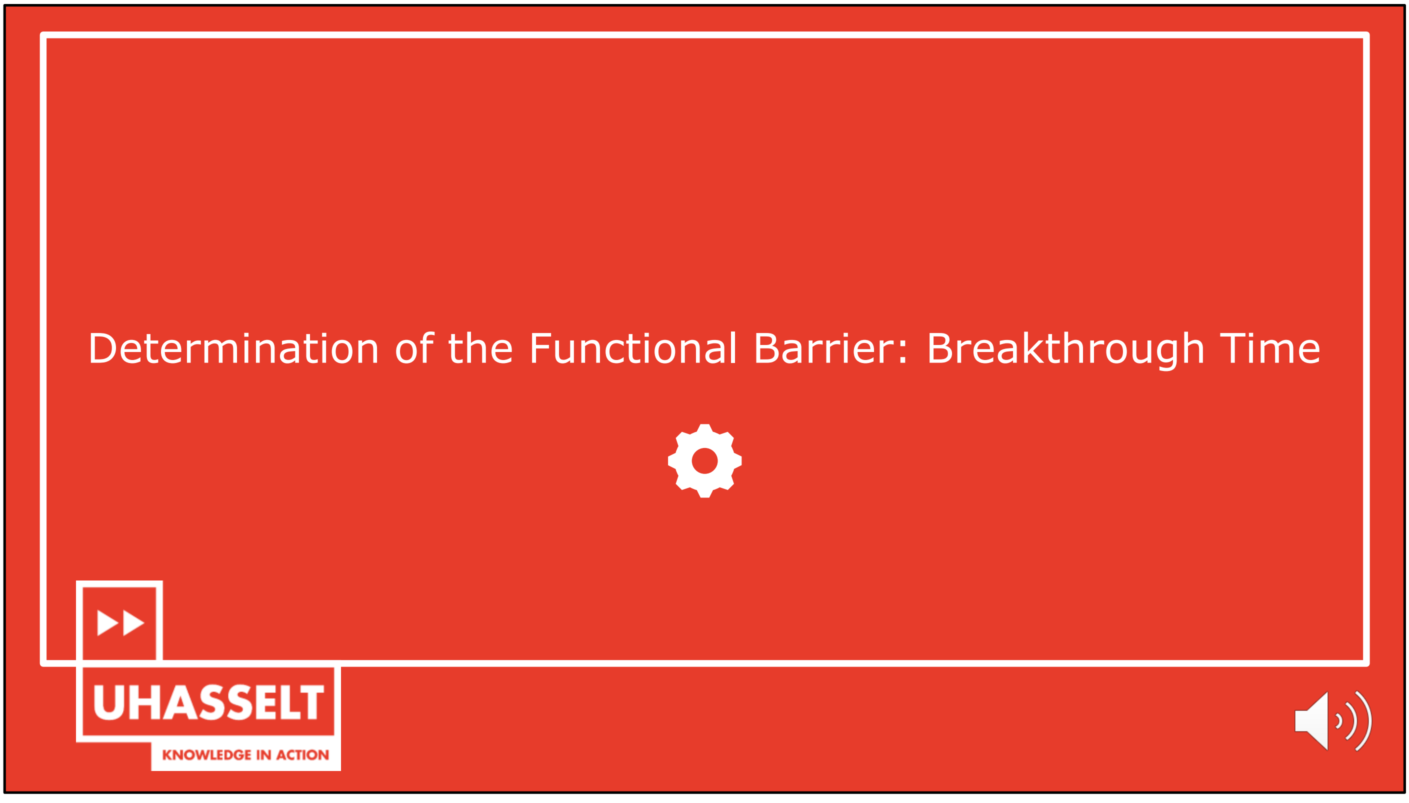
We measured both oxygen and nitrogen permeation using this system.
In order to effectively compare different materials with each other we can convert the permeation values to a permeability coefficient by taking the thickness into account.
However, comparison if often difficult because not all materials have been tested at the same temperature.
In this graph the results of three EVOH grades are given and compared with other barrier materials the three EVOH grades outperform other polymers such as HDPE, PP, PET and even PA. Especially EVOH32 shows very high barrier properties against oxygen as this grade contains the highest mol percentage of vinyl alcohol units.
These results clearly show that EVOH has outstanding oxygen barrier properties. PA and PET are considered medium barriers.



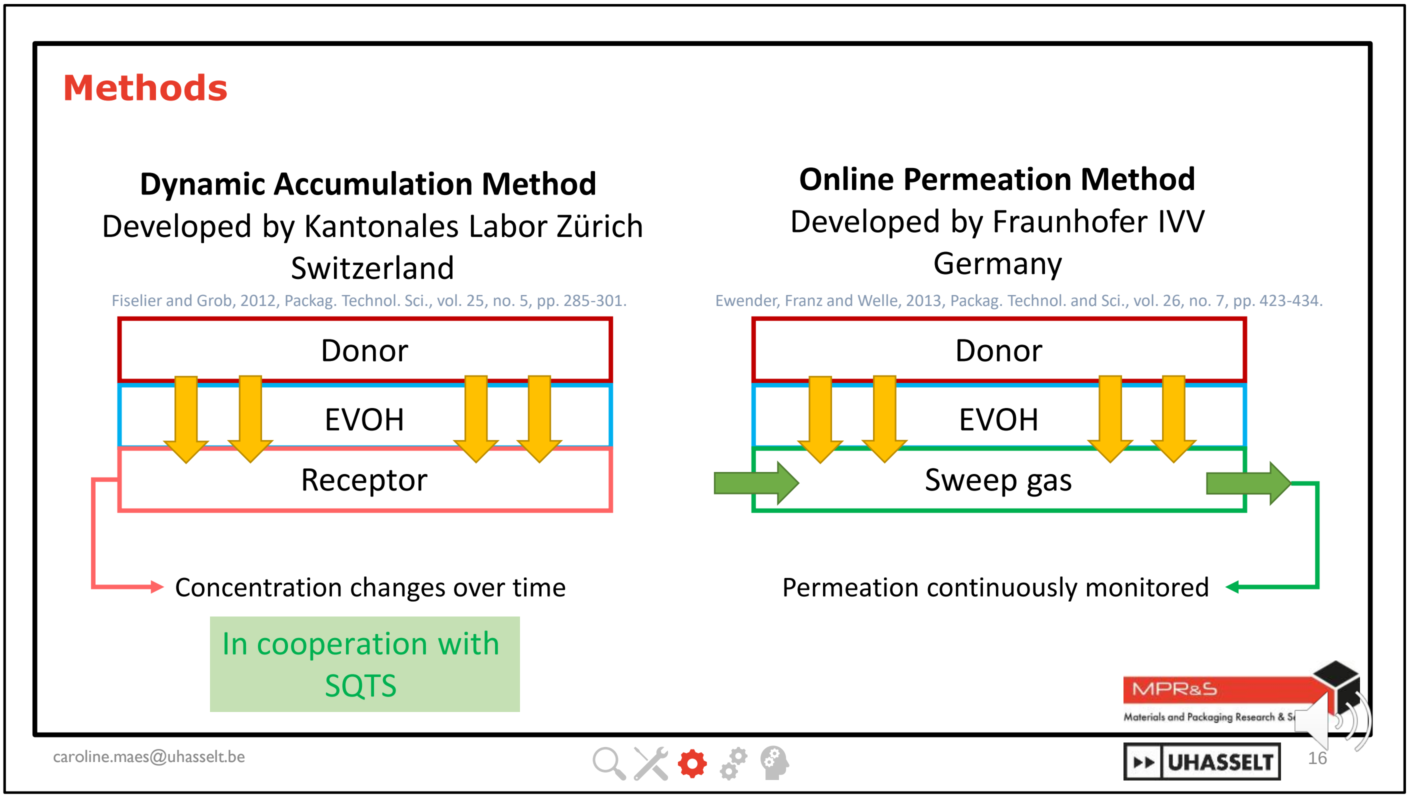
The same was done for the nitrogen permeation experiments, in this graph we see that the nitrogen permeability coefficient is lower for all polymers compared to the oxygen.

Again EVOH shows outstanding barrier properties, it easily outperforms PET and PA even under more stringent conditions by several orders of magnitude.

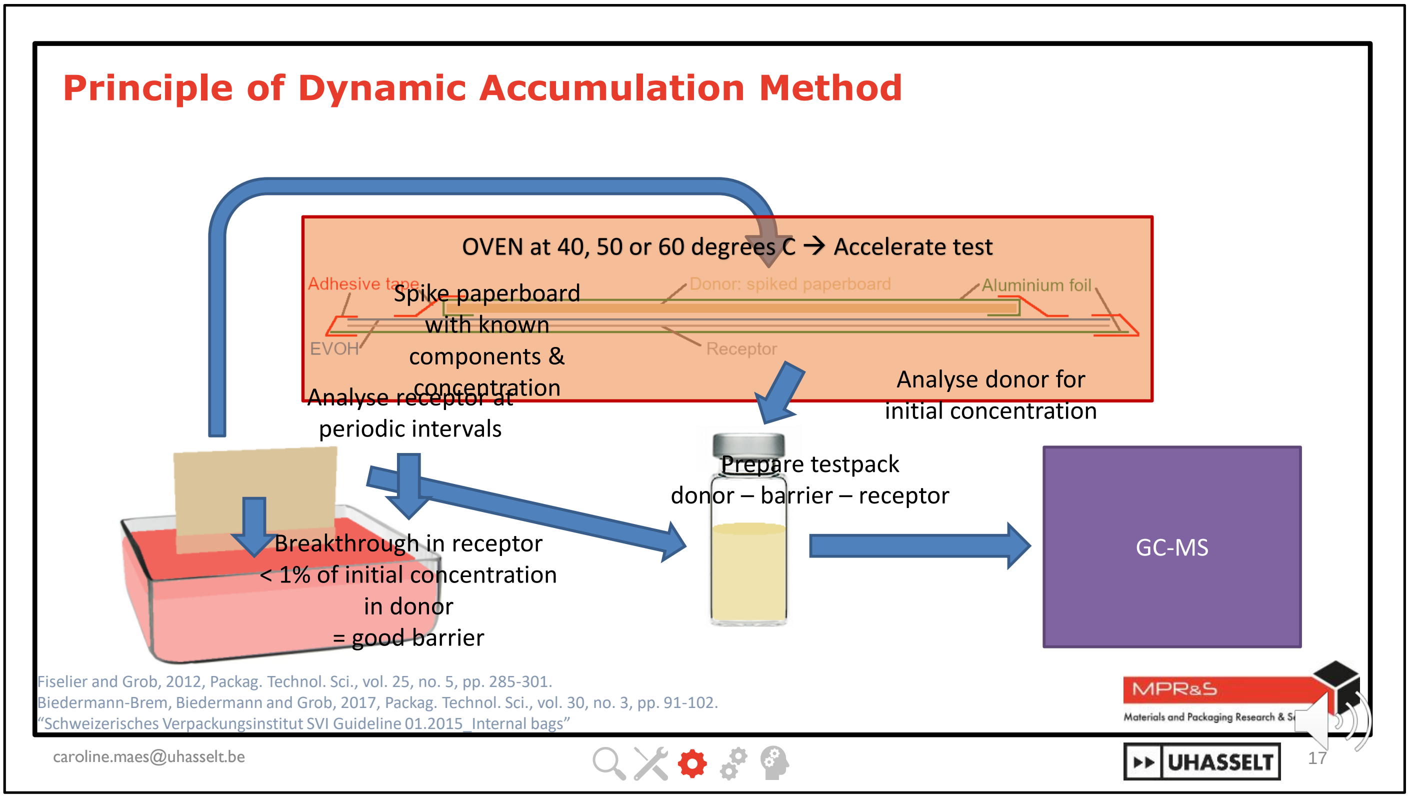
From these experiments we can conclude that EVOH is a good barrier against both oxygen and nitrogen.



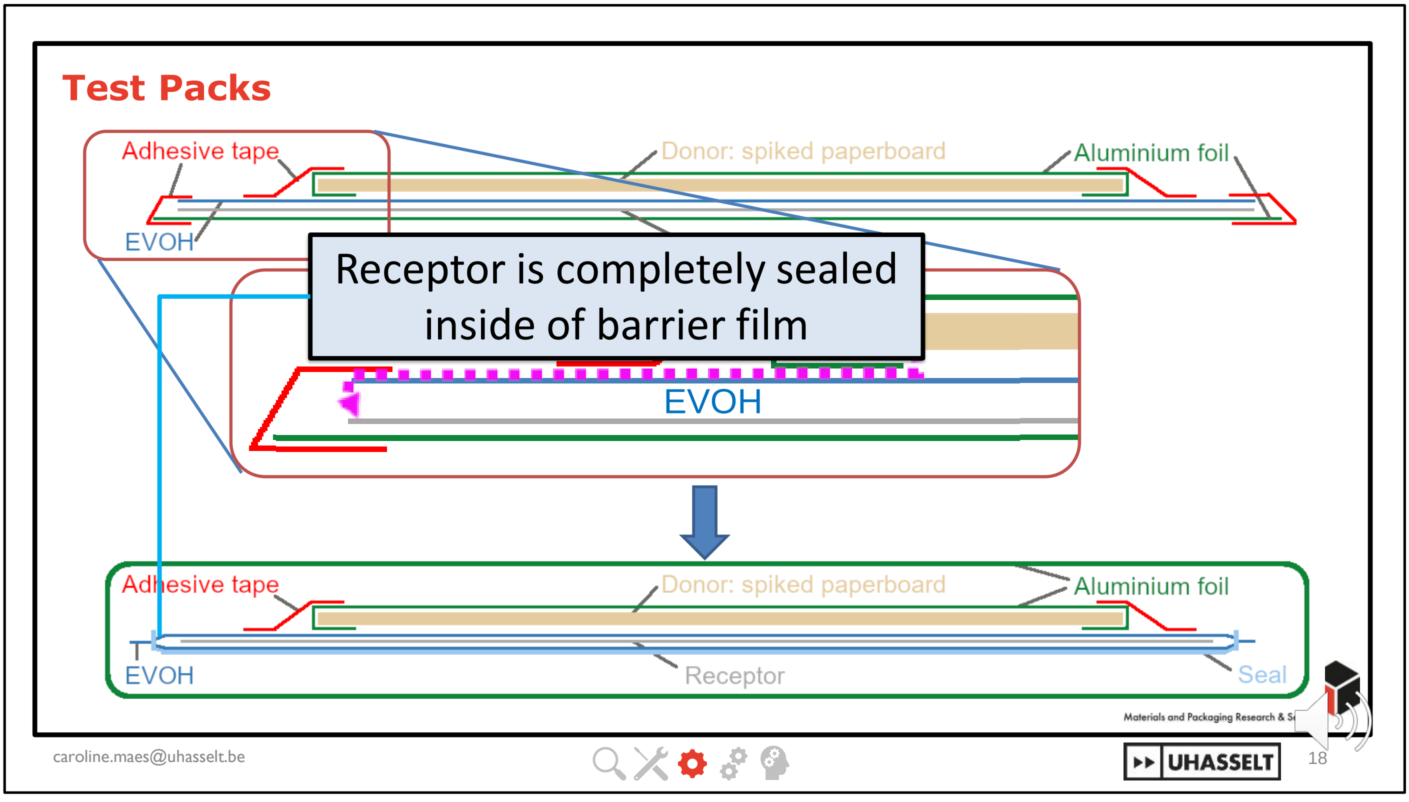
Next is the determination of the functional barrier.



Two different methods were used for this. The breakthrough time or Dynamic Accumulation Method was developed by the Kantonales Labor in Zürich. The first method uses a contaminated donor, a barrier material and receptor. The contaminants migrate from donor to receptor and are blocked and delayed by the barrier. Concentration in the receptor changes over time.
These experiments were performed in cooperation with SQTS, a independent lab in Switerland.

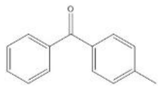
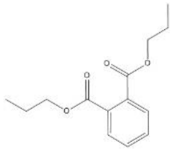
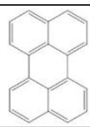
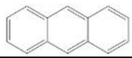


The test set-up starts with spiking paperboard with known components and concentrations by submerging the paperboard in a solution.
After conditioning the paperboard for 2 weeks, a piece is analysed for the initial concentration by GC-MS.
The spiked board is used as donor material in a test pack, where it is taped on top of the barrier. On the other side of the barrier a receptor is placed to collect the components that break through.
The test packs are placed in an oven at elevated temperatures to accelerate the test.
At periodic intervals a piece of the receptor is analysed by GC-MS.
The Guideline provided by the Swiss Packaging Institute states that the barrier is good when the values remain below 1% of the initial concentration in the spiked donor at the end of the shelf life.



When we take a closer look at the test pack, we can see that the barrier material is secured on top of the receptor.
There has been some concern that the components might migrate sideways into the receptor when testing a good barrier as this is the path with least resistance, this effect can be more pronounced at higher temperatures.
Therefore, a series of test packs were made with the receptor sealed inside of the barrier material.

Surrogate Components

Name	Abbrev.	Structure	Simulant for
4-methyl benzophenone (1)	**MBP**		**Photo-initiator**
di-*n*-propyl phthalate (1)	**DPP**		**Plasticiser**
n-heptadecane (1)	**C17**		**MOSH**
perylene (2)	**PER**		**MOAH**
anthracene (2)	**ANT**		**MOAH**

(1) Biedermann-Brem, Biedermann and Grob, 2017, Packag. Technol. Sci., vol. 30, no. 3, pp. 91-102. and "Schweizerisches Verpackungsinstitut SVI Guideline 01.2015_Internal bags"
(2) Additional components added for this study

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In the spike solution we used the following components as described in the method developed by Dr. Grob and his team:

4-methyl benzophenone as a photo-initiator
di-n-propyl phthalate as a plasticiser
n-heptadecane as a MOSH

Both perylene and anthracene were added to simulate MOAH components.

Samples

Barrier	**Average layer distribution** LDPE/tie/**Barrier**/tie/LDPE [µm]
EVOH27	22/5/**3**/5/21
EVOH32	21/5/**3**/5/20
EVOH32	21/4/**5**/5/20
PA6/6.6 (Polyamide 6/6.6)	20/5/**3**/4/18
PET (Polyethylene terephthalate)	**12**

Films extruded on Dr. Collin 5-layer blown film pilot line
Layer distribution determined by microscopic analysis
O_2GTR determined on MOCON OXTRAN® 2/21 (ASTM F1927)

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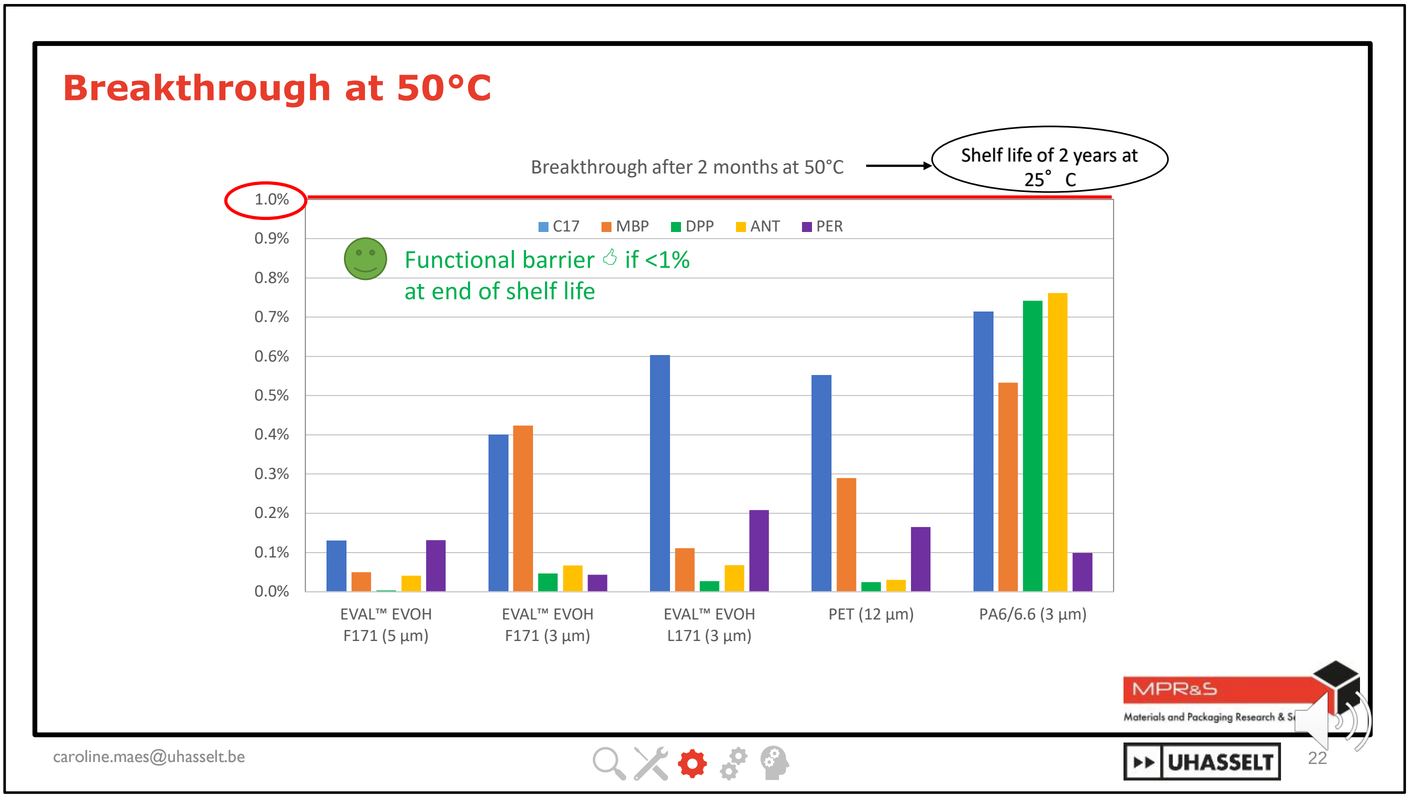
As for the samples we used 5 different films. Of which 4 were multilayer films where the barrier is sandwiched between two PE layers.
One film contained a layer of EVOH27 of only 3 µm.
Two films contained a layer EVOH32 of 3 and 5 µm.
One film with 3 µm of PA.
And finally a monolayer PET film of 12 µm.

Samples

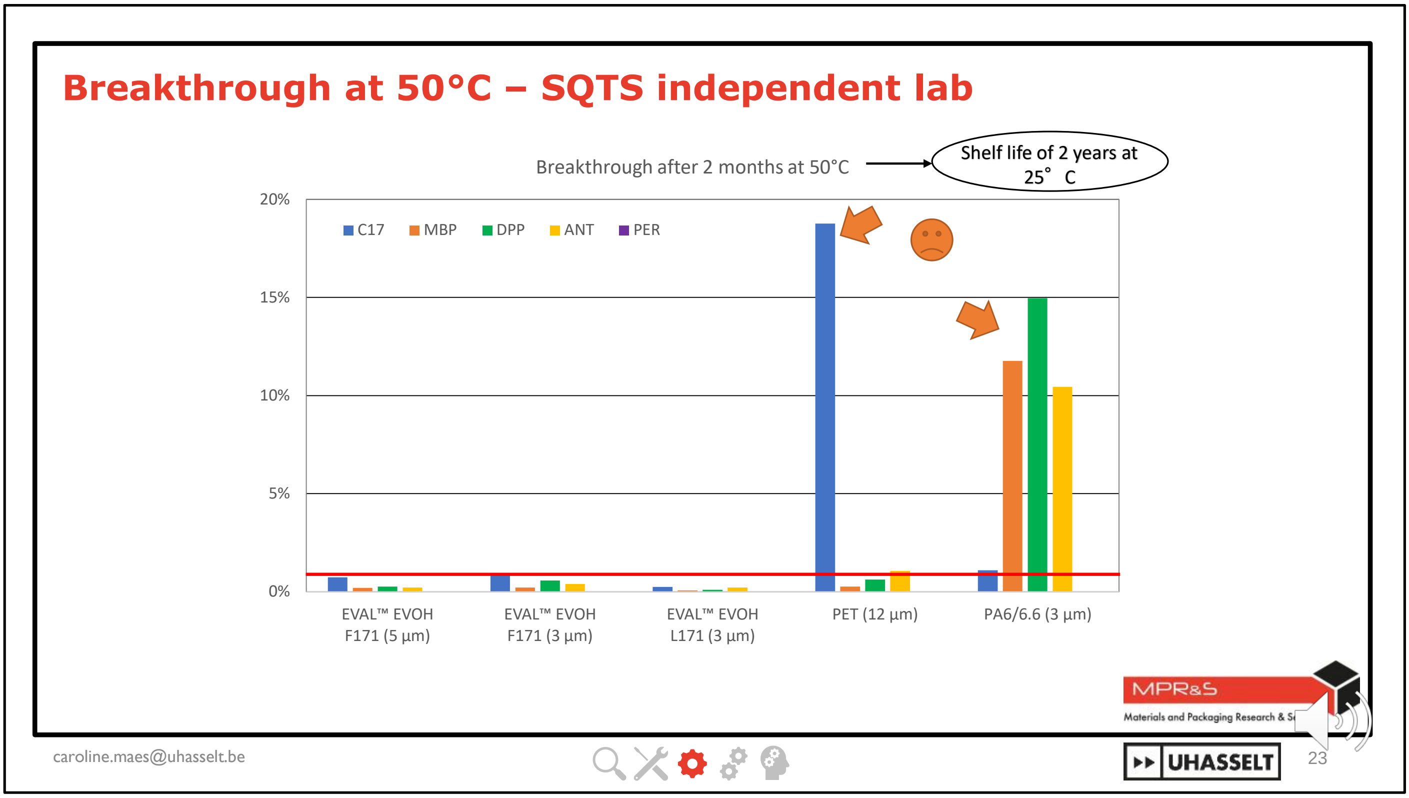
Barrier	**Average layer distribution** LDPE/tie/Barrier/tie/LDPE [µm]	**O_2GTR** @ 20°C, 65% RH [cm³/(m².day.atm)]
EVOH27	22/5/**3**/5/21	**0.7**
EVOH32	21/5/**3**/5/20	**1.7**
EVOH32	21/4/**5**/5/20	**0.7**
PA6/6.6 (Polyamide 6/6.6)	20/5/**3**/4/18	**479**
PET (Polyethylene terephthalate)	**12**	**91**

Films extruded on Dr. Collin 5-layer blown film pilot line
Layer distribution determined by microscopic analysis
O_2GTR determined on MOCON OXTRAN® 2/21 (ASTM F1927)

The O2GTR values are also given to compare the different barriers. And clearly show that the EVOH grades are high barrier resins and easily outperform PET and PA at the given thickeness.

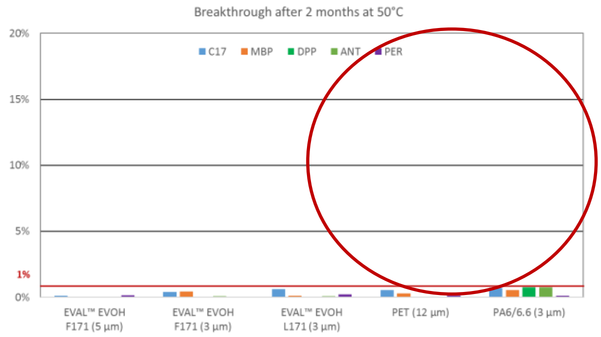


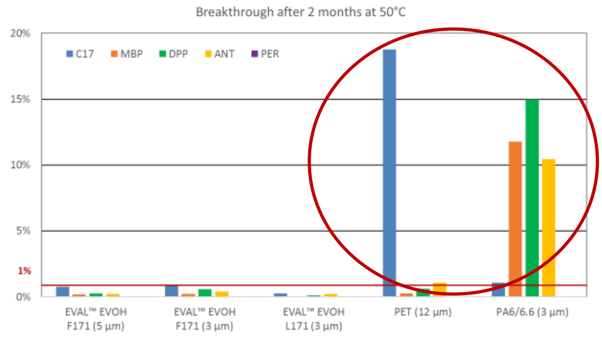
We measured the breakthrough after 2 months at 50°C which represents a shelf life of 2 years at 25°C.
For this test the receptors were sealed inside the barriers to omit all possibilities of sideways migration from occuring.
The barriers all showed values below the 1% thresshold value.
This graph shows that the two different EVOH grades at both 5 and 3 µm are sufficient and can easily compete with a 12 µm PET film.
EVOH barriers mainly showed higher breakthrough values for heptadecane, the 3 µm F-grade or EVOH32 also had a higher value for 4-methyl benzophenone next to heptadecane.
This was the same for the PET. PA showed higher breakthrough values for all components with the exception of perylene.



The test at 50°C was also performed at SQTS. However, here the barrier was placed on top of the receptor, covering it in the conventional way as described in the SVI Guideline.
While the films with EVOH still showed values below the 1% thresshold values, this was not the case for PET which had a very high breakthrough for n-heptadecane and PA showed very high breakthrough for 4-methyl benzophenone, di-propyl phthalate and anthracene. n-Heptadecane also exceeded the 1% thresshold, but at a lower value than the other three components.

Conclusion of Dynamic Accumulation Method





Discrepancy between tests, also found at other temperatures

In general if breakthroug is noticed: EVOH & PET susceptible to C17
PA6/6.6 susceptible to MBP, DPP & ANT

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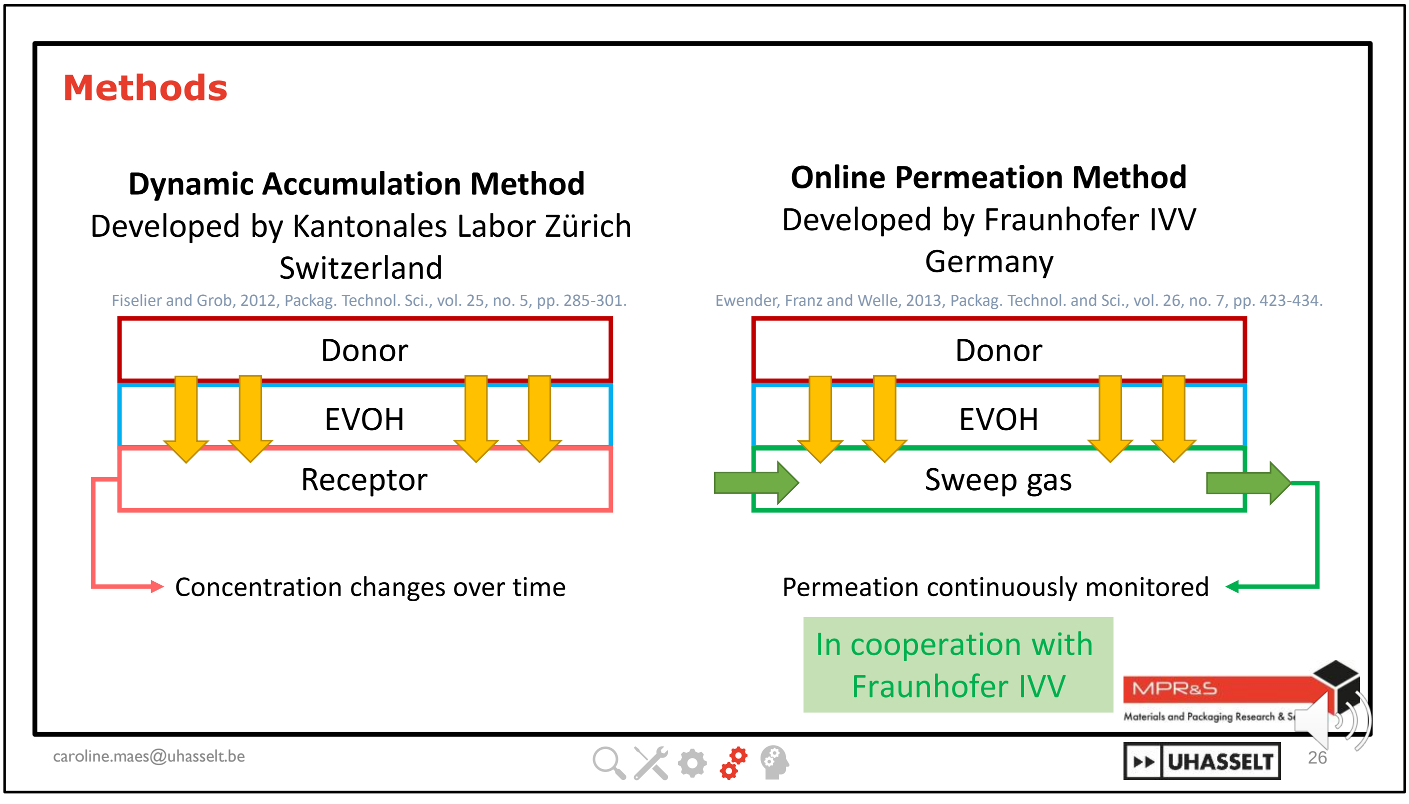
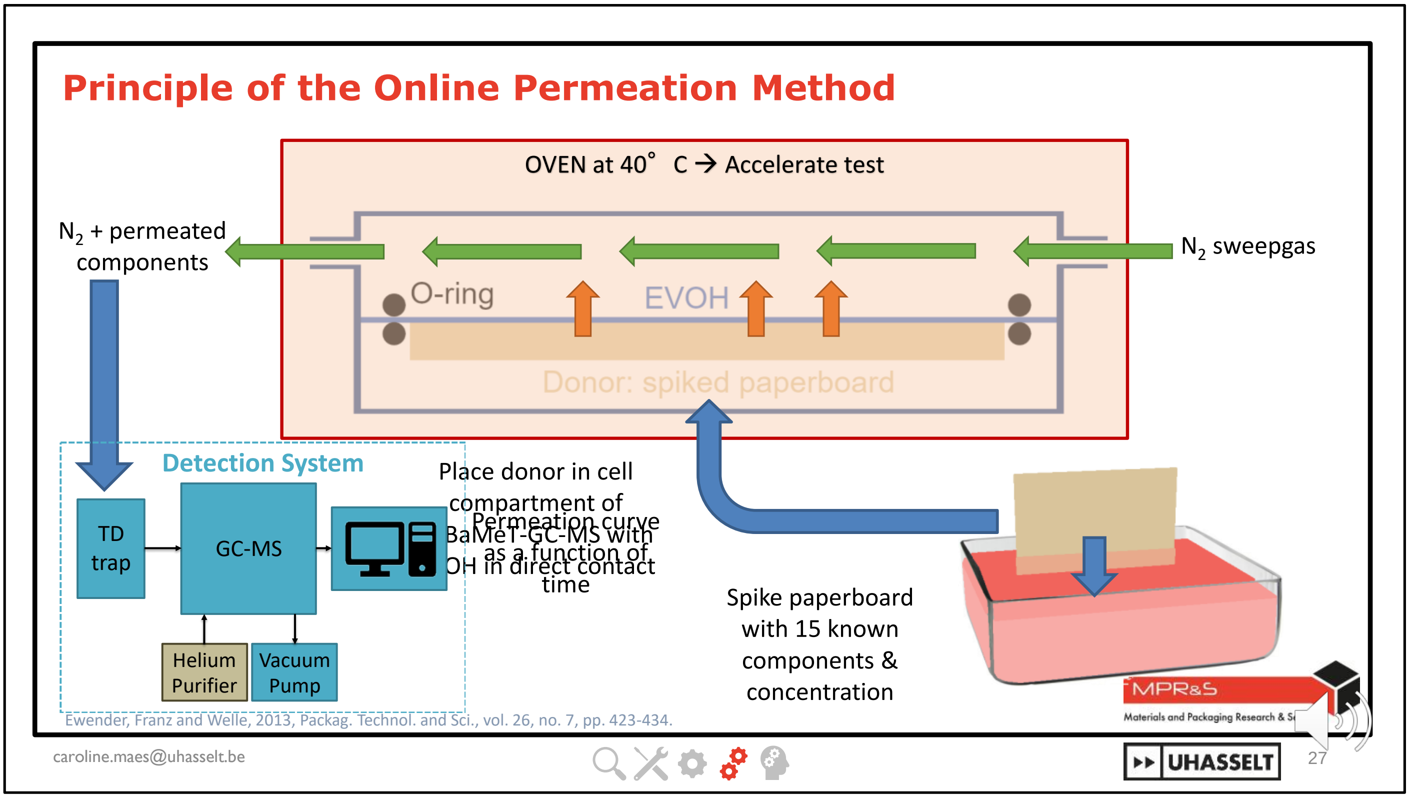
When comparing the results there was some discrepancy between the tests for PET and PA. We also noticed this at other temperatures for EVOH as well.
These can be due to many causes such as a small defects in the film in combination of elevated temperatures.
Or because of the intial contaminations and cross-contaminations due to the many manual manipulations, as well as sideways migration.
If breakthrough was noticed: EVOH and PET are most susceptible to C17 whereas PA was more susceptible to 4-methyl benzophenone, di-propyl phthalate and anthracene.
Conclusion: this test gives a good indication, is relatively easy to perform and many samples can be analysed simultaneously, but due to many manipulations, contamination is possible.

Now let’s move on to the final part of this research. The determination of the functional barrier via online permeation.



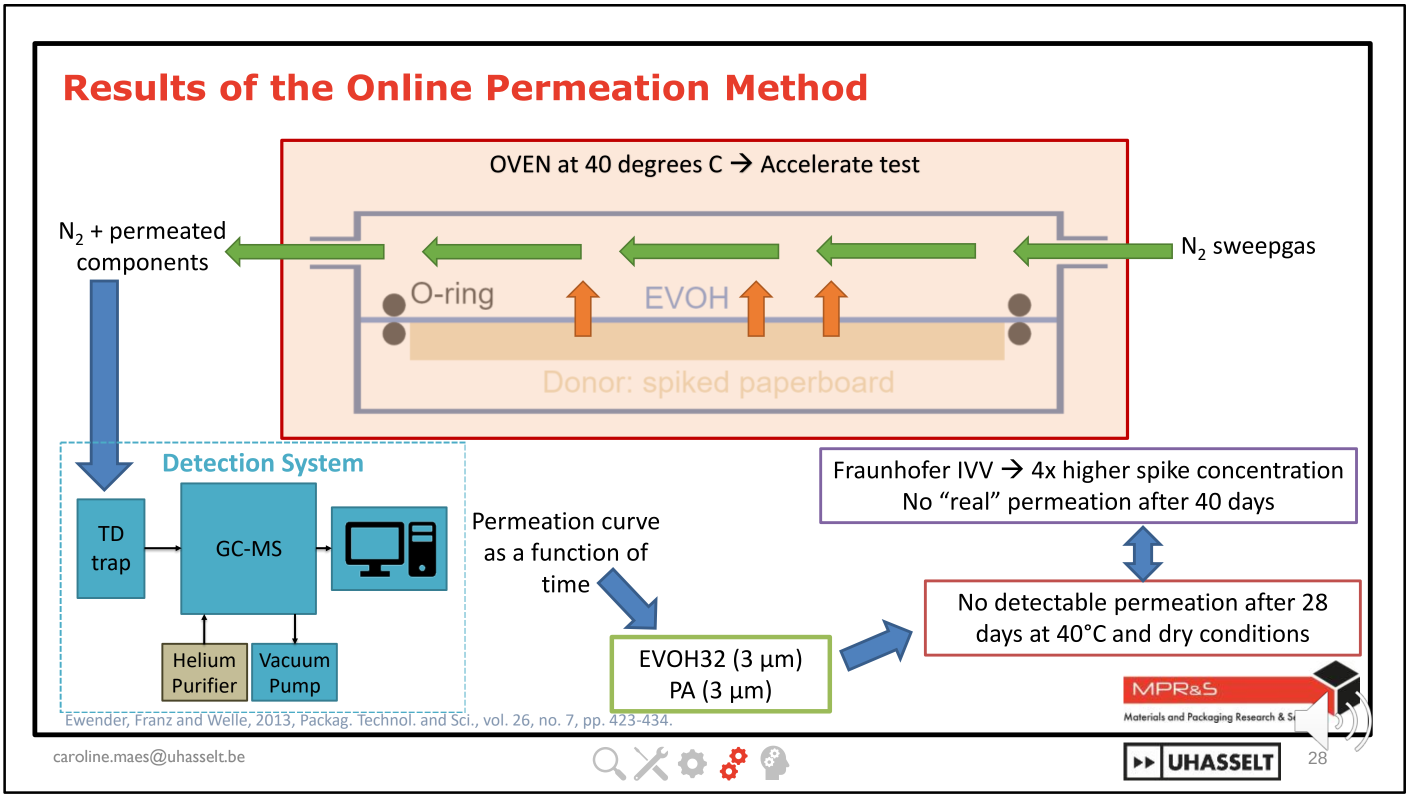
The second method, or the Online Permeation Method was developed by Fraunhofer IVV.
In this method there is no receptor, but the contaminants are collected by a sweep gas which is continuously monitored.



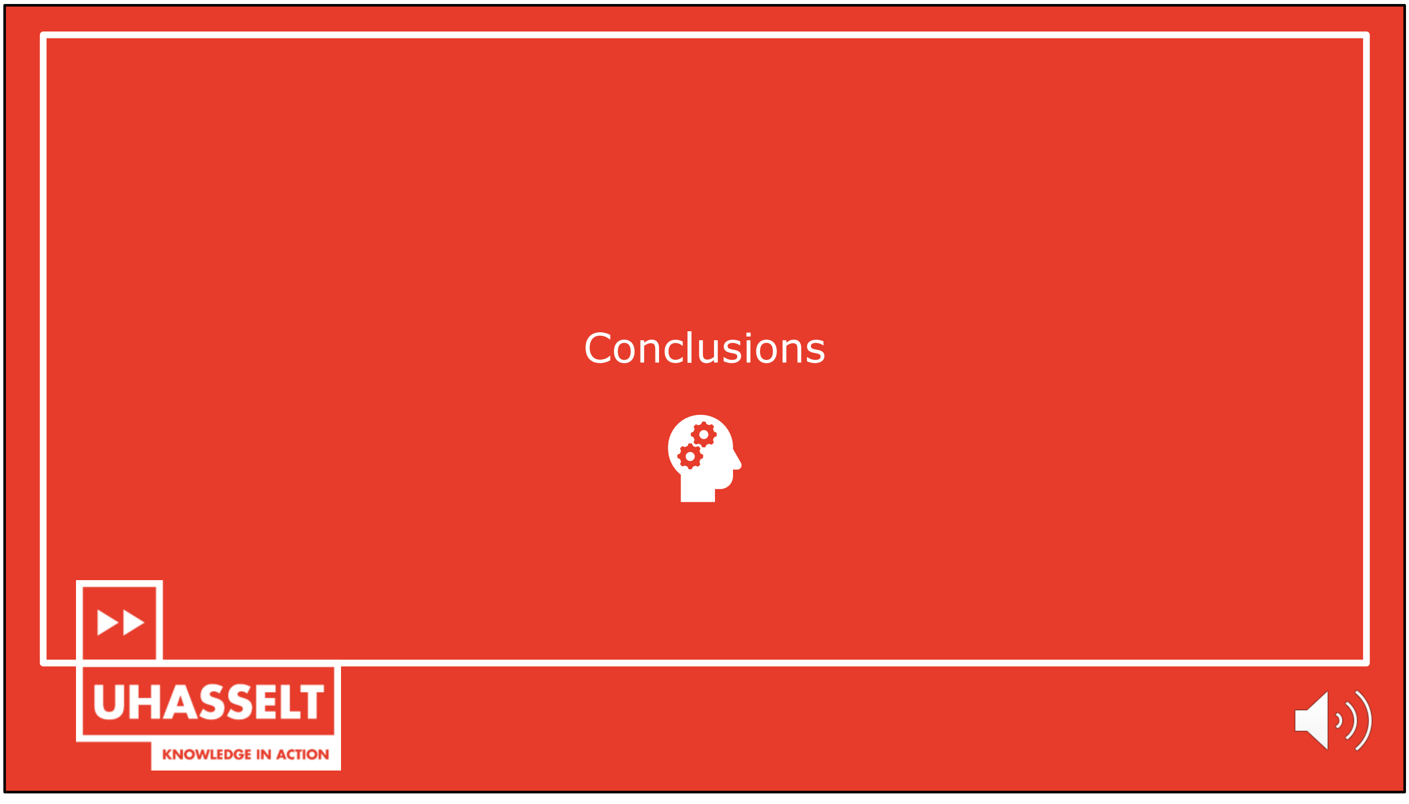
Similar to the previous method this test also uses spiked paperboard with known components and concentrations.

But here the donor material is placed inside a permeation cell, with the film placed on top.

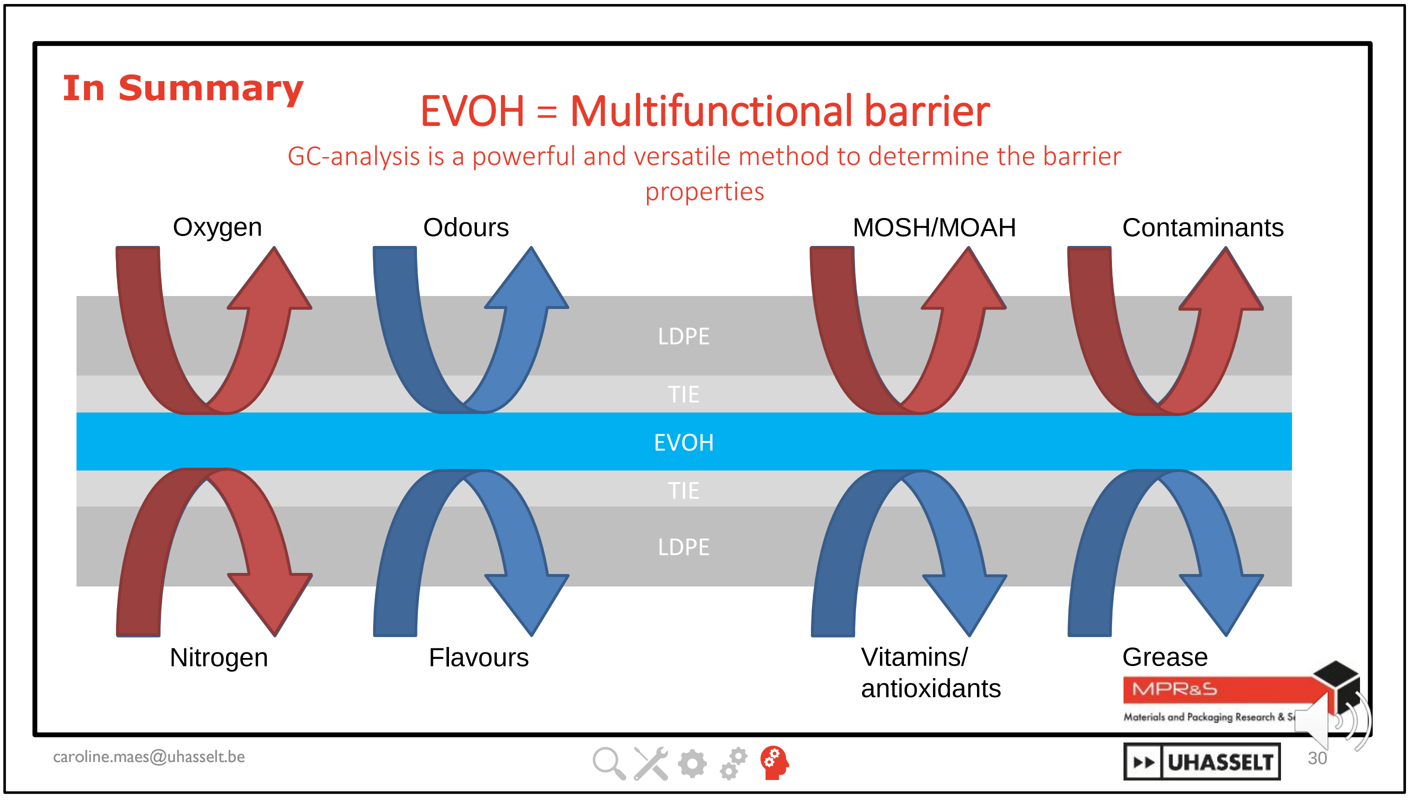
Just like the PEBaMeT-HPA which was used for gas permeation, three of theses cells are inside a permeation system which can be heated to 40°C to accelerate the test and the top compartment is swept with a nitrogen flow. This flow takes the permeated componens to a pre-trap and enrichment unit before being analysed by GC-MS. This results in permeation curves as a function of time and steady-state permeation values.



Two multilayers containing 3 um EVOH32 or 3 um PA were tested using this method at 40°C in dry conditions. There was no detectable permeation after 28 days. This is in line with the experiments performed at Fraunhofer, with a spike concentration of 4 times higher. No real permeation was observed after 40 days in the same conditions.



And then we've arrived at the conclusions.



As was already established in other research. EVOH is a multifunctional barrier. We were able to measure the barrier of EVOH against oxygen, nitrogen, mineral oils and other contaminants migrating from paperboard by using Gas chromatography. GC proves to be a powerful and versatile analysis method to determine the barrier properties of EVOH and other polymers.

External Partner & Funding

- Partner & Funding

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- Co-funded by

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Then I would like to thank you all for your attention.