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Detection of honey adulteration of high fructose corn syrup by Low Field Nuclear Magnetic Resonance (LF ^{1}H NMR)

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ABSTRACT

The effect of honey adulteration by high fructose corn syrup in different concentrations from 0% (pure honey) to 100% (pure high fructose corn syrup) was investigated using Low Field Nuclear Magnetic Resonance spectroscopy (LF ^{1}H NMR) and physicochemical analytical methods. The LF ^{1}H NMR data were analyzed by bi-exponential fitting and compared with physicochemical data. The physicochemical parameters demonstrated that water content, water activity, pH and color differed significantly in honey samples adulterated with different concentrations of high fructose corn syrup. These differences were also observed by transverse relaxation (T_2). Bi-exponential fitting of T_2 resulted in the observation of two water populations in all samples, T_{21} and T_{22}, with relaxation times in the range of 1.26–1.60 ms and 3.33–7.38 ms, respectively. Relaxation times increased with higher percentages of high fructose syrup in adulterated honey. Linear correlations were observed between the T_2, T_{21} and T_{22} parameters and physicochemical data, suggesting that LF ^{1}H NMR can be used to discriminate pure blossom honey from honey adulterated with high fructose corn syrup.

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1. Introduction

In recent years, limited production of honey caused a rise in honey prices, and in turn, an increase in honey adulteration by producers through the addition of different commercial sugar syrups. Honey has become the target of adulteration with cheaper sweeteners in Brazil as well as in other countries. Honey is subjected to adulteration with inexpensive sweeteners, such as refined cane sugar, beet sugar, high fructose corn syrup and maltose syrup, resulting in higher commercial profits. Consequently, discrimination between adulterated and unadulterated honey and authenticity of honey has become a very important issue for processors, retailers and consumers as well as regulatory authorities. Research for newer, simpler, more sensitive and more economical procedures is ongoing (Ruiz-Matute et al., 2010).

Adulteration of honey can be detected by different analytical techniques, such as near infrared spectroscopy (Zhu et al., 2010), Elemental Analysis – Isotope Ratio Mass Spectrometry (EAIRMS) (Simsek et al., 2012), chromatographic (Cordella et al., 2003, 2005; Morales et al., 2008), and mass spectrometry (Cotte et al., 2007). Although these methods are useful to assess the adulteration of honey, they are time-consuming and can be expensive, requiring the development of fast, nondestructive, easy-to-use and sensitive analytical methods.

Recently, LF ^{1}H NMR has gained wide acceptance in the field of food sciences as a powerful method because of its advantages over other analytical techniques. It is a rapid, non-destructive, highly reproducible, and sensitive technique. In combination with chemometric techniques, LF ^{1}H NMR methods are successfully applied in quality control of food products such as porcine muscle (Bertram et al., 2001; Bertram and Andersen, 2007; Straadt et al., 2007), processed pork (Hullberg and Bertram, 2005), salmon (Aursand et al., 2009 and Aursand et al., 2010), shrimp (Gudjónsdóttir et al., 2011; Carneiro et al., 2013), crude oil (Ramos et al., 2009), egg (Laghi et al., 2005), ice cream (Lucas et al., 2005), herbs (Preto et al., 2013), cod (Erikson et al., 2004 and Aursand et al., 2008) and acidified milk drinks (Salomonsen et al., 2007).

In LF ^{1}H NMR studies, proton relaxation is described by the relaxation time constants T_1 (longitudinal) and T_2 (transverse), where T_2 relaxation decay in food is multiexponential, indicating the presence of different water populations in the foods matrixes (Belton, 1990; Bertram et al., 2001; Finch et al., 1971). Different tissue water populations can be studied because protons in different

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environments exhibit different T_2 relaxation properties. Most studies have reported 2 or 3 different water populations in food matrix, with transversal relaxation times dependent on the environment of the protons in each water population. Honey is a very complex multi-component system and its LF ^{1}H NMR relaxation profile can be modeled as a linear combination of characteristic relaxation times from the measurable hydrogens present in their structure. (Ribeiro et al., 2014).

The aim of this study was to evaluate the potential of LF ^{1}H NMR parameters and physical and chemical measurements (pH, water activity, color, moisture and ash contents) to differentiate between adulterated (high fructose corn syrup added) and unadulterated pure blossom honey samples.

2. Materials and methods

2.1. Collection and storage of samples

This study was carried out at a farm in the mountainous region of Rio de Janeiro in the South-East of Brazil. Bee colonies were kept in Teresópolis (22° 24′ 44″ S, 42° 57′ 56″ W). Pure blossom honey samples ($n = 30$) were collected by beekeepers and stored at room temperature (18–23 °C) from the time of collection to spectral analysis (a maximum of 2 weeks after extraction from the hives). Honey samples were stored in the dark in screw-cap jars at moderate temperatures, to prevent significant changes during storage.

2.2. Sample preparation

Mixtures were prepared using pure blossom honey samples and high fructose syrup. Pure model mixtures were prepared by adding high fructose syrup to honey samples at a ratio of 0%, 10%, 25%, 50%, 75% and 100% by weight. After adding the high fructose syrup, samples were kept in a water bath at 35 °C for 20 min and stirred for 1 min followed by cooling in an ice bath.

2.3. Physicochemical measurements

Moisture was determined with an Abbe refractometer. All samples were measured at 20 °C after a 6 min wait time to allow them to reach temperature equilibrium with the refractometer. The refractive index of honey samples was correlated using Chataway Charts (AOAC, 1990).

The pH of honey was measured with a pH meter (Digimed® Model DM-32, São Paulo, Brazil). The electrode was immersed in a suspension made by mixing 10 g of honey with 75 mL of distilled water (AOAC, 1990).

Color intensity was measured with a Minolta CR-400 colorimeter (Konika Minolta®, Tokyo, Japan) according to the manufacturer's instructions.

Ash contents were determined with a weighed sample ignited in a muffle furnace at 550 °C until a constant weight for carbonization was reached.

Water activity (A_w) was measured with a Pawkit meter, by Decagon Devices, USA, using a small aliquot of honey with a weight of approximately 1 g. This measure of water activity is based on the equilibrium relative humidity (ERH) of the sample. Measurements were performed in triplicates for each sample and the mean was determined.

2.4. Low field NMR measurements

For the LF ^{1}H NMR measurements, a bench-top NMR analyzer with a working frequency of 13 MHz was used (MARAN DXR 2, Oxford Instruments®, Osney Mead, Oxford, UK). Measurements were performed on 15 g samples at 25 ± 1 °C in NMR tubes (50 mm diameter). All samples were analyzed in triplicate. The transverse relaxation time (T_2) was measured with a Carr–Purcell–Meiboom–Gill (CPMG) pulse sequence (Carr and Purcell, 1954; Meiboom and Gill, 1958), with 10 scans, 256 points, 100 ms between scans, and 100 μs between pulses of 90° and 180°. The LF-NMR relaxation curve was fitted to a multi-exponential curve with the software RI-WINFIT (version 2.5, Oxford Instruments®). Analysis of the exponential fits indicated that two exponentials were sufficient to describe the system for all samples. Bi-exponential fitting thus resulted in two water populations, with corresponding relaxation times T_{21} and T_{22}. T_2 distributions were obtained using the software WinDXP, version 1.8.1.0 from Resonance Instruments®, distributed by Oxford Instruments®.

2.5. Statistical analysis

A one-way analysis of variance (ANOVA) with repeated measures was used to identify differences between pure and adulterated honey for each relaxation time (T_2 and T_{21}, T_{22}) and physicochemical parameters. When a significant F was found, additional post hoc tests with Bonferroni adjustment were performed. Pearson correlations were used to examine the relationship between each physicochemical (moisture, pH, water activity, ash content, sugar content and color) and each transversal relaxation parameter (T_2 and T_{21}, T_{22}). Statistical significance was set at the 0.01 confidence level. All analyses were performed with a commercially available statistical package (SPSS Inc., Version 17.0 Chicago, Illinois).

3. Results and discussion

The range of the honey samples adulterated with high fructose syrup and of unadulterated pure blossom honey samples for LF ^{1}H NMR data and physicochemical obtained is given in Tables 1 and 2 respectively. In order to get an overview of the main variation between the pure blossom honeys samples and the effect of the experimental adulterated honeys.

3.1. Low field NMR results

We measured the LF ^{1}H NMR of honey samples adulterated with high fructose syrup and of unadulterated pure blossom honey samples and established their physical and chemical properties. Our purpose was to evaluate the relationship between these parameters, and to test its applicability to the discrimination of pure honey from adulterated honey of different percentages. A

Table 1
Range of the LF ^{1}H NMR parameters obtained in honeys according to samples adulterated with high fructose corn syrup.

Adulteration (%)	T_2 (ms)	T_{21} (ms)	T_{22} (ms)
Pure honey	5.90 ± 0.07[a]	1.60 ± 0.08[a]	7.38 ± 0.10[a]
	(5.74–5.94)	(1.45–1.79)	(7.23–7.54)
10	5.30 ± 0.10[b]	1.51 ± 0.10[b]	6.55 ± 0.28[b]
	(4.73–5.55)	(1.36–1.67)	(5.90–6.91)
25	5.19 ± 0.11[c]	1.57 ± 0.12[b]	6.26 ± 0.25[c]
	(5.05–5.31)	(1.42–1.79)	(6.15–6.53)
50	4.21 ± 0.07[d]	1.48 ± 0.10[c]	5.69 ± 0.19[d]
	(4.11–4.34)	(1.41–1.72)	(5.44–6.00)
75	3.26 ± 0.12[e]	1.32 ± 0.16[d]	4.00 ± 0.18[e]
	(3.08–3.79)	(1.16–1.36)	(3.78–4.55)
100	2.67 ± 0.6[f]	1.26 ± 0.8[d]	3.33 ± 0.07[f]
	(2.61–2.75)	(1.12–1.32)	(3.54–3.87)

[a,b,c,d,e,f] Different letters in a column indicate significant differences ($p < 0.01$) between treatments (ANOVA).

Table 2
Ranges of physicochemical parameters (moisture, pH, ash, A_w and color) for honey adulterated with different percentages of high fructose corn syrup.

Adulteration (%)	Moisture (g/100 g)	pH	Ash (g/100 g)	A_w	Color		
					L^*	a^*	b^*
Pure honey	17.60 ± 0.5[a] (17.40–17.80)	3.10 ± 0.04[a] (3.08–3.15)	0.15 ± 0.1[a] (0.13–0.17)	0.51 ± 0.02[a] (0.50–0.53)	48.17 ± 2.12[a] (46.86–50.35)	7.88 ± 0.44[a] (7.61–7.98)	40.22 ± 1.84[a] (38.59–40.96)
10	18.20 ± 0.8[b] (18.00–18.60)	3.30 ± 0.03[b] (3.29–3.42)	0.17 ± 0.2[b] (0.16–0.18)	0.55 ± 0.3[b] (0.54–0.57)	51.79 ± 1.57[b] (49.98–53.21)	3.25 ± 0.49[b] (3.03–3.96)	38.19 ± 2.61[b] (37.52–39.97)
25	19.40 ± 0.10[c] (19.00–19.60)	3.68 ± 0.05[c] (3.66–3.69)	0.20 ± 0.1[c] (0.20–0.21)	0.58 ± 0.08[c] (0.57–0.60)	55.95 ± 2.29[c] (53.17–57.68)	8.44 ± 1.18[a] (8.28–9.49)	36.65 ± 1.59[b] (34.28–38.09)
50	20.20 ± 0.7[d] (20.0–20.60)	3.82 ± 0.02[d] (3.80–3.84)	0.25 ± 0.3[d] (0.23–0.26)	0.60 ± 0.01[c] (0.59–0.60)	68.65 ± 3.02[d] (67.44–70.81)	10.35 ± 1.3[c] (9.45–11.25)	33.28 ± 1.43[c] (32.81–33.45)
75	20.80 ± 0.6[e] (20.40–21.00)	3.98 ± 0.03[e] (3.97–4.00)	0.29 ± 0.3[e] (0.27–0.30)	0.66 ± 0.02[d] (0.65–0.67)	72.24 ± 1.10[e] (62.38–63.27)	11.33 ± 1.14[c] (10.12–13.25)	30.31 ± 1.51[d] (28.13–31.68)
100	22.80 ± 0.7[f] (22.60–23.00)	4.70 ± 0.08[f] (4.65–4.80)	0.31 ± 0.2[f] (0.30–0.32)	0.71 ± 0.01[e] (0.70–0.72)	74.60 ± 1.36[f] (63.46–65.26)	6.57 ± 0.62[d] (6.20–7.42)	27.74 ± 2.25[e] (26.87–29.47)

L^* (darkness), a^* (redness), and b^* (yellowness), A_w (water activity).
[a,b,c,d,e,f] Different letters in a column indicate significant differences ($p < 0.01$) between treatments (ANOVA).

variety of methods was used to examine the T_2 relaxation data: continuous distributed NMR relaxation curves, biexponential fitting of T_2 relaxation curves, and comparison of NMR and physical and chemical data.

3.1.1. Continuous distributed NMR (T_2) relaxation curves

Comparison of the continuous distributed curves revealed visible differences in the distribution of water mobility among the different percentages of adulterated honeys. The 100% adulterated samples tended to show a slightly broader T_2 distribution than other treatments. This behavior can be explained by high water activity in fructose syrup. T_2 has been related to water activity in other matrixes (Bertram and Andersen, 2007; Aursand et al., 2010; Carneiro et al., 2013). These differences can be explained by the amount of syrup added, which affects the water activity in adulterated samples.

3.1.2. Bi-exponential fitting of T_2 relaxation curves

Fig. 1 shows the distributed T_2 relaxation-time spectra of honey samples adulteration by high fructose corn syrup. The adulteration had a pronounced effect on the T_2 distributions. Comparison of the continuous distributed curves revealed visible differences in the distribution of water mobility between the adulterated honeys and unadulterated honeys. The LF ^{1}H NMR relaxation time method was used to investigate water mobility in honey samples. By bi-exponential fitting of the transverse relaxation data we were able to discriminate two water populations in all samples, one with a faster relaxation time T_{21} in the range of 1.26–1.60 ms, and another with a slower relaxation time T_{22} in the range of 3.33–7.38 ms, depending on the percentage of adulteration with high fructose syrup (Table 1). T_{21} (faster relaxation time) was slower in pure blossom honey (1.26–1.51 ms), indicating that water mobility was lower in unadulterated honey compared to the adulterated honey.

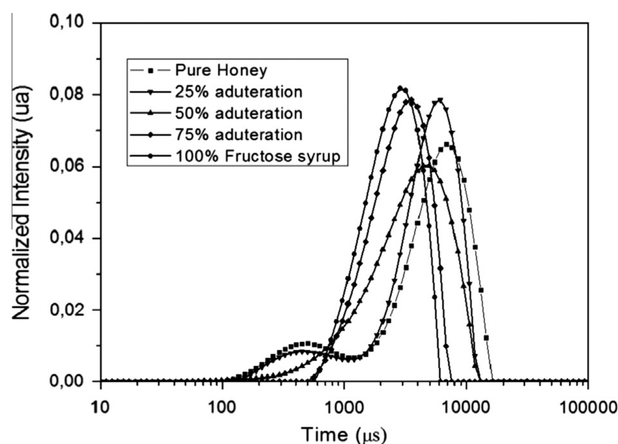

Fig. 1. Continuous relaxation time spectra of adulterated honeys and pure honey.

3.1.3. Comparison of NMR and physical and chemical data

Table 2 shows the means, standard deviations and ranges of the data obtained from the analysis of the different physical and chemical parameters (moisture, water activity, pH, color and ash contents). The results confirmed the hypothesis that the effects of addition of HFCS improved the quality characteristics of the honey.

We detected significant differences of moisture, pH, water activity, ash content and color ($p < 0.01$) between adulterated and pure blossom honey. ANOVA results (Table 2) showed that at relaxation time T_{21} all adulterated honey samples, including those at the 10% level, differed significantly from pure honey. This indicates that the relaxation time T_{21} changes in honey adulterated with high fructose syrup. Additionally, relaxation times T_{22} of all honey samples differed significantly from each other ($p < 0.01$), allowing to discriminate different percentages of adulteration. This model thus confirms the effectiveness of the screening and suggests that it can be a time-saving method for detecting high fructose corn syrup adulteration of honey.

Moisture, water activity and pH increase were associated with less T_{21} and T_{22} relaxation times in honey and were related to the percentage of adulteration with HFCS. Morales et al. (2008) described that adulteration with HFCS resulted in modifications of the honey samples' sugar composition. The modification on sugar composition with increase on HFCS can be associated with the increase on those parameters. Knowledge of the moisture in honey is useful to improve conservation and storage. High levels of humidity are important for honey because they affect other characteristics such as viscosity, fluidity and conservation (Acquarone et al., 2007). The moisture content of pure honey (17.65%) increased gradually as the percentage of the adulterant was raised (Table 2). As shown in Fig. 2, we observed a significant negative correlation between T_{21} and moisture ($r = -0.92$). At the 50% adulteration level the moisture content of 20.2% was close to the allowed limit for natural honeys (20%), which represents the critical moisture level for the keeping quality of honey (Codex Alimentarius, 2001 and EU Council, 2002). In contrast, at the 75% and 100% adulteration level, moisture exceeded the recommendation by the legislation.

Water activity was negatively correlated with T_{21} and T_{22} ($r = -0.86$ and $r = -0.91$, respectively). This parameter is important for stability, preventing or limiting microbial growth (Pelizer et al.,

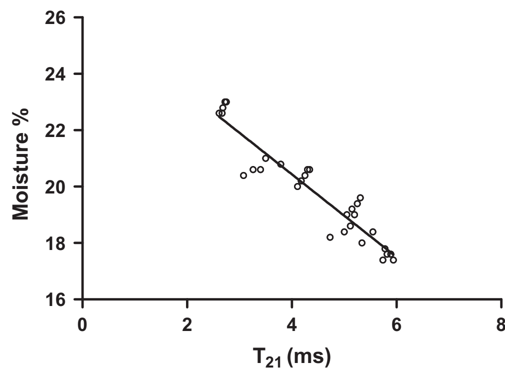

Fig. 2. Correlation between Transverse relaxation time (T_{21}) and water activity (A_w) in honeys, according to the different botanicals origins.

2003). Furthermore, other differences in the experimental conditions such as high fructose syrups content can affect the relaxation times (T_2 and T_{21}, T_{22}).

The pH values ranged from 3.10 to 4.70 for pure honey and adulterated honey samples. This parameter is of great importance during extraction and storage of honey because it influences its texture, stability and shelf life (Gomes et al., 2010). The low pH of honey inhibits the presence and growth of microorganisms and causes the honey to be compatible with many food products in terms of pH. A raise the percentage of the adulterant resulted in significantly increased pH values, and was also reflected in longer T_{21} and T_{22} relaxation times of adulterated honeys.

Ash values depend on the mineral content of honey and directly measure inorganic residue after carbonization. In this study, the ash content of pure blossom honey (0.15%) increased gradually as the percentage of adulterant was increased. Ash content was highly negatively correlated with relaxation time T_{22} ($r = -0.90$). The higher ash content of HFCS (0.17–0.31 g/100 g) may be related to the residues of acidic and alkaline solutions added to it. This increment was such that the ash for honey adulterated with 100% HFCS was more than twice that for pure honey (Table 2). The variability in the ash content of pure honeys could be due to harvesting processes, beekeeping techniques and the material collected by the bees during foraging (Finola et al., 2007), but in our studies the increases of ash content was observed in all samples adulterated with HFCS.

The color of the analyzed samples ranged from yellow to brown, depending on the percentage of adulteration. The color characteristics are summarized in Table 2 (means, standard deviations and ranges of the parameters L^*, a^* and b^*). Relaxation times (T_{22}) were correlated with the parameters L^* ($r = -0.87$), a^* ($r = -0.52$), and b^* ($r = -0.29$). The plot of parameters a^* and b^* shows that the analyzed honey samples had red, yellow and green components. Green components were indicated by the presence of negative a^* values in all samples, although a^* and b^* did not significantly differ in adulterated honeys. The parameter a^* in samples for this study are irregular, fact also previously reported for Bertoncelj et al. (2007), that demonstrated variation in honeys from same botanical origin.

The highest correlation coefficient found was for the relationship between T_{22} relaxation time and the L^* value of honey color ($r = -0.87$). The correlation was negative, indicating that lighter honeys have higher L^* values due to the percentage of adulteration. The progressively lighter colors and an increase in the relaxation time T_{22} were closely correlated with the decrease of the ash content ($r = 0.84$). The mineral content influences the color (González-Miret et al., 2005). The higher the content of metals and the darker the color, the stronger the honey will taste (Sancho et al., 1991). Surprisingly, the color of honeys in this study was also noticeably different and varied from pale yellow to dark brown.

4. Conclusions

In the present study, LF ^{1}H NMR was used to discriminate pure blossom honey from honey adulterated with high fructose corn syrup. Our results indicate that adulterated honey samples can be satisfactorily discriminated from pure blossom honey by using LF ^{1}H NMR. Relaxation times were significantly affected by adulterate concentration in pure honey, decreasing at higher fructose syrup concentrations. Significant correlations were found between relaxation times and physical–chemical parameters (pH, water activity and moisture content). We therefore conclude that LF ^{1}H NMR can be used to discriminate pure blossom honey from honey adulterated with high fructose syrup. However, in order to improve the model accuracy and stability, further studies need to test additional types of honey.

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