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Short communication

Comparison between Karl Fischer and refractometric method for determination of water content in honey

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ABSTRACT

The aim of this work was to compare refractometric index (RI) and Karl Fischer (KF) titration methods for water content measurement in honeys. In addition, the effectiveness of two different solvents (methanol (M) and methanol:formamide in the ratio 1:1 (M + F)) was evaluated.

Results indicated that RI and KF methods yielded similar results for water content determination in honeys; mainly, when the solvent M + F was used. This solvent mixture (M + F) also allowed a reduction in titration time which may be a potential advantage for measuring water content in honey.

1. Introduction

Water content is a quality parameter important for honey shelf life and is critical in order to prevent from microbiological spoilage; water content also affects some physical properties of honey, such as viscosity and glucose crystallization (Bogdanov, Ruoff, & Persano Oddo, 2004; Isengard, Schultheiß, Radović, & Anklam, 2001).

Water content of honey is usually determined by an indirect method based on soluble solids content estimation through the refractometric index (RI). Since the composition of honey solids may vary in different honeys, this affects the conversion of RI into water content. Thus, water content determination in honeys by refractometry does not yield exactly the "true" water content; nevertheless it is a simple, fast and reproducible method and for this reason is successfully used in routine honey control.

Gravimetric methods based on drying (with conventional oven or infrared drying) have been also used to determine water content of honey, but the high viscosity of the rubbery matrix formed during drying makes water diffusion difficult, which leads to an underestimation of water content. Besides, other volatile substances present in honey may evaporate, even those which might be produced by chemical reactions during the process itself (Isengard et al., 2001).

Karl Fischer (KF) titration is known to determine water selectively by a chemical reaction (Scholz, 1984). Despite it is an expensive and time-consuming method, it is considered the most accurate for determining water content; is to be noted that values obtained may somewhat depend on experimental conditions of titration (solvent utilized, temperature).

The aim of this work was to compare RI and KF titration methods for water content measurement in honeys. Moreover, in the case of KF the effectiveness of two different solvent systems were also evaluated.

2. Materials and methods

2.1. Honey

Honey samples of the 2006/2007 harvest were collected and packaged in glass flasks hermetically sealed. Sampling was carried out in honey production and bee-hive product areas of Santa Fe province, Argentina (28–35°SL; 58–62°WL). Twenty-two samples of floral origin were used in this study; about 50% were monofloral clover and 50% were monofloral alfalfa.

2.2. Fructose solutions

Model solutions consisting of supersaturated solutions of fructose (Laboratorio Ciccarelli, Buenos Aires, Argentina) in the water

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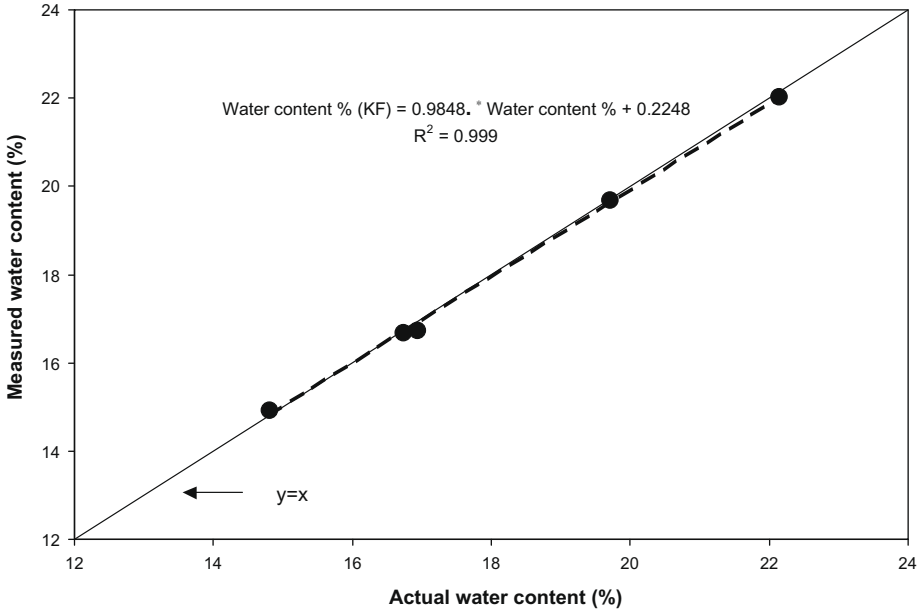

Fig. 1. Comparison of measured (KF method, solvent methanol) and actual (*) water content in model solutions of fructose.

Table 1
Water content (%) in honeys determined by three methods: (a) Karl Fischer titration (KF) using methanol; (b) KF titration using methanol:formamide, and (c) refractometric index (RI). The water activity (a_w) of each honey sample is also reported.

Honey sample	Water content (% w/w): method used			a_w
	KF (methanol)	KF (methanol:formamide)	RI	
1	14.07	14.03	14.6	0.517
2	14.20	14.92	14.7	0.525
3	14.92	15.65	15.6	0.536
4	15.10	15.45	15.8	0.540
5	15.81	16.56	16.5	0.559
6	16.11	16.53	16.8	0.561
7	17.52	17.52	17.6	0.563
8	16.63	16.74	17.6	0.565
9	16.38	16.80	16.9	0.568
10	17.09	17.02	17.3	0.569
11	17.21	17.69	17.2	0.575
12	18.32	18.24	18.0	0.578
13	17.99	17.81	18.2	0.581
14	17.60	17.96	18.0	0.582
15	17.77	17.97	18.1	0.584
16	17.79	18.41	18.5	0.585
17	18.26	18.68	18.5	0.586
18	17.55	17.78	18.4	0.587
19	17.87	17.54	18.2	0.588
20	17.90	18.11	18.8	0.592
21	19.36	18.17	18.4	0.593
22	21.12	19.05	19.3	0.602

content range of 14.8–22.1% (resembling total soluble solids in honeys) were prepared by adding distilled water to fructose. Solutions were heated in sealed flasks to reach complete solubilization; it was verified that no fructose crystallization from these supersaturated solutions occurred over the time frame of measurements. These model solutions were used, because they allowed us to know accurately the actual water content.

2.3. Water content of honeys

Water content was determined either by refractive index (RI) or Karl Fischer (KF) titration. Crystallized or partially crystallized honey samples were liquefied at about 42–45 °C in hermetically sealed glass containers before water content determination.

A digital honey moisture refractometer Pal-22S, Atago (Japan) was used to obtain water content (%); measurements were made by duplicate at 25 ± 1 °C and the average taken.

KF titration were carried out at 25 ± 1 °C with a Karl Fischer titrator DL 31 from Mettler-Toledo, applying the one-component technique with Hydranal Titrant Composite 5 from Riedel-de Haën, Germany. Pure methanol or a methanol:formamide mixture (1:1) were used as solvent and they were purchased from Merck, Darmstadt, Germany. Sample sizes were approximately 100 mg and were analyzed twice each. The standard deviation for KF titration using as solvent methanol or methanol:formamide mixture, was calculated from six replicate measurements performed on a honey sample of about water content 17% , and found to be 0.24 and 0.16 (water content %), respectively.

2.4. Determination of water activity

Water activity of honey samples were also measured in order to test the appropriateness of water content, as determined by KF method, to predict water activity of honeys. Water activity was measured using an electronic dew-point water activity meter Aqualab Series 3 model TE (Decagon Devices, Pullman, Washington, USA), equipped with a temperature-controlled system which maintains a temperature-stable sampling environment. The equipment was calibrated with saturated salt solutions in the water activity range of interest (Favetto, Resnik, Chirife, & Ferro Fontán, 1983). For each determination three replicates were obtained and the average reported.

3. Results and discussion

As mentioned before, refractive index measurements are frequently used for water content determination in honeys. However, it has been reported that the Karl Fischer (KF) method may give more accurate values (Bogdanov et al., 2004).

The reliability of the KF method to accurately determine water content in model solutions of fructose of known water content values, was first evaluated. Fig. 1 shows the correlation between

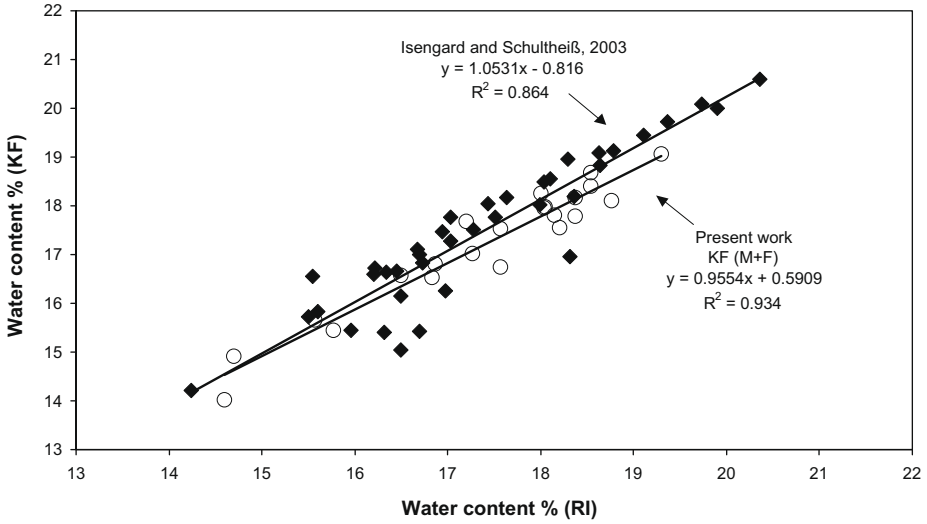

Fig. 2. Correlation between KF method and RI measurements of water content in several honeys: data from present work (○); data from Isengard and Schultheiß (2003) (♦).

measured (determined by KF; solvent methanol) and actual water content values. An excellent linear correlation (R^2 = 0.999) was observed. The average percentage error ($\overline{\varepsilon}\%$) from measured and actual data (Fig. 1) was calculated using the following equation:

$$\overline{\varepsilon}\% = \frac{\sum |x - x_a|}{n} \cdot 100 \quad (1)$$

where x is the measured water content % (KF method), x_a is actual water content %, n is the number of data.

The value of ($\overline{\varepsilon}\%$) was 0.56% indicating that KF yields very accurate water content values in highly concentrated fructose solutions.

An important aspect in KF titration is the total solubilization and availability of water from the sample. In the case of honey, high viscosity could affect the water transfer to the titration solvent. For this reason two solvent systems were evaluated for water content determination in honeys, methanol (M) and methanol:formamide in the ratio 1:1 (M + F), at room temperature. Table 1 compares water content values of honeys obtained either by RI and KF method with different solvent systems. It is to be noted that the use of M + F mixture as solvent for KF method allowed a notable reduction in titration time (about fifty percent), which is a potential advantage. The following observations can be made form the data shown in Table 1: (a) for water content below 17% the values obtained by KF using the solvent mixture (M + F) were approximately 3.6% (relative difference percent) higher than those obtained with methanol; (b) in the whole water content range (14–22%), the relative difference percent between RI and KF (M + F) was 1.7%, while the correspondent to RI and KF (M) was 3.3%, indicating that the values obtained by KF using the solvent mixture were closer to RI than using methanol as a solvent.

Other authors have used different conditions during KF titrations to optimize the measurement time and water solvation from the sample. Isengard et al. (2001) reported a shortening in determination times increasing the temperature of titration to 50 °C. Fig. 2 shows the correlation between water content % measured by RI and water content % measured by KF titration using (M + F) at room temperature; the data of Isengard and Schultheiß (2003), at 50 °C using (M) solvent were also plotted for the purposes of comparison. In both cases, present work and Isengard and Schultheiß (2003), a similar behavior was observed and good linear regressions were obtained, although a higher regression coefficient (R^2 = 0.934 vs. 0.864) was achieved in present work.

Previous literature reports indicated that values of water content determined by KF are a little different from those measured by RI. These differences could be attributed to the botanical origin and the nature of dry matter of honey (Isengard & Schultheiß, 2003; Isengard et al., 2001).

In last years water activity was studied as criterion of microbiological stability of honeys as alternative to water content (Chirife, Zamora, & Motto, 2006) and efforts were made to correlate water activity with refractometric water content. Eqs. (2) and (3) show linear regression equations between water activity and water content (for present honeys) determined either by RI or KF measurements with (M + F) solvent. It can be seen that both equations are almost identical,

$$a_w = 0.2748 + 0.0171 \cdot \text{Water content \% (KF)} \quad (R^2 = 0.928) \quad (2)$$

$$a_w = 0.2702 + 0.0172 \cdot \text{Water content \% (RI)} \quad (R^2 = 0.959) \quad (3)$$

The similarity between Eqs. (2) and (3) confirms that both methods for measuring water content (RI or KF with (M + F) solvent), can be satisfactorily used to predict water activity from knowledge of water content of honey.

References

Bogdanov, S., Ruoff, K., & Persano Oddo, L. (2004). Physico-chemical methods for the characterization of unifloral honeys: A review. *Apidologie, 35*, 4–17.

Chirife, J., Zamora, M. C., & Motto, A. (2006). The correlation between water activity and % moisture in honey: Fundamental aspects and application to Argentine honeys. *Journal of Food Engineering, 72*, 287–292.

Favetto, G. J., Resnik, S. L., Chirife, J., & Ferro Fontán, C. (1983). Statistical evaluation of water activity measurements obtained with the Vaisala Humicap humidity meter. *Journal of Food Science, 487*, 534–538.

Isengard, H.-D., & Schultheiß, D. (2003). Water determination in honey – Karl Fischer titration, an alternative to refractive index measurements? *Food Chemistry, 82*, 151–154.

Isengard, H.-D., Schultheiß, D., Radović, B., & Anklam, E. (2001). Alternatives to official analytical methods used for the water determination in honey. *Food Control, 12*, 459–466.

Scholz, E. (1984). *Karl Fischer titration*. Berlin: Springer.