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Water determination in honey—Karl Fischer titration, an alternative to refractive index measurements?

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Abstract

Honeys must not contain too much water if they were to be protected from microbiological spoilage. Water content is usually measured via the refractive index (RI). From the value measured, the water content is calculated by an empirical formula or by "conversion" tables. Creamy honeys must be heated before analysis, a procedure that may result in a loss of water and makes a comparison with liquid honey measurements at room temperature difficult. Another problematic point is that the composition of the solid content, which in fact is determined by RI measurements (and not water content), varies from one type of honey to another. The formula used for calculation and the tabulated values are therefore necessarily not equally correct for every honey. The objective of this work was to establish a generally applicable method to determine the real water content of honeys. As the Karl Fischer (KF) titration is known to determine the water selectively by a chemical reaction, this technique was chosen.
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Keywords: Honey; Water determination; Karl Fischer titration; Refractive index; Reference method

1. Introduction

To protect honey from microbiological spoilage the water content must not exceed 21% by mass; for clover and heather honey the value must not be more than 23%. Water content is usually determined via refractive index measurement, converting the values found into water content by using tables or a formula (see later). In the case of creamy or crystallised honeys, a preheating at 50 °C is necessary. Measurements are then carried out at 20 °C (Method A below) or 40 °C (Method B below). According to another method (AOAC, 1995), all samples are preheated at 40 °C and then measured at 20 °C.

It can be expected that the preheating process will change the original water content of the sample. The refractive index depends on the solid matter of the sample. As the components of the solid matter vary from one type of honey to another, the same conversion table or formula cannot be expected to be equally appropriate for all honeys, to convert the refractive index measured into water content.

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The Karl Fischer titration is a selective method for water determination. It does not depend on the composition of honey samples and can therefore be applied to different types of honey in the same way. A preheating is not necessary. The Karl Fischer method thus avoids the drawbacks of refractive index measurements for analysing water content.

2. Materials and methods

Honey samples from different countries and different floral origins were investigated (Isengard, Schultheiβ, Radović, & Anklam, 2001).

RI measurements were carried out with an Abbe refractometer from Atago, Japan, applying two methods:

Method A, according to German law (Amtliche Sammlung von Untersuchungsverfahren, 1992): honeys are liquefied at 50 °C, if necessary, and then the RI is measured at 20 °C. The water content is read from a table according to Chataway (1932, 1935).

Method B: honeys are liquefied at 50 °C, if necessary, and then the RI n is measured at 40 °C.

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The dry matter, DM, is calculated using an empirical formula (Auerbach & Borries, 1924):

$$DM[\%] = 78.0 + 390.7 \cdot (n - 1.4768)$$

The water content, WC, is the difference from 100%:

$$WC[\%] = 100\% - DM[\%]$$

KF titrations were carried out with a KF Titrino 701 from Metrohm, Herisau, Switzerland, applying the two-component technique, with Hydranal-Titrant 5 and Hydranal-Solvent from Riedel-de Haën, Seelze, Germany. Titrations are principally possible at room temperature, but a temperature of 50 °C was eventually preferred (using a titration vessel with thermostatic jacket), because of clearly shorter determination times (see Fig. 1). Samples were introduced into the titration cell by means of a 5 ml disposable syringe without needle.

3. Results and discussion

Preheating at 50 °C is necessary for creamy honeys to render them liquid for RI determinations. This procedure entails a slight water loss as is shown in Table 1. As the time necessary for liquefying the samples is usually shorter than 1 h (in the range of 20–30 min), the effect is smaller than the amounts cited in Table 1. The original water content of such honeys can, nevertheless, not be measured exactly by the RI technique.

Table 2 contains results for honeys of various botanical and geographical origins. For every sample, the highest value is highlighted with grey; the lowest is not highlighted. The same highlighting means that the values are not significantly different. If all of three values differ significantly from each other, the middle value is highlighted with light grey. Different highlighting always indicates a significant difference.

Table 1
Water content of a sample of creamy honey before and after preheating (from Isengard et al., 2001)

Preheating	Karl Fischer result	
	Water content (g/100 g)	Confidence interval (95% level)
None	17.32±0.033 (n=10)	17.30; 17.34
1 h at 40 °C	17.24±0.026 (n=10)	17.22; 17.26
1 h at 50 °C	17.12±0.030 (n=10)	17.10; 17.14
2 h at 50 °C	17.08±0.050 (n=8)	17.04; 17.12

The KF results have (in most of the cases) a lower standard deviation and are therefore more precise than the RI results. Within the RI techniques, method B (measurement at 40 °C) is usually more precise than method A (measurement at 20 °C), possibly due to the fact that small crystals may be formed again when the honeys cool down for measurement, an effect that is less reproducible when the decrease in temperature is higher and, thus, the time longer. Method B, with only a few exceptions, yields significantly lower results than method A.

It is reported that RI values are lower than Karl Fischer results (Zürcher & Hadorn, 1980, 1981). This could be confirmed for honeys from chestnut, acacia, heather and lime blossom, as well as for the liquid eucalyptus honeys. Sunflower (but for one sample) and, to a great extent, oil-seed rape honeys, were exceptions to the general tendency. The botanical origins of the honeys and, thus, the nature of the dry matter, seem to have an influence on the refractive index which may be relatively strong in certain cases. The application of the same formula to calculate the water content from the refractive index or the use of the same conversion table is therefore not appropriate.

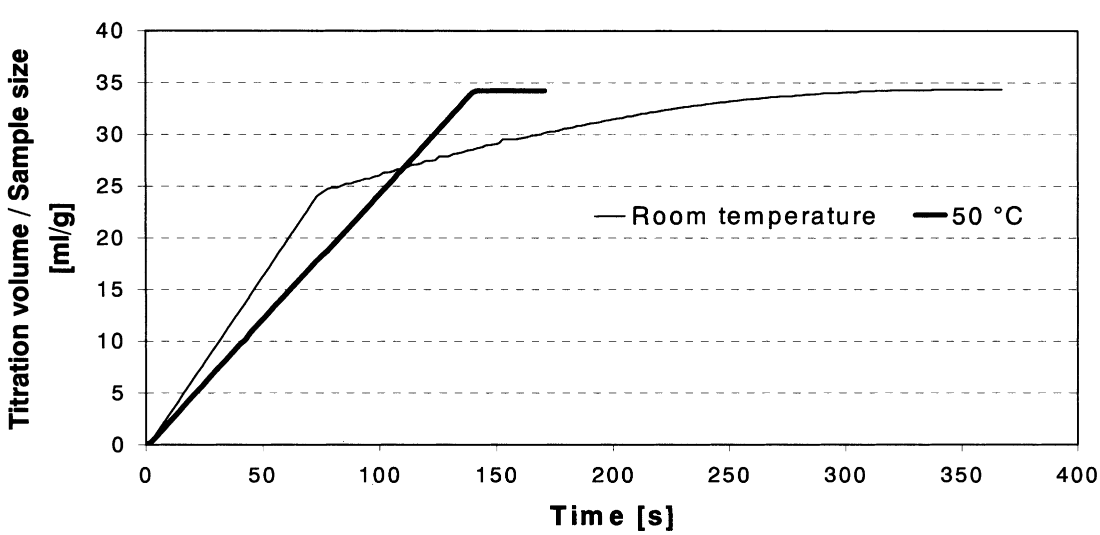

Fig. 1. Karl Fischer titration curves for honey at different temperatures (from Isengard et al., 2001).

Table 2
Water content (*n* replicates) of various honeys measured by Karl Fischer titration (KFT) and two RI methods [RI A (measurement at 20 °C) and RI B (measurement at 40 °C)]

Origin of honeys (sample number)	KFT ($n=5$)	RI A ($n=4$)	RI B ($n=4$)
Chestnut honeys (preheating for RI measurements necessary only for the two French samples)			
Italy (10)	18.56±0.031	18.10±0.120	17.96±0.035
Italy (16)	17.77±0.025	17.03±0.069	16.85±0.020
Italy (21)	18.48±0.034	18.04±0.118	17.99±0.035
Italy (23)	19.73±0.023	19.36±0.046	19.22±0.038
Italy (24)	19.08±0.030	18.63±0.060	18.69±0.060
France (29)	16.72±0.020	16.22±0.095	16.24±0.023
France (35)	17.46±0.020	16.94±0.050	16.86±0.023
Germany (42)	17.27±0.023	17.03±0.020	16.89±0.020
Germany (43)	17.76±0.033	17.51±0.020	17.42±0.020
Acacia honeys (no preheating for RI measurements necessary)			
Germany (1)	16.55±0.037	15.55±0.058	15.28±0.033
Germany (2)	15.73±0.013	15.50±0.078	15.44±0.034
Italy (11)	16.60±0.032	16.21±0.068	16.11±0.020
Italy (19)	17.00±0.038	16.70±0.077	16.47±0.017
Italy (20)	16.66±0.025	16.45±0.038	16.07±0.020
Italy (22)	18.03±0.018	17.99±0.020	17.79±0.060
France (31)	16.83±0.037	16.73±0.020	16.46±0.020
Lime-blossom honeys (preheating for RI measurements necessary)			
Germany (3)	15.82±0.019	15.60±0.030	15.46±0.023
Netherlands (38)	19.44±0.030	19.11±0.020	18.95±0.046
Netherlands (41)	17.10±0.028	16.67±0.082	16.47±0.023
Germany (44)	16.64±0.031	16.34±0.077	16.03±0.020
Heather honeys (preheating for RI measurements necessary)			
Germany (6)	19.13±0.012	18.78±0.023	18.78±0.023
Germany (7)	18.16±0.021	17.63±0.144	17.65±0.038
France (33)	20.08±0.034	19.73±0.020	19.36±0.023
France (36)	18.83±0.039	18.64±0.046	18.30±0.020
Netherlands (37)	18.95±0.016	18.29±0.050	18.26±0.060
Netherlands (39)	20.60±0.063	20.36±0.033	20.01±0.033
Great Britain (47)	23.14±0.021	22.30±0.115	22.11±0.038
Great Britain (49)	22.60±0.068	21.43±0.020	21.19±0.038
Great Britain (50)	22.47±0.031	20.79±0.020	20.63±0.057
Eucalyptus honeys (preheating for RI measurements necessary only for the two Italian samples)			
Italy (14)	16.15±0.038	16.50±0.069	15.91±0.052
Italy (17)	14.21±0.030	14.24±0.046	14.09±0.023
Spain (25)	17.52±0.032	17.28±0.046	17.39±0.046
Portugal (52)	18.05±0.031	17.43±0.038	17.23±0.033
Sunflower honeys (preheating for RI measurements necessary)			
Italy (13)	15.45±0.031	15.96±0.098	15.62±0.020
Italy (15)	16.26±0.021	16.98±0.033	16.67±0.040
France (34)	20.00±0.026	19.90±0.040	19.61±0.020
France (40)	18.19±0.019	18.36±0.033	18.26±0.050
Oil-seed rape honeys (preheating for RI measurements necessary)			
Germany (4)	15.04±0.024	16.49±0.068	16.19±0.100
Germany (5)	15.41±0.025	16.32±0.145	16.08±0.023
Denmark (8)	15.42±0.021	16.70±0.100	16.12±0.040
France (30)	16.96±0.027	18.32±0.033	18.22±0.020

4. Conclusions

The Karl Fischer titration, preferably at 50 °C to shorten analysis time, using the two-component technique, was found to be applicable to all of the investigated honey samples from different countries and from various biological sources. The results are very precise and the titration curves indicate a complete and correct detection of the water. The results were compared to those obtained by refractive index measurements. It could be shown that creamy honeys do lose small amounts of water during the necessary preheating and, thus, refractive index measurements do not yield the original water content. In most cases, the Karl Fischer results were higher. In some cases, however, the refractive index results were higher. This seems to depend on the botanical origin of the honeys. As it can be assumed that the Karl Fischer method yields the correct water content of the samples, this deviation confirms that the same empirical formula and the same conversion table are not equally applicable to all types of honey. This procedure leads to more or less incorrect results.

It is therefore proposed that the Karl Fischer titration be established as an international standard or reference method for determining the water content of honeys. The results are accurate and the precision is as good as that of the refractive index technique.

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