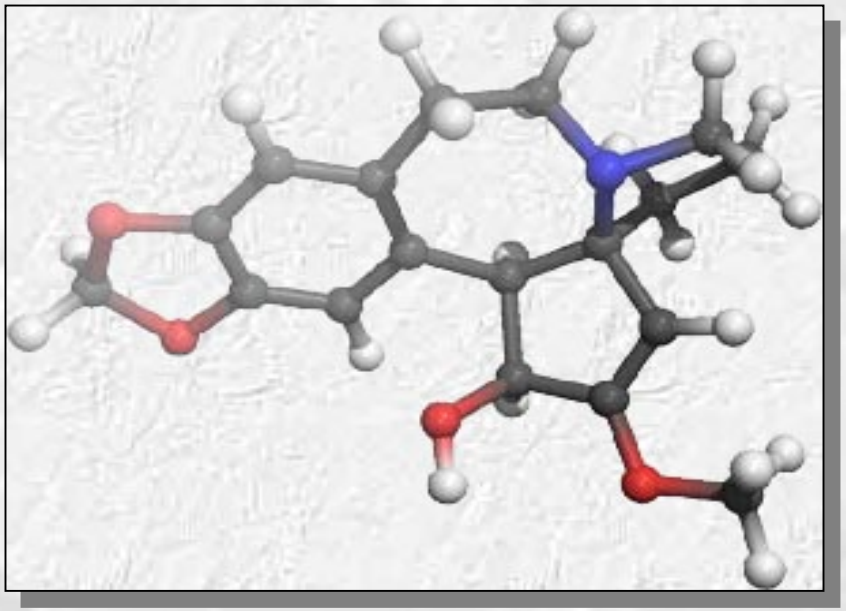
EQUINLAB
Equipos para la Industria y Laboratorio

novasina
The Art of Precision Measurement

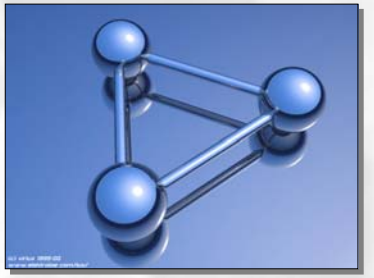
Theory of
Water Activity (a_w)



Quality control of food !!

AGENDA

1. Definition of water activity
2. Hurdle technology
3. Microbial growth
4. Measurement of water activity
5. Sorption isotherms
6. Novasina product range



- **Raoult's law**:

$$p = \gamma \cdot p_S$$

p : Partial vapour pressure
γ : mole fraction
p_S: Saturation pressure

- **chemical potential** of **water** in a real solution:

$$\mu_W = \mu_W + R \cdot T \cdot \ln a_W$$

thus the Raoul's law becomes: $p = p_S \cdot a_W$

- the **osmotic pressure** is given as:

$$V_W \cdot \pi = R \cdot T \cdot \ln a_W$$

V_W: molar volume of water
π : osmotic pressure

The activity a_W of an aqueous solution is called **water activity**.

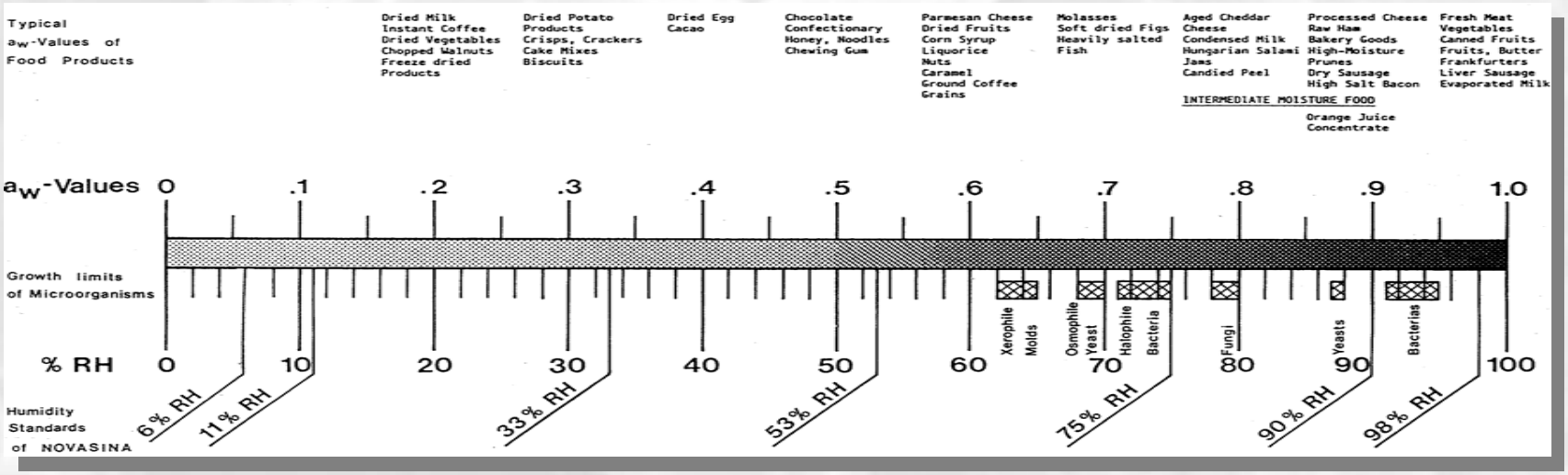
Definition of water activity

The water activity is defined as:

$$a_w = \frac{\text{water vapour pressure over sample*}}{\text{saturation vapour pressure of pure water*}}$$

* at the same temperature °C

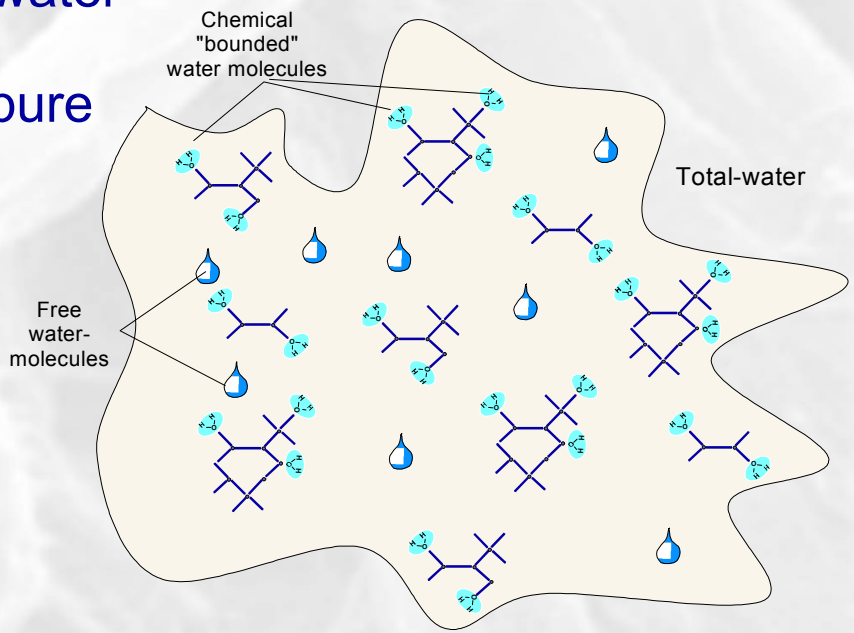
$a_w = p/p_0$ = equilibrium humidity = EHR (%) / 100



a_w = water activity

- The degree of availability of water is measured by water activity (a_w)
- Water activity is a measurement of the energy status of the water in a system
- The water activity states how much the water vapour pressure of a product is reduced compared to the saturation pressure of pure water at the same temperature
- Water activity is the amount of „free“ or „available“ water in a product
- „Free“ is also defined as:

  same physical properties
  as pure water



Water activity (aw)

Moisture content

Moisture content

Quantitative amount of water in a sample on a wet or dry basis

An extensive property that depends on the amount of material

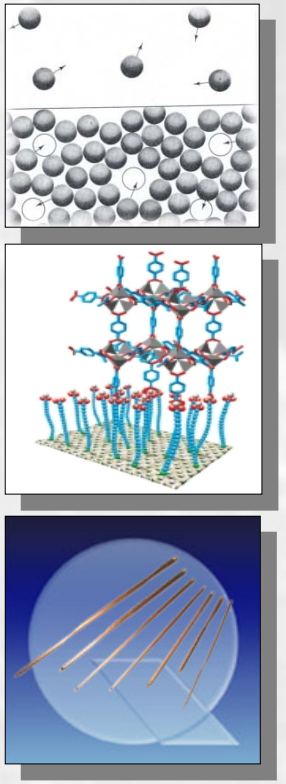
Water activity

A measure of the energy status of the water in a system (qualitative)

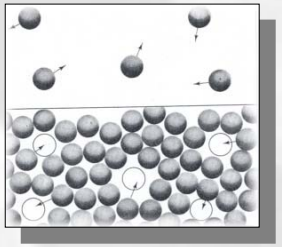
An intensive property that does not depend on the amount of material

Factors that control water activity:

- Colligative effects or solute interactions
- Matrix effects or surface interactions
- Capillary effects



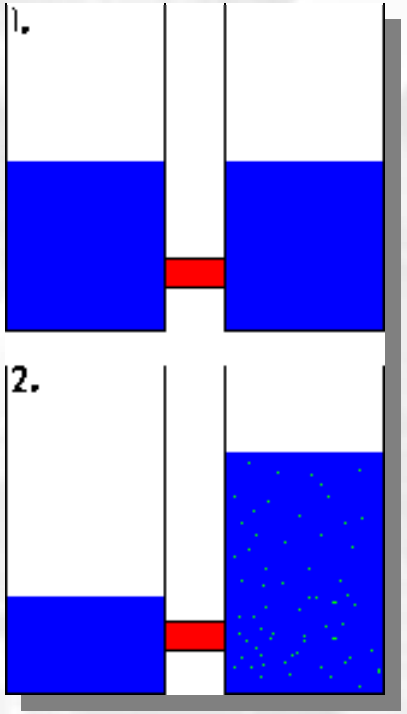
It is a combination of these factors in a food or pharmaceutical product that reduces the energy of the water compared to pure water.

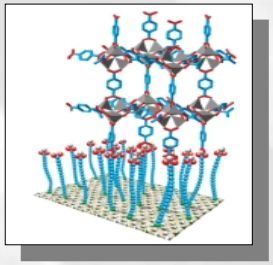


Colligative properties

Depend on the number of solute particles present in solution.

Solute particles interfere with the kinetic motion of water.

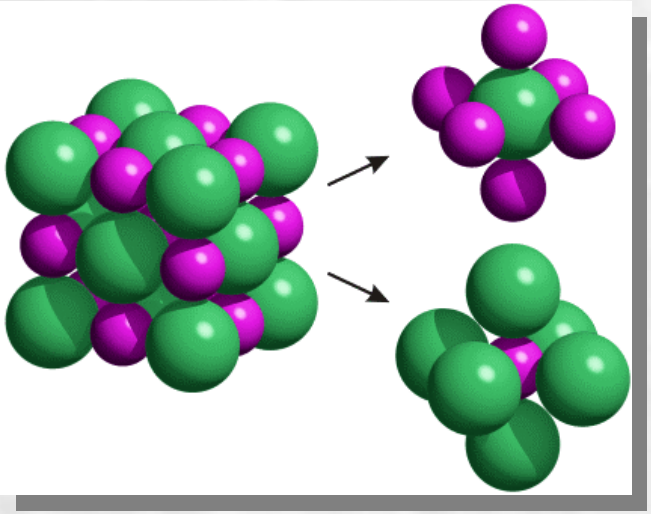


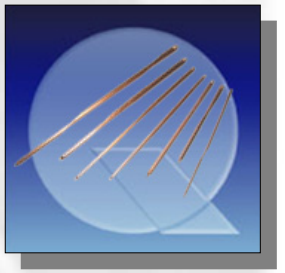


Matrix effect

The sample matrix affects a_W through physical binding of water to particle surface

Reduction in energy is the result of direct physical binding of water to the matrix by hydrogen bonding, ionic (H_3O^+ or OH^-), dipole-dipole and van der Waal forces

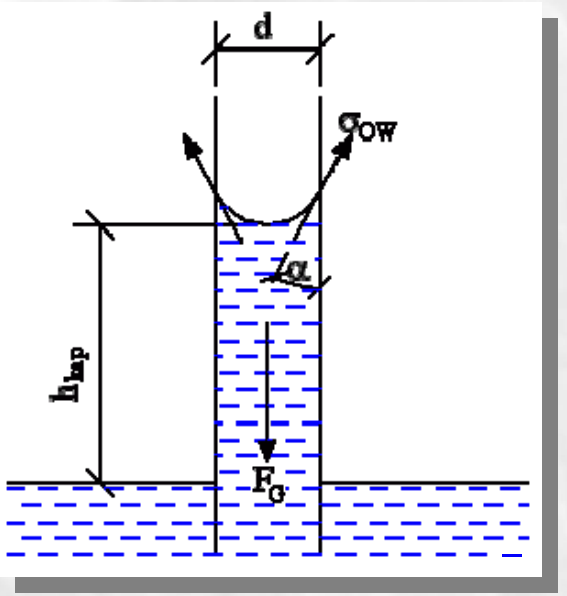




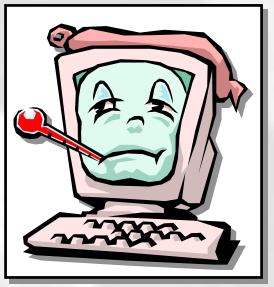
Capillary effects

The surface curvature and surface tension changes the hydrogen bonding between water molecules and lowers the escaping tendency of water.

The Kelvin equation predicts this lowering



Water activity (a_w)
and its influence

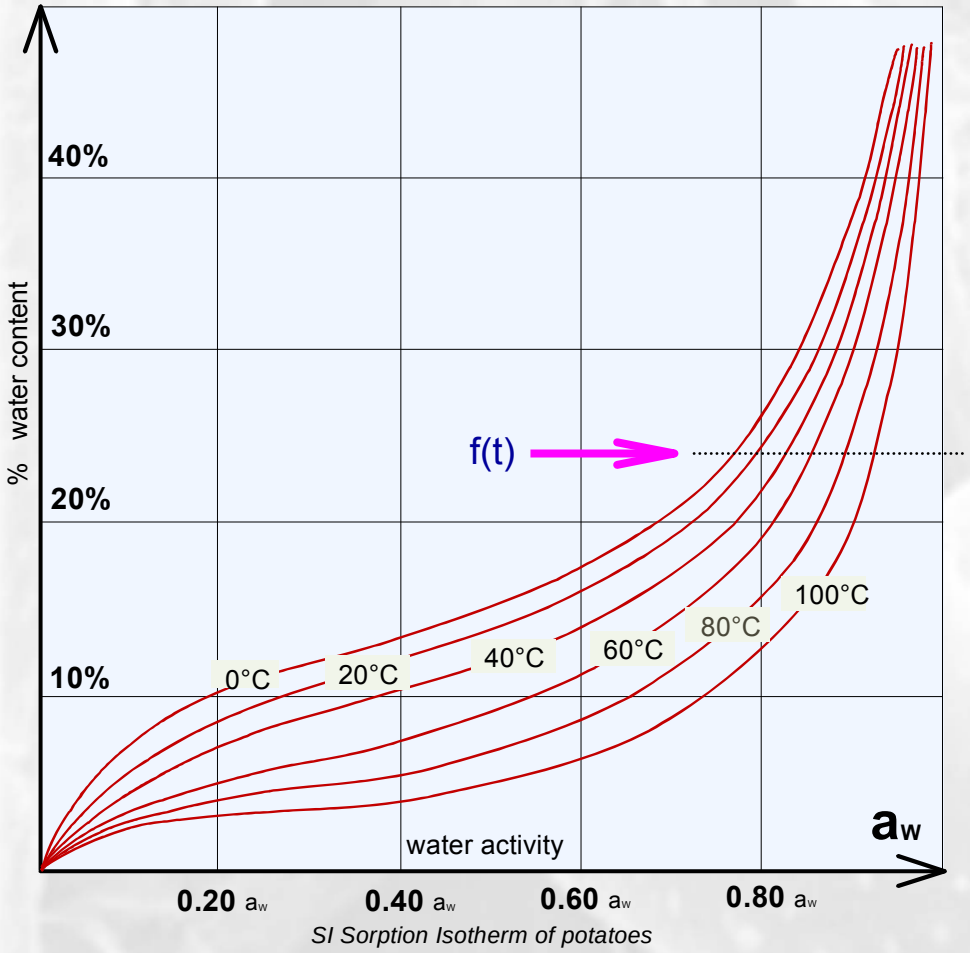


Temperature → a_w

The water activity depends on temperature.

- The water activity of a product changes with its temperature at constant moisture content!
- -> Thus changes in temperature can cause a water migration between different components

Temperature effect



SI Sorption Isotherm of potatoes

Water activity changes with temperature thus:

- It is necessary to control temperature.
- Compensate for temperature difference between sample and sensor.

Purposes for temperature control:

- Aw-measurement at a defined temperature
- Lab to lab sample comparison
- Isotherm determination
- Compliance with government or internal regulations
- Eliminate extreme ambient temperature fluctuations

Temperature effect

The temperature dependence of the vapour pressure

Follows the Clausius-Clapeyron relationship:

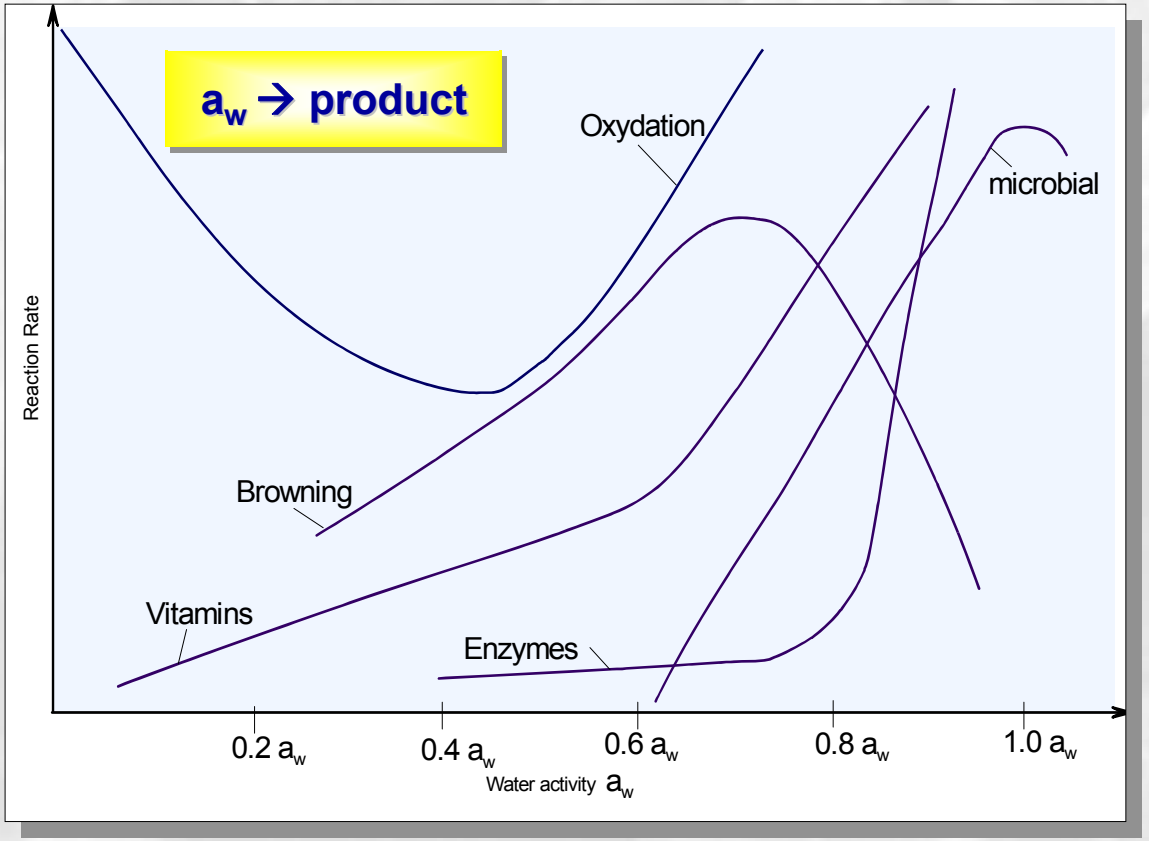
$$\ln \frac{a_{W2}}{a_{W1}} = -\frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Where a_W is a_{W1} and a_{W2} at the temperatures T_1 and T_2, respectively

ΔH is the heat of sorption and R is the gas constant.

Influence of the water activity on the product

Water activity is jointly responsible for the growth of undesirable organisms such as bacteria or fungi, which produce “toxins” or other harmful substances. But also chemical/biochemical reactions (e.g. Maillard reaction) increasingly take place



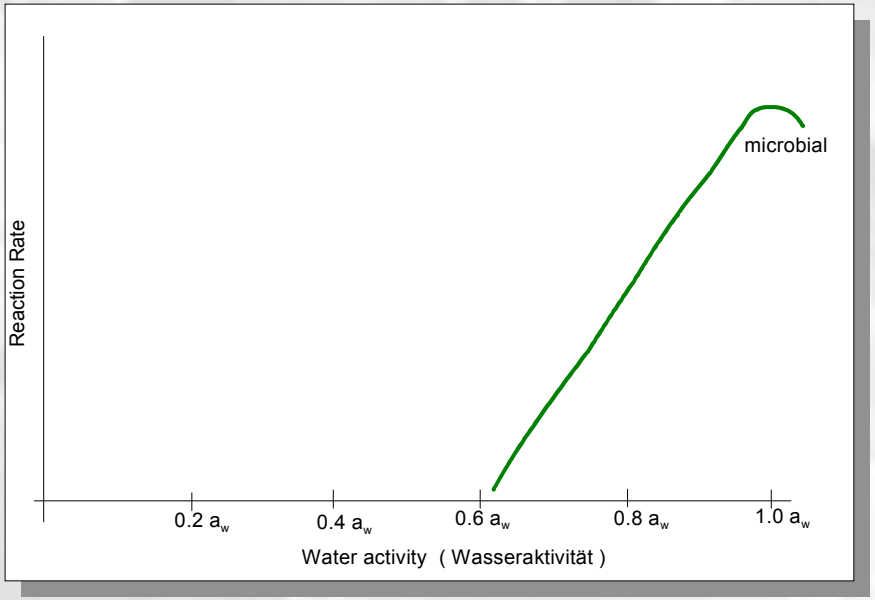
The following properties of a product are affected:

- Microbiological stability
- Chemical stability
- Content of proteins and vitamins
- Colour, taste and nutritional value
- Stability and durability
- Solubility and texture

Influence of water activity on the reaction rate

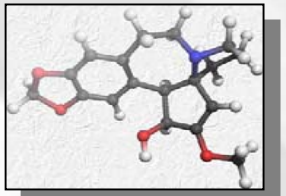
- Most reaction rates increase with increasing water activity
- Most reaction rates correlate better with the water activity than moisture content
- Water may act as:
  - Solvent
  - Reactant
  - Change the mobility of reactants (viscosity)

Microbial Growth



- Decreasing quickly with declining aw-value.
- There is no more microbial growth **under 0.6a_w** !

Enzyme Activity



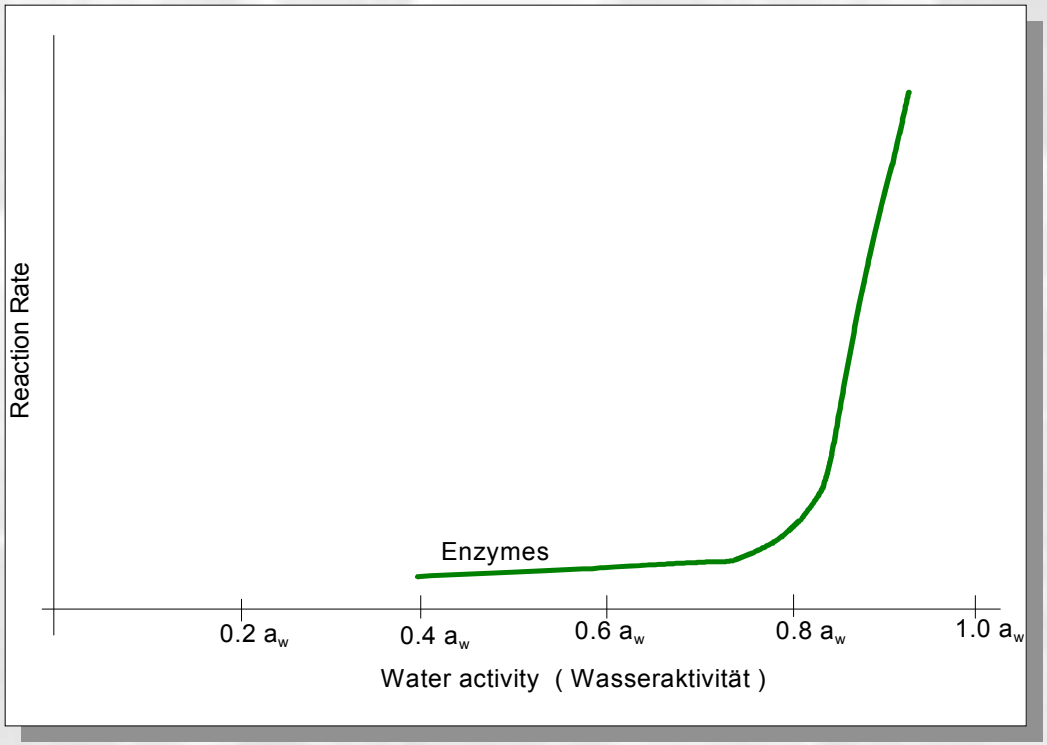
- For various enzymes a minimal water content is necessary
- It leads to changes in nutritional value, colour and flavour
- The most enzyme activity slows down below an a_w-value of 0.8

Enzyme activity water effects：

- Dissolve substrate
- Increase substrate mobility
- Water can be a reactant

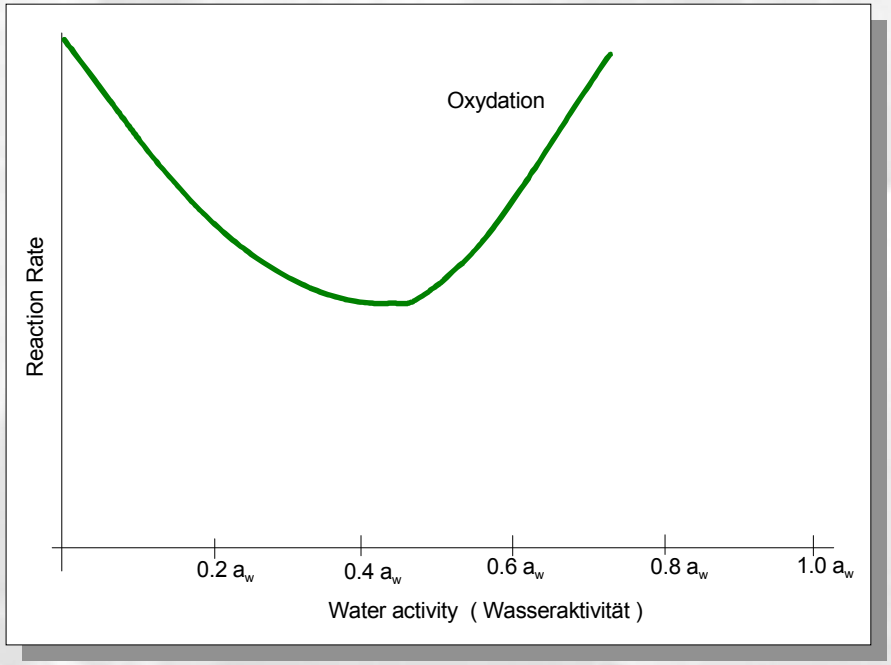
Enzyme stability water influences：

- The denaturations:
  - Hydrolysis
  - Deamidation
  - Oxidation



Lipid Oxidation

- **Oxidation** is one of the major causes of food spoilage and it is initiated by metal ions.
- The reaction rate falls with a lower a_w-value and increases again.
  The minimum is at 0.3 a_w



Causes of anti-oxidative effect
(range 0 – 0.3 a_w)

- Reduced oxygen diffusion
- Less available metal ions due to bonding with water molecules
- Free radicals are bounded

Causes of pro-oxidative effect
(range 0.3 – 1 a_w)

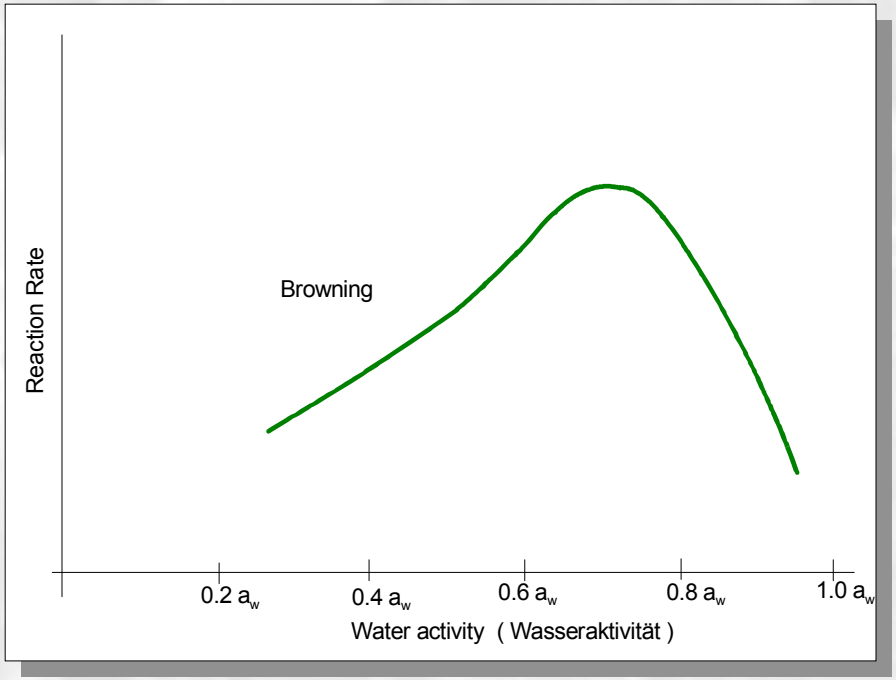
- Increased mobility of the reactants (metal ions and oxygen)
- Increased dissolution of catalysts
- The food swells what causes a surface extension

Non-enzymatic reactions

For non-enzymatic reactions you can mainly mention the protein denaturation and the non enzymatic browning. Mostly the non-enzymatic browning causes the most noticeable changes. The extent of browning reactions depends on the water content respectively the **water activity** of a product.

The probability of the non-enzymatic reaction is more probable with increased a_w-value and reaches a :

Maximum at 0.6 – 0.7a_w



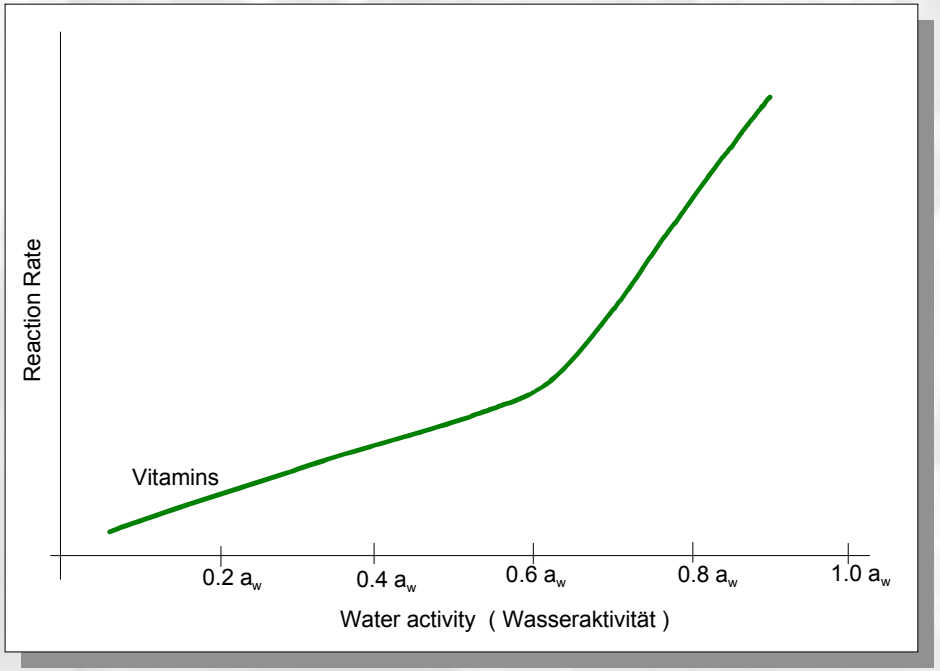
Maillard reaction

The Maillard reactions are a complex series of reactions, whereas free amines (amino acids) and carbonyl groups (reducing sugars) are involved.

- Affects nutritional value, colour, taste, aroma and texture of a product
- May increase or decrease the acceptability of food
- Desirable changes: caramelization, roasted coffee, bread crust, etc.
- Undesirable changes: darkening of milk powder, changes of dried meat (becoming hard and bitter), loss of proteins

Nutrient Degradation

Vitamins are **essential food components** therefore its preservation during the processing of food is of prime importance.



The reaction rate of vitamins increases with **increasing aw-value**. This leads to degradation and loss of vitamins.

Physical Properties

- Texture
- Water migration
- Flow properties of powders
- Caking and Clumping

Texture (1)

Hard or crispy products

- low water activity
- break when physically stressed
- soften when exposed - aw ↑

Soft products

- intermediate to high aw
- bend when physically stressed
- are moist, juicy, tender and chewy
- harden when exposed - aw ↓

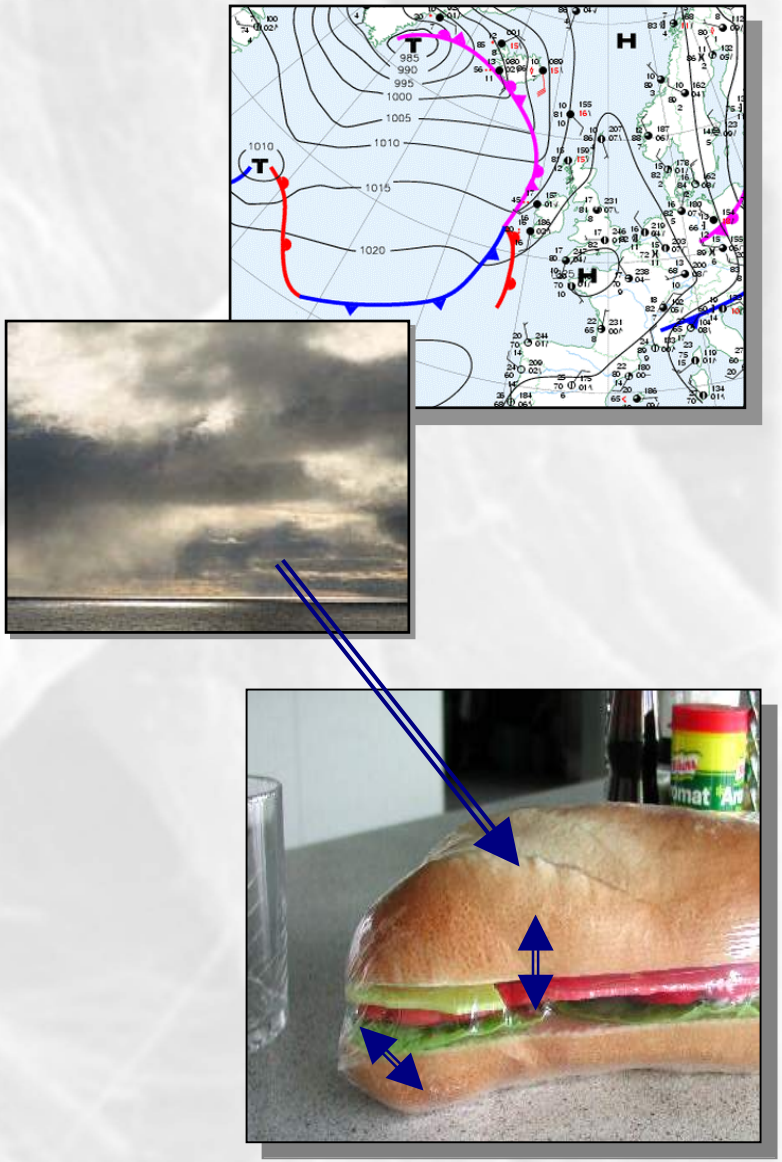
Texture (2)

Solutions to maintain texture

- maintain water activity within critical limits for proper texture characteristics
- prevent moisture migration in multi-component products
- barrier packaging

Water migration (1)

- Two ingredients may have the *same* moisture content, but totally *different* a_w-values.
- The water migrates from regions of high $\mathbf{a_w}$ to regions of low $\mathbf{a_w}$, and *not* between areas of unequal moisture content!
- Water migration between different layers of a **multi-component food** causes un-desirable textural changes.
- Rate of migration depends on structure/ diffusion properties.



Water migration(2)

Moisture migration can lead to:

- texture changes
- microbial growth
- degradation reactions
- organoleptic changes

Examples of „multi-component“ products:

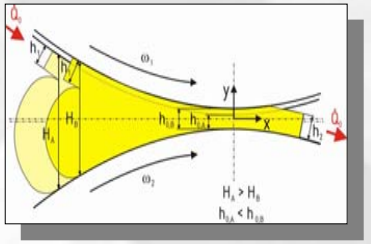
Bakery products
ice cream in cone
frozen pizza crust - sauce
etc.

Water migration (3)

Solutions

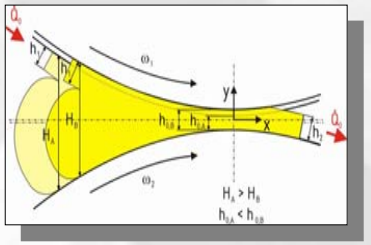
- Water migration can be reduced by knowing and influencing the various levels of **a_w-values**
- Equal the water activity of the different components
- Retard diffusion process within components (viscosity ↗)
- Edible barrier
- Separate packaging

Flow properties caking and clumping (1)



- Caking is a water activity, time and temperature dependent process
- Free flowing powder is transformed into lumps or an agglomerated solid
- This problem is ubiquitous in the food and pharmaceutical industries

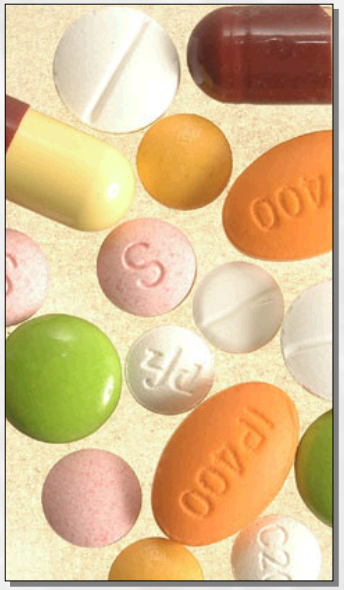
Flow properties
caking and clumping (2)



To preserve the good free flowing property of a powder and to prevent the caking of a powder the following methods can be applied:

- dehydration on a low water content
- conditioning at low air humidity and packaging in airtight packing
- storage at low temperature
- agglomeration
- additives and anti-caking-substances

Why is the measurement of the water activity (aw-value) in foods and pharmaceuticals so important?



The importance of „a_w“ measurement :

microbial safety	*to predict shelf life*
HACCP requirements	*as part of QC*
fulfil government regulations	*EU, USA, Japan ….*
control chemical reactions, physical properties	*to guarantee product quality, good taste, colour, crispness*

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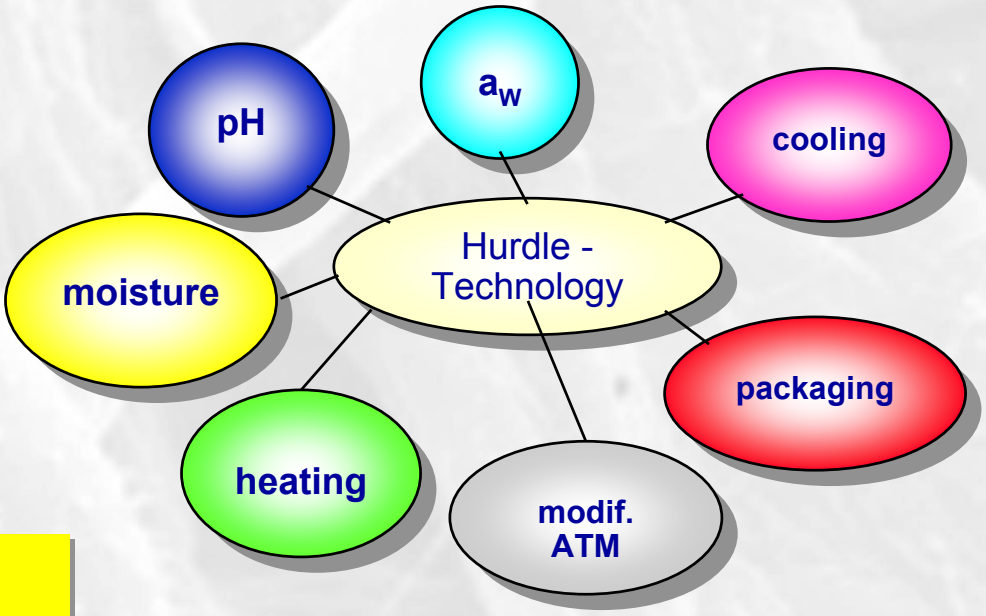
„*Hurdle*-Technology“ in food

Since centuries food was preserved by different methods. Often these methods are applied in combination.

The principles which form the basis of the traditional methods are made quantitative ascertainable by:

- f-value (heating)
- t-value (cooling)
- pH-value (acidification)
- aw-value (drying, salting, sugaring)
- eh-value (deoxygenation)
- competitive flora (fermentation)
- preservatives



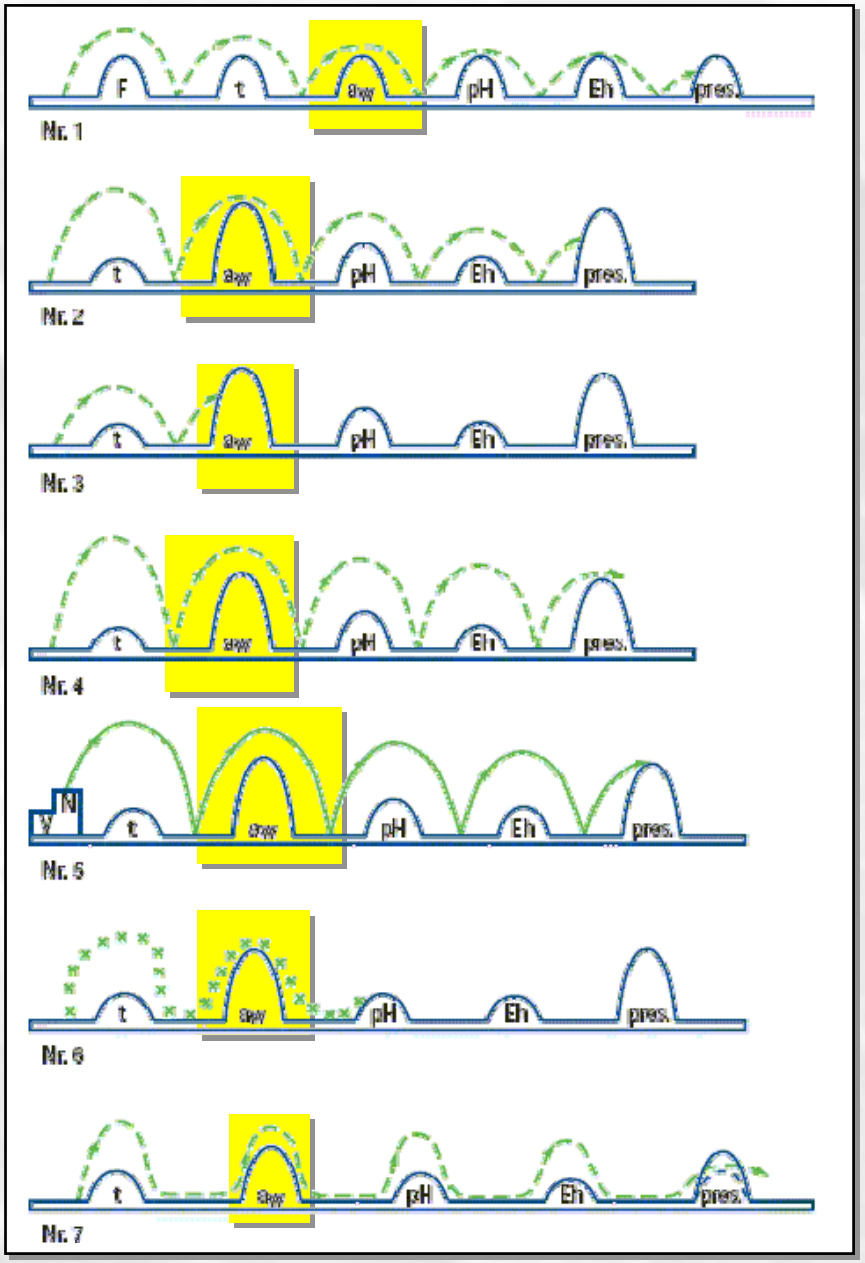
An intelligent application of a combination of these factors is called **Hurdle-Technology**

„*Hurdle* Technology“

(Illustration of the hurdle technology by 7 examples)

The symbols have the following meaning :

f	:	heating
t	:	cooling
a_w	:	water activity
pH	:	acidity
eh	:	redox potential
pres.	:	preservatives



Measures to
Lowering the water activity

- Sun-drying, adding **salt** or **sugar** are practices known for **centuries**
- **Dehydration/freezing** or drying are **modern techniques**
- **Humectants;** decreasing availability by binding water; like honey or corn syrups (sugar), polyols (e.g. glycerine, glycerol, propylene glycol, sorbitol), but also proteins, amino acids etc. are today commonly found in foods !
- A **smart combination** results in an optimum texture, flavour, taste, colour of the final product.

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Requirements for the growth of microorganisms

Nutrients

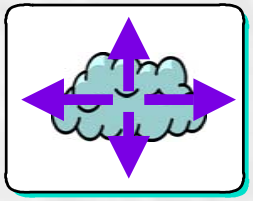
- Yeasts prefer food rich on carbohydrates (dessert, sauces, fruit juices)
- Salmonella splits protein and grows on food (meat, sausage, fish, egg and cheese)

Temperature

- Most microorganisms show an optimal growth between 15°C and 40°C
- The growth of mircroorganisms depends on temperature

Water

- Not only the water content is responsible for the growth of microorganisms, but the free available fraction of the water (a_w-value) is determining
- An high sugar- and salt content is responsible for an well binding of the free water into an probe. This is a possible way to bring the free water content down.



Requirements for the growth of microorganisms

pH value

- Bacteria prefer a lightly acid respectively neutral environment, **pH-value 4.5 – 7**
- For yeasts and molds a **pH 4.5** is **optimal**

Oxygen

- Molds and yeast need oxygen
- Certain bacteria (e.g. clostridium) grow without oxygen
- Other bacteria can adapt to changing environmental conditions

Way of infection and sources
of food poisoning

Primary contamination :

Production animal is contaminated with pathogens
(often without symptom of disease respectively pool of pathogens
Salmonella, Campylobacter, EHEC, Shigella, ...)

Secondary contamination :

- Contamination during the winning of the food by smear infection via unclean equipment, lack of hygiene or insufficient care, ...
  (all pathogens possible: Intestinal bacteria, Clostridium, Staphylococcus)
- Food contaminated by pathogens
- Food poisoning (by toxins)

For innumerous food spoilage organisms a **minimum a_w-value** is known!

Below this value its growth and toxin production is inhibited

Bacteria, for example:	Minimum aw-value
Staphylococcus aureus :	$0.86a_w$
Clostridium botulinum A *and* ***Escherichia coli***	$0.95a_w$
Salmonella	$0.92a_w$
Molds, for example.:	
Aspergillus flavus : produces toxin above $0.83a_w$, but does not grow below	$0.78a_w$.
Fungi, other molds, mildew, yeasts go lower, but *not beyond*	$0.60a_w$.

Growth and sources of different **bacteria**

	meat	milk	poultry	egg	fish	fruits & vegetables
Salmonella	■	■	■	■		■
Pathogenic E. coli	■	■				■
Campylobacter		■	■			
Y. enterolytica	■		■			
C. perfringens	■		■			
C. botulinum	■				■	■
L. monocytogenes	■	■	■		■	■
Vibrio sp.					■	■
S. aureus	■	■	■			

a_w-range of **food** and its microflora

a_w-range	food	microorganisms
> 0.98	Fresh meat Fresh fish Fresh fruits & vegetables	Pseudomonas, Escherichia, Proteus, Shigella, Bacillus, Clostridium perfringens
0.92 – 0.98	Sausages Cheese Bread	Salmonella, C. botulinum, Lactobacillus, Pediococcus, some yeasts and molds

a_w-range of food and its microflora

a_w-range	food	microorganisms
0.92 – 0.87	Fermented sausages, Biscuits, cheese, margarine	Various yeasts (Candida, ...) Micrococcus
0.87 – 0.80	Fruit juice concentrate, Condensed milk, chocolate syrup, flour, fruit cake, ham	Most molds, Staphylococcus aureus, most Saccharomyces, Debaryomyces

a_w-range of **food** and its microflora

a_w-range	food	microorganisms
0.80 – 0.60	Dried fruit Spices Cereals Nuts	Xerophilic fungi (Aspergillus candidus, ...) Osmophilic yeasts
> 0.60	Confectionery Honey Noodles egg- and milk powder cookies, cracker, etc.	No microbial growth but may remain viable

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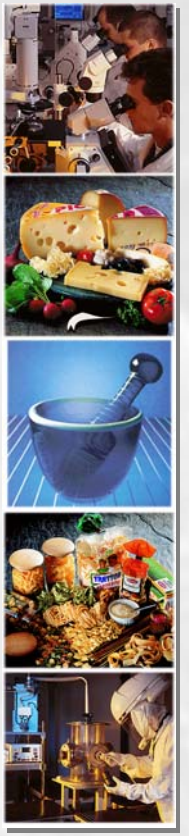
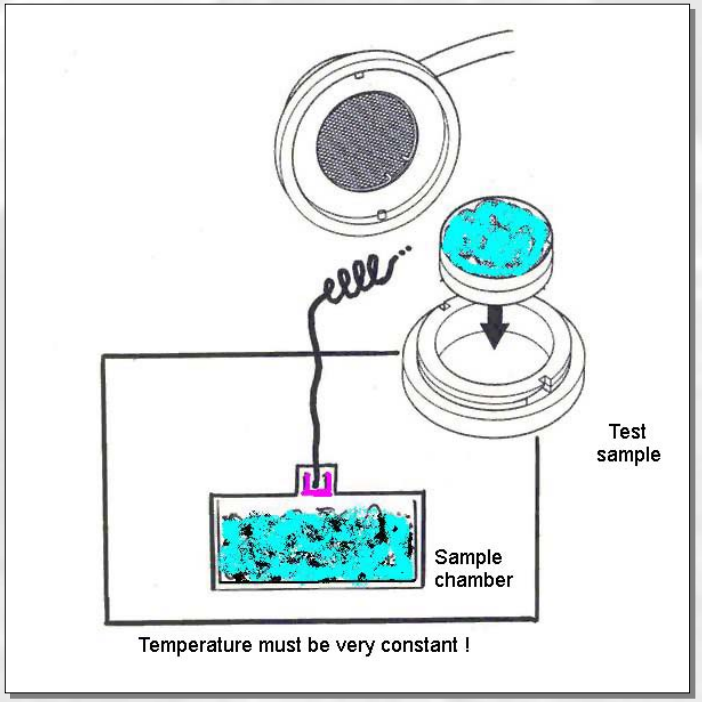


Measurement of water activity

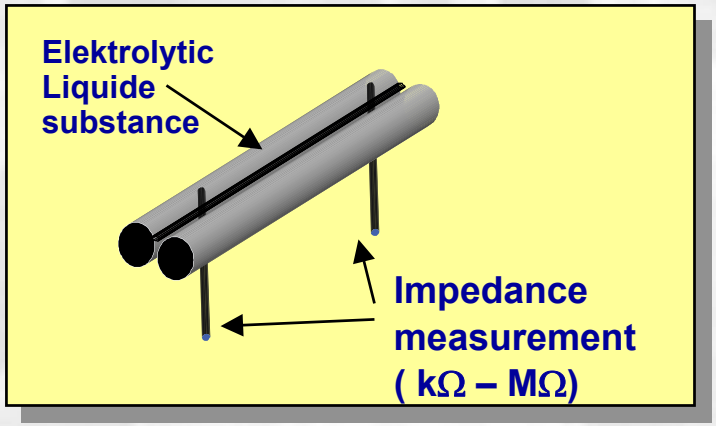
The „offline“ measurement :

The test sample is placed in a completely sealed measuring chamber and the sample humidifies or dehumidifies the air volume inside the chamber till the **equilibrium humidity** is reached.
This exchange takes place due to the **partial water vapour pressure difference** between the sample and the air.
The measuring speed is largely dependent on the sample properties.



The humidity/aw measurement element

Resistive Electrolyte Cell

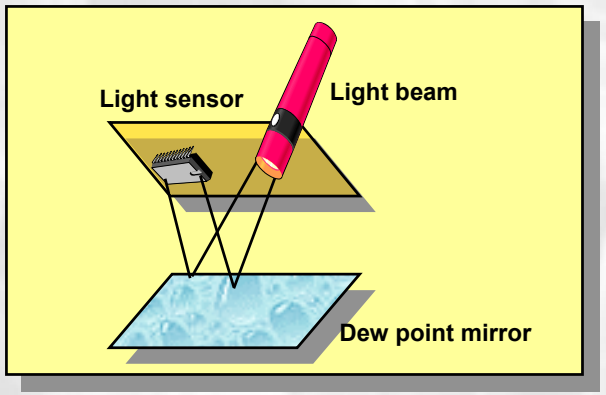


Function :

Liquid electrolyte changes resistance when the humidity around is changed

- directly measuring the a_w-value
- virtually hysteresis-free
- accurate to **0.003a_w** (0.3%rh), from below **0.03a_w** up to **1.00a_w**
- excellent repeatability of **0.002a_w** (0.2%rh)
- very easy and simple to change a calibrated measurement element (full accuracy)
- simple to calibrate the aw-system with saturated salt solutions

The dew point measurement method

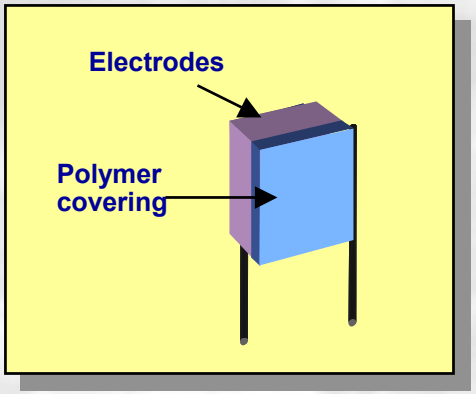


Function :
Optical identification of condensation on mirror temperature

- needs a lot of electronics and control tools
- is not easy to handle and maintain (daily mirror cleaning)
- indirect measurement; gets a result by ***calculating*** the $\mathbf{a_w}$ from both, mirror dew point and sample temperature
- tremendous errors can be caused by volatiles (eg. **alcohols**!) as well as from sample surface colour and structure, which influence the infrared surface temperature measurement
- results are sometimes **calculated too fast**, so repeated measurements are recommended and frequent mirror cleaning is advisable

The humidity/aw measurement element

Capacitive measurement

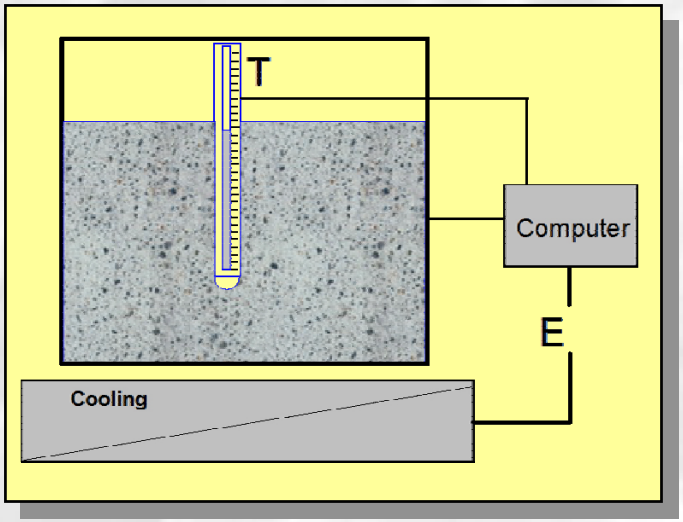


Function :

Polymer expands with increasing humidity, thus changing capacitance

- easy and simple to handle
- quick reading of (+/- 0.04-0.05 a_w)
- directly measuring rh, have a physically given hysteresis of min. 1.5%rh (0.015a_w)
- “second sorption effect” in the high range: they absorb additional water molecules, which leads to a higher reading
- Problematic against chemical contamination

Freezing point determination (aw-cryometer)



Function :

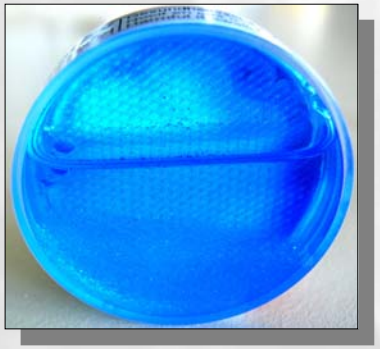
Accurate determination of the depression in freezing point relative to pure water

- simple to handle
- accurate and not affected by volatiles
- limited aw-range (>0.90aw)
- small sample size
- aw-value determined at the freezing point, the result is than extrapolated on 25°C.

Saturated salt solutions

The saturated salt solutions can be used over many years as often as desired to verify and calibrate water activity instruments.

Advantages of saturated humidity standards :



- Simple handling
- Long term stability of the standards
- Simple control of lifetime

Sample preparation

A special sample preparation is **not needed**, but larger samples should be cut into small pieces: a volume of 8…15ml (ccm) is sufficient. Depending on the product, crushing or grinding may change the a_w-value, so manually cutting and immediately testing is the safest procedure.

Multicomponent products may take a **very long time** to establish a final, common a_w-value (several days, even weeks!), so it might be advisable to separate the different components and measure them individually.

Special Samples

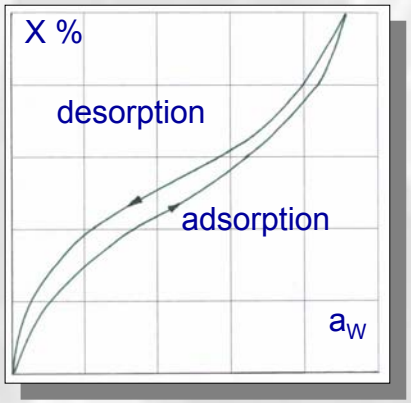
- Coated products
- Emulsion
  - oil in water (e.g. cream)
  - water in oil (e.g. butter)
- Glassy products
- Low water emitting samples
- Volatiles or aggressive substances (➡protection filters)

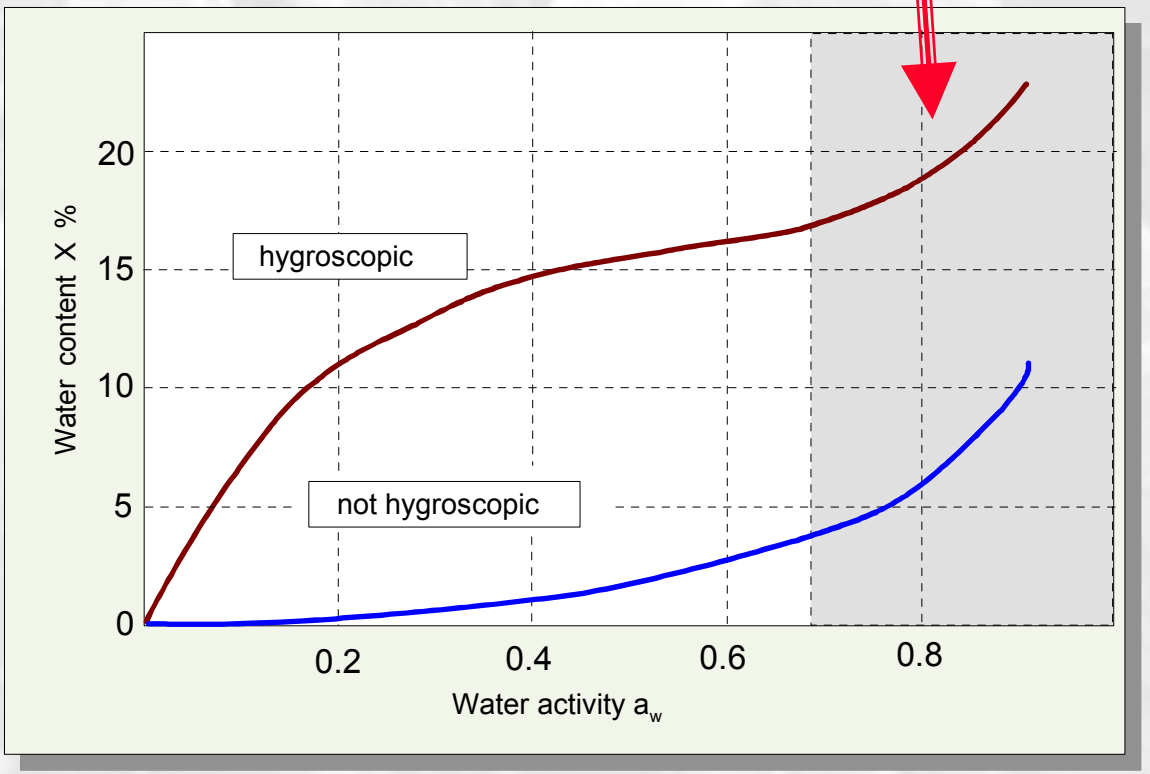
AGENDA

1. Definition of water activity
2. Hurdle technology
3. Microbial growth
4. Measurement of water activity
5. Sorption isotherms
6. Novasina product range

Record of the sorption isotherm

- Relation between water content and water activity of a product
- Product specific and temperature dependent
- Desorption – or adsorption isotherm (hysteresis)

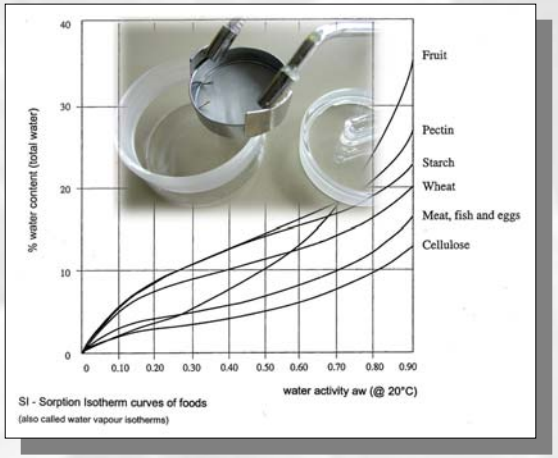


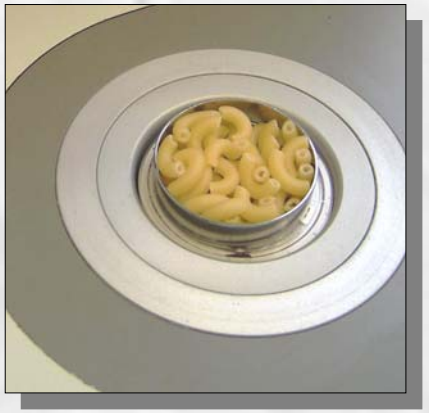


Record of the sorption isotherm

It is possible to record a sorption isotherm (SI curve) with the new water activity instrument **LabMaster-aw** thanks to:

- temperature controlled measuring chamber+/-0.2K
- temperature range 0°C ... 50°C
- 7 Novasina humidity standards





AGENDA

1. Definition of water activity
2. Hurdle technology
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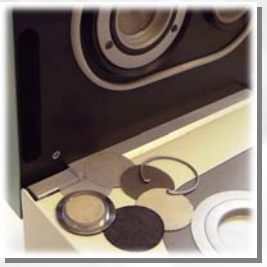
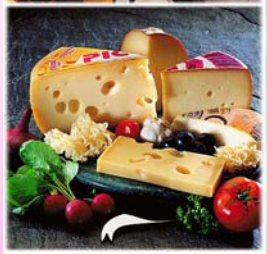
5. Sorption isotherms
6. Novasina product range

*Lab*Master-*aw*



- Best accuracy (+/- 0.003 a_w)
- High precision temperature controlled chamber
- Wide measurement range 0.03a_w up to 1.00 a_w
- Single or multi chamber version
  (1 LabMaster and max. 9 LabPartner)
- Precondition chamber for sample
- Large, back-lighted LC display
- Simple to maintain and service
- 6 to 7 point calibration available
  (with Novasina SC standards)
- High temperature range
  (0....50°C and accuracy : +/-0.2°C)
- SI set to measure the sorption isotherm available


Measurement of the water activity on a probe in the food, pharmaceutical and cosmetic industry

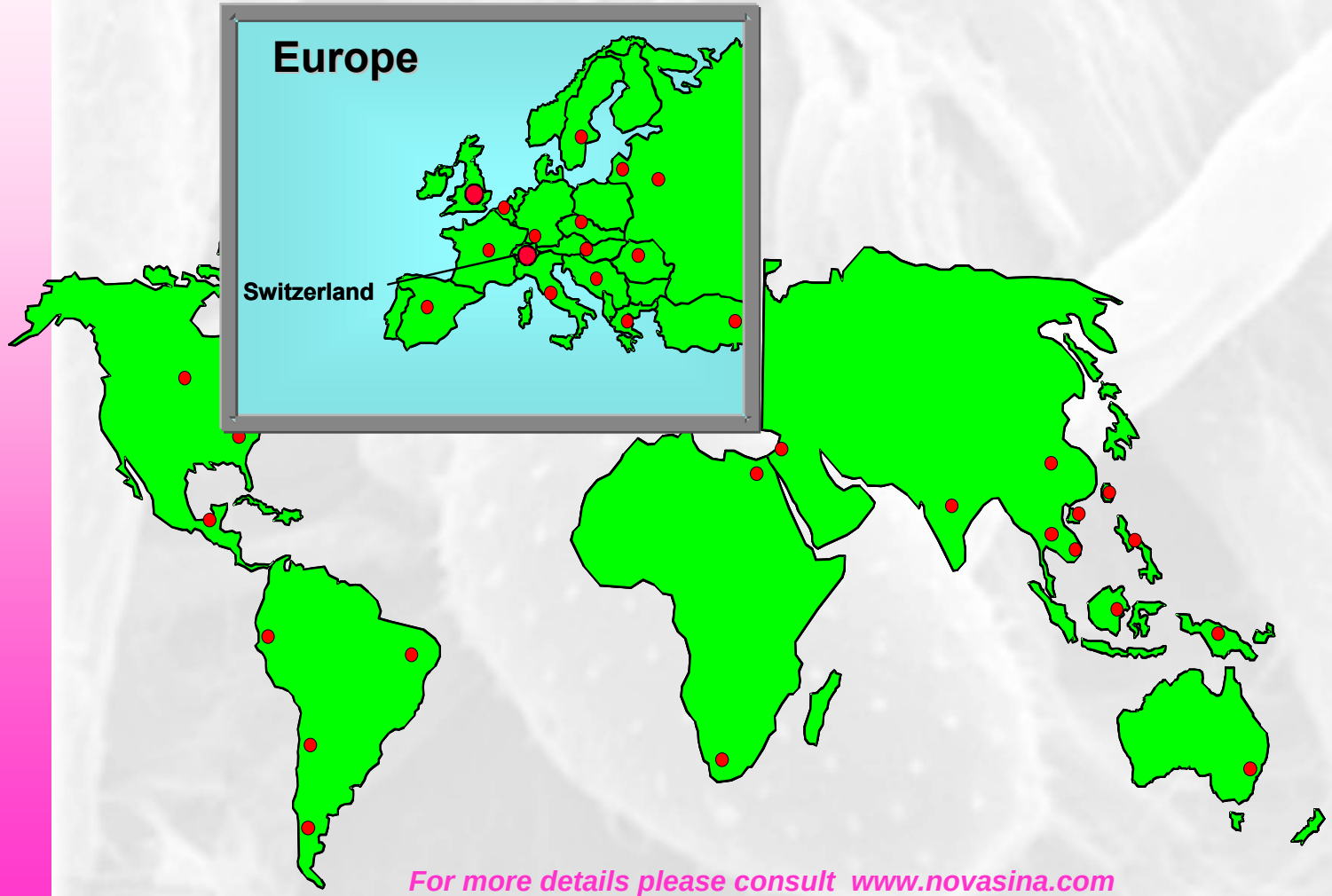
aW

Products:

- ***Lab*Master-aw / *Lab*Partner-aw**
- **AW LAB set H / F**
- ***LabSwift*-aw**




International representatives :



worldwide

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Indonesia	
Iran	

For more details please consult www.novasina.com

International references :