Tackling the Fraudsters: Using NMR to Detect Adulterated Honey

Lea Heintz, Business Development and Product Management, Applied NMR, Bruker BioSpin

Honey has been valued throughout history, not only as a sweetener, but also as a medicinal remedy. It has been found in ancient Egyptian pyramids, preserved by its natural antibiotic and preservative properties, and in 1851 the creation of a worldwide beekeeping industry began with the invention of a practical movable-frame hive.

With the global honey market set to grow by 70% a year to 2023 [1], it comes as no surprise that increasing demand is placing strain on the industry. This demand, and the lack of international standardised rules for honey production, has become an incentive for fraudsters to adulterate honey. This poses a huge problem for many, including beekeepers who produce the honey and are undercut by cheaper products in supermarkets, and consumers who are unaware that there is fake honey on the market.

Elemental analyser isotope ratio mass spectrometry (EA-IRMS)/stable isotope ratio analysis (SIRA) is a common method used to detect honey adulteration, but it has proven unreliable as fraudsters have altered their fake honey to pass under the radar. Therefore, several methods have been developed to deal with the deficiencies of SIRA, with nuclear magnetic resonance (NMR) spectroscopy emerging as a more holistic approach to fighting honey fraud.

Powerful technologies, such as 1H-NMR, are emerging as a solution to this problem, enabling laboratories to identify fraudulent honey quicker.

Economically motivated adulteration (EMA) of honey globally

The high value of honey provides a strong economic incentive and puts it at risk of economically motivated adulteration (EMA). The product's perceived health benefits among consumers worldwide, who are willing to spend more for natural products, is a key driver in the projected growth of the honey market. For example, consumers in countries such as the United States, Japan, and Australia are demanding more mono-floral honeys or specialty honeys. As this demand continues to rise, supply grows short, as production in most countries has remained constant or declined, affected by bee diseases, deterioration of bees' natural habitats, and adverse climatic conditions. According to the U.S. Pharmacopeia's Food Fraud Database, honey ranks as the third food target for adulteration, behind milk and olive oil, and in Europe it is classed as one of the 10 most faked food products [2, 3].

With there being no U.S. federal standard of honey identity at this moment, regulatory efforts to ensure the safety and quality of the product are hindered. Currently, several types of EMA have been linked to the honey industry, including dilution with cheap sugar syrups, intensive supplemental feeding of honeybees, and masking the true country of origin. Ultrafiltration (or resin technology) enables fraudsters to mask the true origin and botanical varieties by removing the pollen as well as the chemical components which give color and flavor to honey. Additionally, a common practice in some countries is the harvest of unripe honey, which is done to increase the production yields. The honey is harvested with a moisture content of around 50% and is then artificially dried down to achieve a content of around 18%. As this honey is not properly ripened by the bees, it results in a product of an inferior quality that does not have the same properties as ripe honey.

While several countries have reported significantly increasing their honey exports, there has been little to no increase in beehive numbers and evidence highlights that fraudulent activity is vastly increasing (*Figure 1*).

Despite regulatory efforts, governing agencies and trade organisations have struggled to ensure safe, high quality, correctly labelled honey in the market. This lack of quality control has potentially far-reaching consequences for global honey prices and the livelihood of beekeepers.

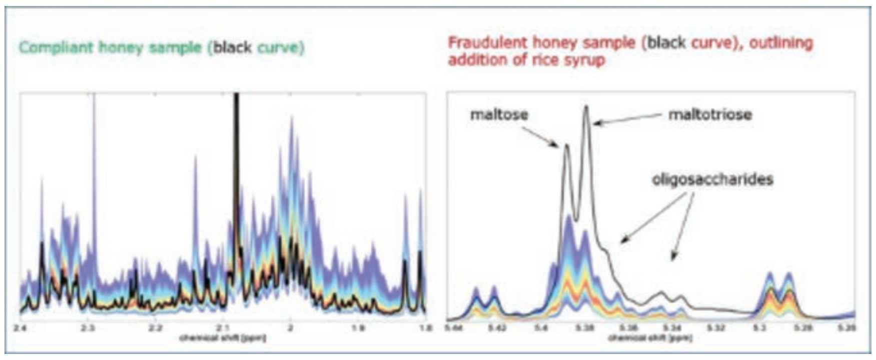

Figure 1: NMR Fingerprints of one sample of compliant honey and one sample of rogue honey.

Current testing methods

Several targeted methods currently exist for the detection of sugar syrups in honey. These methods are based either on the detection of foreign enzymes used to change the starches into sugars (e.g. β-fructofuranosidase, foreign amylases), or on specific markers of syrups (e.g. SM-R and TM-R). Evidence indicates that techniques have been found to remove these markers, and the cost of looking for specific markers of adulteration and the inability to keep up with the ever-evolving methods of adulteration have resulted in the amount of fake honey soaring tremendously in the last decade. As a result, non-targeted and multi-markers methods, which are not specific to a certain type of adulterant, are gaining more and more adoption.

The AOAC International method based on EA-IRMS/SIRA is only able to detect sugar syrups from C4 plants, such as corn and sugar cane, and is blind to sugar syrups from C3 plants, such as rice and beet. Fraudsters have exploited this and altered their methods to include beet and rice syrup to increase product volume. The new NMR honey database suggests that the EA-IRMS test only detects the adulteration in 23.9% of adulterated samples. A negative result with EA-IRMS therefore cannot be considered as proof of honey authenticity and is no longer a reliable method.

Liquid chromatography combined with isotope ratio mass spectrometry (LC-EA-IRMS) can also detect different kinds of sugar additions. However, the methods developed based on LC-EA-IRMS suffer from a lack of inter-laboratory reproducibility due to the usage of non-standardised methods for data acquisition and processing, as well as the usage of different parameters and related reference values (purity criteria) to assess the presence of sugar syrups in honey. Furthermore, some syrups that have a similar isotopic pattern to honey make detection challenging.

Over the years, the amount of adulteration detected by these methods has decreased massively, therefore the necessity for a more harmonised, universal, analytical method is required in order to tackle honey fraud.

NMR: the solution

NMR offers a more holistic approach and over the past ten years research has been undertaken to demonstrate its potential for food authenticity analysis. With 1H-NMR spectroscopy, the honey composition is analysed as hundreds of chemical constituents are observed simultaneously, ranging from high concentration of several hundred g/kg down to the low parts per million (ppm) range, including sugars, acids, and amino acids. This generates a 'fingerprint' and, using a database of honey fingerprints, users can compare the tested sample with all reference samples, in order to check for compliance. This quickly allows to detect the presence of sugar syrups, but also to check compliance of declared country of origin and botanical source. Furthermore, comparison with reference samples from the same floral source allows quick deduction of atypical profiles which can then be investigated further, detecting new methods of fraud as they are implemented.

It is the high reproducibility of NMR that allows it to create such a robust database of reference samples (fingerprints) and to make sure that the variations observed between spectra are real and not due to analytical drift. Once the fingerprint is acquired, the data can be reprocessed at any time using new techniques and algorithms, even years later and compare this to the honey database, which currently contains 18,000 reference samples, covering more than 50 countries and 100 botanical varieties. It also includes 1,900 known adulterated honeys with sugar syrups, which is necessary to identify the specific markers of adulterated honeys compared to pure honey. An example comparison of a single compliant honey sample and a fraudulent honey sample (*Figure 1*) shows how the adulterants can be identified.

Due to its unique universal capabilities, 1H-NMR, combined with multivariate statistical chemometrics, is proving to be a powerful tool for determining the authenticity and quality of honey which permits the preparation of a detailed analysis report (*Figure 2*).

Results Summary

Type of Analysis	Result	Status
Analysis of declared information		
Origin New Zealand	Consistent	●
Variety Manuka	Consistent	●
Detection of Sugar Syrups	No	●
Codex Alimentarius and EU-Directive 2001/110/EC	Compliant	●
Quantitative Analysis	Typical concentrations	●
Monofloral Manuka: 3-phenyllactic acid	Compliant	●
Non-Targeted Analysis		
Univariate Verification	Consistent	●
Multivariate Verification	Consistent	●

The data analysis is performed at Bruker BioSpin GmbH (Rheinstetten, Germany) according to testing method AA-54-03 (DIN EN ISO/IEC 17025:2005 Accreditation Certificate D-PL-19229-01-00). All results solely refer to the tested sample as provided by the customer.

Figure 2: Detailed analysis report for a single honey sample showing compliance.

Fighting fraud in the future

Food fraud is a major issue threatening the beekeeping community. As fraud continues to grow, consumers will lose confidence in honey and standard methods for determining authenticity are proving no longer effective.

The combination of NMR with statistical analysis represents a powerful alternation for the analysis of honey authenticity and its country of origin. Technologies, such as the FoodScreener™ platform, are meeting the demand for reliable testing, with emerging software modules such as Honey-Profiling™, to tackle these issues and make it very hard, likely impossible, for fraudsters to continue to deceive tests by the addition of foreign chemicals and syrups. In doing so, fraud can be exposed quickly and successfully without unreasonable expense.

For more information on the FoodScreener Honey Profiling 2.0, please visit https://www.bruker.com/products/mr/nmr-food-screening/honey-profiling-module-of-the-nmr-foodscreener.html.

References:

1. Marketresearchfuture.com. (2018). Honey Market Size, Share, Trends, Global Industry Analysis, 2023 | MRFR. [online] Available at: https://www.marketresearchfuture.com/reports/honeymarket-5139

2. Norberto L. García (2018) The Current Situation on the International Honey Market,
Bee World, 95:3, 89-94, DOI: 10.1080/0005772X.2018.1483814

3. Enhanced honey authenticity surveillance (2018 to 2019 Report), Government of Canada, https://inspection.gc.ca/about-the-cfia/science-and-research/our-research-and-publications/report/eng/1557531883418/1557531883647

About the author

Léa Heintz graduated with a Master of Science in Analytical Chemistry. She worked several years as an application scientist at Bruker, developing NMR methods for food matrices to monitor authenticity and quality. She is now working as a business development and product manager for the Applied NMR portfolio which comprises the FoodScreener platform and its screening methods.