CHEMICAL ENGINEERING TRANSACTIONS
VOL. 44, 2015
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet
Guest Editors: Riccardo Guidetti, Luigi Bodria, Stanley Best
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ISBN 978-88-95608-35-8; **ISSN** 2283-9216

Characterization of Pears During Drying by Conventional Technique and Portable non Invasive NMR

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Drying is an important process for the conservation and subsequent marketing of fruits due to their high water activity which makes them highly perishable. Dried products have to meet high quality standards, and one of the most important aspects in fruit drying is the need to obtain products with uniform organoleptic properties. Therefore, the knowledge and the optimization of drying process are very important in order to minimize thermal damage and quality loss.
In the case of pears, sugar concentrations are relatively high (60–75 g/100 g dry basis) and greatly increase as water evaporates, offering, combined with fruit shrinkage, an additional resistance to moisture transfer from the fruit.
In this study, the effect of drying on properties of pear samples (Pyrus Communis 'Conference') was analysed. In particular, the water transport mechanism was investigated in pear during drying process at 50 °C. The drying kinetics were obtained by standard weight measurements and the water loss in chosen sample sections (exterior, intermediate and central sections) was evaluated.
The drying moisture profiles of samples were also investigated by portable NMR, a non-invasive and non-destructive technique. The water loss obtained by standard weight measurement and the extent of shrinkage obtained by means of a vernier calliper were found to be in a good agreement with the results obtained by portable NMR

1. Introduction

The pear (Pyrus communis L.) is a typical fruit of temperate zones and is cultivated in Europe, among other regions. Due to its nutritive properties, good taste and low caloric level, the pear is highly considered by consumers. Although pears can be consumed fresh, they are also commonly used in processing techniques such as in syrup conserves, purees for use in nectars and yogurts and drying (Park et al., 2003). The dehydration of fruit is one of the most common processes used to improve food stability as it considerably decreases the water activity of the material, reduces microbiological and enzymatic activity, and minimizes physical and chemical reactions during its storage. The expansion of the dehydrated food market demands high quality products that maintain the physicochemical properties of the initial fresh product at a very high level. In previous research, we have evaluated the change of several physical properties (porosity, pore-size distribution, microstructure, shrinkage) of eggplant during the drying process (Russo et al., 2012) also with the use of MRI technique (Adiletta et al., 2014). In the case of eggplant drying (Brasiello et al., 2013) a mathematical model accounting for the shrinkage effect have been developed and discussed. Moreover, the effect of pre-treatments on the drying process has been investigated both experimentally (Di Matteo et al., 2003) and theoretically (Brasiello et al., 2011).

The chemical and sensorial transformations that occur during the drying process influence the end-product quality and have a decisive influence on its attractiveness to the consumer. In the case of fruit, and especially pears, the sugar concentrations (on wet basis) are relatively high and increase very significantly with water evaporation, offering, combined with fruit shrinkage, an additional resistance to moisture transfer from the fruit throughout the drying process (Guiné & Castro, 2002). Therefore, the drying of pears becomes critically dependent on the temperature as well as water and sugar concentrations inside the fruit during drying. Hence, the study of the water transport mechanism and of shrinkage is fundamental for the choice of the optimal drying condition without compromise the quality of the product.
In the literature, various fruits and vegetables such as banana (Raffo et al., 2005), kiwifruit (Panarese et. al., 2012), and eggplant (Adiletta et al. 2014) have been investigated by means of low field NMR (Tylewicz et al., 2011) or MRI (Taglienti et al., 2009) giving important information on food texture, quality, ripening and processing. The main advantage of low field NMR techniques is that they do not require any pretreatment of the sample and once developed, standard protocols based on fast measurements can be easily transferred to quality control applications. ^{1}H pulsed low field NMR allows to obtain information on water compartmentalization and diffusion by detecting proton signal predominantly due to H_2O contained in vegetable tissue. In particular portable NMR has been used to monitor, fully non-invasively, kiwifruit growth (Capitani et al., 2010, 2013), and to investigate the water status of fresh and withered blueberries (Capitani et al., 2014).
In this study the water transport mechanism and shrinkage were evaluated in pear during drying process at a temperature of 50 °C. The drying kinetics was obtained by standard weight measurements and the water loss in exterior, intermediate and central parts of samples was evaluated. The extent of shrinkage was also assessed. Both the drying kinetics and the extent of shrinkage were also investigated by portable NMR, which allows non destructive and non invasive analysis.

2. Materials and Methods

2.1 Sample preparation

Fresh Pear (Pyrus communis L. cultivar Conference) samples with dimensions of 2.5 x 2.5 x 2 cm^3 and initial moisture content of 5.14 ± 0.96 kg/kg dry basis were obtained from peeled fruit.
The parallelepipeds were sampled from the whole fruit using a suitable steel mould. The dimensions of the samples were chosen on the basis of the NMR probe head size and in order to obtain a detectable signal also at high drying times (i.e. when the water content is definitively low).

2.2 Drying experiments

The drying experiments on parallelepiped samples were conducted in a convective dryer (Zanussi FCV/E6L3) at temperature of 50 °C and air velocity at 2.3 m/s until the constant mass was reached. For drying kinetics, the weight of five samples was recorded using a digital balance (mod. Gibertini E42, Italia) at suitable time intervals during the drying process, until a constant mass was achieved. Moisture ratio (M_t/M_0) was calculated as the ratio between the actual (M_t) and the initial (M_0) moisture content on dry basis.
At specific times during the same drying experiment, ten parallelepiped pear samples were collected. From each of them, the core part (cylinder of 0.9 cm diameter and 2 cm initial length) was sampled. Three parts (exterior, intermediate and central one) were obtained by cutting the cylinder at two positions: 2/3L and 1/3L as shown in Figure 1. For these three parts the moisture content was measured according to AOAC standards (1997).

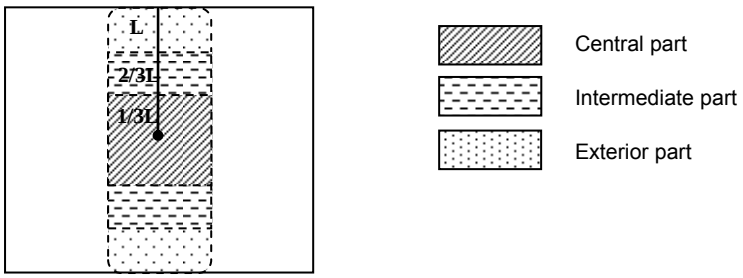

Figure 1. Scheme of the sampling of the three parts: exterior, intermediate and centre

2.3 Shrinkage measurements

At given drying time pear samples were removed from the oven and their dimensions were measured by means of a vernier calliper. The shrinkage of the samples was then expressed as the ratio between the sample thickness at a given drying time (L) and initial one (L_0).

2.4 Low resolution portable NMR measurements

Measurements were carried out at 13.55 MHz with an NMR instrument from Bruker Biospin interfaced with a single-sided sensor by RWTH Aachen University, Germany (Perlo et al., 2005). This sensor generates a magnetic field with an extremely uniform gradient to resolve the near surface of arbitrary large samples.

^{1}H NMR profiles were obtained as the addition of the first eight echoes acquired with a Carr Purcell Meiboom Gill (CPMG) sequence with an echo time of 56 ms and a nominal resolution of 57 μm. Profiles were acquired by repositioning the single-side sensor in steps of 100 μm to cover the desired spatial range, from the surface to a depth of 20 mm. A recycle time of 10 s was used and 64 scans were collected.

The average loss of water in dried samples was calculated by integrating the profiles and reported as the ratio between the integral (I_t) of the profile at different drying times and the integral (I_0) of the profile of fresh fruit. The shrinkage of the samples was also obtained by the thickness reduction of ^{1}H profiles, calculated as the ratio between the thickness of the profile at a given drying time (L_{NMR}) and the profile of the fresh fruit (L_{0NMR}).

2.5 SEM analysis

Images of pear structure during drying were captured using a scanning electron microscope (SIGMA ZEISS, featuring GEMINI® technology). Prior to analysis, samples were coated with a thin layer of silver in a sputter coater (AGAR Auto Sputter Coater, mod.108 A, England) for 5 min.

3. Results and Discussion

3.1 Drying kinetics

The curve of M_t/M_0 versus drying time is shown in Figure 2a for parallelepiped pear samples. It can be observed that M_t/M_0 of samples decreases with drying time. A total drying time of 48 h was necessary to reduce the moisture content of pear samples from the initial moisture content M_0=5.14 g/g dry basis to the final value of 0.11 g/g dry basis.

In Figure 2b the temporal profiles of M_t/M_0 in exterior, intermediate and central parts of pear samples are reported vs drying time at 50 °C. As expected, during drying process the water content decreased more rapidly in the exterior part of the pear sample than in the intermediate and central parts. After 15 h at 50 °C the difference in the water content between the three parts was reduced, and at 48 h the water content of the central part reaches approximately the same value as the exterior part.

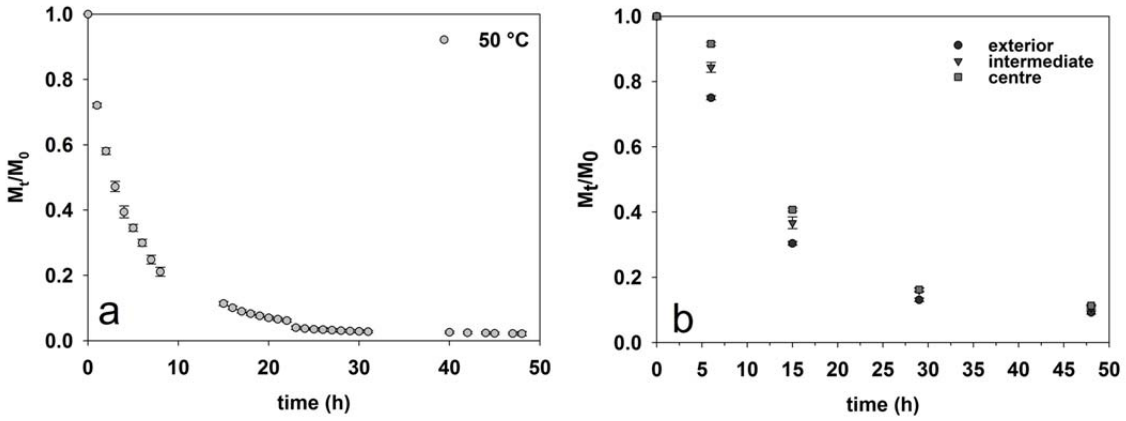

Figure 2: Moisture ratio of a) parallelepiped pear samples and b) exterior, intermediate and central part of pear samples during drying at 50 °C

3.2 Drying kinetics 1H NMR depth profiles

Information on drying kinetics can be obtained by measuring the intensity of ^{1}H NMR signal as a function of the thickness of the sample. Figure 3 shows the comparison among profiles of fresh pear and pears dried for 3, 6, 15, 20, 29 and 48 h. The amplitude of profiles measured in dried samples was found to be progressively lower than that measured on fresh pear, indicating a progressive loss of water with increasing the drying time. In Figure 4a the ratio of I_t/I_0 vs drying time is reported. The trend is very similar to that found in the case of

M_t/M_0 curves (Figure 2a). In fact, a very good agreement (r^2=0.978) was found between M_t/M_0 values, obtained by gravimetric measurements, and I_t/I_0 values obtained by integrating NMR profiles with micrometric resolution (Figure 4b).

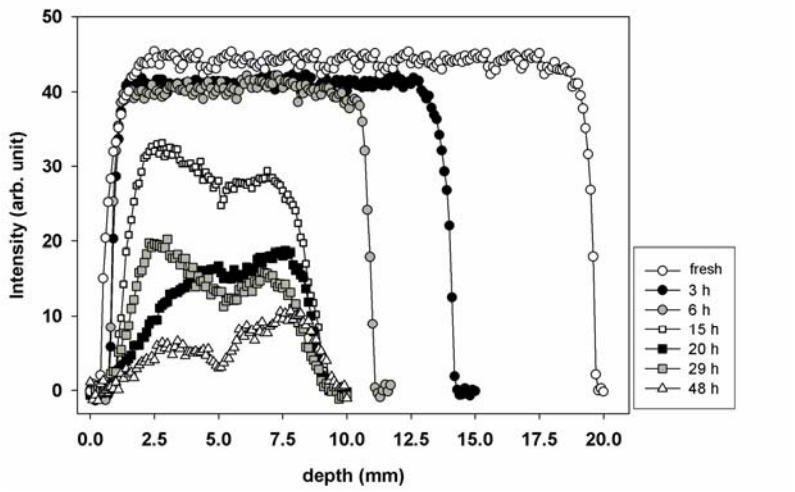

Figure 3: Depth profiles of fresh and dried pear samples at 50°C for 3, 6, 15, 20, 29, 48 h

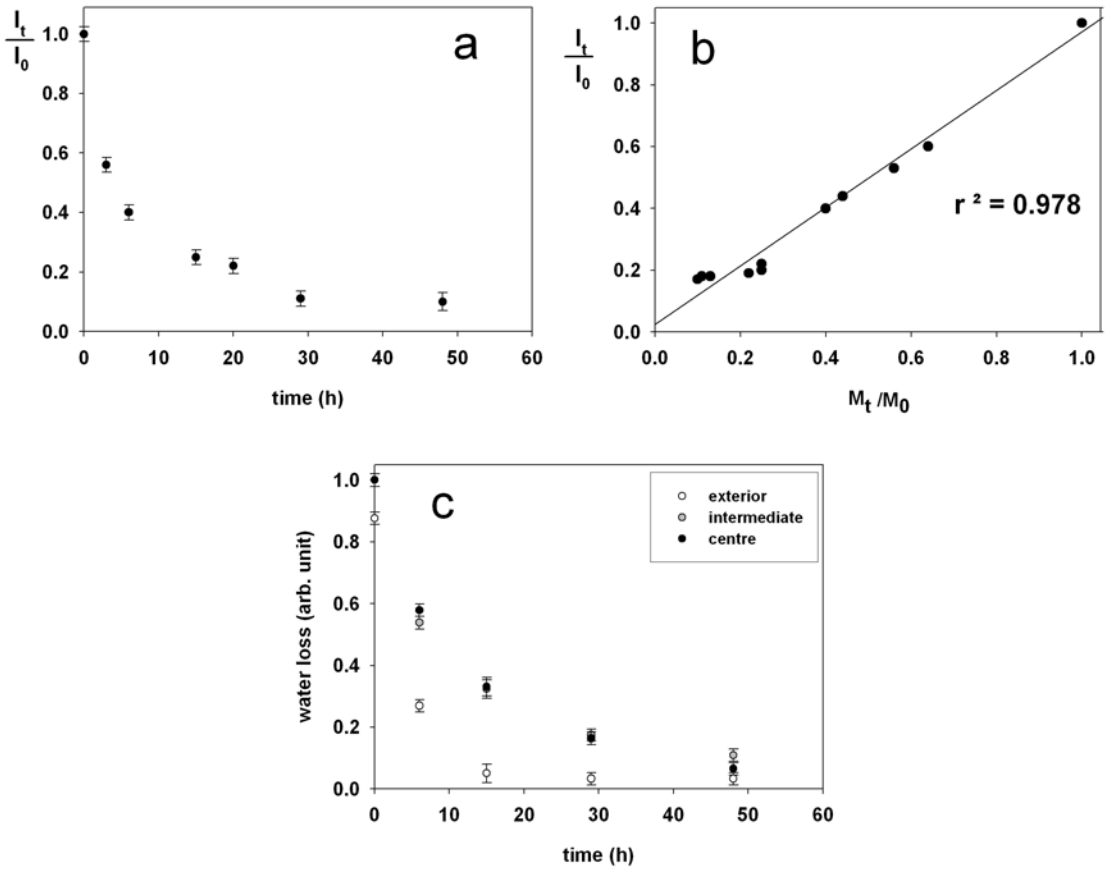

Figure 4: a) Variation of moisture content (I_t/I_0) measured by NMR; b) relationship between M_t/Mo and NMR integral ratio I_t/I_0; c) water loss in exterior, intermediate and central part of pear samples measured by NMR

An evaluation of the loss of water in the outer, intermediate and central regions of pear samples can be obtained by integrating the profiles in the three corresponding regions. The results are reported in Figure 4c.

As expected the water content of outer region decreases more quickly than that in the intermediate and in the central one. Such differences are mostly reduced after 29 and 48 h. This behavior is in good agreement with that obtained by conventional methods (Figure 2b).

3.3 Shrinkage

During the drying process, the size of pear samples reduced considerably. The reduction of thickness (L/L_0) vs drying time is shown in Figure 5a. A net reduction of L/L_0 was observed up to about 15 h thereafter the decrease was smoother. During the final step of drying, the development of porosity increased sharply as observed by SEM images (Figure 6) and probably caused the observed behavior in figure 5a.

As expected, due to the shrinkage of the fruit with drying time, the thickness of NMR profiles was reduced and also the shape of the NMR profiles was affected at long drying time (15-48 h). The correlation between L_{NMR}/L_{0NMR} and L/L_0 obtained by conventional method is reported in Figure 5b.

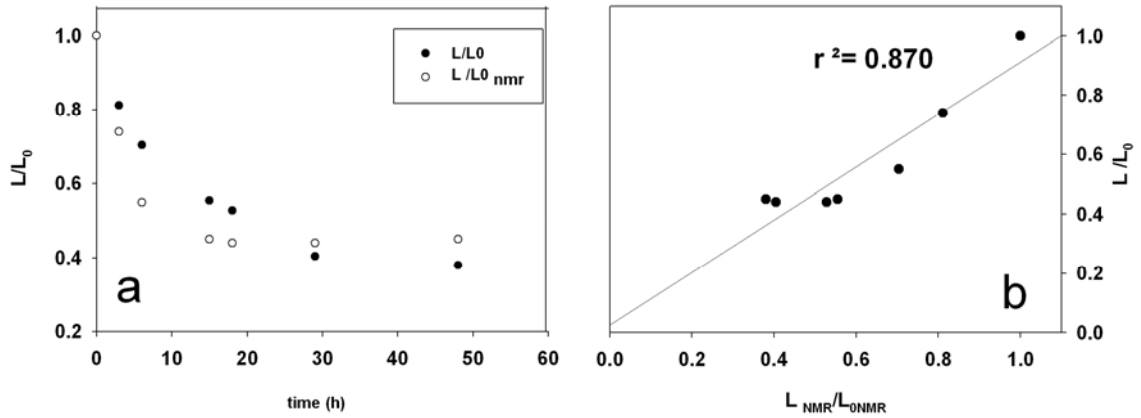

Figure 5: a) Shrinkage vs. drying time in pear samples dried at 50°C: comparison between size measurement and NMR. b) relationship between size measurements and NMR methods

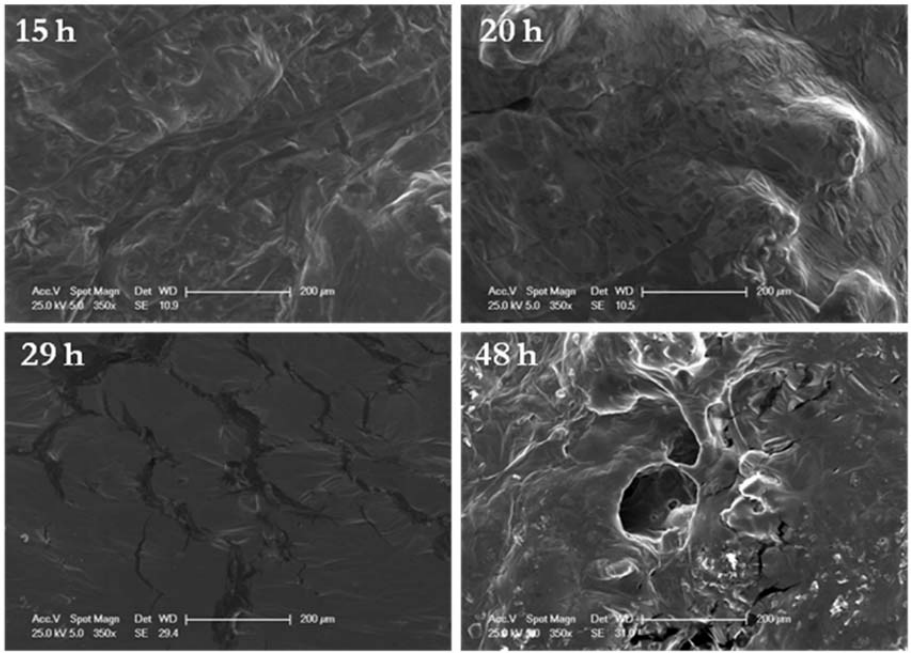

Figure 6: SEM images of pear samples at different drying time

4. Conclusions

Non-invasive, non-destructive portable NMR technique allows studying water status in food during drying processes. The M_t/M_0 curve obtained by gravimetric method showed that the final moisture of 0.11 g/g dry basis was reached t 50°C after 30 h and then the sample mass remained constant. The drying kinetics was followed by NMR measurements. A good agreement (r^2=0.978) was found between M_t/M_0 values obtained by gravimetric measurements and I_t/I_0 values obtained by integrating NMR profiles with micrometric resolution. With regards to shrinkage a net reduction of size L/L_0 was observed up to about 15 h. Information on shrinkage of the fruit by NMR profiles was also obtained, the reduction of thickness of profiles showed a good correlation with the L/L_0 values (r^2=0.87).

In conclusion, results obtained by NMR combined with those obtained by the standard gravimetric method, size measurement and SEM images allow to elucidate the effect of drying on textural and physical structure of fruit.

References

Adiletta, G., Iannone, G., Russo, P., Patimo, G., De Pasquale, S., Di Matteo M., 2014, Moisture migration by magnetic resonance imaging during eggplant drying: a preliminary study, Int. J. Food Sci. Technol., 49, 2602-2609.

AOAC, Official methods of analysis. Association of Official Analytical Chemist, Arlington, Virginia, USA, 1997, 16th ed.

Di Matteo, M., Cinquanta, L., Galiero, G., Crescitelli, S., 2003, A mathematical model of mass transfer in spherical geometry: plum (*Prunus domestica*) drying, J. Food Eng., 58, 183-192.

Brasiello, A., Adiletta, G., Russo, P., Crescitelli, S., Albanese, D., Di Matteo, M., 2013, Mathematical modeling of eggplant drying: Shrinkage effect, J. Food Eng., 114, 99-105.

Brasiello, A., Crescitelli, S., Adiletta, G., Di Matteo, M., Albanese, D., 2011, Mathematical modeling with shrinkage of an eggplant drying process, Chem. Eng. Trans., 24, 451-456.

Capitani, D., Mannina, L., Proietti, N., Sobolev, A.P., Tomassini, A., Miccheli, A., Di Cocco, M.E., Capuani, G., De Salvador, R., Delfini, M. 2010, Monitoring of metabolic profiling and water status of Hayward kiwifruits by nuclear magnetic resonance, Talanta, 82,1826-1838

Capitani, D., Mannina, L., Proietti, N., Sobolev, A.P., Tomassini, A., Miccheli, A., Di Cocco, M.E., Capuani, G., De Salvador, R., Delfini, M. 2013, Metabolic Profiling and Outer Pericarp Water State in Zespri, CI.GI, and Hayward Kiwifruits, J. Agr. Food Chem., 61(8), 1727-40.

Capitani, D., Sobolev, A. P., Delfini, M., Vista, S., Antiochia, R., Proietti, N., Bubici, S., Ferrante, G., Carradori, S., De Salvador, F. R. , Mannina, L. 2014 NMR methodologies in the analysis of blueberries, Electrophoresis, 35, 1615-1626..

Guine´, R.P.F., Castro, J.A.A.M., 2002, Pear drying process analysis: drying rates and evolution of water and sugar concentrations in space and time, Drying Technol., 20, 1515-1526.

Monsalve-Gonzalez, A., Barbosa-Canovas, G.V., McEvily, A.J., Lyengar, R., 1994, Inhibition of enzymatic browning in apple products by 4-hexylresorcinol, Food Technol., 4, 110-118.

Panarese, V., Laghi, L., Pisi, A., Tylewict, U., Dalla Rosa, M., Rocculi, P., 2012, Effect of osmotic dehydration on *Actinidia deliciosa* kiwifruit: a combined NMR and ultrastructural study. Food Chem., 132, 1706−1712.

Park, K.J., Bin, A., Brod, F.P.R., 2003, Drying of pear d'Anjou with and without osmotic dehydration, J. Food Eng., 56, 97-103.

Perlo, J., Casanova, F., Blu¨mich, B., 2005, Profiles with microscopic resolution by single-sided NMR, J. Magn. Reson.,176, 64-70.

Raffo, A., Gianferri, R., Barbieri, R., Brosio, E., 2005, Ripening of banana fruit monitored by water relaxation and diffusion1H-NMR measurements, Food Chem., 89 (1),149-158.

Russo, P., Adiletta, G., Di Matteo, M., 2012, The influence of drying air temperature on the physical properties of dried and rehydrated eggplant, Food Bioprod Process, 91(3), 249-56.

Taglienti, A., Massantini, R., Rotondi, R., Mencarelli, F., Valentini, M., 2009, Postharvest structural changes of Hayward kiwifruit by means of magnetic resonance imaging spectroscopy, Food Chem., 114, 1583–1589.

Tylewicz, U., Panarese, V., Laghi, L., Rocculi, P., Nowacka, M., Placucci, G., Dalla Rosa, M., 2011, NMR and DSC water study during osmotic dehydration of *Actinidia deliciosa* and *Actinidia chinensis* kiwifruit. Food Biophys., 6, 327−333.