MRI AND BULK NMR T_2 MEASUREMENT OF POTATOES HEATED BY MICROWAVE

Sharifudin Md. Shaarani[1], Kevin P. Nott[2] & Laurence D. Hall[2]

[1]School of Food Science and Nutrition, UniversitI Malaysia Sabah. Locked Bag 2073. Kota Kinabalu 88999, Sabah. Malaysia.
[2]Herchel Smith Laboratory for Medicinal Chemistry, University of Cambridge School of Clinical Medicine, University Forvie Site. Robinson Way, Cambridge, CB2 2PZ, U.K.

ABSTRACT. *Magnetic resonance (MR) imaging and bulk T_2 measurements of the tissue water protons were performed to investigate whether the variability of cooking potatoes in a microwave oven reflects differences either of the raw materials or of the heating process. Sixteen whole potatoes, eight from the same plant and eight from different plants were individually heated in a microwave oven for four minutes. Segmentation of the pith, parenchyma and cortex tissues of the raw potato could be achieved from MR images of the spatial distribution of the T_2 values. The experimental data from bulk NMR T_2 measurements were best analysed by bi-exponential fitting. The long T_2 component (T_{21}) decreased (from 254 to 73 ms for potatoes from the same plant and from 298 to 115 ms from different plants) upon cooking; this reflects gelatinisation of the starch plus water loss induced by microwave heating. The T_{21} values of cooked potatoes (55 – 91 ms same plant, and 73 – 141 ms different plants) covered a wider range than those of raw potatoes (250 – 265 ms same plant and 299 – 301 ms different plants) indicating that the variability of cooking could not be accounted for solely by the differences measured for the raw product.*

KEYWORDS. *NMR; MRI; Potato; Plant variability; Microwave heating*

INTRODUCTION

A major challenge for the food industry is that the variability of both the raw materials and the processing conditions can affect the quality of the final product. As a consequence, it is important to understand not only the fundamental properties of the raw materials used but also the processes that they undergo (Tijkens et al., 2003). Hence the food industry needs methods that can be used either 'on-line' or 'at-line' to evaluate batches of the raw materials prior to processing, so that the subsequent processing conditions can be adjusted to optimise the final product (Thybo et al., 2004).

The quality of cooked potatoes is important for many consumers and food producers alike. It is already well known that the structural and chemical composition of a potato depends on many factors including species, maturity, growing- and storage-conditions (Burton, 1989); in particular, texture is one of the most important attributes in its acceptance by both consumers (Thybo et al., 2000) and food processors (Povlsen et al., 2003). Consequently, there has been extensive research to quantify and understand factors that affect the texture of cooked potatoes; these include sensory perception (Collison et al., 1980; Van Marle et al., 1997), and instrumental approaches which relate to the rheological, biochemical and physical properties of potato (Martens and Thybo,

2000; Thybo et al., 2000; Kaaber et al., 2001; Alvarez and Canet, 2002; Bu-Contreras and Rao, 2002; Van Dijk et al., 2002).

'Bulk' and 'Imaging' Nuclear Magnetic Resonance (NMR) techniques have already been used to study potato structure at both the macroscopic (tissue) and microscopic (cellular) level. Thus, Toussaint et al., (1999), used MRI to develop a model that was capable of predicting the gelatinised fraction of starch in boiled potato as a function of time, temperature and penetration of the gelatinisation front. Thybo et al. (2000) used low field proton (^{1}H) NMR combined with near-infrared reflectance (NIR) and uniaxial compression and chemical analysis to predict the sensory texture quality of boiled potatoes. Subsequently, Thygesen et al., (2001) explored correlations between low field ^{1}H NMR relaxation times, sensory texture and chemical constituents of boiled potato; they concluded that NMR measurements at low field can be used to evaluate certain "mouth-feel" variables due to its sensitivity to the state of moisture in the sample. Martens et al., (2002), used T_1 weighted Magnetic Resonance (MR) images to cross correlate sensory descriptive analysis with Magnetic Resonance Imaging (MRI) data.

Recently MRI techniques were used in this laboratory to investigate the effects of microwave heating of potato (Nott et al., 2003); prior to shrinkage, MRI phase mapping gave spatial measurements of temperature that are independent of the moisture content and structural changes. In addition, the spatial distribution of the water proton spin-spin relaxation times (T_2 values) showed three distinctive tissues, the pith, the parenchyma tissue and the cortex, the T_2 values of which decreased and converged as the potato homogenised during cooking. It is also suggested that moisture loss is another factor besides starch gelatinisation that caused the significant reduction of T_2 values upon microwave heating.

Thybo et al., (2003) investigated relationships between the dry matter content of potatoes and the parameters determined from both bulk NMR and MR images. Both components of the spin–spin relaxation times determined by bulk NMR were found to be highly correlated with dry matter; as a consequence, MR images showed large visual differences due to variations in the water distribution. A subsequent study by Thybo et al., (2004), investigated the ability of MRI to evaluate the sensory texture quality of cooked potatoes; although there was no correlation between MRI data from raw potato and the specific gravity, it was suggested that MR data identifies anatomic structures within the raw potato which are important for the perceived textural properties after cooking.

To complement the substantial body of work already reported for raw potato, this present study was designed to use a combination of MR imaging and bulk NMR for two purposes: first, to study the variability within species for both raw and cooked potato; second, to quantitate structural changes that occur during microwave heating.

MATERIALS AND METHODS

Heating experiments

Sixteen potatoes (Desiree variety) from a local farm were used; eight from the same plant whereas the other eight were randomly picked from different plants; all were cleaned and weighed before and after heating. A 900W domestic microwave oven (Sharp model R383SL) with a turntable was used at 100% power. Each potato was attached to a perspex sheet which had a triangular end to allow accurate repositioning in the MR probe before, during and after heating. For every experiment, the oven was pre-warmed by heating 2 litres of water for 5 minutes; then each potato was placed individually in the centre of the turntable and heated for 4 minutes.

MRI hardware

All MRI measurements were acquired using a 2.35 Tesla, 31cm horizontal-bore superconducting magnet (Oxford Instruments, Oxford, UK) connected to a Bruker Medzintechnik Biospec II imaging console (Karlsruhe, Germany). A gradient set (14.5 cm internal diameter) was built 'in house' with each axis powered by a pair of Techron gradient amplifiers (Model 7790, Crown International Inc., Elkart, U.S.A). A cylindrical, eight strut bird cage radiofrequency (RF) probe (internal diameter of 9.4 cm), built 'in house', was used in the quadrature mode to transmit and receive the MR signal.

MRI quantitation and data processing

The protocols for MRI quantification of the spin-spin relaxation times (T_2-values) gave 313 μm (matrix 256 × 256) in-plane spatial resolution for a 3 mm slice thickness. A set of 16, T_2-weighted echo images was acquired using a multi-echo, spin echo sequence with TE 12 ms and TR 7.5 s, scan time 33 minutes. The data for the equivalent pixels in each series of images were fitted to the corresponding mono-exponential decay curve for T_2 given by Equation 1

$$M_{xy} = M_0 \exp(-TE/T_2) \quad (1)$$

where M_{xy} is the magnetisation in a particular pixel, M_0 is the equilibrium magnetisation, TE is the echo time and T_2 is the spin–spin relaxation time.

The sets of raw data were transferred to a network of Linux workstations where the subsequent data processing used a curve fitting program written-in-house by Dr P. Watson, based on the method of Levenberg–Marquandt (1963) least-squares optimisation. The images were visualised using image display software (Cmrview) written by Dr N.J.Herrod. Segmentation was carried out by manually drawing a region of interest (ROI) on the three tissues of raw potato.

Bulk NMR T_2 measurement

All the measurements of the raw and cooked potatoes were made at room temperature (20°C). Bulk NMR T_2 measurements were acquired from the potatoes using a Carr-Purcell-Meiboom-Gill (CPMG) sequence with 256 points, TE 1.6ms and TR 10 seconds. The T_2 data were fitted to the bi-exponential decay curves using Equation 2, with the aid of Marquardt least-squares optimisation method (Gnuplot software, Linux version 3.7)

$$M_{xy} = M_{01}exp(-TE/T_{21}) + M_{02}exp(-TE/T_{22}) \quad (2)$$

where T_{21} and T_{22} are the two T2 components.

RESULTS AND DISCUSSION

MRI quantitation

Figure 1 demonstrates that the T_2 contrast between the pith, parenchyma and cortex of the raw potato in a T_2 map is sufficient to distinguish between those three tissues; as a result, they can be segmented and analysed separately. The fact that the water in the pith has longer T_2 values than that in the parenchyma and cortex tissues may reflect the fact it is present in larger amounts than in those other two tissues (Karlsson & Eliasson, 2003).

The mean and standard error (n=8) for T_2 of the pith of the raw potatoes was 80 ± 4 ms for the same plant (Figure 2(a)), and 100 ± 5 ms for the different plants (Figure 2 (b)). The values for parenchyma and cortex of the same plant were 61 ± 4 ms and 58 ± 6 ms, respectively; the corresponding T_2 values for both tissues from different plants were slightly higher, 80 ± 1 ms and 74 ± 4 ms, respectively. Martens and Thybo (2000) suggested that the three types of tissues are distinct in raw potato because of the differences in their starch and water contents.

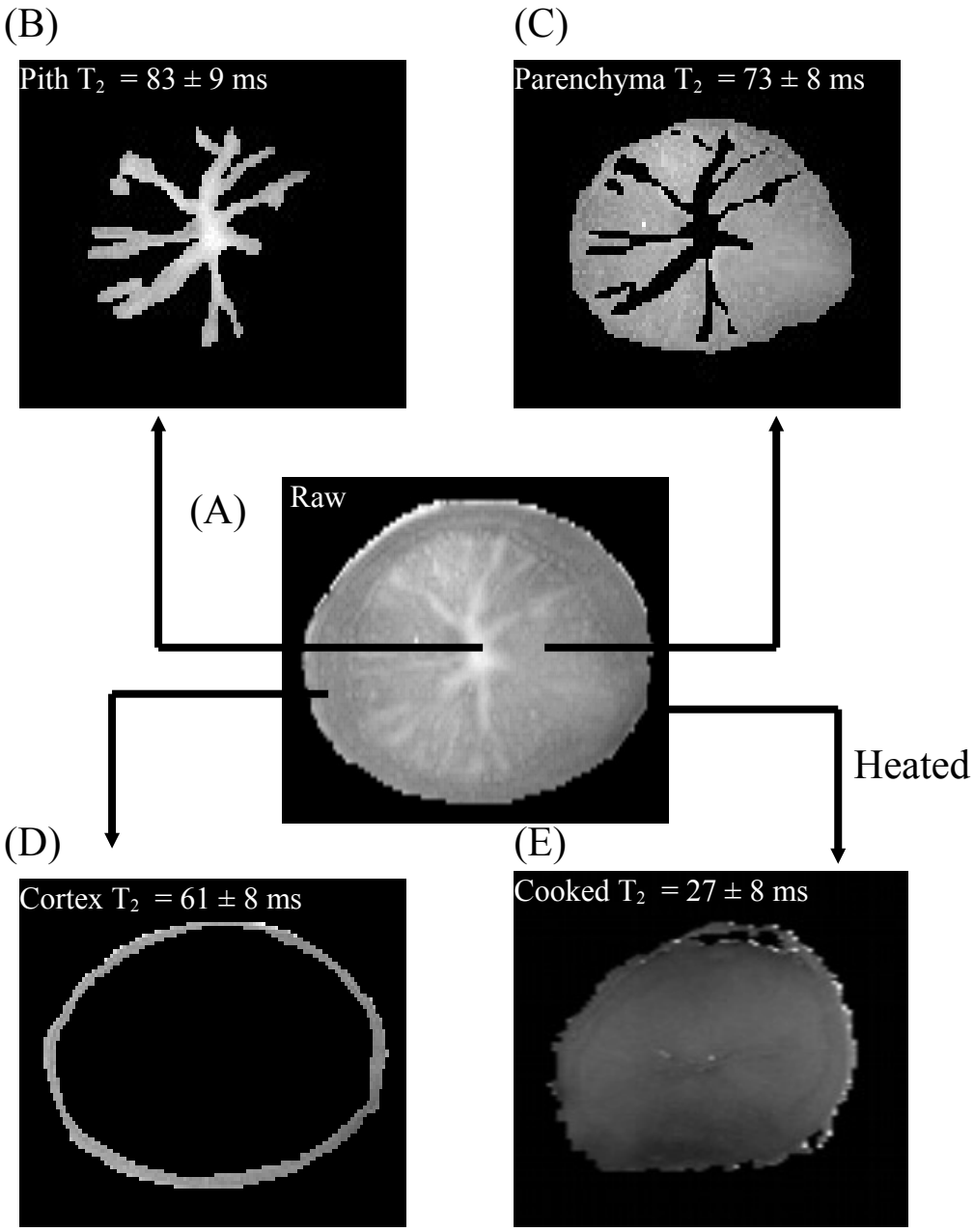

Figure 1. (A) Experimental MRI image of an intact raw potato, together with the location following manual segmentation: (B) the pith, (C) the parenchyma and (D) the cortex. (E) Shows a 2D slice from the MR image of a cooked potato at ambient temperature.

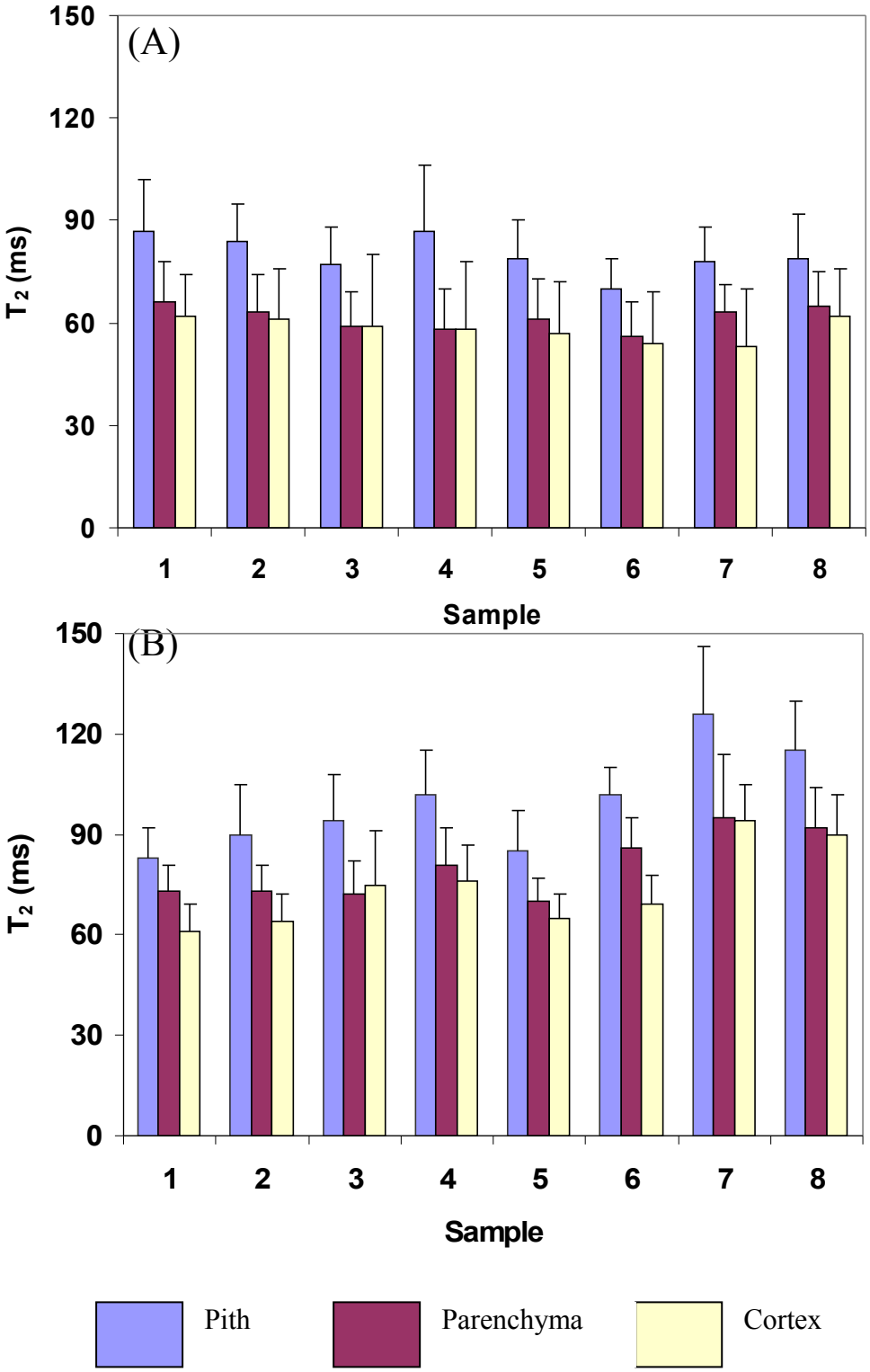

Figure. 2. T_2 values for the water protons in the three different tissues of raw potatoes measured by MRI: (A) from the same plant, and (B) from different plants.

However, in cooked potatoes (Figures 3 (A) and (B)), the difference in the T_2 values between the three tissues was not large enough for them to be distinguished by segmentation, which implies that the texture of the cooked potatoes had become more homogenous due to cellular disruption. Nott et al. (2003) previously reported that microwave heating caused cellular disruption, which resulted in an even distribution of water, effectively homogenising the texture as observed in the T_2 maps. Although heating also results in moisture loss, the content cannot be absolutely quantitated by MRI measurements of the liquid proton density (M_0) since those protocols cannot detect the water which is strongly bound to the starch granules before cooking. Interestingly, re-analysis of data from that earlier study showed a highly negative correlation ($r = -0.956$, $p<0.01$) between the T_2 values of the cooked potatoes from MR imaging and measurements of water loss (Figure 4). This suggets that after the structural changes have taken place the T_2 values from MR imaging may represent the moisture distribution even though the M_0 values extrapolated from T_2 decay do not. As a consequence, the role of M_0 values was not further considered in the present study. The standard deviation of T_2 indicates the spatial heterogeneity of cooking across the potato. The data measured after 1 minute of heating, clearly demonstrates that the potato was only partly cooked, as did the data after 2 minutes. Thereafter, the standard deviation decreased progressively with increasing cooking time as the potato structure became more homogenous until it was fully cooked (after 4 and 5 minutes of heating).

Bulk NMR measurement

Figure 5 shows the results from bi-exponential fitting of the T_2 decay of water protons for raw and cooked potatoes from the same, and from different plants which is in agreement with previous studies (Thybo et al., 2003; Thygesen et al., 2001 and Thybo et al., 2000). It has been suggested that the long T_2 component (T_{21}) is associated with intracellular water whereas the short T_2 component (T_{22}) is ascribed to extracellular water in the vascular tissue and pith (Thybo et al., 2000). In the present study, the mean values for T_{21} and T_{22} of the water in the raw potatoes from the same plant were 254 ± 8 ms and 41 ± 2 ms respectively, whereas the values for the different plants were 298 ± 10 ms and 38 ± 2 ms respectively. That the standard deviation for the values from different plants is slightly higher than for those from same plant suggests that there may be a higher 'biological' variation between different plants than within the same plant.

Figure 5 also shows there is a decrease in the T_2 values from raw to cooked potatoes; thus the mean values of T_{21} and T_{22} for the cooked potatoes from the same plant were 73 ± 14 ms and 29 ± 6 ms respectively whereas the values for different plants were 115 ± 22 ms and 39 ± 8 ms, respectively. This decrease in the T_2 values is due to the starch gelatinisation process during which starch granules progressively absorb water from outside, swell, and then on disruption release amylose, with which the water can associate (Olkku and Rha, 1978). Thybo et al., (2000) suggested that the difference between the long T_2 components of the raw and cooked potatoes is due to the gelatinisation process, which provides a more accessible molecular environment for the water and hence restrict its motion in the intra-cellular matrix. The difference between the short T_2 components of the raw and cooked tissues was attributed to extra cellular water situated in the vascular tissue and pith which is diffusion-hindered.

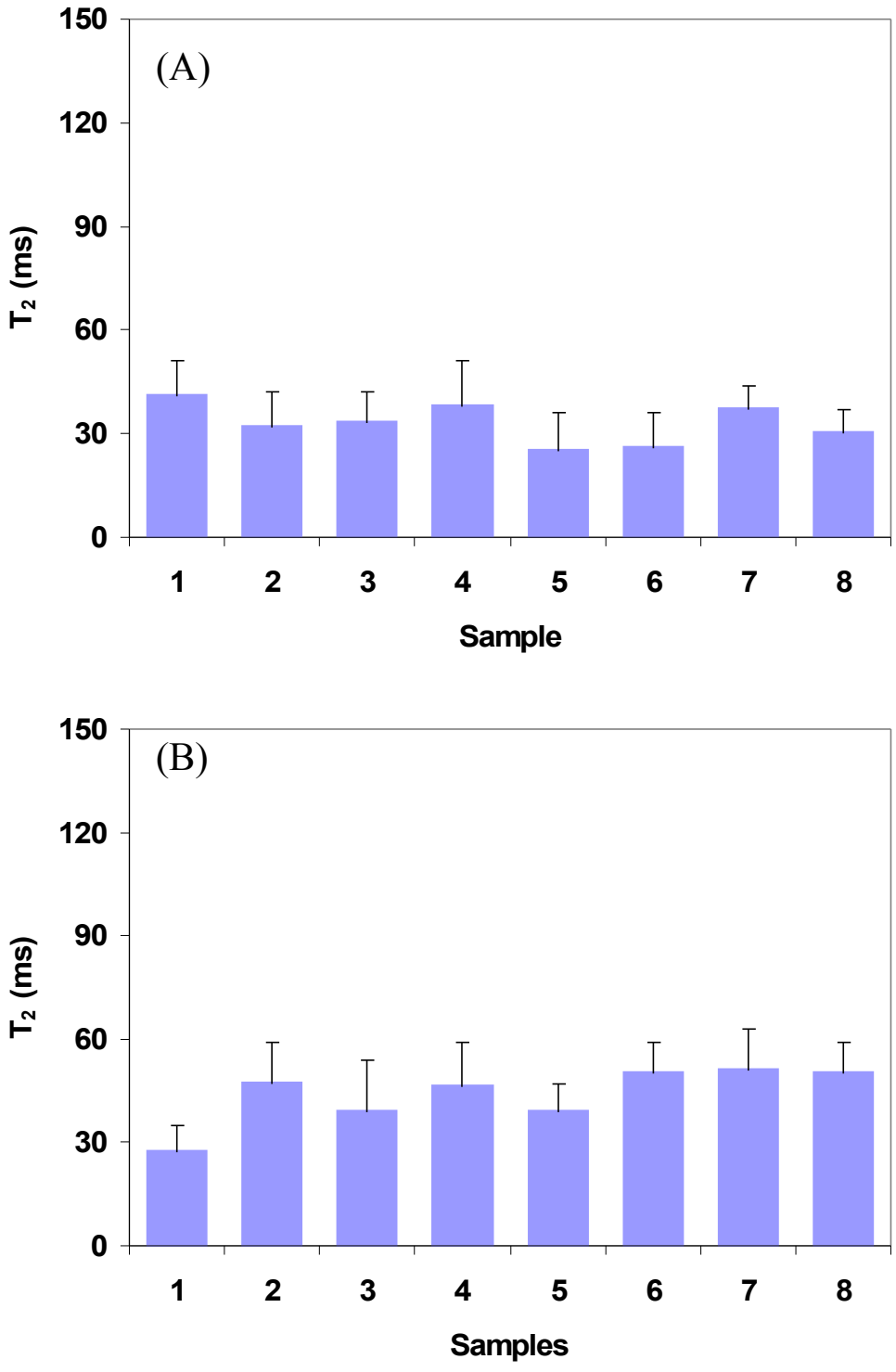

Figure. 3. Mean T_2 values for cooked potatoes measured by MRI: (A) from the same plant, and (B) from different plants

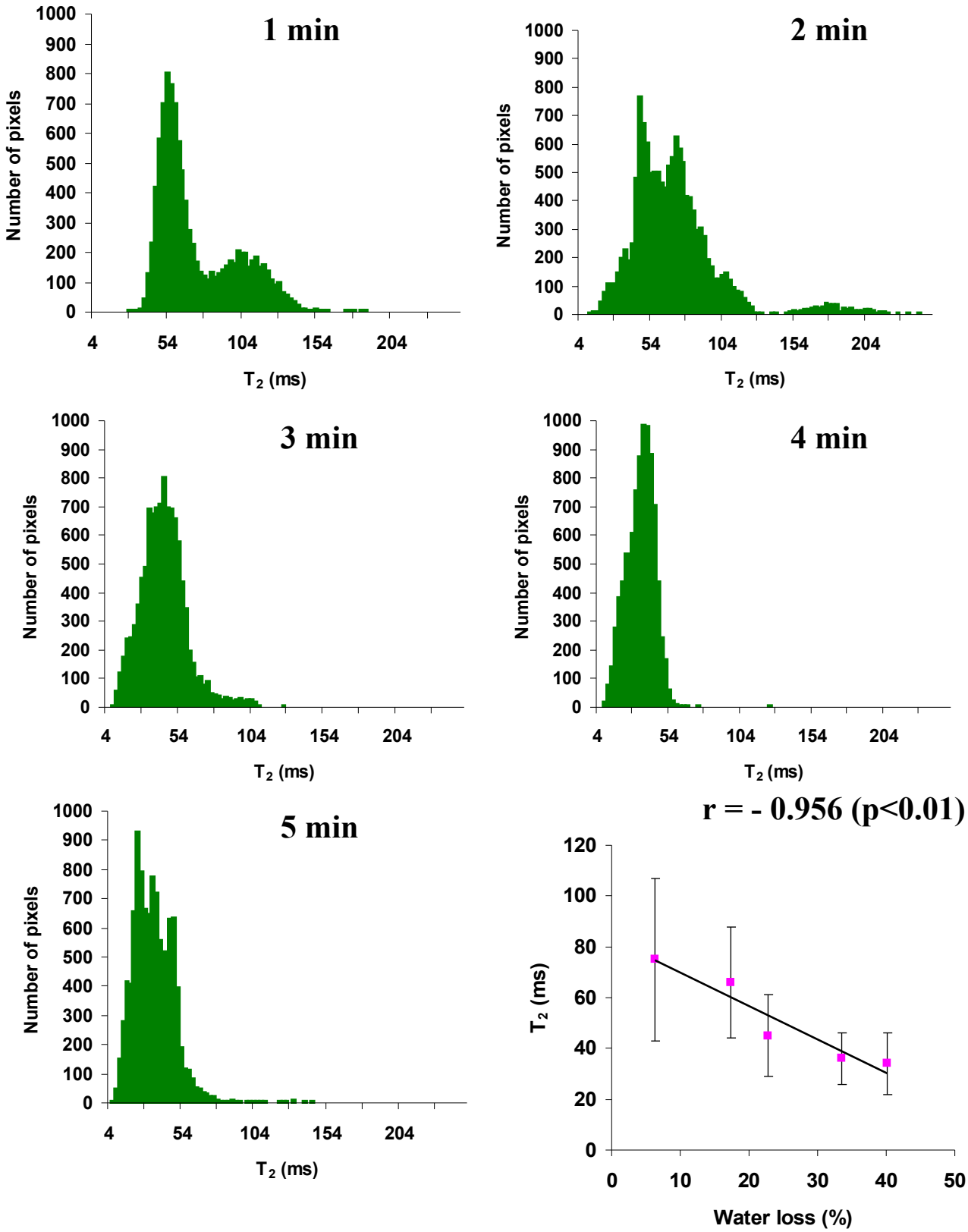

Figure 4. Histogram plots for the T_2 values of the water proton determined by MRI for different potatoes heated for 1, 2, 3, 4 and 5 minutes. The correlation with percentage water loss is shown in the graph on the lower right of the figure.

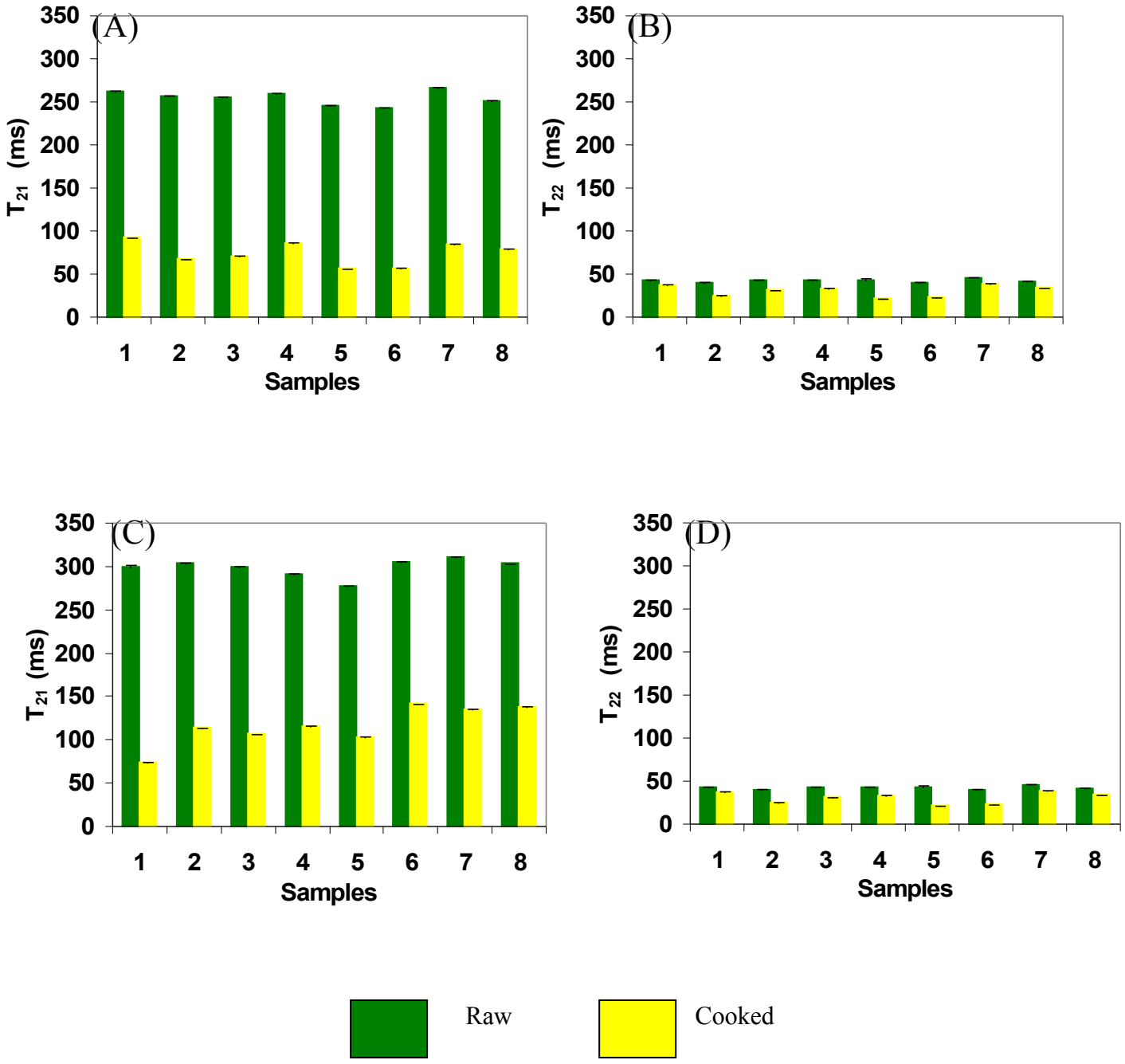

Figure 5. Two components of the T_2 relaxation times measured by bulk NMR: (A) T_{21}, and (B) T_{22} values for raw and cooked potatoes from the same plant; (C) T_{21}, and (D) T_{22} values of raw and cooked potatoes from the different plants.

Although the difference between T_2 values of the three tissues was large enough for them to be separately observed in the MR images, it was too small to enable then to be distinguished in the bulk T_2 measurement; typically such analyses requires an order of magnitude difference between the individual components. Consequently the bulk T_2 measurement reflects the cellular distribution of water, and the fit of the NMR data to a mono-exponential decay is the weighted average of two of the bulk components. The echo train used for MRI is too short (12 ms x 16 = 192 ms) to be significantly influenced by the longer T_2 component observed in the bulk data, which is also the major component. Although there is good overall agreement between these results with those from other studies (Thybo et al., 2000) there are numerical differences in the actual T_2 values; these reflect the different field strengths used (100MHz in this study compared to 23.2MHz), and also the different heating methods (microwave heating in this study as opposed to boiling).

CONCLUSIONS

This study provides a clear demonstration of the fact that MRI can be used to measure intact samples of food materials which undergo physical changes due to cooking; specifically, that T_2 measurements by either MR imaging or bulk NMR can be used to evaluate the variability of cooking potatoes by microwave heating. The T_2 measurements can be used to rationalise changes in texture between raw and cooked potato; microscopically, T_2 values indicate the different molecular associations between water and starch in the tissues of the raw versus cooked potatoes.

The present study demonstrates two potential benefits of MRI measurements: first, the use of whole potato as opposed to excised sections to obtain non-invasive measurements for the quality of intact potatoes; second, it demonstrates that the three types of tissues in raw potato can be analysed quantitatively, rather than qualitatively. More broadly, this study also suggests that MRI measurements may be able to help agriculturalists and food scientist to determine the fundamental variability of "raw food" materials and thereby understand the changes which occur when they are cooked.

ACKNOWLEDGEMENTS

LDH gratefully acknowledges the late Dr Herchel Smith for his endowment which established the Herchel Smith Laboratory for Medicinal Chemistry; SMS thanks the University Malaysia Sabah for a scholarship. KPN would like to thank the UK Biotechnology and Biological Sciences Research Council (BBRSC) for funding (Grant No. D15646). Thanks are also due to Richard Smith, Simon Smith and Cyril Harbird for maintenance of the MRI hardware; Dr Da Xing and Dr Nicholas Herrod for the computer facilities; and Dr Paul Watson for the curve fitting software.

REFERENCES

Alvarez, M. D. & Canet, W. 2002. A comparison of various rheological properties for modelling the kinetics of the thermal softening of potato tissue (c.v. Monalisa) by water cooking and pressure steaming. *International Journal of Food Science and Technology,* **37**: 41-55.

Bu-Contreras, R. & Rao, M. A. 2002. Review: Dynamic rheological behaviour of heated potatoes. *Food Science Technology International*, **8 (1)**: 3-10

Burton, W.G. 1989. *The potato*. 3rd edition. New York. Longman Scientific &Technical.

Collison, R., Johnson, K., Olufolakime, O. O. & West, A. 1980. Subjective and objective assessments of the degree of cooking of potatoes heated by different methods. *Journal of Food Technology,* 15, 1-8.Kaaber, L., Brathen, E., Martinsen, B. K. & Shomer I. 2001. The effect of storage condition on chemical content of raw potatoes and texture of cooked potatoes. *Potato Research,* **44**: 153-163

Karlsson, M. E. & Eliasson, A. C. 2003. Gelatinization and retrogradation of potato (Solanum tuberosum) starch in situ as assessed by differential scanning calorimetry (DSC). *Lebensmittel-Wissenschaft Und-Technologie*, **36**: 735-741.

Lisinska, G. & Leszczynski, W. 1989. *Potato science and technology*, London & New York. Elsevier Applied Science.

Martens, H., Thybo, A. K., Anderson, H. J., Karlsson, A. H., Dønstrop, S., Stødkild-Jørgensen, H., & Martens, M. 2002. Sensory analysis for magnetic resonance-image analysis: using human perception and cognition to segment and assess the interior of potatoes. *Lebensmittel-Wissenschaft Und-Technologie,* **35**: 70-79.

Martens, H. J., & Thybo, A. K. 2000. An integrated micro structural, sensory and instrumental approach to describe potato texture. *Lebensmittel-Wissenschaft Und-Technologie*, **33**: 471-482.

Nott, K. P., Md Shaarani, S. & Hall L. D. 2003. The effect of microwave heating on potato texture as studied with magnetic resonance imaging In Belton P S, Gil, A.M & Rutledge, D. (Eds), *Magnetic Resonance in Food Science: Latest Development*, (pp 38-46) The Royal Society of Chemistry.

Olkku, J. & Rha, C. 1978. Gelatinisation of starch and wheat flour starch - A review. *Food Chemistry*. **3**: 293-317

Povlsen, V. T., Rinnen, Å., Van den Berg, F., Anderson, H. J. & Thybo, A. K. 2003. Direct decomposition of NMR relaxation profiles and prediction of sensory attributes of potato samples. *Lebensmittel-Wissenschaft Und-Technologie,* **36**: 423-432.

Thybo, A. K., Bechmann, I.E., Martens, M. & Engelsen, S.B. 2000. Prediction of sensory texture of cooked potatoes using uniaxial compression, near infrared spectroscopy and low field ^{1}H NMR spectroscopy. *Lebensmittel-Wissenschaft Und-Technologie,* **33**: 103-111.

Thybo, A. K., Szczypiński, P. M., Karlsson, A. H., Dønstrop, S., Stødkild-Jørgensen, H. S. & Andersen, H. J. 2004 Prediction of sensory texture quality attributes of cooked potatoes by NMR-imaging (MRI) of raw potatoes in combination with different image analysis methods. *Journal of Food Engineering*, **61**: 91-100

Thygesen, L.G., Thybo, A.K., & Engelson, S.B. 2001. Prediction of sensory texture quality of boiled potatoes from low-field ^{1}H NMR of raw potatoes. The role of chemical constituents. *Lebensmittel-Wissenschaft Und-Technologie*, **34**: 469-477.

Tijkens, L. M. M., Konopachi, P. & Simcic, M. 2003. Biological variance burden or benefit? *Postharvest biology and technology*, **27**:15-25.

Toussaint, C. A., Langevin, F., Pain, J. P. & Goullieux. 1999. Study and modelisation of starch gelatinisation in potatoes with magnetic resonance imaging. In Belton, P.S., Hills B.P., & Webb G. A. (Eds)., *Advances in magnetic resonance in food science.* (pp256 – 263). The Royal Society of Chemistry.

Van Dijk, C., Fischer, M., Beekhuizen, J.G., Boeriu, C. & Stolle, S. T. 2002. Texture of cooked potatoes (solenum tuberosum), preheating and the consequences for the texture and cell wall chemistry. *Journal of Agricultural and Food Chemistry*, **50**: 5098-5106

Van Marle, J. T., Recourt, K., Van Dijk, C., Schols, H. A. & Voragen, A. G. J. 1997. Structural features of cell walls from potato (solanum tuberosum L.) cultivars Irene and Nicola. *Journal of Agricultural and Food Chemistry*, **45**: 1686-1693.