The Science Behind The Ancient Art of Food Preservation

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Outline of Talk

- The Need for Food Preservation
- What spoils Food
- Techniques discussed
  - Drying
  - Fermentation
  - Curing
- Product
  - Salami
- Importance of food preservation in the ancient and modern world

The need for Food Preservation

- Up until about 10,000 years ago humans were primarily hunter gathers. They would have been faced with a glut of food at some times and shortages at others.
  - Seasonal crops of fruits, cereals and vegetables
  - Spawning runs of fish and animal migrations
- Foods remains edible for only a brief period of time after harvest or death
  - How to use it before it spoils ?

What spoils food?

- Microbial Growth
  - Bacteria
  - Yeasts
  - Fungi

Generate off-flavours and odurs
Alter texture / appearance
Reduce the nutritional quality of the food
Make the food unsafe to eat

What spoils food?

- Enzymatic Reactions
  - Generate off-flavours and odours
  - Alter the texture
  - Reduce the nutritional quality of the food
- Chemical Reactions
  - Off flavours and odours
    - Oxidation – rancidity of fat – off odours
    - Curlding of milk due to low pH
- Insects / Rodents
  - Eat the food

Food Spoilage

- Food products are described as spoiled or “unfit for purpose” if they become unacceptable to the producer or consumer.

  - Unsafe
    - Contain disease causing micro-organisms
    - Contain toxins from microbial growth
  - Taste, look or smell bad.

What Does Food Preservation Achieve ?

- Primary Goals
  - Prevent undesirable **microbial**, chemical and enzymatic changes
  - Enhance shelf-life
  - Enhance safety
- Secondary Advantages
  - Changes sensory characteristics
  - Increases digestability

Start of Food Preservation ?

- Observation
- Trials
- Reflection
- Trials
- Method passed on to others (IP concerns?)
- Technology / Scientific Approach

Drying

- One of the earliest preservation techniques
- All living things, including micro-organisms, need water to grow / survive.
- Removing water - slows microbial growth.
- Eventually a lack of water will prevent microbial growth

FOOD	
Fresh poultry or fish	
Fresh Meat	
Fresh vegetables	
Cooked meat, bread	
Cured meat products, cheese	
Syrups, fermented meat (salami)	
Rice, beans, peas	
Jams, marmalades	
Candies	
Dried fruit, dried meat	
Dried pasta, spices, milk powder	
Crackers	

Last longer

Drier

Spoilage Organisms

Bacteria

- Slime

-Off odours

Drying

- Compare a dried apricot to a piece of dried meat.
- Dried apricots are somewhat juicy and contain about 20 % water
- Dried meat is like leather and contains about 10% water
- Yet both shelf-stable - why.

Moisture Vs Water Activity

- Water in food can be either bound or free.
  - Bound water is held by physical forces to macromolecules within the food and is not available to micro-organisms.

- It is the **availability of water**, not the moisture content, which determines the potential of a food to support the growth of bacteria and hence its shelf-life.

- Moisture content = total water (Bound water + Free Water)
- Water Activity (A_w) is the term given to free water
  - Pure Water has a A_w of 1.00

FOOD	A_w
Fresh poultry or fish	0.98-0.99
Fresh Meat	0.95-0.99
Fresh vegetables	0.97-0.99
Cooked meat, bread	0.95-0.98
Cured meat products, cheese	0.91-0.95
Syrups, fermented meat (salami)	0.87-0.91
Rice, beans, peas	0.80-0.87
Jams, marmalades	0.75-0.80
Candies	0.65-0.75
Dried fruit, dried meat	0.60-0.65
Dried pasta, spices, milk powder	0.20-0.60
Crackers	0.10-0.15

A_w dictates what can grow in a food

Group/ Species of Microorganism	Minimum A_w for Growth
Most Bacteria	0.90-0.97
Campylobacter	0.99
Pseudomonads (spoilage)	0.96
E. coli (pathogen)	0.93
Lactobacillieae (spoilage)	0.94
Salmonella (pathogen)	0.92
Listeria monocytogenes (pathogen)	0.92
Most yeasts (spoilage)	0.88
Most filamentous fungi (spoilage)	0.80
Xerotolerant Moulds (spoilage)	0.61

A_w Vs Moisture

- In general:
  - Lipids / protein have low water binding capacity;
  - Cellulose binds water weakly;
  - Starch and sugars bind water strongly.

- Reason why “dried apricots” contain more moisture than “dried meat” yet are still shelf-stable.

- A lot of the water in the apricots is bound to the sugars they contain and is not available for the micro-organisms to use.

"Drying" Preserves Food by reducing its A_w

- Physical removal:
  - drying, smoking, freezing
    baking
  - solar or mechanical
    - apricots, beef jerky

- Binding of water by addition of osmotically active compounds
  - Addition of salt or sugars
    - Jam, candy

Sugar

75 % sugar

63 % sugar

75.7 % sugar

9 % sugar

25 % sugar

45 % sugar

60 % sugar

Fermented Foods (low pH / high acid, acidic)

- The actions of micro-organisms on the food cause changes which:
  - Extend shelf-life,
  - Improve aroma and flavour characteristics,
  - Increase digestibility

- No other single food group or category of foods or food product has been as important in history through-out the world.

History and origins of some fermented foods

Food	*Approximate year of introduction*	*Region*
Mushrooms	4000 BC	China
Soy sauce	3000 BC	China, Korea, Japan
Wine	3000 BC	North Africa, Europe
Fermented milk	3000 BC	Middle East
Cheese	2000 BC	Middle East
Beer	2000 BC	North Africa, China
Bread	1500 BC	Egypt, Europe
Fermented Meats	1500 BC	Middle East
Sourdough bread	1000 BC	Europe
Fish sauce	1000 BC	Southeast Asia, North Africa
Pickled vegetables	1000 BC	China, Europe
Tea	200 BC	China

Worldwide production of some fermented foods

Food	*Quantity (t)*	*Beverage*	*Quantity (l)*
Cheese	15 million	Beer	100,000 million
Yoghurt	3 million	Wine	35,000 million
Mushrooms	1.5 million		
Fish sauce	300 000		
Dried stockfish	250 000		

Individual consumption of some fermented foods: average per person per year

Food	*Country*	*Annual consumption*
Beer (l)	Germany	130
Wine (l)	Italy, Portugal	90
	Argentina	70
Yoghurt (l)	Finland	40
	Netherlands	25
Kimchi (kg)	Korea	22
Tempeh (kg)	Indonesia	18
Soy sauce (l)	Japan	10
Cheese (kg)	UK	10
Miso (kg)	Japan	7

Fermented milk

- Developed as a means of preserving milk against spoilage.
- Most fermented milk products are made from cow’s milk, but sheep, goat, buffalo and horse milks are also used.
- Over 56 traditional fermented milk drinks are produced in a range of countries around the world.
  - Ranging from Aoules made in Algeria out of Goats milk to
  - Zimne sour milk made in Yugoslavia out of Ewe’s milk

- More familiar products include Buttermilk and Yoghurt

Yoghurt

- Two species of Lactic Acid Bacteria are used:
  - *Streptococcus thermophilus*
  - *Lactobacillus delbrueckii* subsp. *bulgaricus*.
- Commercially fermentation takes place at 42^{o}C for 3 – 4.5h.
- A prolonged period of incubation at 27-30^{o}C can be also be used.
- Although they can grow independently, the rate of acid production is much higher when the two LAB are used together

Yoghurt

- The streptococci are responsible for the initial pH drop of the yogurt mix to approximately pH 5.0
  - Responsible for typical yoghurt flavour and texture.
- The lactobacilli are responsible for a further pH decrease to pH 4.0 and produce the fermentation products which contribute to flavour:
  - lactic acid
  - acetaldehyde
  - acetic acid
  - diacetyl

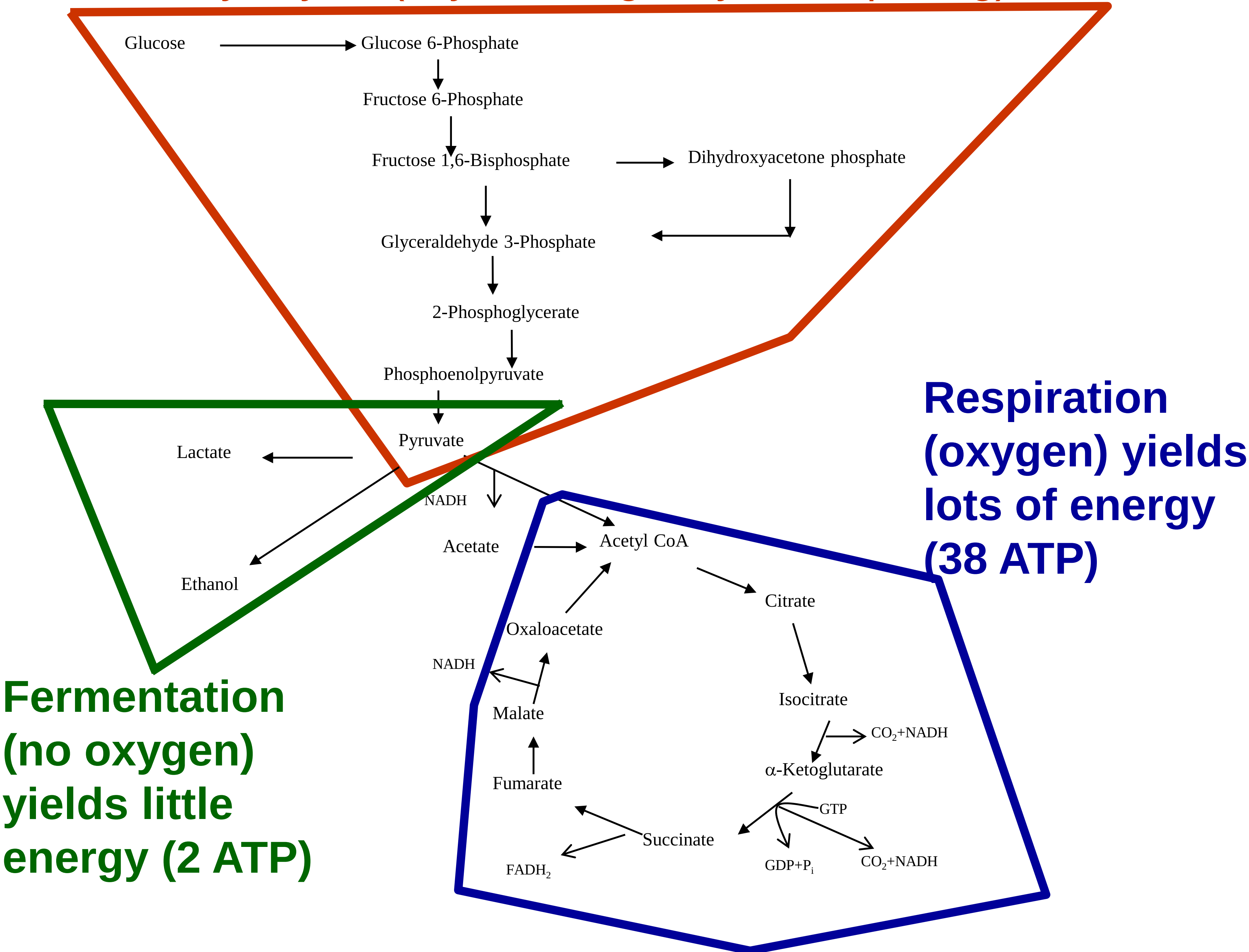
Yoghurt

- The end results of this
  co-operation is that both species are actively involved in the conversion of lactose (sugar in milk) to lactic acid.
  - The metabolites produced by the two organisms give the yoghurt its distinct flavour
  - Acidity is 1.2. to 1.4 % lactic acid,
  - pH is around 4.2 to 4.3
  - The population of each organism is around 2×10^7 cells /ml

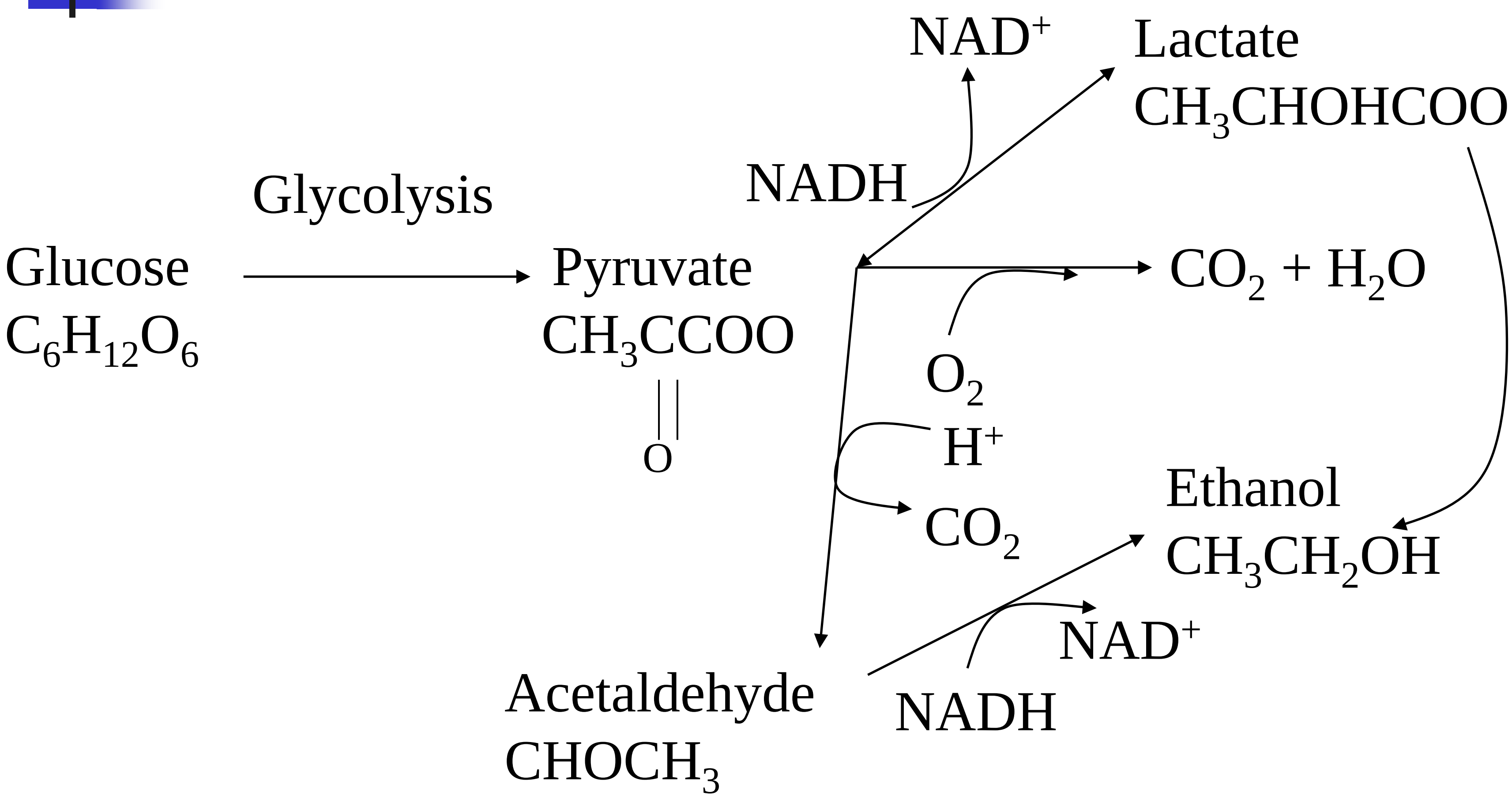
Lactic Acid Bacteria

- 11 different species of bacteria
- Use sugar (lactose, glucose) as a source of energy
- Grow in the presence or absence of oxygen
- In the absence of oxygen the end products of their metabolism are either:
  - Solely lactic acid (**homofermentative)**
  - A variety of compounds including lactic acid, ethanol, CO_2, acetylaldehydes and diacetyl (**heterofermentative)**

Glycolysis (Glyco = sugar; lysis = splitting)



Anaerobic breakdown of sugar



Lactic Acid Bacteria

- Generally grow over a temperature range of 10-40^{o}C
- Most can grow in the pH range from 4 to 8
- Their primary function is the production of lactic acid from sugars
  - Drop the pH of the food to between 4.3 to 4.5
- Other functions may include:
  - flavour, aroma, and alcohol production
  - proteolytic and lipolytic activities
  - inhibition of undesirable organisms

Many Foods Owe Their Stability To Their Low pH

- Low pH achieved by:
  - The action of micro-organisms (LAB)
    - Sauerkraut, yoghurt, salami
  - The addition of organic (acetic, lactic) or inorganic (phosphoric) acids
    - Pickled vegetables, marinated mussels, mayonnaise, sauces
- Other foods are characterised by inherent acidity:
  - Fruit, fruit juices

The pH of a food is a major factor in determining which microorganisms grow.

What spoils acidic (pH 4.5) foods?

Organism	pH		
	Minimum	Optimum	Maximum
Bacteria (most)	4.5	6.5 – 7.5	9.0
Escherichia coli	4.3 – 4.4	6.0 – 8.0	9.0– 10.0
Clostridium botulinum	4.8 – 5.0	6.0 – 8.0	8.5 – 8.8
Lactobacillus (most)	3.0 – 4.4	5.5 – 6.0	7.2 – 8.0
Pseudomonas (most)	5.6	6.6 – 7.0	8.0
Salmonella (most)	4.5 – 5.0	6.0 – 7.5	8.0 - 9.6
Staphylococcus aureus	4.0 – 4.7	6.0 – 7.0	9.5 – 9.8
Yeasts	1.5 – 3.5	4.0 - 6.5	8.0 – 8.5
Saccharomyces cerevisiae	2.0 – 2.4	4.0 – 5.0	
Molds	1.5 – 3.5	4.5 – 6.8	8.0 – 11
Aspergillus niger	1.2	3.0 – 6.0	
Penicillium	1.9	4.5 – 6.7	9.3

Chemistry of organic acids in food

- In foods acidity is due to the presence of weak organic acids (mainly acetic, lactic, propionic, sorbic and benzoic acid).
- In solution such acids form an equilibrium.

$$HA \Leftrightarrow H^{+} + A^{-}$$

Undisassociated Form Disassociated Form

- A neutral solution has a pH of 7.

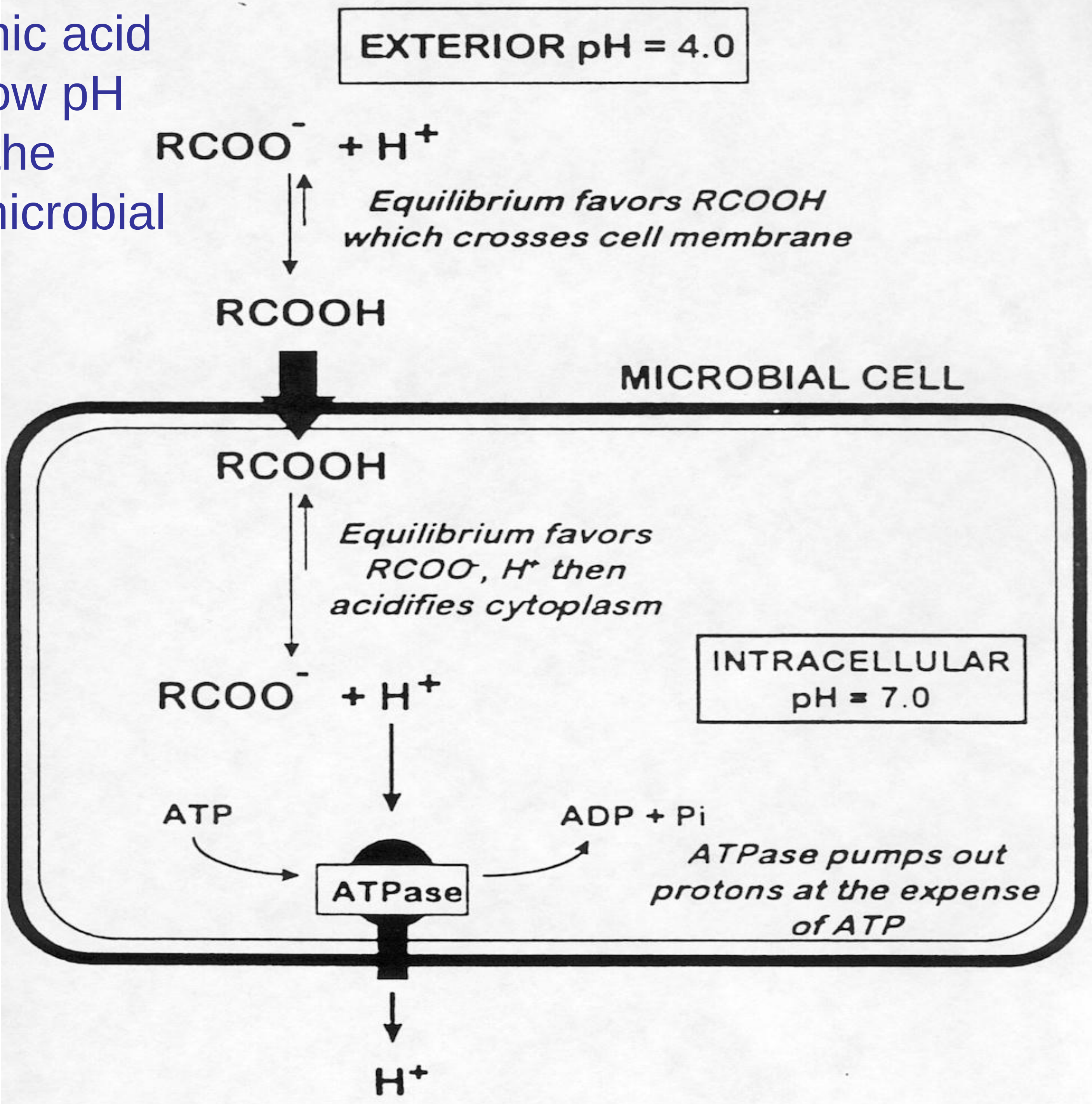
- As the solution becomes more acidic (pH gets lower) the H+ concentration increases and the equilibrium is moved towards HA
- As the solution becomes more alkali (pH gets higher) the H+ concentration decreases and the equilibrium is moved towards H+ and A-

The cell walls of micro-organisms regulate what enters the cells

– critical for cell survival and growth

- in general charged molecules (eg H^+ , A^-) cannot cross the membrane

Fate of an organic acid (RCOOH) in a low pH environment in the Presence of a microbial cell



Cell uses energy to pump H^+ out

- slows growth

If it runs out of energy it dies

Chemistry of organic acids in food

In foods acidity is due to the presence of weak organic acids (mainly acetic, lactic, propionic, sorbic and benzoic acid).

In solution such acids form an equilibrium. $HA \Leftrightarrow H^+ + A^-$,

The equilibrium constant for this process K_a, is given by

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

This expression can be rearranged $\frac{1}{[H^+]} = \frac{1}{K_a} + \frac{[A-]}{[HA]}$

Taking logarithms to the base 10 we get:

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

Chemistry of organic acids in food

$$\log 1 = 0$$

$$pH = pK_a + \left[\log \frac{[A^-]}{[HA]}\right]$$

- When the pH = the acids pK_a - half of the acid will be undissociated

    - Acetic acid, pK_a= 4.75
    - Lactic acid, pK_a = 3.79;
    - Propionic acid, pK_a = 4.87

Chemistry of organic acids in food

Log 10 =1

$$pH = pK_a + \left[\log \frac{[A^-]}{[HA]}\right]$$

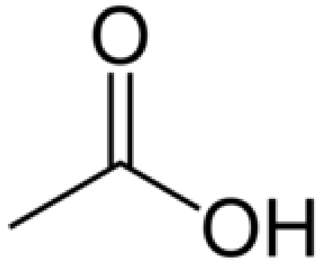
$HA \Leftrightarrow H^+ + A^-$

- As pH increases ($[H^+]\downarrow$) dissociation of the acid increases $\rightarrow$.
- As pH decreases ($[H^+]\uparrow$) dissociation decreases $\leftarrow$

- Small changes in pH have a dramatic impact on an acids effectiveness against micro-organisms.

- Increasing the pH by 1 unit increases the ratio of dissociated acid to undissociated acid by 10
  - Consider when pH = pKa + 1

Acetic Acid



$C_2H_4O_2$

- **Acetic acid**, also known as **ethanoic acid**, E260 is best recognized for giving vinegar its sour taste and pungent smell
- Acetic acid is corrosive, and its vapour is irritating to eyes and nose, although it is a weak acid based on its ability to dissociate in aqueous solutions.

Acetic Acid

$C_2H_4O_2$

- In the food industry acetic acid is used under the food additive code as an acidity regulator / preservative.
- It is normally present in sufficient amounts to exert an effect on flavour and product pH.
- By reducing the pH it potentiates its own action by increasing the proportion of undissociated acid present.
- Added to pickles, sauces, chutney

Sorbic acid, or 2,4-hexadienoic acid

$C_6H_8O_2$

- Sorbic acid (E200) and its mineral salts, sodium sorbate (E201), potassium sorbate (E202) and calcium sorbate (E203).
- First isolated from the unripe berries of the Rowan Tree (*Sorbus aucuparia*).
- The pKa of sorbate is 4.80
- At pH of 4.0, 86 % of the compound is undissociated,
- At a pH of 6 only 6% is undissociated
- Works best at pH < 4.8
- Used in of shelf-stable sauces / fillings

Low pH Foods

- Phosphoric acid, 10 % sugar
- Acetic acid, 21.3 % sugar
- No added acid, 5.1 % sugar
- Acetic, citric and sorbic acid, 5.1 % sugar
- Acetic and Lactic acid, 7.6 % sugar
- No added acid, 5.9 % sugar
- Acetic, lactic, and sorbic acid, 17.8% sugar
- Acetic acid, 20.2 % sugar

Curing (Nitrite)

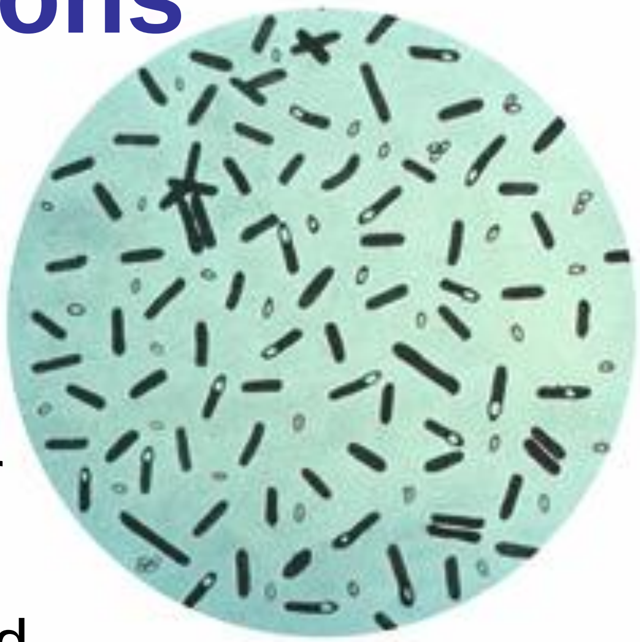
- Meat curing solutions containing "salt" have been used for many centuries.
- The Romans widely adopted this practice and helped to spread the techniques around the "known" world

Nitrite

- As the use of salt (NaCl) as a meat preservative spread, a preference developed for certain salts that produced a pink color and special flavor in meat.
- These salt also seemed to improve the safety of cured products
- It was discovered around 1940 that Nitrite ($NaNO_2$), a "contaminate" in the salt was responsible for enhancing colour, flavor and safety

Nitrite is now a legal requirement in meat curing solutions

- Provides protection against the growth of the bacterium *Clostridium botulinum* and prevents its production of toxin.
- Gives cured meat its characteristic colour and flavour
- No alternatives to its use have been found



Botulinus toxin is the most poisonous substance known
LD_{50} Intravenous
0.0003 ug/kg

Nitrite

- In cured meats nitrite, is reduced to nitric oxide.

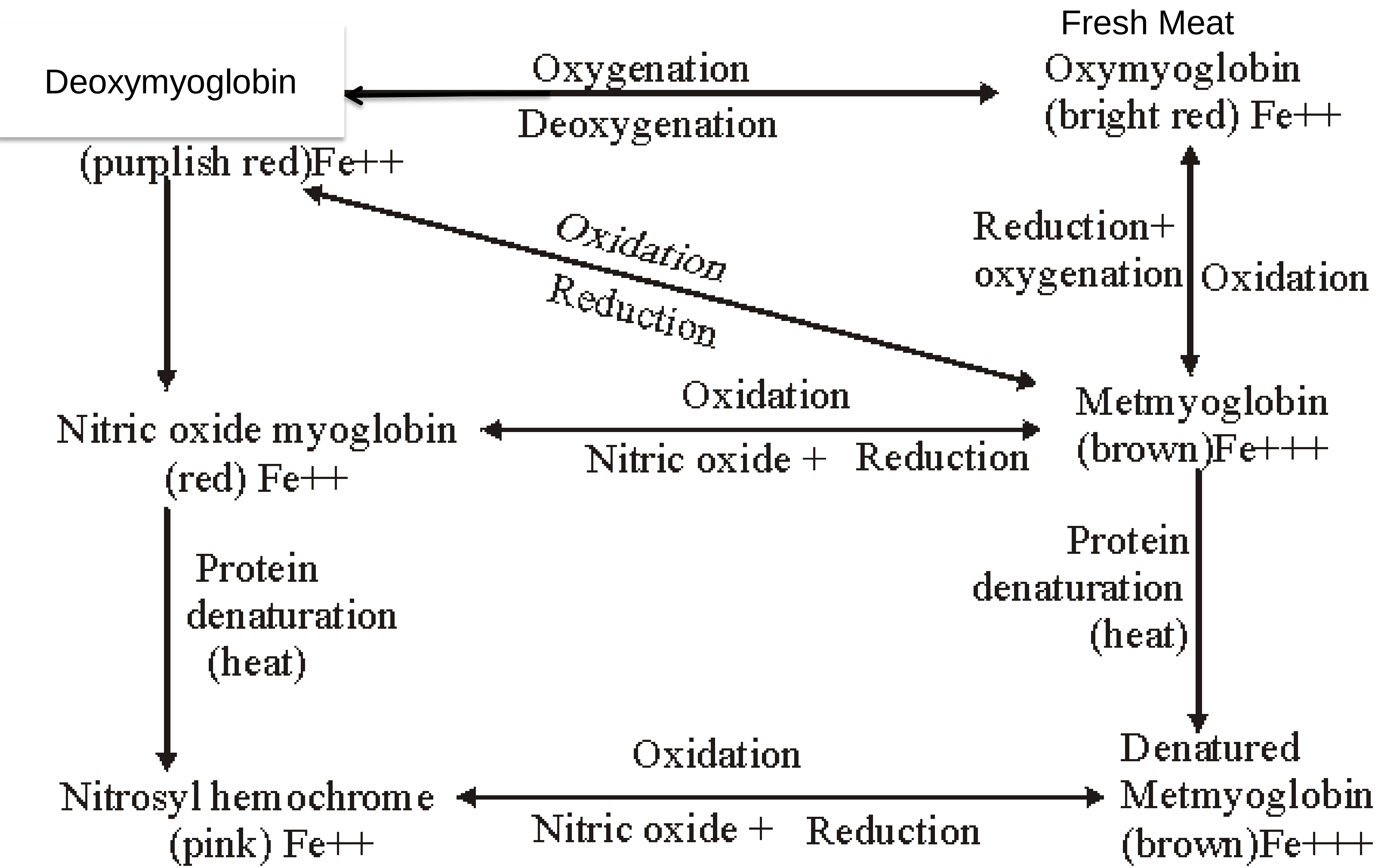
$NaNO_3$------------> **$NaNO_2$**-------------> **HONO**------------> **NO**

Sodium nitrate Sodium nitrite Nitrous acid Nitric oxide

- Nitric oxide reacts with many components in meat such as proteins, lipids, carbohydrates and the myoglobin.

- These reactions are responsible for the meat's colour, flavour and microbial stability.

Nitric Oxide Reactions in Meat



Nitrite / Myoglobin Reactions

Oxymyoglobin – bright red

Nitrosyl haemochrome - pink

nitric oxide myoglobin - red

Fermented Meat Products.

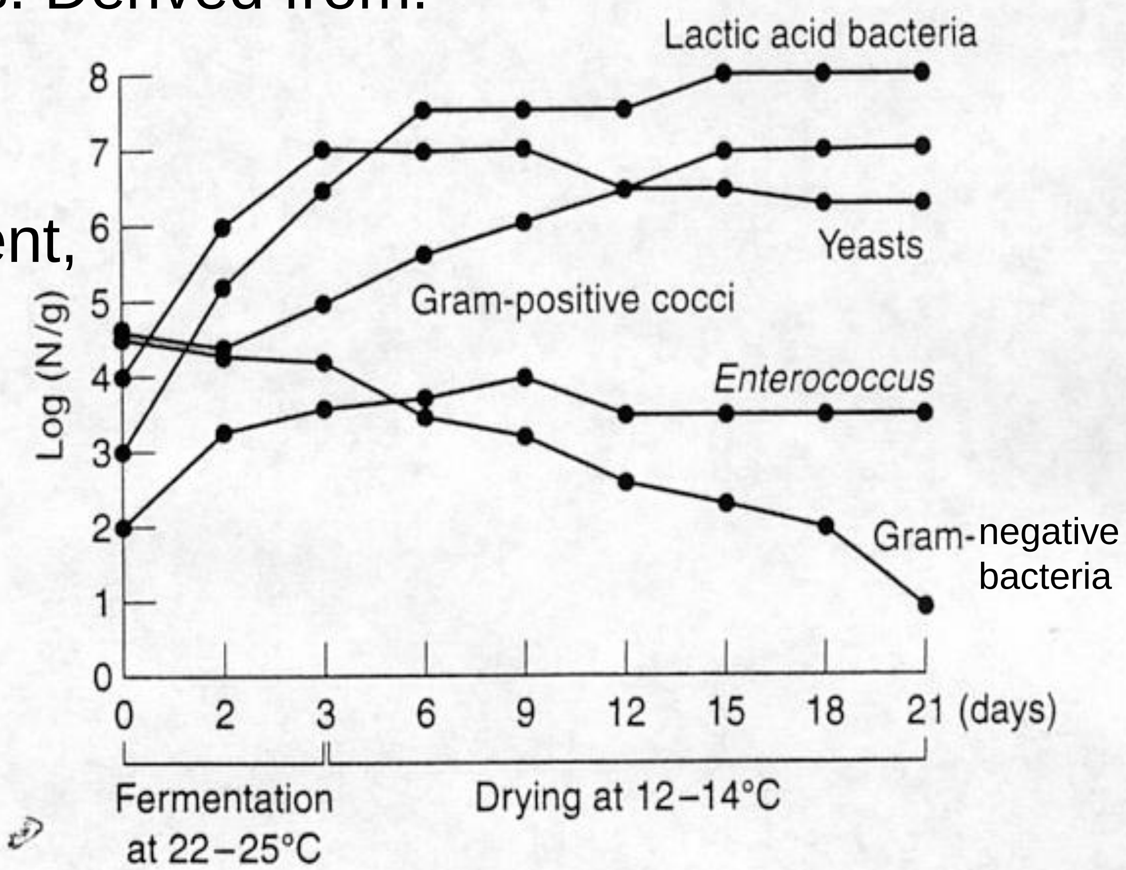
- First recorded around 1500 BC
- Rely on a number of “hurdles” to enhance safety and shelf-life.

Manufacture of Fermented Sausages

- Meat is minced with additives
  - nitrate, nitrite, NaCl and ascorbate
- Seasonings
  - sugar, garlic and pepper.
- The meat mixture is stuffed into casings
- Fermented and air dried
- A wide variety of fermentation conditions are used.

Microbiology of Fermentation

- The raw mixture is naturally contaminated with many kinds of micro-organisms. Derived from:
  - raw meat,
  - casing,
  - processing environment,
  - seasonings and
  - workers.



Microbiology of Fermentation

- At the end of the fermentation period LAB are generally the dominant bacterial flora
  - Give the desired appearance, texture and flavour
  - Contribute to the inhibition of spoilage organisms and pathogens

- The gram-positive cocci include, *Kocuria* and coagulase negative stapyloccocci
  - Contribute to the development of colour and flavour.

Many factors are responsible for inhibiting undesirable bacteria

- Drying at temperatures below 25^{o}C and the addition of nitrite, nitrate or sodium salts, inhibit *Salmonella* and *Clostridium*.

- Reduction of oxygen during fermentation suppresses the aerobic bacteria (*Pseudomonas)* and favours LAB.

- The reduction of water activity during drying to between 0.96 to 0.86 inhibits *Clostridium* and *Staphylococcus* aureus*.*

- LAB produce lactic acid and reduce the pH (pH 4.3 to 5.0)

Many factors are responsible for inhibiting undesirable bacteria

- The prevention of botulinum toxin (*Clostridium botulinum*) is achieved by a combination of
  - NaCl,
  - Nitrite,
  - Reduced water activity (< 0.97),
  - Low pH and
  - Low temperature storage

Sensory Properties

Development of Texture

- At pH values below 5.4 meat proteins are denatured and coagulated and their water binding capacity decreases.

Development of Colour

- Chemical reactions involving the myoglobin of the meat with nitrite and the presence of Staphylococci and *Kocuria*.

Development of Flavour

- Bacterial metabolites, sausage ingredients, smoking agents and enzymatic reactions.

Importance of food preservation in the ancient and modern world

Cornerstone of advancement

- Facilitated the establishment of permanent settlements
- Aided exploration and travel
- Aided in warfare
- Enabled the development of large cities
- Enabled the building of large monuments
- Enabled individuals within societies to pursue cultural activities.

Food Preservation

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Civilisation

Future for New Zealand's Food Industry

- How does the WORLD see New Zealand ?

How does the WORLD see Italy?

Italian Foods

- Identifiable
- High Priced
- Sought after

Future for NZ Food Industry

- Move away from selling commodities
  - Lamb
  - Beef
  - Cheese
  - Milk Powder

Future for NZ Food Industry

- Move towards selling
  - “Added value”,
  - High quality products
- Target at
  - Specific markets
  - Wealthy markets
- Food Preservation Technologies
  - Desirable characteristics
  - Ensure food safety and shelf-life