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HONEY ADULTERATION AND CRYSTALLISATION

Honey Technology online seminar

Presented by Sandra Meixner

Intertek Food Services GmbH

AGENDA

01 **Honey**

02 **Adulteration and detection possibilities**

03 **Honey crystallisation and influencing factors**

04 **Process optimization**

05 **CRYSTEK**

QUALITY CONTROL OF HONEY
SENSORY

Test of the organoleptic characteristics

- Colour
- Texture
- Smell
- Taste

Background

- Consumer expectation
- Botanical Origin (Characteristics)
- Defects (e.g. Fermentation, Smoke, Thymol, Heat, …)

CODEX STANDARD FOR HONEY / DIRECTIVE 2001/110/EG CATEGORIES

Type	Legal name	Definition according Annex I
Source	Blossom Honey	Honey which comes from nectars of plants
	Honeydew Honey	Honey which comes mainly from excretions of plant sucking insects (*Hemiptera*) on the living parts of plants or secretions of living parts of plants
Removal from the comb / Style	Extracted Honey	Honey obtained by centrifuging decapped broodless combs
	Pressed Honey	Honey obtained by pressing broodless combs
	Drained Honey	Honey obtained by draining decapped broodless combs
	Honey	Honey in liquid or crystalline state or a mixture of the two
	Comb Honey	Honey stored by bees in the cells of freshly built broodless combs and which is sold in sealed whole combs or sections of such
	Cut Cumb in Honey or Chunk Honey	Honey containing one or more pieces of comb honey
	Filtered Honey	Honey which has been filtered in such a way as to result in the significant removal of pollen

ESSENTIAL COMPOSITION AND QUALITY FACTORS

General	Honey shall not have added to it any addition other than honey… No pollen may be removed except where this is unavoidable in the removal of foreign matter. Chemical or biochemical treatments shall not to be used to influence honey crystallisation
Fructose and Glucose Content (Summe)	Not less than 60 g/100 g for Blossom Honey Not less than 45 g/100 g for Honeydew Honey
Sucrose Content	Not more than 5 g/100 g
Moisture Content	Not more than 20 %
Water Insoluble Solids Content	Not more than 0.1 g/100 g
Electrical Conductivity	Not more than 0.8 mS/cm for Blossom Honey Not less than 0.8 mS/cm for Honeydew Honey
Free Acidity	Not more than 50 mmol/kg
Diastase Activity	Not less than 8
Hydroxymethylfurfural Content (HMF)	Not more than 40 mg/kg

SUGAR SPECTRUM OF HONEY

Monosaccharides (78%)

- Fructose 33-42 %
- Glucose 27-36 %

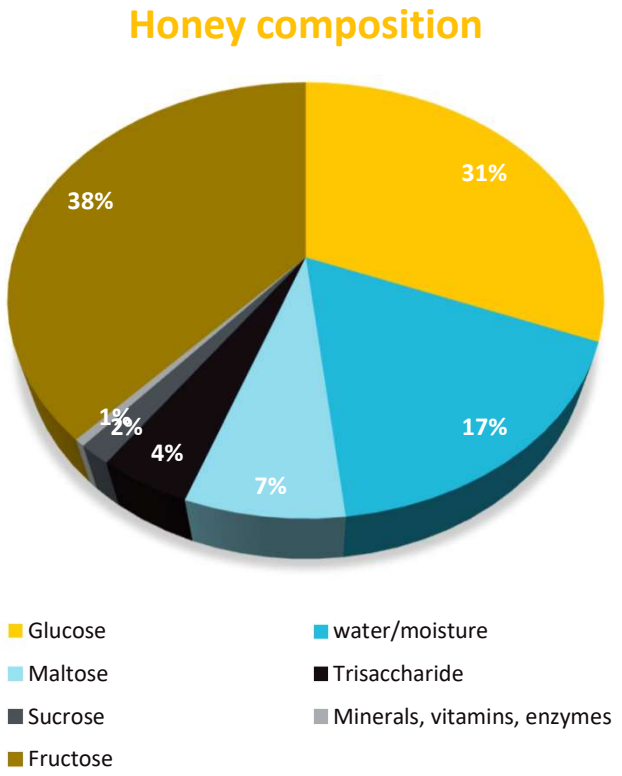
Disaccharides

- Sucrose
- Maltose

Trisaccharide

- Melezitose

Distribution depending on the botanical origin



SUGAR SPECTRUM OF HONEY

Monofloral honeys	F/G ratio
Acacia Honey	> 1,55
Chestnut Honey	> 1,45
Clover Honey	< 1,20
Eucalyptus Honey	> 1,05
Heather (*Calluna*) Honey	> 1,20
Heather (Erica) Honey	> 1,05 – 1,30
Lavender Honey	1,10 – 1,25
Manuka Honey	1,12 – 1,47
Orange Blossom Honey	> 1,10
Rape Honey	<= 1,00
Rosemary Honey	> 1,10
Sunflower Honey	< 1,10
Thyme Honey	> 1,30

Natural range of F/G rate from 0.85 to 1.7 depending on the plant source

THE CHALLENGE

Today, there is more honey traded globally than there are bees to produce the honey hence the obvious concern for adulteration and authenticity across the honey supply chain. As a result testing laboratories are in a race to determine if adulteration exists.

CONSUMER AND INDUSTRY IMPACT

Safety. Food fraud encompass the deliberate and intentional substitution, addition (or dilution), tampering, or misrepresentation of food, food ingredients, or food packaging; or false or misleading statements made about a product, for economic gain.

Financial. Economically-motivated adulteration of food, otherwise known as "food fraud," has been estimated to cost the food industry $30 to 40 billion per year.

OVERVIEW- 2018 FOOD FRAUD ON THE RISE

Figure 4 - *Shows the top 10 product categories (number of requests) in the AAC-FF in 2018*

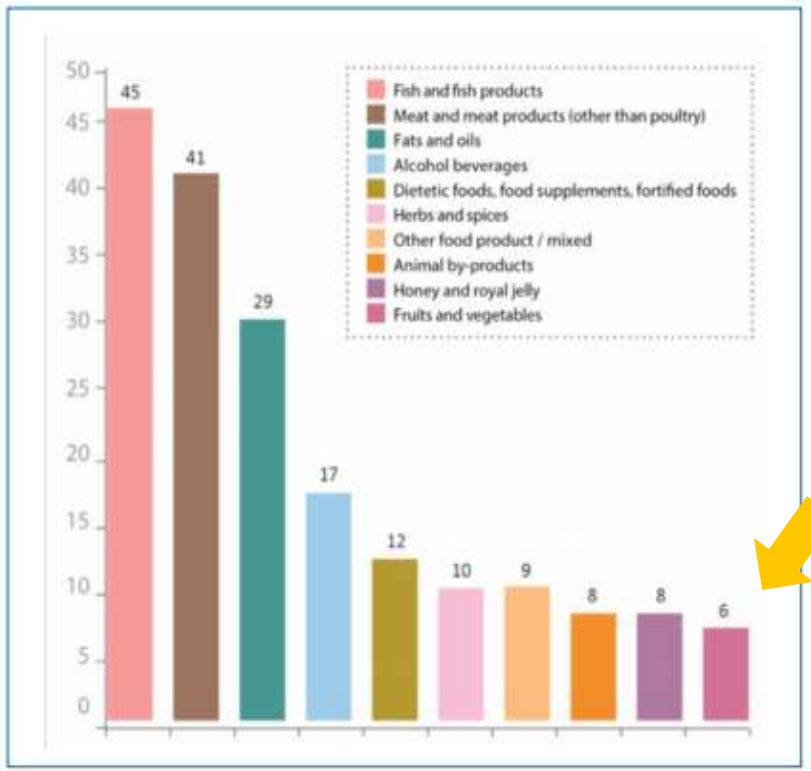


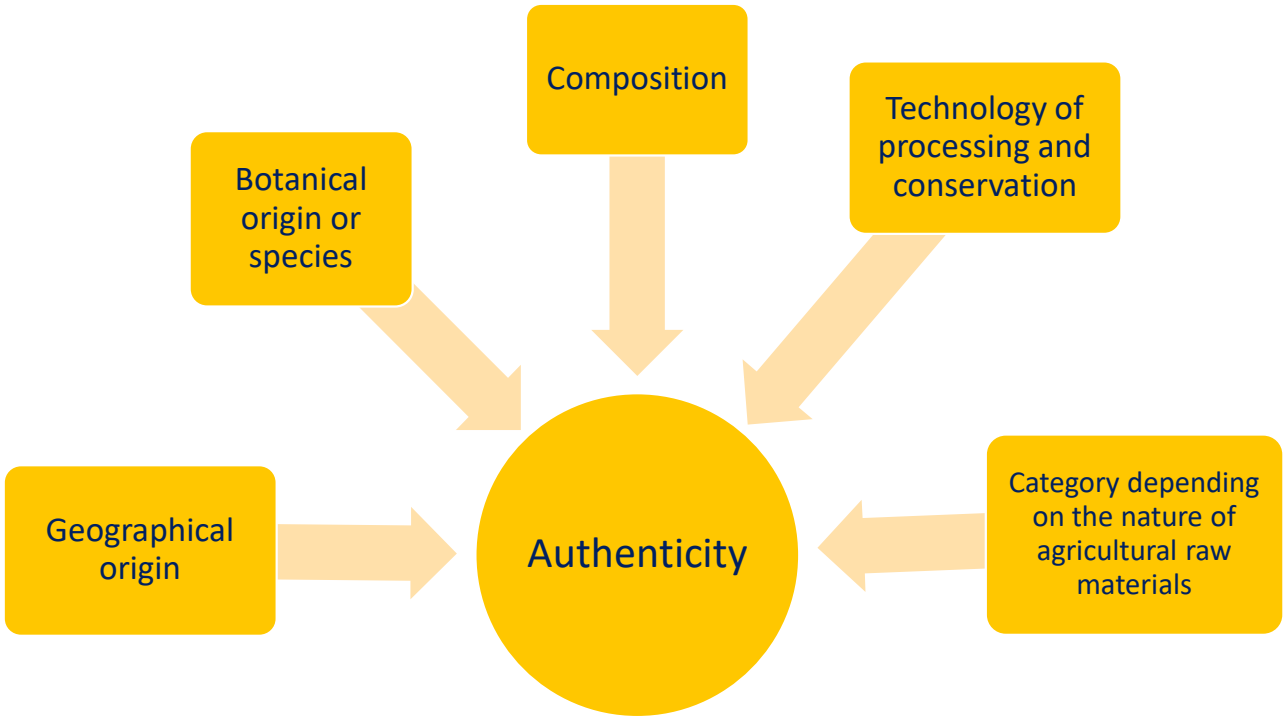
Figure 4 – Top 10 categories in the AAC-FF in 2018

Honey is a high risk food in regards to fraud or adulteration. The honey market shows high numbers of Fraud issues especially compared to the global market size in comparison to other foodstuffs.

Products of interest:

- Wine / alcoholic beverages
- Fruit & vegetables and cereals
- Meat (fresh & products)
- Oils and fats
- Honey, Eggs and other animal origin products
- Fishery
- Spices, coffee, cocoa & tea

OVERVIEW – PARAMETER THAT DETERMINE FOOD AUTHENTICITY



sume. In Europe, geographic origin is one of the main authenticity issues for food products. A recent trend in European legislation is the protection of 'mountain products' and 'products of island farming' (EU regulation 1151/2012). These two labels are the latest companions to the protected designation of origin (PDO) and protected geographical indication (PGI) labels. High quality products with geographical indications and designations of origin command higher retail price and bring in a higher financial benefit to the PDO/PGI producers than other similar products. There is a need to protect such products from possible commercial fraud. These products are defined by geographical origin, special know-how or traditional processing methodology, use of certain farming methods (e.g. organic or 'free range' foods), and in some cases by special animal diet and animal breed [1].

SENSORY HONEY AND MELISSOPALYNOLOGY

Organoleptic properties	
Color	Egg yolk yellow
Odor	Mild, fruity, aromatic
Taste	Fruity, aromatic
Consistency	Cristalline, tends to separate

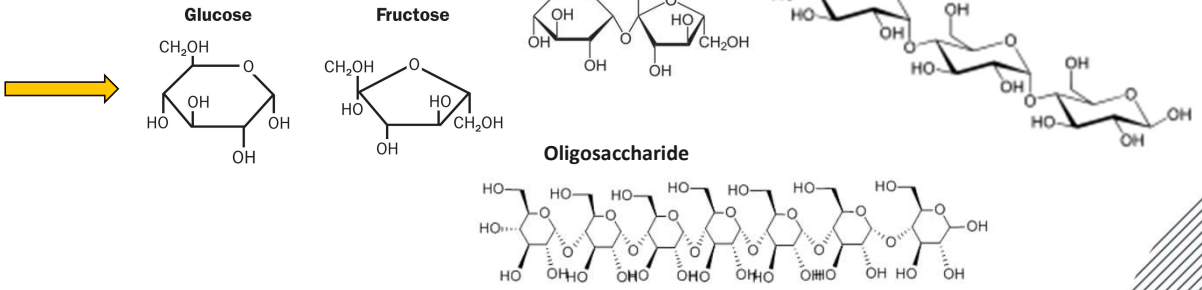
Microscopic and physio-chemical characterisitics	
Helianthuspollen [%]	At least 50
Electrical conductivity [mS/cm]	0,20 to 0,40
F/G ratio	Max 1,10
Color [mm Pfund]	40 to 60

HONEY ADULTERATION

Since the 1970s : **H**igh **F**ructose **C**orn **S**yrup

- cheap to produce
- first product to adulterate honey
- often used

Meanwhile a lot of different syrups on the market which are produced from **starch (**Maize, Rice, Wheat**)** and **Sucrose** (beet, cane) with the help of enzymes



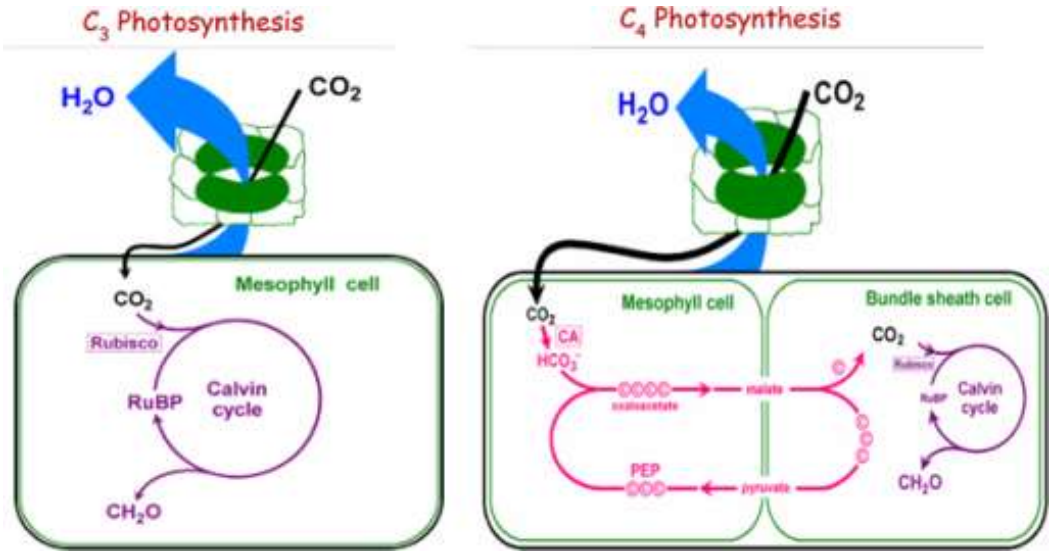
INTRODUCTION OF ANALYTICAL METHODS FOR AUTHENTICITY & FOOD FRAUD DETECTION

Element Analyser/Liquid Chromatography Isotop Ratio Mass Spectroscopy => EA/LC-IRMS	
• carbon isotopic profiling • traceability of botanical origin • foreign sugar use	
Nuclear Magnetic Resonance => NMR	
• organic substance profile • traceability of geographical origin • detection of quality parameter	
Liquid Chromatography Mass Spectroscopy => LC-HRMS	
• trace organic substance profile • traceability of botanical origin • foreign syrup markers	
Inductively Coupled Plasma - Mass Spectrometry => ICP-MS	
• inorganic substance profile • trace element profiler • traceability of geographical origin	accepted in the US market

HONEY ISOTOPIC ANALYSIS
C_3 AND C_4 PHOTOSYNTHESIS

CO_2 Fixation of plants

Photosynthesis: $6\ CO_2 + 6\ H_2O \rightarrow C_6H_{12}O_6 + 6\ O_2$



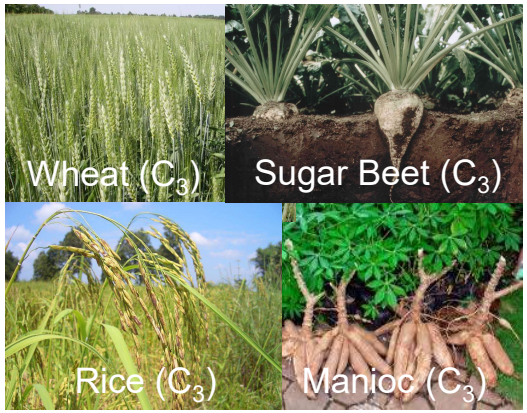
C_3-Plants, Calvin Cycle, Enzyme RuBisCo

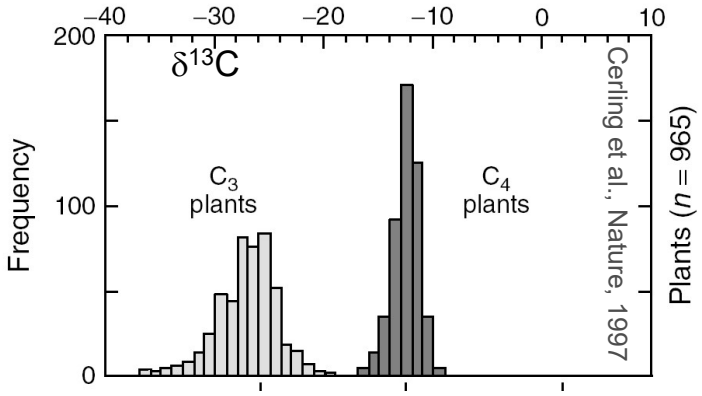
Intermediate product: 3-Phosphoglyceryt (sugar with **3** C atoms)

C_4-Plants, Hatch-Slack Cycle, Enzyme PEP carboxylase

Intermediate product : Oxalacetate (sugar with **4** C atoms)

HONEY ISOTOPIC ANALYSIS
C_3 SYRUP ISSUE





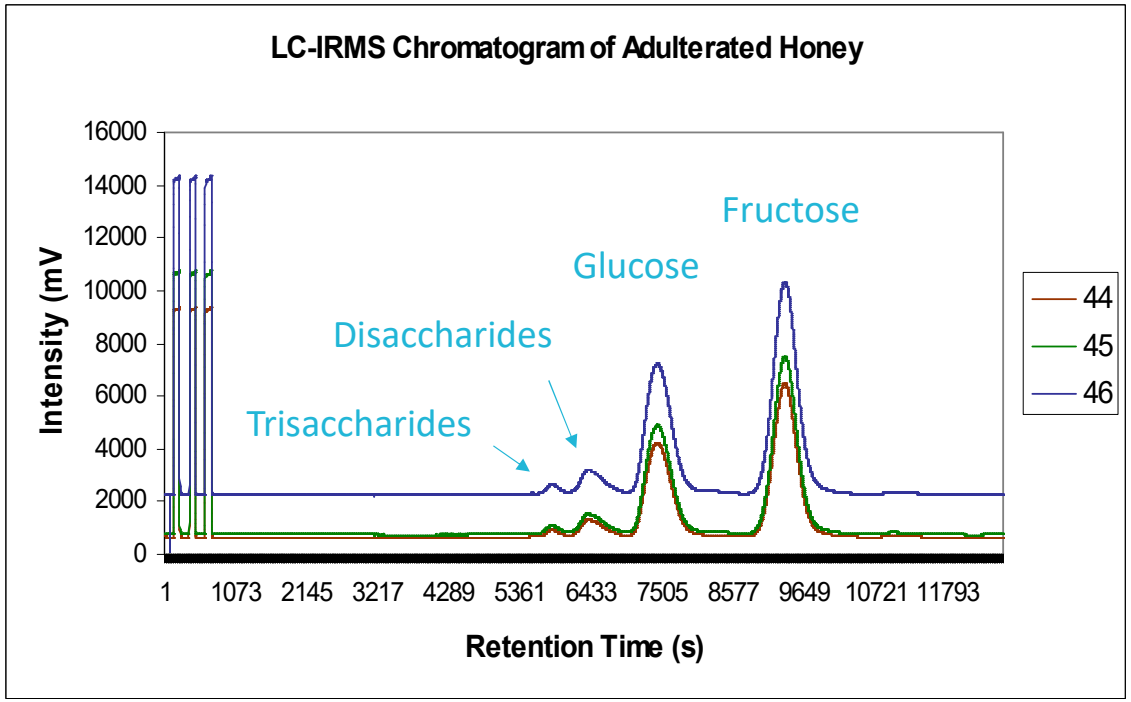
CO_2 Fixation	Syrup from	$\delta^{13}C$ Honey-Value (vs. V-PDB)	Method
C_4-Plants	Maize, Sugar Cane	-8 to -13 ‰	**EA-IRMS** (AOAC 998.12)
C_3-Plants	Rice, Wheat, Manioc, Sugar Beet	-22 to -30 ‰	**LC-IRMS** (inhouse)

Starch based / sucrose based

Cabanero et al., 2006, Elflein and Raezke 2008

^{13}C ISOTOPIC ANALYSIS BY EA-LC/IRMS: DETECTION OF C3 AND C4 SUGARS

SEPARATION OF SUGARS (LC-IRMS): ADULTERATED ACACIA HONEY



Parameter	δ^{13}C [‰] vs. VPDB
Protein	-25.2
Honey	-24.6
Fructose	-23.79
Glucose	-25.96
Disaccharides	-25.71
Trisaccharides	-24.96
Delta 13C (F-G)	2.17
Delta 13C (max.)	2.17

EA-IRMS
C4-Zucker 3.9 %

Result EA-IRMS: ok
LC-IRMS: **adulterated**

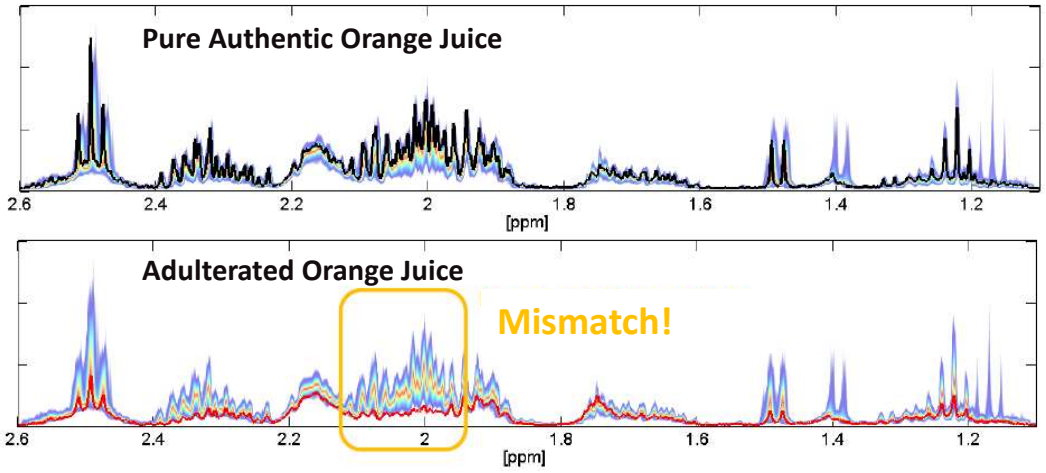
Adulterated with Fructose syrup!

^{1}H NMR PROFILING

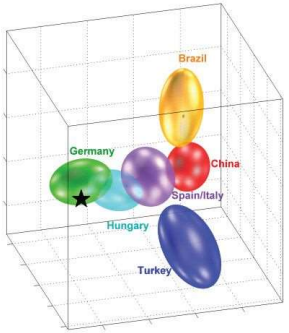
- A rapid screening technique, with simple sample preparation
- This system is currently used for wine, juice and honey authenticity testing
- Targeted and non-targeted analysis
- Identification and quantification of typical honey substances (e.g. sugars, acids, HMF)

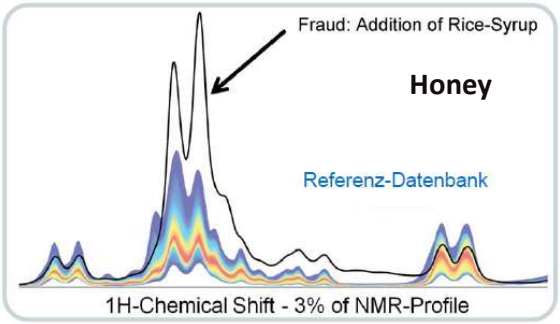
NMR (NUCLEAR MAGMETIC RESONANCE) PROFILING

NMR Profiling



Geographical Differentiation





Quantitative parameters

Compound	Result	Unit	A.I.J.N. (Apple) Flag	min	max	SGF-Profiling n =2733
ethanol	<10	mg/l	●	-	3000	0 619
formic acid	<5	mg/l	○	-	-	0 17
fructose	62.6	g/l	●	45.0	85.0	47.9 77.9
fumaric acid	<5	mg/l	●	-	5	0 6
glucose	25.2	g/l	●	15.0	35.0	12.6 34.9
lactic acid	52	mg/l	●	-	500	0 414
malic acid	6.5	g/l	●	3.0	-	2.2 9.8
methanol	N/Q	mg/l	○	-	-	0 194
pyruvic acid	22	mg/l	○	-	-	4 44
quinic acid	810	mg/l	○	-	-	143 1192

Examples taken from Bruker NMR Presentation at IFS Bremen, July 24th, 2015

LC-HRMS AT A GLANCE

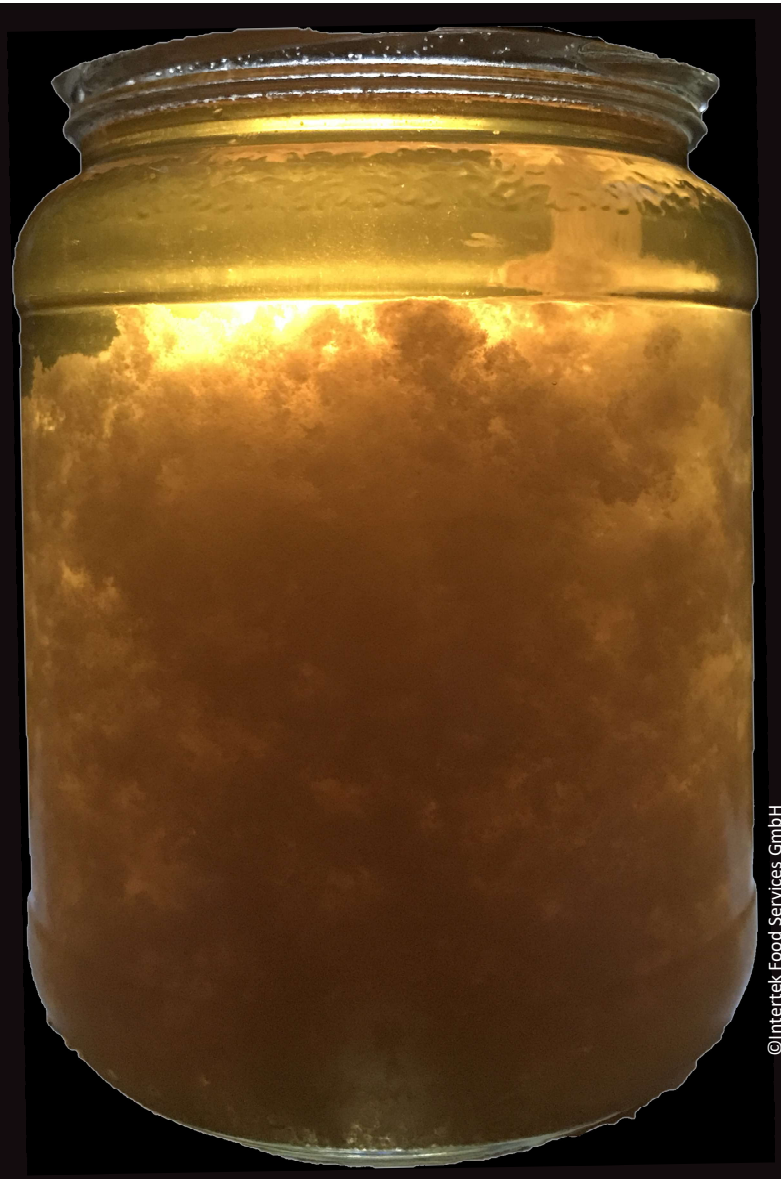
- Enables the detection of known and unknown honey adulterants in one analytical test.
- Has a significant higher detection sensitivity for foreign sugar adulterants compared to established honey authenticity testing methods.
- Is suitable as a multi-method with hundreds of identified marker substances for the simultaneous detection of additions of different types of sugar syrups used for adulteration.
- Can replace various single methods for certain types of adulteration and thus helps to reduce the analytical effort in terms of analysis costs and testing efficiency.

- **Combined with 1H NMR-Profiling and 13C stable isotope analysis (EA/LC-IRMS), it is the most advanced and reliable testing method for honey authenticity on the market.**

SUGAR SPECTRUM OF HONEY

Fructose

Glucose

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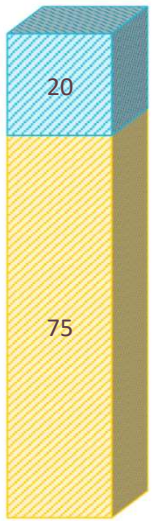
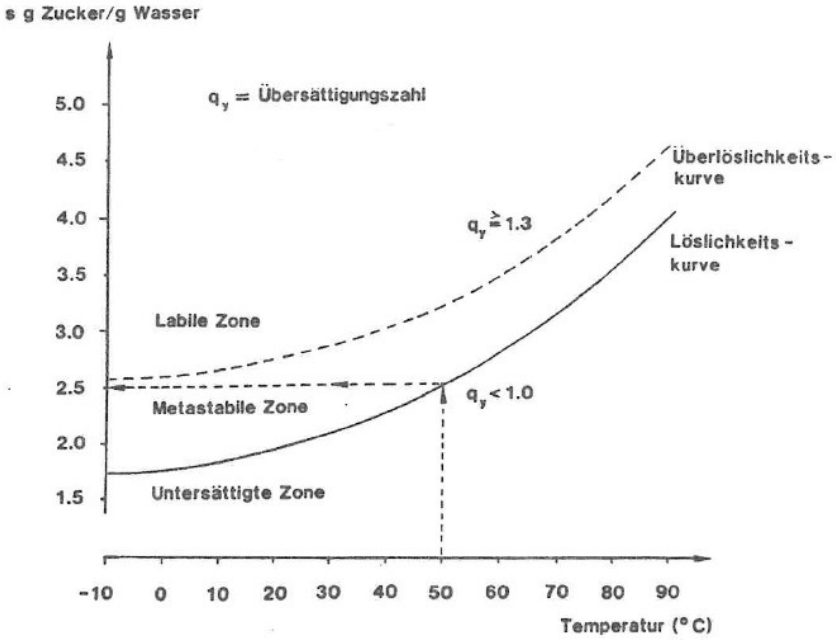
DESCRIPTION OF HONEY CRYSTALLISATION

- Honey crystallizes as it is a supersaturated solution.

- Metastable zone = Only already existing crystals
- Unstable zone = Spontaneous crystallization

- Saturation concentration
  - Fructose in honey 79% (liquid)
  - Glucose in honey 32 % (crystallized)





INFLUENCING FACTORS

Fructose/Glucose content

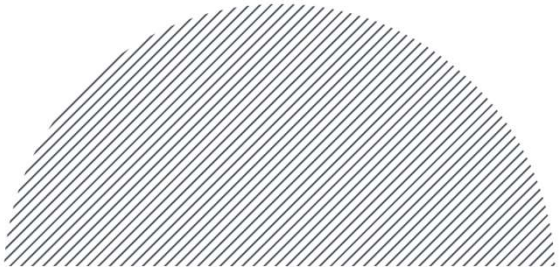
- < 1,15 Fructose/Glucose
- Glucose content >32 g/100 g

Crystallization trend

- > 1,5 Fructose/Glucose (z.B. acacia honey)
- Fructose 79 g/100 g
- Glucose < 32 g /100g

Lower crystallization trend

- A low F/G, indicates a trend for a *fast* crystallization



INFLUENCING FACTORS

Water content

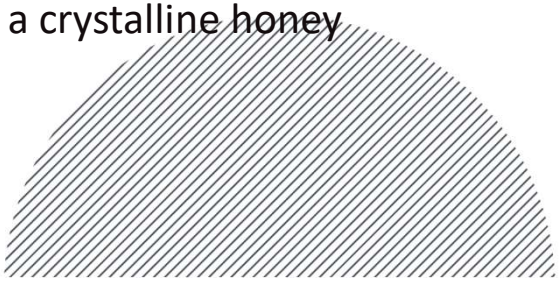
- > 2,1 Glucose / Water ratio
- Water content 15-18 %

Crystallization trend

- < 1,7 Glucose / Water ratio
- Water content > 18 %
- Water content < 15 %

Lower crystallization trend

- A high water content, would create a *softer* consistency of a crystalline honey



INFLUENCING FACTORS

Temperature

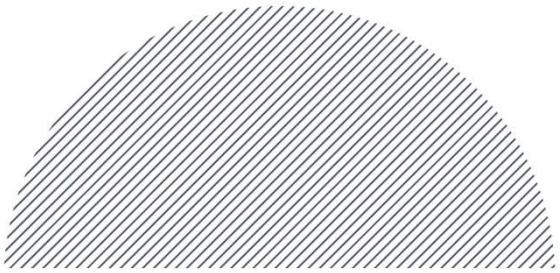
- ≈ 14 °C

Ideal for Crystallization

- 25 °C

No crystallization

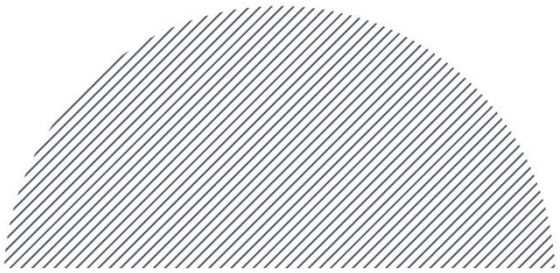
- Temperature changes around 14°C accelerate the crystallization



INFLUENCING FACTORS

Crystallization indicators / initial nucleus

- Pollen
- Bee remains
- Dust particles
- Air
- Sugar crystals
- Bees wax
- Filtering agent

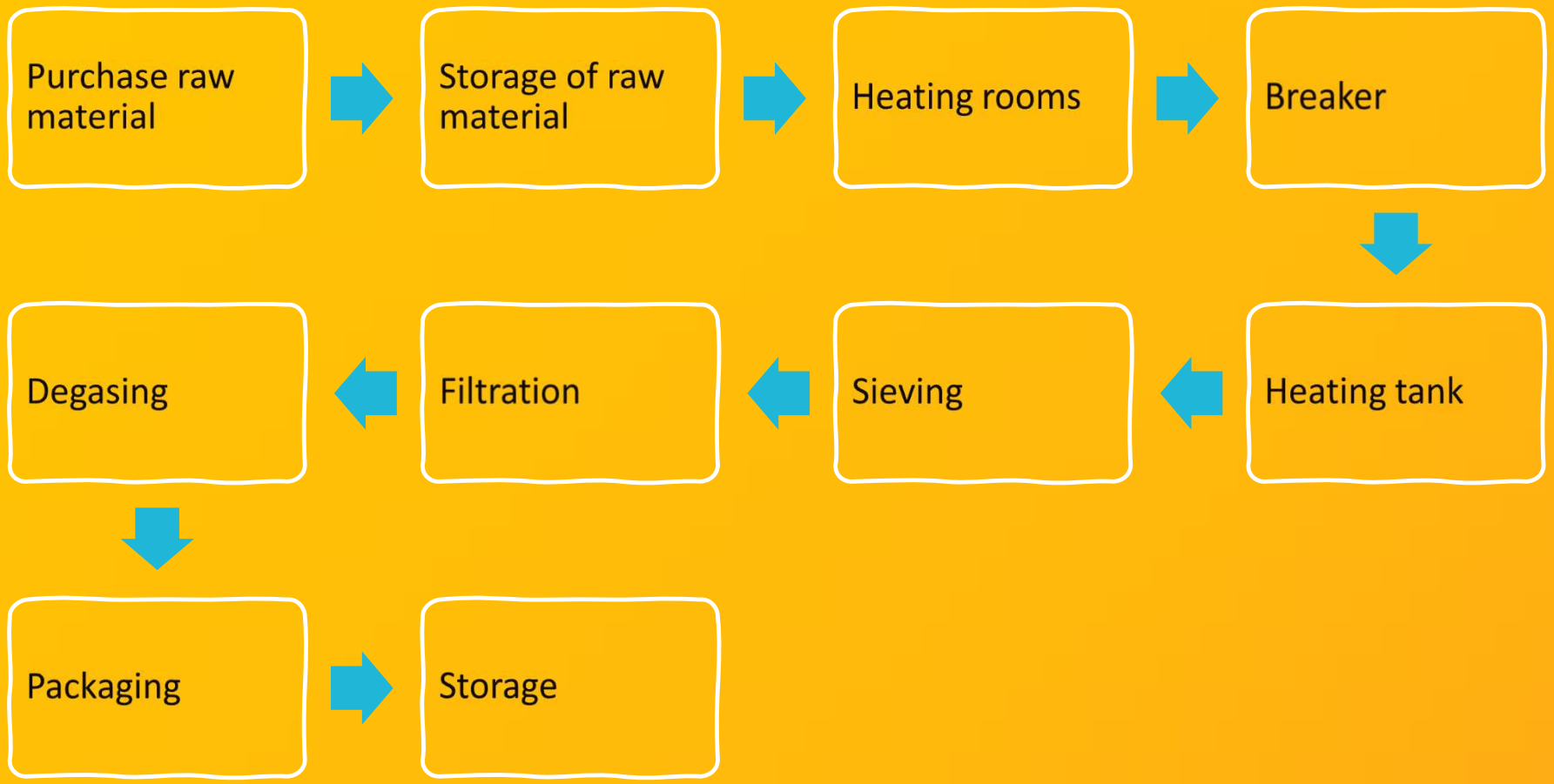


INFLUENCING FACTORS

Packaging

- Round
- Without edges
- Without indentation
- Smooth surface structure

PROCESS OPTIMIZATION FOR LIQUID HONEY BATCHES



PROCESS OPTIMIZATION

Before Production

- Purchase Raw material
  - Honey type
  - Honey quality
  - F/G ratio
  - Water content
- Simulation crystallization
- Storage temperature
- Choice of machines/equipment

During Production

- Slow production speed
- Avoid crystallization starters
  - Melted wax
  - Bee particels
  - Air
  - Sugar crystals
- Select the right temperature
- Maintenance plan

After Production

- Packaging type
- Storage temperature
- Transport temperature
- BBD
- Simulation crystallization

CRYSTEK

Crystallized/Creamy honey is also a typical product that has different challenges. This presentation is focused on the liquid products.

The re-crystallization of liquid honey is a problem that honey producers fight since decades.

Visualization of sugar crystals before your eyes are able to detect them

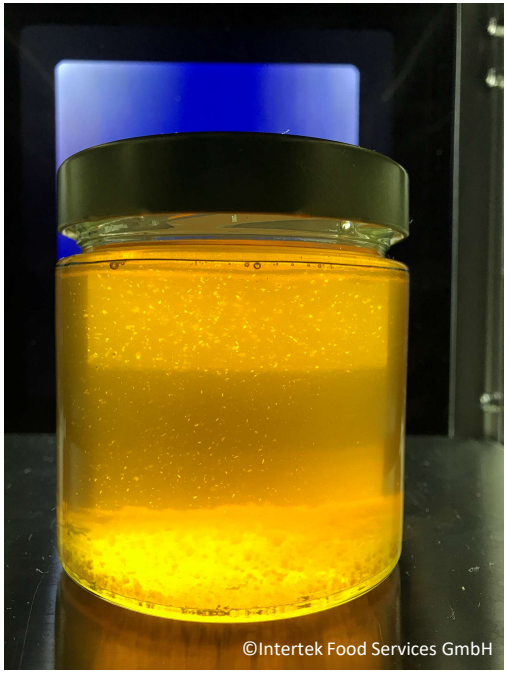
Several areas of application

Recommendation of accelerated storage condition

Recommendation for result evaluation

CRYSTEK

Without CRYSTEK



With CRYSTEK

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