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**Utilization of NMR Technology for Internal
Nondestructive Quality Evaluation of Fruits
and Vegetables**

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Table of Contents

	Page
Cover page	i
Table of Contents	ii
Abstract	1
Objectives (as stated in the original research proposal)	2
Relevant data, methodology, results and discussion	2
NMR imaging	2
Single-pulse FID spectrum	3
One-dimension NMR signal projection	4
Real-time on-line system	5
Evaluation of the research achievements	6
Description of cooperation	7
Conclusions	7
List of Publications	7
Figures	9-10
Appendix I	11

Abstract

Project Title: Utilization of NMR Technology for Internal Nondestructive Quality Evaluation of Fruits and Vegetables

Objective: The objective of this research was to investigate the potential use of NMR for evaluating various internal quality factors of fruits and vegetables, leading to the eventual development of practical techniques that are useful for future development of NMR sensors.

Summary: Investigation on NMR imaging, one-dimension NMR projection, and single-pulse free-induction-decay (FID) spectrum led to the development of high-speed NMR techniques for real-time sensing of internal quality of selected fruits.

NMR imaging can be used for detecting internal defects and various quality factors such as bruises, dry regions, worm damage, stage of ripeness, tissue breakdown, and the presence of voids, seeds, sprouts, and pits. The one-dimension (1-D) image profile technique, in which the 1-D projection of the NMR signal of a selected slice of the intact fruit is recorded, is suitable for detecting tissue breakdown regions, presence of pits, and other defects in fruits. The oil and sugar content of fruits can be determined from the single-pulse FID spectrum measurement, in which a surface coil is used to acquire the FID spectrum and the ratio of the resonance peaks is used as the quality index. The latter two techniques are suitable for high-speed sorting of fruits.

The most important accomplishment is the successful development of high-speed NMR techniques for determining internal quality of fruits while they are moving at speeds up to 30 cm/s. This accomplishment is an important step toward the development of NMR techniques for on-line sorting of fruits and vegetables.

Objectives (as stated in the original research proposal)

The general objective of this research is to investigate the potential use of NMR for evaluating various internal quality factors of fruits and vegetables, leading to the eventual development of practical techniques that are useful for future development of NMR sensors. Specific objectives are:

1. To continue to identify additional NMR parameters that correlate well with internal compositions (oil and sugar content) and tissue breakdown (bruised, overripe, and watery tissue) of selected fruits and vegetables.
2. To develop new and/or search for existing rapid procedures for measuring these parameters.
3. To develop design criteria for an experimental NMR quality sensor.

An in-depth study will be carried out on selected commodities with as-yet-unsolved problems in evaluating internal quality. This study, leading toward the development of the necessary sensing techniques, should serve as a model for other commodities.

Relevant data, methodology, results and discussion

We investigated three major techniques: NMR imaging, single-pulse FID spectrum, and one-dimension NMR projection.

NMR imaging. Two-dimensional images were acquired using a General Electric CSI-2 NMR spectrometer, operating at a proton resonant frequency of 85.5 MHz; a Biospec-7T, operating at 300 MHz; and a Tecmag (0.6T), operating at 26 MHz. Results of our study indicate that NMR imaging technique can be used for detecting internal defects and various quality factors such as bruises (apple, peach, pear, onion), dry regions (apple, pear, avocado), worm damage (Asian pear, potato), stage of ripeness (tomato, avocado), tissue breakdown (cantaloupe, mango) and the presence of voids (apple, pears, cantaloupe), seeds (apple, pomelo), sprouts (garlic) and pits (olive, cherry, prune, peach). Although NMR imaging is a very powerful technique for detecting internal quality of fruits and vegetables, there still remain two problems that must be solved before this technique can be viable for on-line sorting. First, the imaging speed must be increased to a sustained speed of about 3 to 5 images/s. Second, the time required to analyze the image and extract useful information for making sorting decision should be within 100 ms. A method for processing and analyzing two-dimensional NMR images of apples for detection of bruises was developed. It was tested with 40 images of apples. Test results showed that by counting the number of pixels whose distances from the center of the apple were more than 0.75 of the apple's mean radius, and whose intensities are greater than a preset level, the algorithm was able to discriminate between all bruised and non-bruised apples. The method, which requires only two scans of the image and simple computations, is fast and

efficient. Detailed information of this method is given in Appendix I (Zion, B., P. Chen, and M. J. McCarthy. 1995. Detection of bruises in magnetic resonance images of apples. *Comp. and Elect. in Agric.* 13(4):289-299).

A study was made to find out why the bruised tissue regions appear brighter than intact tissue regions in NMR images of bruised apples. The cause of the contrast was investigated. The spin-spin relaxation rates ($1/T_2$) of the bruised regions were found to be greater than those of firm tissue regions, ruling out this mechanism as a cause for the contrast. By comparing spin-echo images with gradient-recalled-echo images, it was concluded that the contrast may be attributed to the decrease in the partial destruction of the cellular structure caused by bruising. A detailed report of this study is given in Appendix I (McCarthy, M. J., B. Zion, P. Chen, S. Ablett, A. H. Darke, and P. J. Lilliford. 1995. Diamagnetic susceptibility changes in apple tissue after bruising. *Journal of the Science of Food and Agriculture* 67:13-20).

Single-pulse FID spectrum. The single-pulse free-induction-decay (FID) spectrum measurement, in which a surface coil is used to acquire the FID spectrum, and the ratio of the resonance peaks is used as a quality index, can be used to determine the oil and/or sugar content of fruits and vegetables (avocado, prune, pear, mango, kiwi). Tests were made using a General Electric CSI-2 NMR spectrometer with a 2-cm diameter surface coil, operating at a proton resonant frequency of 85.5 MHz. A Tecmag 0.6 Tesla spectrometer with a 30-cm diameter bore was also available for use with large samples. This technique has many features desirable for high-speed sorting of fruits. First, it is very fast. It requires only a fraction of a second to acquire the signal and process the data. Second, the use of the surface coil facilitates easy measurements of intact fruits. Third, measurements made with the surface coil are less sensitive to varying fruit size and are not so affected by the core, pit, or seeds of the fruit. A 2-cm diameter surface coil acquires the signal from a small region of the fruit (a volume approximately equal to the product of the area of the coil and a depth of half the coil diameter). The volume of this active region is relatively independent of the fruit size and does not contain part of the core, pit, or seeds of the fruit. Therefore, the NMR signal, which is proportional to the volume of this active region, is also less sensitive to fruit size and is less likely to be affected by the core, pit, or seeds. Fourth, this technique can tolerate greater non-homogeneity of the magnetic field. Therefore, shimming for every fruit, which is a lengthy procedure, is not required. Since the active volume is small compared to the entire fruit, the equivalent field homogeneity required for the active volume is much easier to attain than that for the entire fruit. For example, the volume of a 7-cm spherical fruit is 180 cm^3 , which is about 60 times the 3-cm^3 active volume of a 2-cm surface coil. Therefore, it would be much easier to produce a field homogeneity of 2 parts per million (ppm) within the active region of the 2-cm surface coil than to do it within the volume of the entire fruit. Fifth, the quality index, which is expressed as the

ratio of two resonance peaks of the spectrum, is less sensitive to variation due to sample geometry and instrument variability.

A study was made to determine the soluble solids content (SSC) of fresh prunes by this single-pulse FID spectrum measurement technique. The FID of the prunes were measured in the General Electric CSI-2 NMR spectrometer. Results show that the ratio of the soluble solids resonance peak to the water resonance peak was closely correlated with the SSC of the prunes, with a coefficient of correlation $r = 0.907$. Furthermore, we found that detection of the SSC was better with the surface coil when the magnetic field was not shimmed (the shim coil turned off). This is an important finding, since the requirement of magnetic-field shimming for each fruit is a major obstacle to high-speed sorting. The signal acquisition time per fruit was approximately one second. However, in real applications it could be reduced to less than 100 ms per fruit. Additional information on this study is given in Appendix I (Zion, B., P. Chen, and M. J. McCarthy. 1995. Non-destructive quality evaluation of fresh prunes by NMR spectroscopy. *Journal of the Science of Food and Agriculture* 67, 423-429).

The single-pulse FID spectrum measurement technique appeared to have good potential for on-line sorting. In previous studies, the FID signals were acquired while the fruits were stationary. The next step was to develop a high-speed NMR technique that can detect the quality of moving fruits. A specially designed fruit conveyor, that can convey fruits through the spectrometer at different speed, was used to evaluate high-speed on-line sensing and real time sorting of fruits. Using this conveyor, we have shown for the first time that it is possible to acquire an NMR signal from a moving fruit. We successfully acquired FID spectra of avocados while they were moving at speeds up to 25 cm/s. The oil/water resonance peak ratio, obtained from the spectrum, correlates very well ($r^2 = 0.98$) with the dry weight of the fruit. Additional information on this study is given in Appendix I (Chen, P., M. J. McCarthy, S.-M. Kim, and B. Zion. 1996. Development of a high-speed NMR technique for sensing maturity of avocados. *Transactions of the ASAE* 39(6):2205-2209).

One-dimension NMR signal projection. One-dimensional (1-D) projections or 1-D profiles of the 2-D images of fruit samples were obtained to evaluate the potential use of such signals to determine internal defects. The intensity, $S(x)$, of the 1-D profile is defined as

$$S(x) = \int \rho(x,y) dy$$

where $\rho(x,y)$ is the intensity at location (x,y) of the 2-D image. The signal represents the 1-D projection of the NMR signal of a selected slice of the intact fruit. This single-pulse technique (using a bird-cage coil) has the advantages of being fast and being able to provide information on the distribution of water concentration across the fruit. This technique is suitable for

detecting tissue breakdown regions in melons, watercore in apples, presence of pits in cherries and olives, and other defects in fruits.

A simulation of 1-D NMR projections of cherries showed a significant difference between projections of cherries with pits and those without pits. Tests were made on 1-D projections of cherries acquired with a Birdcage coil which could accommodate three cherries at a time. The projections were analyzed and their shapes were characterized by a single value. The routine detected 88% of cherries with pits and 63% pitted cherries when randomly oriented in the magnet. A great improvement was achieved by orienting the cherries with the pitting holes out of the excited plane: 29 out of 30 pitted cherries, and 29 out of 30 cherries with pits were correctly classified. A complete report of this study is included in Appendix I (Zion, B., M. J. McCarthy, and P. Chen. 1994. Real-time detection of pits in processed cherries by magnetic resonance projections. *Lebensmittel-Wissenschaft und-Technologie* (Food Science and Technology) 27(5):457-462).

The 1-D NMR projection technique was used to detect pits in olives under motion. One-dimensional magnetic resonance projections of pickled olives were acquired while the olives were traveling on a conveyor belt mounted through a 2-Tesla NMR magnet and a 150 mm imaging coil. The projections were used to distinguish between pitted and non-pitted olives. The effect of fruit position in the coil was tested and coil edge effects were noticed when projections were generated under dynamic conditions. Sorting of 300 pitted and non-pitted olives at various belt speeds (up to 25 cm/s) was tested. Classification errors (pitted olives classified as non-pitted and vice versa) were 4.3, 4.7, 2.3, and 4.0% at 0, 5, 15, and 25 cm/s belt speeds, respectively. Additional information on this study can be found in Appendix I (Zion, B., S.-M. Kim, M. J. McCarthy, and P. Chen. 1997. Detection of Pits in Olives under Motion by Nuclear Magnetic Resonance. *Journal of the Science of Food and Agriculture* 75:496-502).

Real-time on-line system. Results of previous studies show that both the single-pulse FID spectrum measurement and 1-D projection techniques can be done while the fruit is moving at speeds up to 30 cm/s, indicating that these techniques are viable for real-time on-line sorting of fruits. In previous studies, only one fruit at a time was placed on the conveying belt at a marked location. The relative position of the marked location to the NMR sensing coil could be determined from a sensor which detected a mark on the belt. Also, the NMR signal was acquired by the spectrometer and stored in the computer for later analysis.

A real-time on-line system was developed based on the existing conveying system. The system was modified to add the capability for real time data acquisition and analysis. The real-time sensor system, which is illustrated schematically in Figure 1, has the same control unit that contains a programmable controller and motor driver, a stepper motor, and a conveyor system as used in the previous study. The conveyor system can run at speeds up to 300 mm/s. The data

acquisition (DAQ) system consists of a sample-and-hold (Model: SC-2040, National Instruments, Austin, TX) and a PCI DAQ board (Model: PCI-MIO-16E-4, National Instruments, Austin, TX). The DAQ system was hosted by a 200 MHz MMX personal computer. The DAQ control software was programmed using a graphical programming software. A laser diode position sensor was used to determine the position of the sample relative to the surface coil. A 2-cm diameter surface coil was used to acquire NMR spectra of intact samples. The cross-section drawing of the real-time on-line NMR sensor is shown in Figure 2 showing the position of the position sensor. Since the distance between the position sensor and the surface coil is known, and the displacement of the belt can be precisely controlled by the stepper motor, it is possible to activate the RF pulse when the fruit is at a given position relative to the coil. Thus, the system can be programmed such that a fruit that is placed at a random position on the belt will always be sensed at the right time (e.g., when it is directly on top of the surface coil). A photograph of the real-time system is shown in Figure 3. A preliminary test was made to test the sensitivity of the surface coil. A series of NMR spectra were acquired from an avocado when it is at nine different locations (-30, -20, -10, 0, 10, 20, 30, 40 and 50 mm) relative to the coil center (minus sign means before the coil center) while the belt speed was set at 300 mm/s. The spectra at different locations are shown in Figure 4. The NMR signal decreases gradually as the distance between the fruit and surface coil increases. No magnetic resonance signal of avocados was observed when the sample was 50 mm away from the coil center. Thus, in order to avoid interference between fruits, a 10-cm spacing between fruit centers is required for on-line sorting of avocados with this conveyor system.

Evaluation of the research achievements

We have achieved all the objectives of this project.

1. We continued to show that NMR imaging can be used to detect numerous internal quality factors in fruits and vegetables. In addition to 2-D imaging, we have found that the ratio of resonance peaks of an FID spectrum of a fruit correlates well with oil content and sugar content of the fruit. Internal tissue breakdown and presence of pits or seeds can be detected by the 1-D NMR projection technique.
2. We have developed high-speed techniques for acquiring the FID spectrum and the 1-D NMR projection of individual intact fruits.
3. Based on these techniques, we have designed, built, and successfully tested an experimental on-line NMR sensor for sensing oil content, sugar content, internal tissue breakdown, and presence of pits in fruits and vegetables. At the end of the project, we obtained enough information to design and build an experimental NMR sorting system

for real-time on-line sorting of fruits. We plan to conduct tests on this system in the future.

Description of the cooperation

The Israel and U.S. teams have made plans to complement each other's research and to avoid unnecessary overlapping of work. The Israel team has focused on the one-dimension (1-D) image profile techniques for detecting the internal tissue breakdown in melons, detection of pits in olives and cherries, and detection of bruise in apples. The U.S. team has concentrated on developing high-speed techniques for maturity evaluation of avocados, mangos, kiwi fruits, oranges, and plums.

The two teams frequently exchanged findings and discussed problems via electronic mail (E-mail) and postal airmail. The Israeli team leader has traveled to Davis to conduct experiments on high-speed 1-D profile measurement of fruits using the experimental conveyor that can move through the magnet at a speed up to 30 cm/s. Researchers from the two teams also met during this time to compare results and to discuss future research plans. They also met at international conferences to review and update the project.

Conclusions

We have successfully shown that NMR techniques can be used for nondestructive evaluation of various internal quality factors, such as bruises, dry regions, worm damage, stage of maturity, oil content, sugar content, tissue breakdown, and the presence of voids, seeds, and pits. Further study on the correlations between various NMR parameters and certain quality factors of selected fruits and vegetables led to the development of high-speed techniques for detecting oil content in avocado, sugar content in prunes, soft tissue in melons, and the presence of pits in cherries and olives. The most important accomplishment in this project is the successful development of high-speed techniques for determining internal quality of fruits while they are moving at speeds up to 30 cm/s. This accomplishment is an important step toward the development of NMR techniques for on-line sorting of fruits and vegetables.

List of Publications

1. Chen, P., M.J. McCarthy, S.-M. Kim, and B. Zion. 1996. Development of a high-speed NMR technique for sensing maturity of avocados. Transactions of the ASAE 39(6):2205-2209.

2. McCarthy, M. J., B. Zion, P. Chen, S. Ablett, A. H. Darke, and P. J. Lilliford. 1995. Diamagnetic susceptibility changes in apple tissue after bruising. *Journal of the Science of Food and Agriculture* 67:13-20.
3. Zion, B., P. Chen, and M. J. McCarthy. 1995. Detection of bruises in magnetic resonance images of apples. *Comp. and Elect. in Agric.* 13(4):289-299.
4. Zion, B., P. Chen, and M. J. McCarthy. 1995. Non-destructive quality evaluation of fresh prunes by NMR spectroscopy. *Journal of the Science of Food and Agriculture* 67, 423-429.
5. Zion, B., S.-M. Kim, M.J. McCarthy, and P. Chen. 1997. Detection of Pits in Olives under Motion by Nuclear Magnetic Resonance. *Journal of the Science of Food and Agriculture* 75:496-502.
6. Zion, B., M. J. McCarthy, and P. Chen. 1994. Real-time detection of pits in processed cherries by magnetic resonance projections. *Lebensmittel-Wissenschaft und-Technologie (Food Science and Technology)* 27(5):457-462.

Figure 1. Schematic diagram of the Real-time On-line NMR Sensor.

Figure 2. Cross-section drawing of the Real-time On-line NMR Sensor.

Figure 3. Photograph of the Real-time On-line NMR Sensor.

Figure 4. Avocado spectra at various positions relative to RF coil center at 300 mm/s.