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Method for the determination of water content in sultana raisins using a water activity probe

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Abstract

A new method for the fast (less than 5 min) and accurate (better than 0.5% error in water content) measurement of water in sultana raisins without the need for sample weighing has been developed. The method is based on a commercially available water sensor and probe. Additionally, a raisin press has been developed to prepare the sample for analysis in one step. The results obtained with the proposed method correlate well ($R^2 = 0.999$) with those obtained using a high speed blending Karl Fischer auto-titrator. The method shows good analytical characteristics, the analysis time is short, and no expensive or dangerous chemical consumables are used. The method can thus be used easily by non-experienced personnel, either on site, or in the laboratory.

Keywords: Raisins; Water content; Water activity; Karl Fischer titration

1. Introduction

The water content of foodstuffs has significant importance since it affects the physical characteristics, technological processes, microbiological stability, and shelf life of foods, as well as having legal and economic ramifications (Isengard, 1995). Determination of water content is one of the most frequent analyses performed on foodstuffs. Water determination methods should not only be very accurate but also fast. There are several methods for determining water in foods (Fischer, 1935; Hirschfeld & Stark, 1984; Isengard, 2001; Kraszewski, 1998; Multon, 1997). The nature and special characteristics of each sample, as well as the chemical state of the water in it, determine the appropriate method for the water measurement. Bulk or free water is easy to determine using several methods. On the other hand, the determination of tightly bound water is very difficult and can only be achieved using a limited number of methods (Isengard, 2001).

Raisins were probably discovered by accident thousands of years ago as sun dried grapes on the vine. The key to the quality of raisins is the drying process and their water content. If the raisins are too dry their nutritional value and flavour are diminished, while if they are too wet they degrade very quickly and will not survive storage or transportation. The measurement of water content in raisins is a challenging task due to two main problems: (1) raisins contain sugars and volatile substances besides water, and cannot thus be heated to elevated temperatures, and (2) raisins have a semi-permeable skin which does not allow for fast equilibration of water molecules between the flesh of the raisins and their surrounding environment.

There are two official methods according to AOAC (Official methods of analysis of AOAC International, 1998) for water determination in raisins. The AOAC Method 934.06 for measuring water content in raisins is based on 6 h oven-drying at 70 ± 1 °C under reduced pressure ($\leqslant 100$ mm Hg). The second method (AOAC 972.20) is based on a dried food moisture tester meter developed by DFA of California and the water content is determined by measuring electrochemical characteristics of the sample.

The method proposed in this paper for determining water content in raisins is based on water activity measurements. Water activity and water content are correlated via a sorption isotherm so, if the water activity is measured, water content can be read from the isotherm. Water activity measurements in a solid product are feasible if thermodynamic equilibrium has been attained between the water in the solid and the atmosphere around it. In the case of raisins, this equilibrium is facilitated by the homogenisation of the sample without

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removing the skin with the use of a press. The total analysis time is less than 5 min, while the sensor requires calibration every 6 months.

2. Materials and methods

2.1. Sample preparation

A commercially available manual juicer, which measures 390×190 mm, was modified to a raisin press for the preparation of all raisin samples. The press has a powerful rack-and-pinion gear system, which exerts up to 800 lbs of pressure. The raisins are put in a specially designed cup of 3 cm internal diameter by 3.5 cm depth. Twenty one holes of 4.5 mm are opened at the bottom of the cup. Pressing the raisins with the aid of the plunger will extrude the sample through the holes, without removing the skin.

2.2. Oven drying method

The samples were prepared according to AOAC Method 934.06. Sea sand (Merck, Germany) was used. All samples were dried in an oven (P. SELECTA, Spain, model Vaciotem, 4000571) at 70±1 °C under reduced pressure ⩽100 mm Hg.

2.3. Karl Fischer titration

Volumetric Karl Fischer titrations were performed using a TURBO2 Blending Karl Fischer instrument (Thermo Orion, USA), with an amperometric end-point determination. All the reagents used were obtained from Riedel-de Haën.

2.4. Water activity measurement

For water activity measurements, a Rotronic (Switzerland) A_2 Hygromer and an AwVD probe were used. The raisin sample was placed in a Rotronic PS-14 sample cup. The cup was then placed into the AwVD probe and, after turning on the probe, measurement was taken in 3 min in%RH units.

3. Results and discussion

3.1. General approach

The development of a new analytical method requires the use of calibration standards or a reference method. In the present case, and in the absence of commercially available sultana raisin standards, a reference method had to be chosen, based on accuracy, reproducibility, and overall analytical characteristics.

3.2. Reference methods evaluation

3.2.1. Oven-drying method

The AOAC method 934.06 is an official method, widely used for the determination of water in raisins, and is based on the weight loss after 6 h of drying under vacuum. Fig. 1 shows the effect of oven-drying on weight loss of raisins. The water content, calculated and based on weight loss after 6 h, was 11% w/w. Further

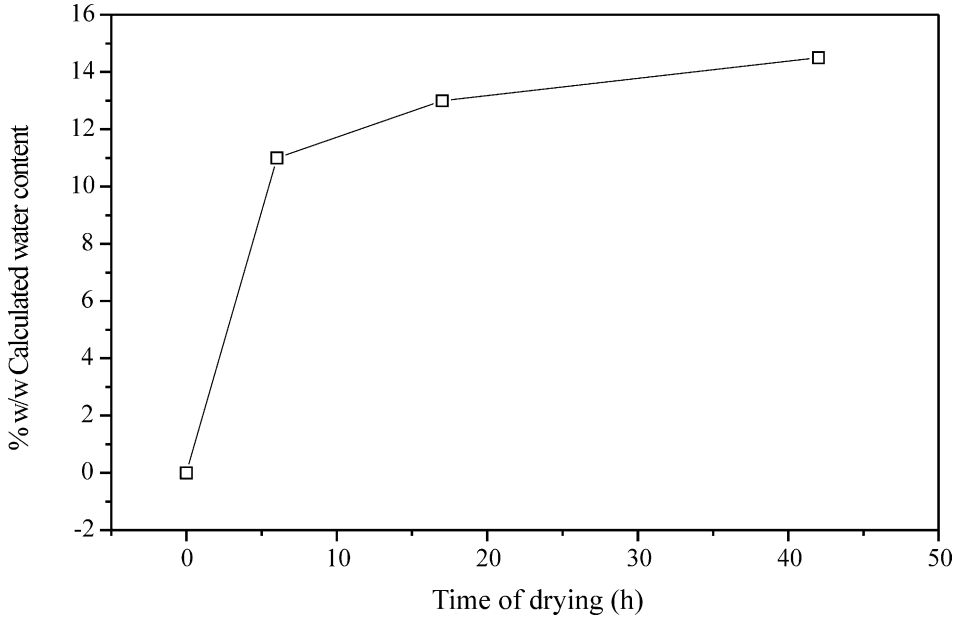

Fig. 1. Calculated (% w/w) water content in a sample of raisins by oven-drying (70 °C, $P \leqslant 100$ mm Hg) vs. time of drying.

sample heating (up to 42 h) resulted in a continuous loss of weight. It should also be mentioned that the water content of samples from the same batch, when analysed using the Karl Fischer method, was calculated to be 15.5%. These results corroborate the fact that water is tightly bound to the raisin matrix, and it is thus very difficult to liberate it under the specific experimental conditions. Generally, oven-drying is not a very accurate method for measuring water content, since it cannot distinguish between water and other volatile substances, either already contained in the original sample or produced by the heating process (Isengard, 1995).

3.2.2. Karl Fischer titration

The second method that was evaluated was that of the automated volumetric Karl Fischer (Fischer, 1935) titration with amperometric end-point determination.

The major problem in the determination of water in raisins by Karl Fischer titration arises from the incomplete extraction of the water of raisins in the solvent. This incomplete extraction leads to sluggish, and difficult to determine titration end-point. For this reason, an automatic high speed blending Karl Fischer instrument was used. Under these conditions reproducible measurements ($CV < 1\%$, $N = 3$) of water content in raisins were obtained. Based on these results, the Karl Fischer

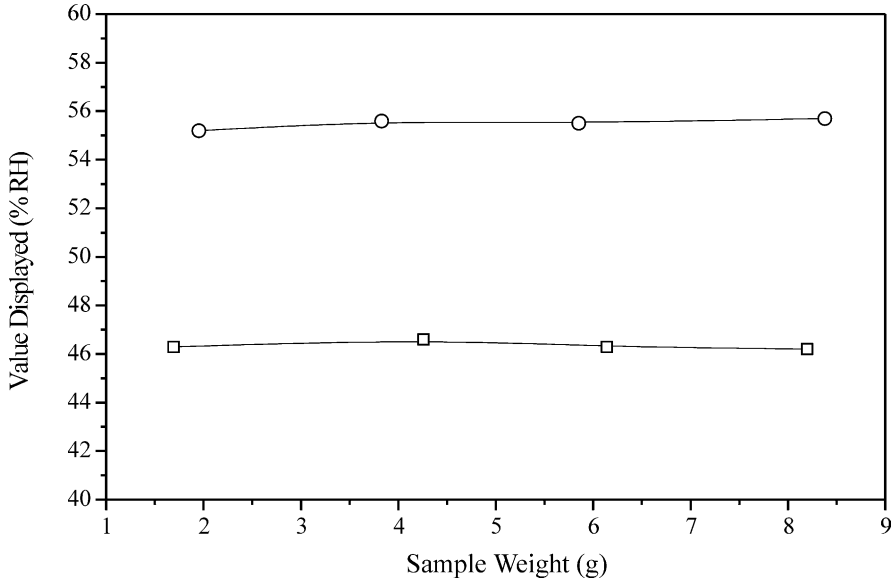

Fig. 2. Effect of sample weight on the value displayed by the hygrometer (%R.H.) for two samples of raisins with different water contents.

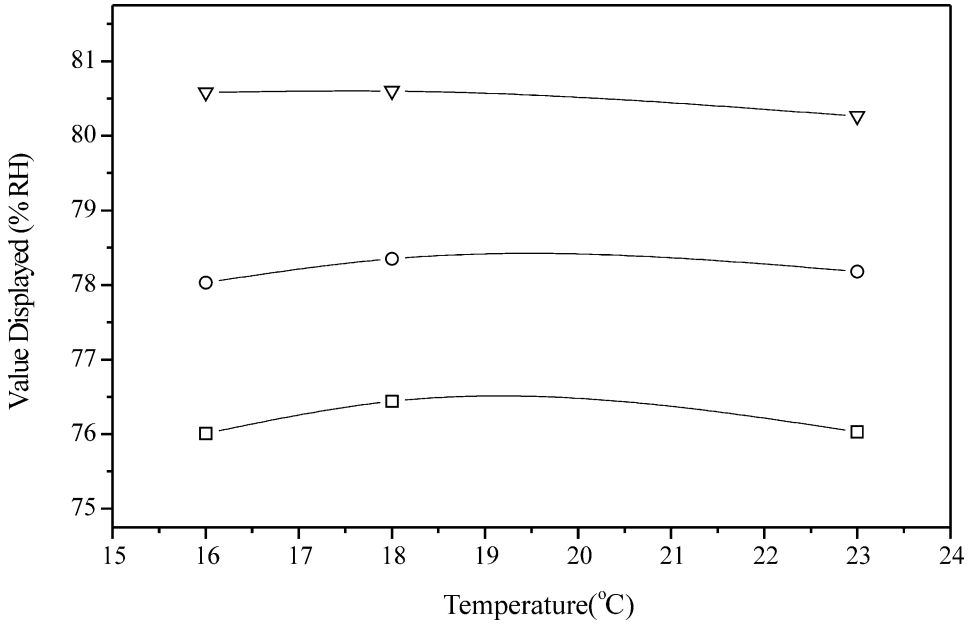

Fig. 3. Effect of temperature on the value displayed by the hygrometer (%R.H.) for three samples of raisins with different water contents.

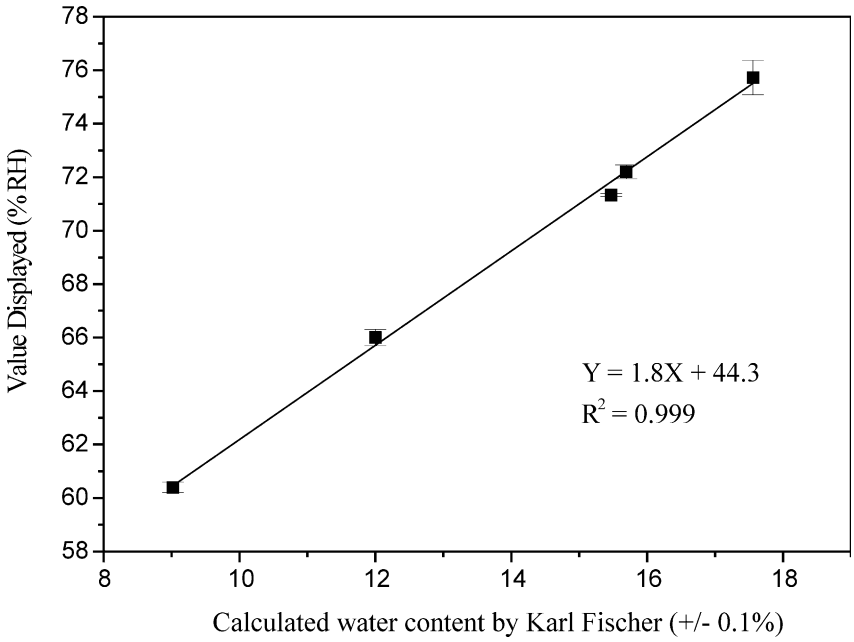

Fig. 4. Calibration curve for the method developed using five samples of raisins with different water content determined by Karl Fischer titration.

method was used subsequently for the calibration of the new method.

3.3. Development of the new method

3.3.1. Effect of sample weight

The elimination of precise sample weighing would be a great advantage of the new method to be developed. In order to evaluate the effect of sample weight on the measured values, two samples, with different water contents, were used. As can be seen in Fig. 2 there is little effect of sample weight, in the range 1–9 g, on the displayed value of the instrument. For this reason, samples in the range of 3–5 g were used, since this amount filled the sample cup without leaving a large empty space, or overflowing.

3.3.2. Effect of temperature

The effect of the temperature is very important for the measurement of water activity. Fig. 3 shows the effect of temperature on the value displayed by the hygrometer. Three samples of raisins with different water contents were used, while the temperature was varied between 16 and 23 °C. There is a slight effect of the temperature on the value displayed by the hygrometer but, if the temperature is carefully controlled within ±2 °C, reproducible measurements can be obtained.

3.3.3. Calibration curve

Fig. 4 is a calibration curve of the instrument, based on the proposed method. Samples with water content in the range of interest for sultanas (9–18 wt.%) are used. The calibration curve is established using different sorts of sultanas, and three different measurements are undertaken for each sample. The total number of measurements used was 15. The data presented are the averages of the three measurements per sample. The temperature was controlled to 20±1 °C, while the different samples used were analysed using the Karl Fischer method. The reproducibility of the method is very good with a CV < 1% for $N = 3$. This data shows the excellent relationship between the actual water content (X-axis) and the relative reading of the instrument (Y-axis), with correlation coefficient of 0.999.

4. Conclusions

In this report a method for the fast, and accurate measurement of the water content in different sorts of sultana raisins is presented. Using a commercially available humidity probe, combined with a raisin press, the measurement of water content in raisins can be achieved very accurately within 5 min. Based on these results, the experimental setup can be easily adopted for the measurement of water content in other varieties of raisins, and other dried fruits and vegetables, if calibration curves are established.

Acknowledgements

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