



NMR a Powerful Technique for Supply Chain Integrity & Brand Protection in the Food Industry



Technical Meeting, 15.04.2021

Thomas Spengler
Sr. Market Manager Food
Bruker BioSpin GmbH

- Food Fraud – A Global Problem
- The Impact of Economically Motivated Adulteration
The Need for Multi-Marker & Non-Targeted Methods to Tackle Dynamic Fraud in Food
- NMR a Powerful Technique for Chain Integrity and Brand Protection in the Food Industry

Food Fraud – a Reality Worldwide

food fraud costs 49\$ billion/year!



FINANCIAL EXPRESS

Food fraud: Ten states unable to ensure food security; 15% of all samples sub-standard

By: FE Online | Updated: Jun 03, 2020 5:08 PM

India is facing a food fraud problem with about ten states unable to ensure food safety and 15% of food samples failing to pass quality tests.

The Gazette

Police seize 1,305 bottles of adulterated olive oil in Greater Victoria

Five establishments were inspected and three brands are being investigated by the Specialized Consumer Protection Department (Decon)

BBC NEWS

Home US Election Coronavirus Video World UK Business More

EL ESPAÑOL

The war between Félix Solís and García Carrión over Valdepeñas wine, on its crucial day due to fraud

Both wineries are by the Castilla-La Mancha Ministry of Agriculture for alleged fraud in the labeling of wine.

July 9, 2020 - 02:55

Blog Sicilia

Nas of Catania seizes seven tons of honey sold without traceability

THE TRADER DENOUNCED

by Editorial staff | 09/03/2020

US beekeepers fear for their future

By Pamela Parker
Business reporter, BBC News, California

26 June 2020

Facebook Twitter Email Share

Olive Oil Times

Brazil Reveals Widespread Olive Oil Fraud

Brazil's Ministry of Agriculture, Livestock and Farming reported that sixty-four percent of olive oil analyzed in the last two years did not meet the quality standards required by their labeling.

Apr. 20, 2017 | By Julie Al-Zoubi

7.6k

Region Murcia Cartagena Lorca Molina Sewer Mazarron Eagles Yecla Pacheco

Extra virgin olive oil leads food fraud cases

15% of the samples analyzed by inspectors in shops belonged to a product of lower quality than advertised

Tuesday, September 8th 2020

THE COURIER.CO.UK

NEWS POLITICS SPORT BUSINESS LIFESTYLE OPINION SUBSCRIBE

The sticky issue of 'honey laundering' and how a new Kitemark aims to protect local produce

Rebecca Shearer lifts the lid on the global problem of fraudulent honey-making and hears how a new initiative aims to give consumers confidence in the products they're buying.

July 13 2020, 6:00pm

by Rebecca Shearer

The Covid Pandemic is Causing a Rise in Global Food Fraud



Extract for the press article:

- *Europol said that its annual Operation OPSON which targets trafficking of counterfeit and substandard food and beverages, last year “found a new disturbing trend” in the infiltration of low-quality products into the supply chain. It said this development was “possibly linked” to the pandemic.*
- *“As countries around the world continue their efforts to contain Covid-19, the criminal networks distributing these potentially dangerous products show only their determination to make a profit,” said Jürgen Stock, Interpol secretary general at the time.*
- *Analysis by the government-backed Food Authenticity Network found a 37% rise in food fraud cases taken from official sources and media reports.*
- *Data from first half of 2020 was compared with same period in 2019. The worst hit categories were spirits, wine and honey.*
- *Research by the Wageningen Food Safety Research Institute, published in October, found food supply chains were increasingly vulnerable to fraud as a result of the disruption caused by the pandemic.*

Published 28.01.2021 <https://www.thegrocer.co.uk/food-safety>

Food Fraud – a Reality Worldwide

Example Honey



A screenshot of an Alibaba.com product listing. At the top, a search bar contains the text "rice syrup for honey" with an orange search icon. Below the search bar is a small image of a glass of yellow liquid. The main product listing is for "Fructose Syrup for Honey (BS SMR TMR C3 C4 C13 test pass F55)". The price is listed as "\$550.00-\$700.00 / Metric Ton" for a "5 Metric Tons (Min Order)". The seller is "Hangzhou Focus Corporation" from China (CN), with 9 years of experience. The listing includes a 97.3% response rate, over \$60,000 in transactions, and a "Good supplier" badge. There are buttons for "Contact Supplier", "Chat Now!", and "compare". A "TOP" button is also visible. At the bottom of the listing, there is a link to "Brix 80% DE28 GMO-FREE Brown Rice" and a "Messenger" icon.

- Sugar Syrups to adulterate Honey can be found in portals like Alibaba, OkChem.

<https://www.downtoearth.org.in/news/health/the-honey-trap-74476>

The Impact of Food Fraud

Example: Honey



IT'S NOT HONEY

DANGEROUS Almost all honey tested was found to be adulterated with sugar syrup

DEBARRATE Chinese companies have imported sugar syrup that can harm almost everyone

DEVASTATING Our health and livelihood of beekeepers are at risk

DOWNLOAD PDF

RAM GOPAL SINGH
Beekeeper
Bharatpur, Rajasthan

OM PRAKASH
Beekeeper/trader

MOHD AZIM ANSARI
Beekeeper/trainer,
Saharanpur, Uttar Pradesh



How can a beekeeper survive? We spend ₹90-100 to produce 1 kg of raw honey. But the prices of raw honey have fallen to ₹60 per kg. No wonder more and more beekeepers are leaving the profession

RAM GOPAL SINGH
Beekeeper
Bharatpur, Rajasthan



Since 2015, the only story you will hear from beekeepers is that they are facing big losses. Prices have been falling and our expenses have risen dramatically. In the last four years, I have suffered a loss of more than ₹20 lakh

OM PRAKASH
Beekeeper/trader



The health of the consumers and the livelihood of beekeepers are affected because traders are illegally adding syrup to honey. If there are no beekeepers and bees who will pollinate the fields? This is the biggest threat to agriculture and to food security

MOHD AZIM ANSARI
Beekeeper/trainer,
Saharanpur, Uttar Pradesh

Threat to viability of beekeeping industry & food security

- “ We spent aprox. 1,30US\$ to produce 1kg of raw honey, but the prices have been fallen to 0,82 US\$/kg.”
- “Prices have been fallen and our expenses have risen dramatically. Last month I suffered a loss of more than 27.000 US\$.”
- “If there are no beekeepers and bees who will pollinate the fields? This is the biggest threat to agriculture and to food security.”

<https://www.downtoearth.org.in/news/health/the-honey-trap-74476>

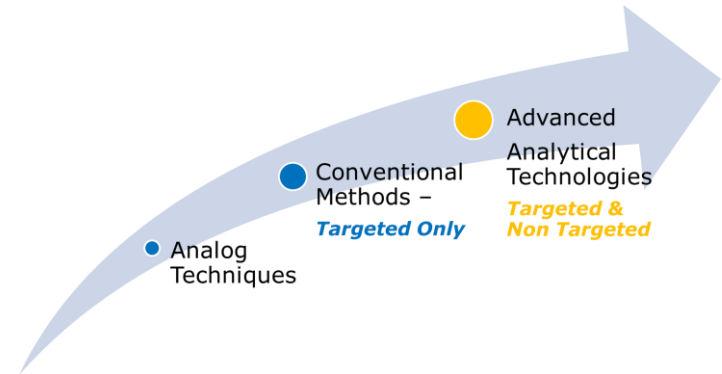
- 79% of consumers that participate in the survey state: it is important for brands to provide guaranteed authenticity, like certifications, when they're purchasing goods.
- Within this group, 71% are willing to pay an added premium (+ 37%) for companies offering full transparency and traceability.

Food Fraud, A Global Problem

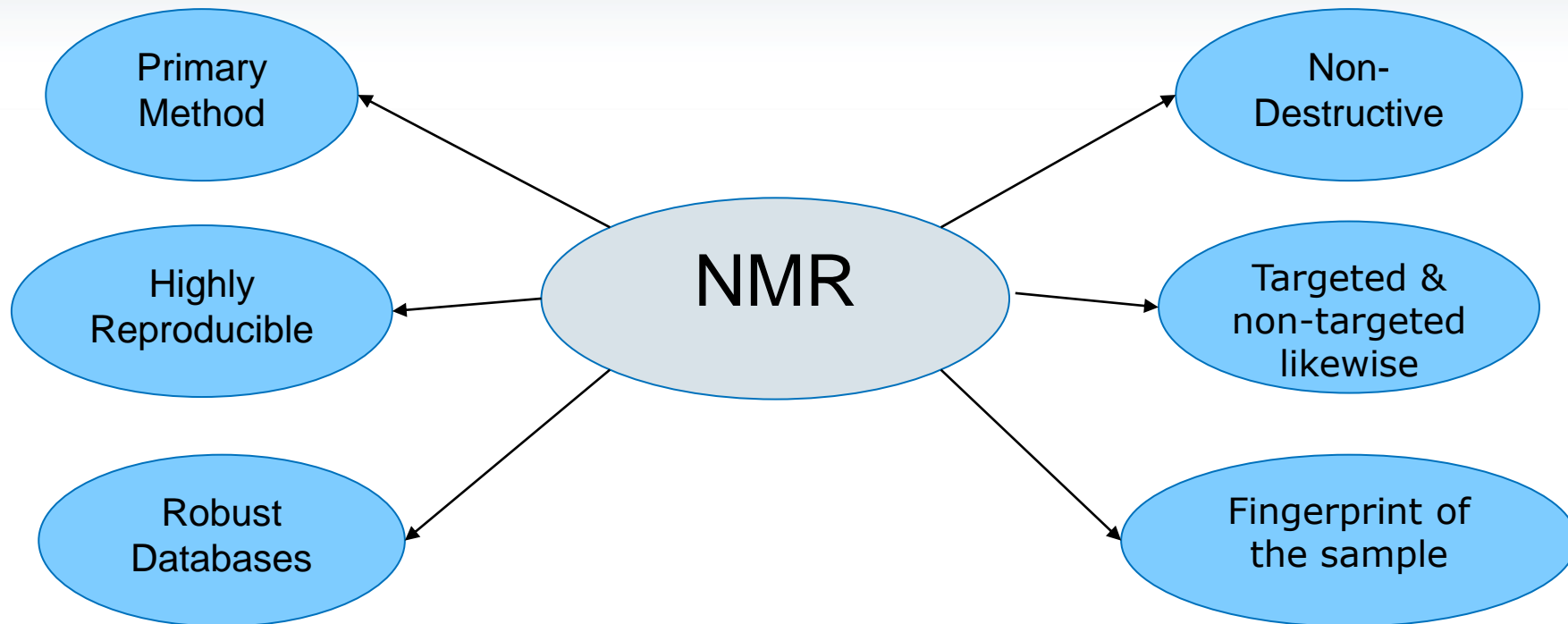
The Need for Non-Targeted Methods to Tackle Dynamic Fraud



- Besides quality and safety, consumers are increasingly concerned about the authenticity of the food products they consume.
- As a consumer I want to know what is in the food I am eating.
- Adulteration of food products is a major concern.
- Adulteration can lead to unfair market competition. It damages reputation of a country, a region or a company and erodes consumer's confidence.
- Current conventional techniques are not able to detect new modes of adulteration.



1H-NMR: A Powerful Technique for Food Authenticity Control



Pre-requisite: usage of **common SOPs**

Food Profiling by $^1\text{H-NMR}$

Process behind it



Non-targeted food profiling, as a fingerprint method, only works with a **representative NMR spectra database** in the background

Strict standardization and, whenever possible, **fully automated routines** of every single step minimizes "homemade" variations

This approach then emphasizes deviating spectral regions and signals of test samples, **indicating abnormalities** (like adulterations)



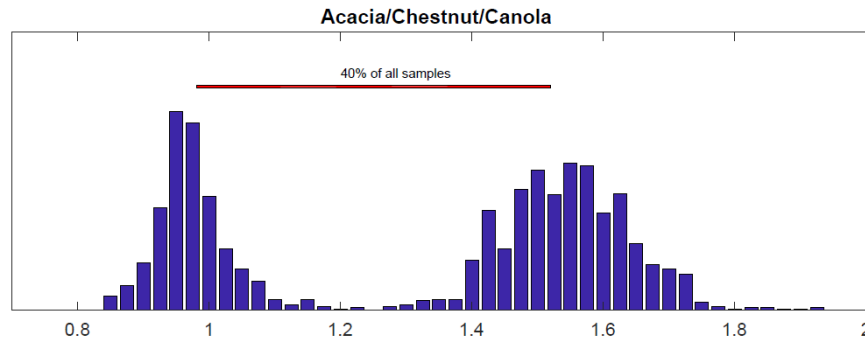
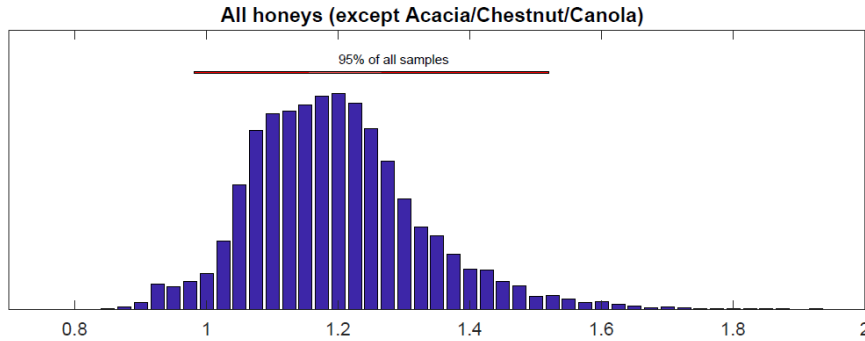
A sufficient number of (authentic) **reference samples** in this database is a prerequisite to generate statistical models

With the database entries and metadata, **models** are generated using a bundle of univariate and multivariate statistical techniques

Continuous feeding of the database with additional reference samples makes the models **increasingly robust and diagnostically conclusive**, and trails factors like climate change or genetic drift, which manifest in metabolic effects

The Importance of Databases:

Validation of Markers and Related Thresholds



Example of Fructose/Glucose ratio

- Independently of the analytical technique used (NMR, MS, HPLC-UV...) and of the parameter measured (unknown compound or identified molecule):

To define what is "normal", it is mandatory to have a set of representative samples, to make sure markers chosen are not naturally present in a specific type of food

➤ **AVOID THE RISK OF FALSE POSITIVE**
(= authentic sample detected as being adulterated)

Current Databases Based on 1H-NMR



	Fruit juice	Wine	Honey
Number of Samples	30.000	25.000	18.000
Quantifications (# compounds)	25	55	36
Statistical models	50 models	50 models	50 models
Version	3.0	3.1	2.0

Current cooperation partners

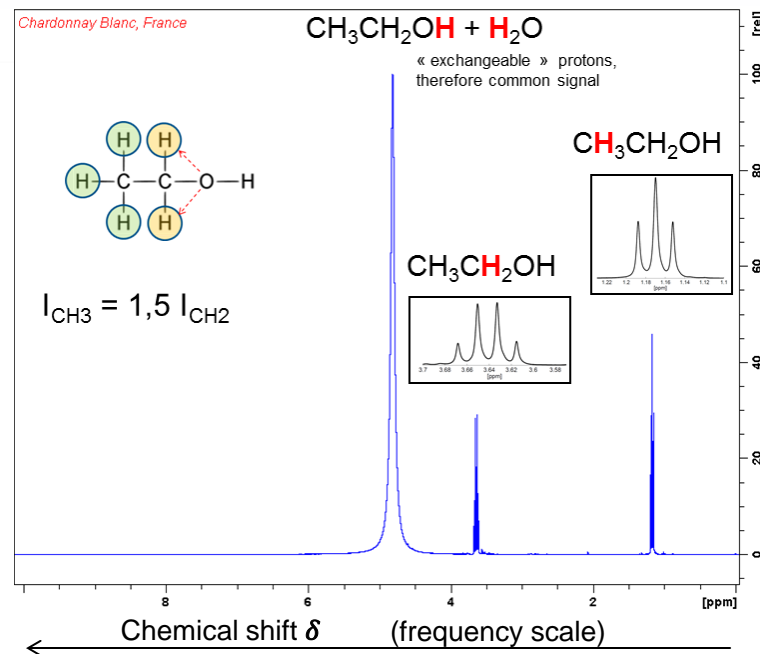


Direct Quantification by $^1\text{H-NMR}$



- The **signal patterns** (number of peaks, relative intensity of peaks, distance between peaks) are unique for each compound and can be used to **identify** them amongst other signals in a mixture.
- The **integral values** can be used to **quantify** the compounds, as long as their chemical structures and signal assignment is known.
- Integration gives concentration value [mg/kg]

Example: ethanol



Direct Quantification by 1H-NMR

Example: Honey



Sugars:

Compound	Value	Unit	LOQ	Reference Range	Flag
glucose + fructose *	71.9	g/100g	20.0	61.7 80.5	●
fructose / glucose *	1.33	-	-	1.17 1.40	●
fructose	41.0	g/100g	10.0	34.2 45.4	●
glucose	30.9	g/100g	10.0	27.1 36.1	●
sucrose	1.4	g/100g	0.5	<0.5 7.9	●
turanose	1.9	g/100g	0.2	0.9 2.4	●
maltose	2.6	g/100g	0.5	1.3 3.4	●
melezitose	<LOQ	g/100g	1.0	<1.0 g/100g in reference dataset	●
maltotriose	<LOQ	g/100g	1.0	<1.0 g/100g in reference dataset	●
gentiobiose	<LOQ	g/100g	0.3	<0.3 g/100g in reference dataset	●
raffinose	0.1	g/100g	0.1	0.1 0.2	●
mannose	<LOQ	g/100g	0.05	<0.05 g/100g in reference dataset	●

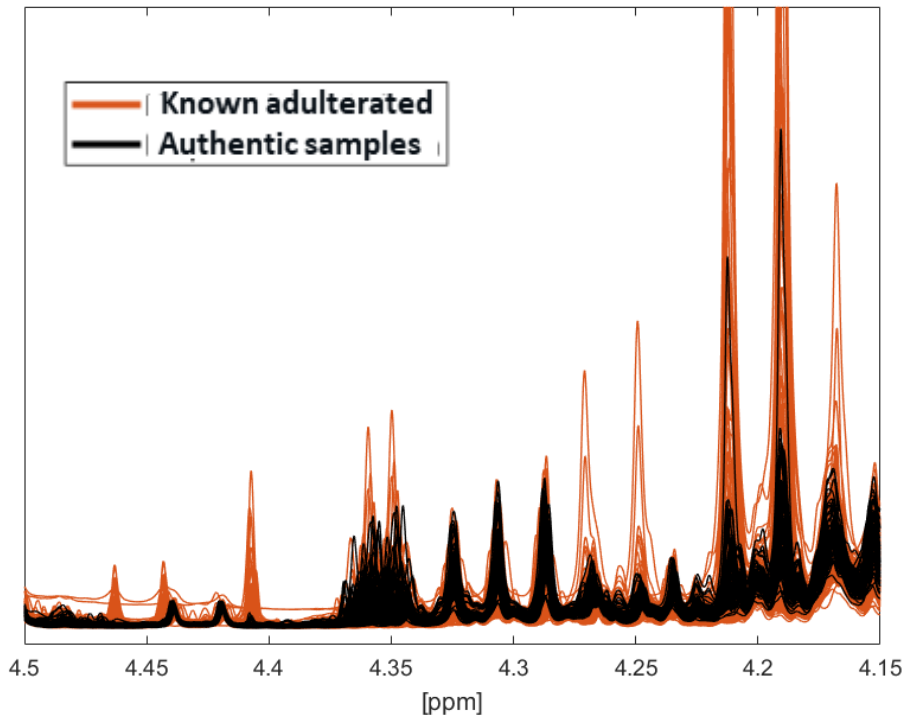
Amino Acids:

Compound	Value	Unit	LOQ	Reference Range	Flag
alanine	11	mg/kg	5	<5 24	●
aspartic acid	<LOQ	mg/kg	150	<150 mg/kg in reference dataset	●
glutamine	<LOQ	mg/kg	200	<200 mg/kg in reference dataset	●
leucine	<LOQ	mg/kg	40	<40 mg/kg in reference dataset	●
proline	428	mg/kg	150	223 723	●
valine	<LOQ	mg/kg	10	<10 13	●
tyrosine	<LOQ	mg/kg	50	<50 88	●
phenylalanine	<LOQ	mg/kg	100	<100 518	●

- **Proline:** <180mg/L) indicates addition of syrup
- **DHA & Mannose:** Presence indicates addition of syrup
- **Turanose:** <0.3% indicates addition of syrup
- **Ethanol** should not exceed 400 mg/kg
- **HMF:** Indicator for heating

Determination of Markers for Adulteration by $^1\text{H-NMR}$

Example: Honey



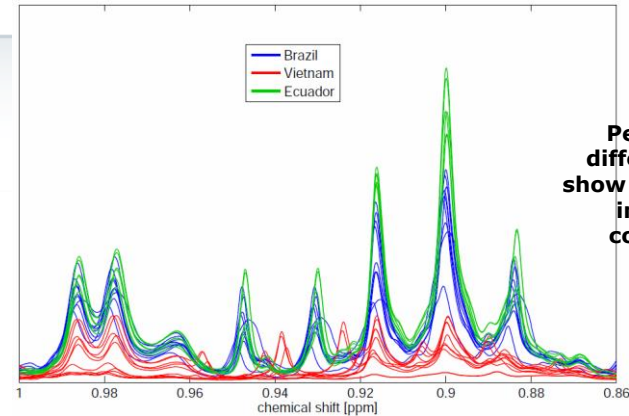
- The markers are identified by comparing authentic honeys with adulterated honeys from all over the world.
- A statistical approach determines the markers that are characteristic, are present or absent in adulterated honeys.
- Optimization: parameters are optimized in order to minimize the false positives results.
- The test is extensively validated and includes true positives, true negatives, false positives, false negatives,

Verification of Origin by $^1\text{H-NMR}$

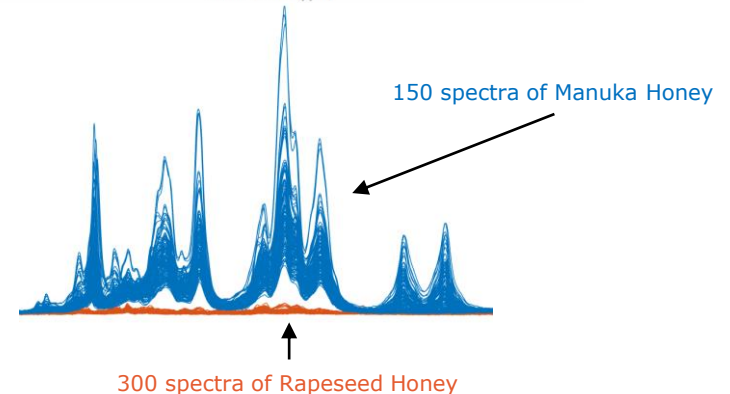
Examples: Pepper (country) & Honey (botanical variety)



- This test uses the complete $^1\text{H-NMR}$ profile, which contains hundreds of signals and is highly reproducible.
- The models are built based on combination of $^1\text{H-NMR}$ with statistical analyses (LDA/QDA).
- **Automated pattern recognition to check consistency with botanical variety.**



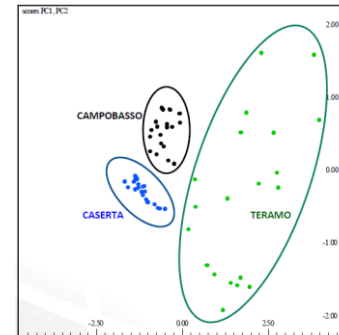
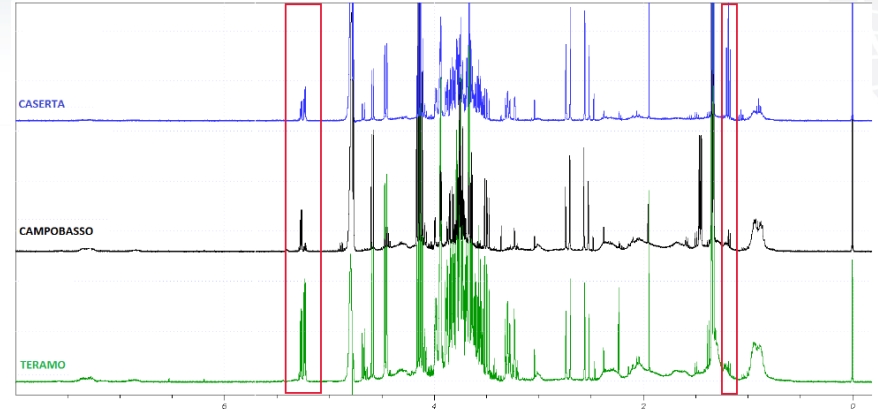
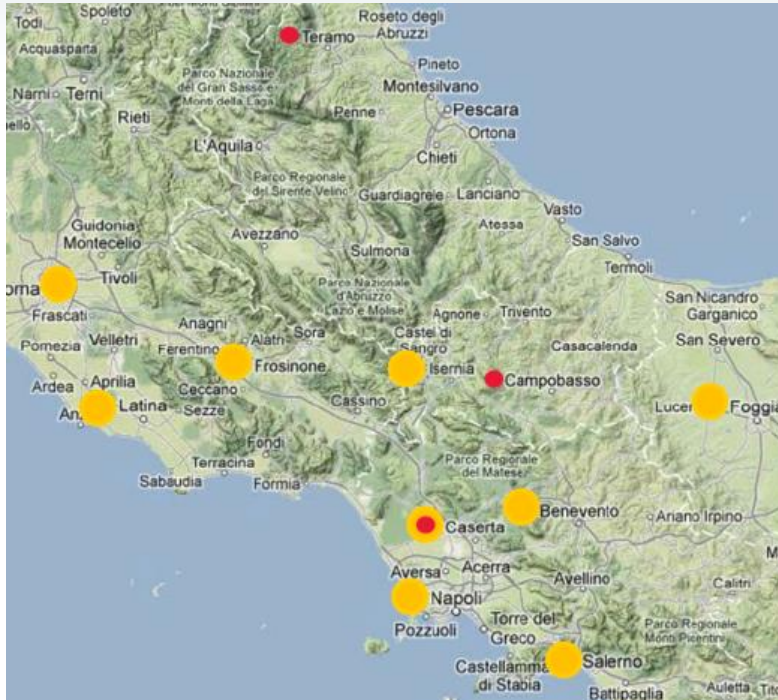
Peppers from 3 different countries show clear differences in component concentrations



Figures shows approx. 3% and 1,5% of NMR-Profiles

Differentiation of Regions by $^1\text{H-NMR}$

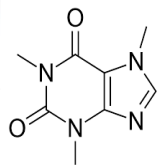
Example: Mozzarella di Campania Cheese



Differentiation of Coffee Types by $^1\text{H-NMR}$

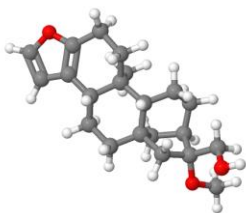
Example: Robusta vs. Arabica

Measured on a 80Mhz Benchtop System

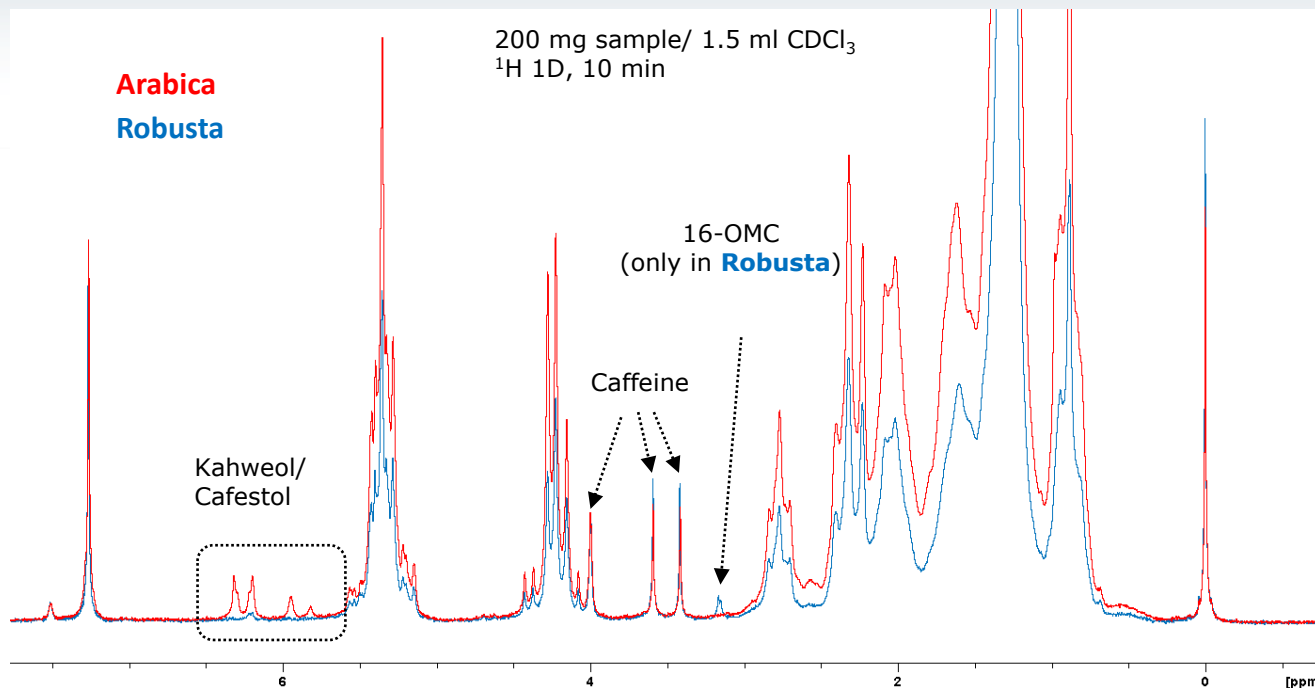


Caffeine

16-OMC is considered a marker for Robusta > 1%



Kemsley et. al.
<https://doi.org/10.1016/j.foodchem.2017.12.034>



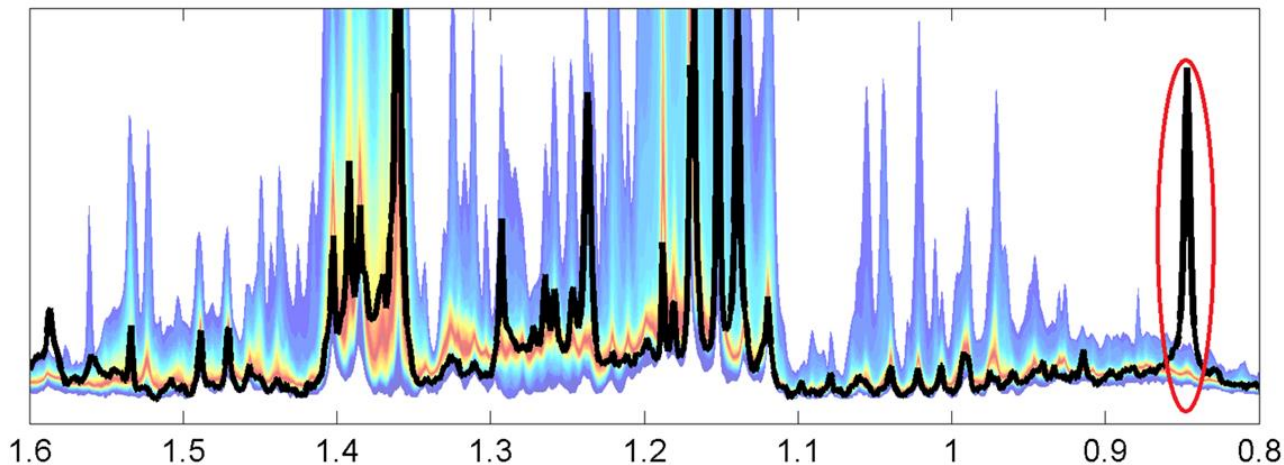
Non-Targeted Analysis by ^1H -NMR

Example: Manuka Honey



Official test for Manuka: **Compliant with mono-varietal Manuka honey**

Result with NMR: **Mixture of 47% Manuka honey with 53% Thyme honey**



Non-Targeted Analysis revealed several deviations in NMR-Profile:

6 elevated signals observed, not typical for Manuka (0.846ppm 0.850ppm 6.359ppm 6.363ppm 6.400ppm 6.404ppm)

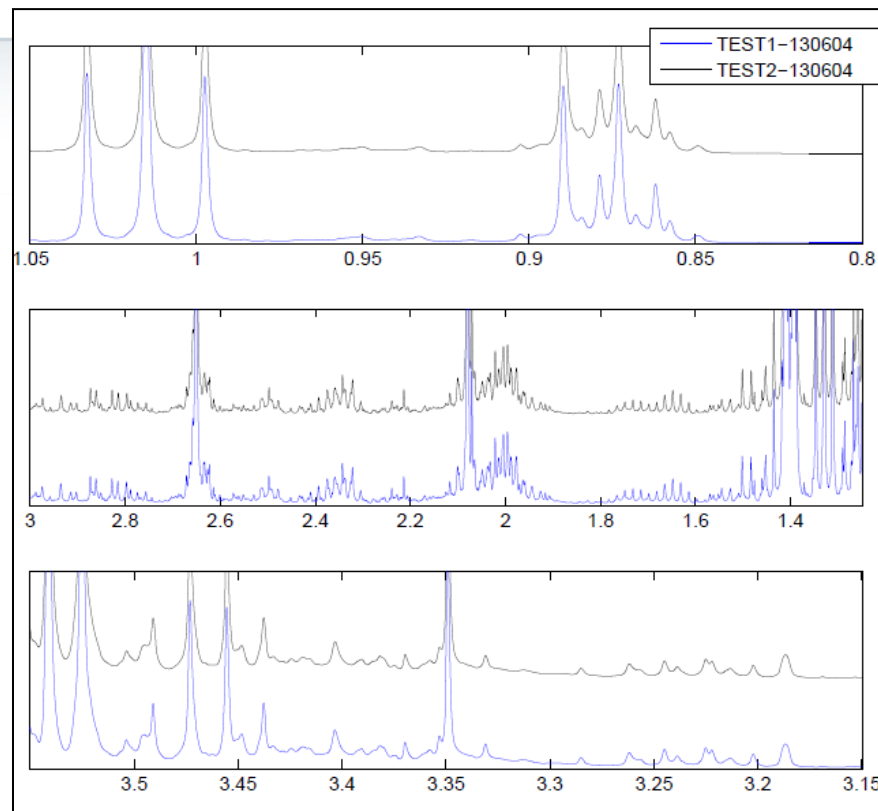
With the courtesy of QSI GmbH

Identity Test using $^1\text{H-NMR}$

Are the two food products the same?



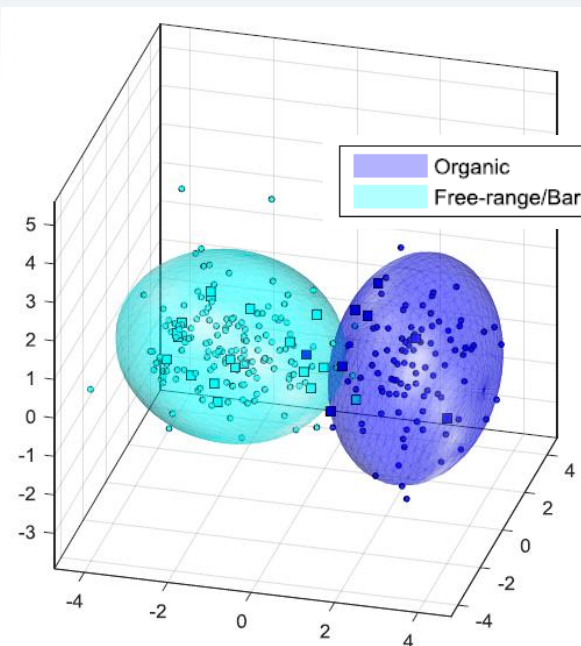
- No need for a reference database
- Analysis of the **whole fingerprint** by comparison to a reference food sample
- NMR as a tool to increase trust between seller and buyer



Examples of Food Products Already Being Tested in Routine Analysis by $^1\text{H-NMR}$

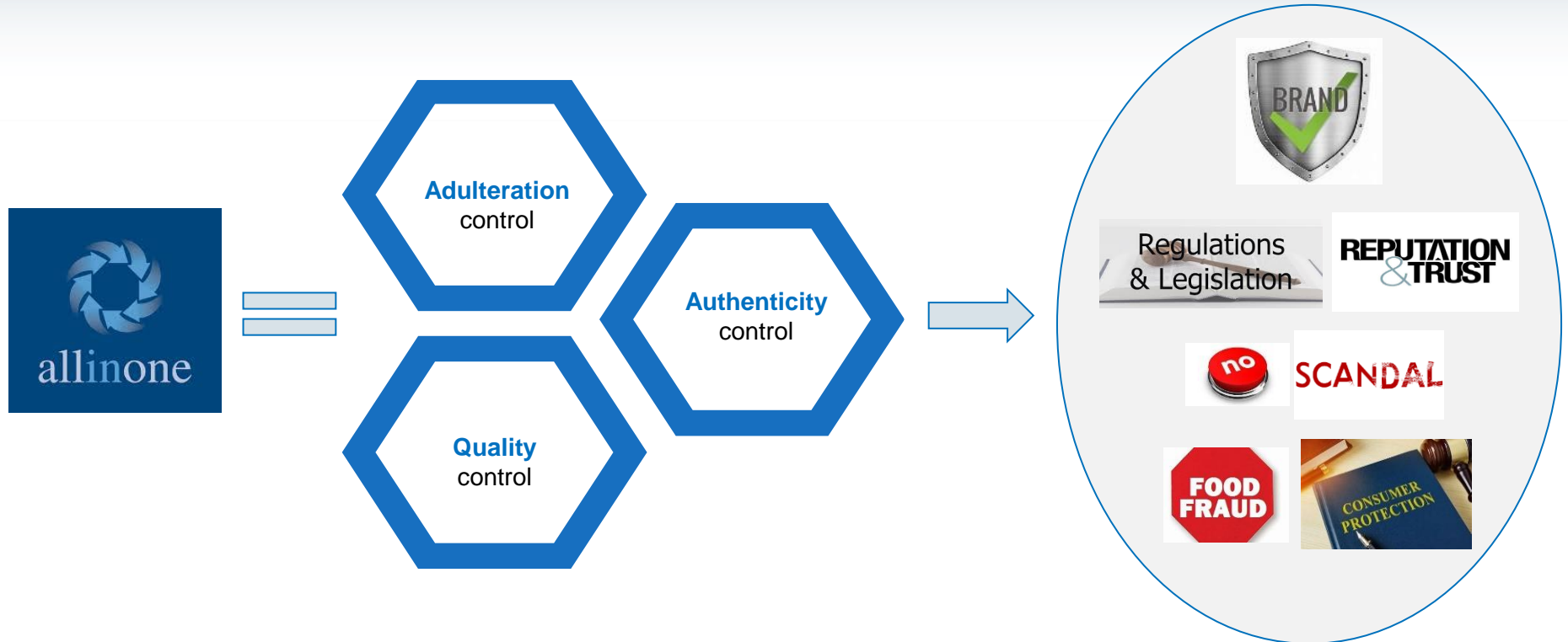


- Honey (authenticity, purity, quality)
- Wine (authenticity, purity, quality)
- Juice (authenticity, purity, quality)
- Coffee (Arabica vs. Robusta)
- Energy Drinks (Taurine, Caffeine, Sugar, Sweeteners)
- Milk / Milk Powder (Melamine, Phospholipid)
- Bread (Propionic Acid)
- Pine Kernels ("Pine Nut Syndrome")
- Spirits (z.B. Thujone in Absinth)
- Beer (Origin, Purity Law)



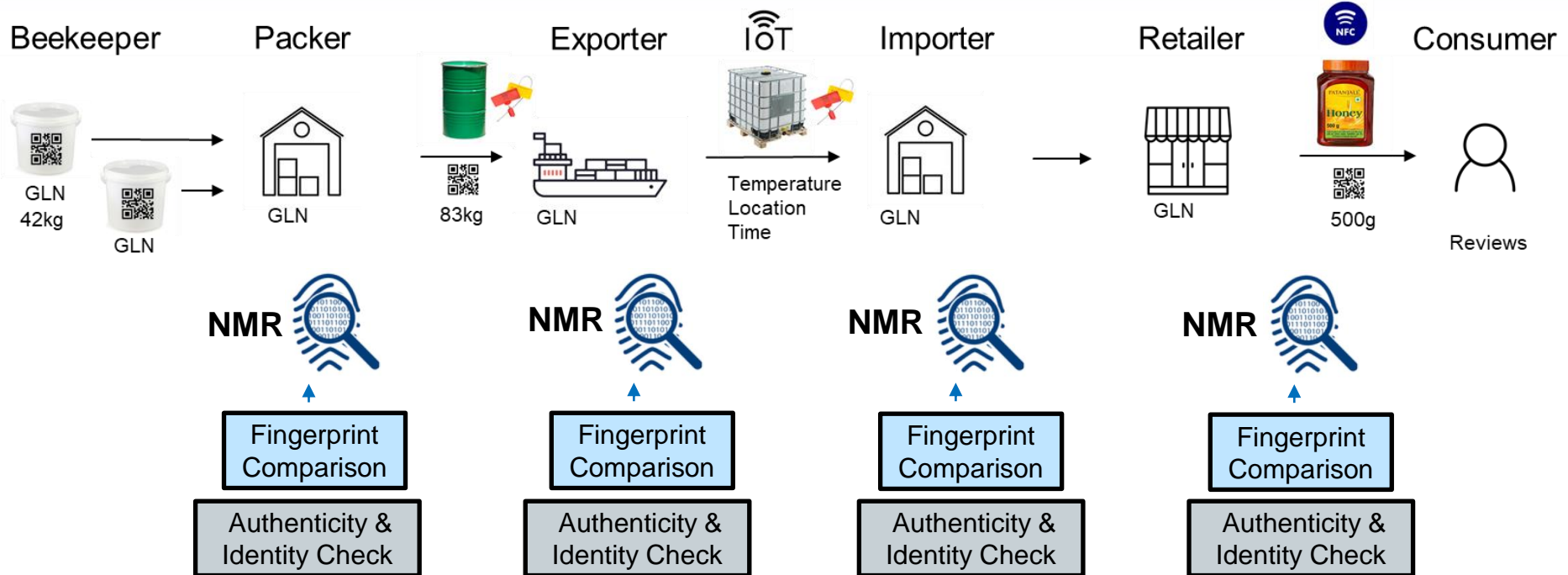
Feasibility Study by Svenja Ackermann
CVUA Karlsruhe

1H-NMR: an All in One Solution for Supply Chain Integrity & Brand Protection



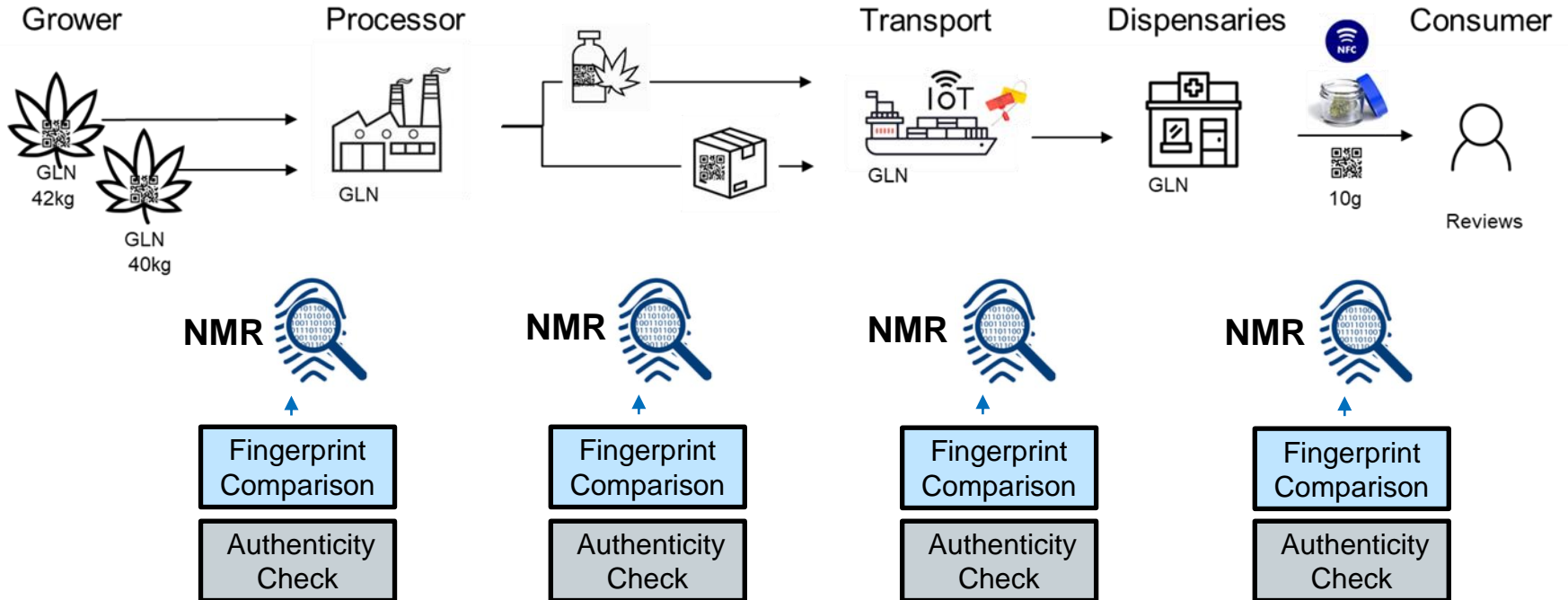
NMR a Powerful Technique for Enhancing Supply Chain Integrity & Brand Protection in the Food Industry

Example: Honey Supply Chain



NMR a Powerful Technique for Enhancing Supply Chain Integrity

Example: Cannabis Supply Chain



**It takes 20 years to build
A reputation and five
minutes to ruin it.
If you think about that
you'll do things
differently.**

-Warren Buffett

