자기공명기술을 이용한 농산물의 품질 판정
Quality Evaluation of Agricultural Products using Magnetic Resonance Techniques

김성민*
정회원
S.M. Kim

1 Introduction

Quality evaluation of agricultural products has been a very important process for grading, processing, sorting, and marketing for a very long time. increasing demand for better quality products has increased research and development related to quality evaluation measurements and techniques. Most fruits and vegetables are not harvested at the same stage of maturity due to biological and environmental differences. While modern mechanical harvesting for products being processed reduces production cost it also increases the need for proper sorting of agricultural products. Even hand-picked fresh market products grading could benefit from additional quality sorting.

Automated sorting machines can sort fruits into several categories according to specified quality evaluation rules. The quality evaluation rules can roughly be divided into two parts: external and internal. Size, shape, surface color and defects and bruises can be categorized as external quality factors and internal voids, solids, disorder, and composition can be categorized as internal quality factors. Detecting external quality factors is relatively easier than detecting internal factors by nondestructive methods. Light reflection and image processing systems are commercially used for external quality evaluation instead of manual sorting. Many internal quality attributes are hard to detect by nondestructive methods. Researchers have been working to find methods for evaluating internal quality attributes of agricultural and food products nondestructively by measuring their physical, acoustical, electrical, optical, X-ray, and nuclear magnetic resonance (NMR) properties (Gunasekaran *et al.*, 1985; Dull, 1986; Chen and Sun, 1991; Self *et al.*, 1993). Most of these techniques detect certain physical properties of the material, and hence, are suitable only for evaluating specific quality

* 전북대학교 농과대학 농업기계공학과

factors. Moreover, some techniques have potential radiation hazards caused by X-ray and gamma ray radiation and sonic and optical methods have limited penetration depth on certain tissues (Chen *et al.*, 1989).

The areas of nondestructive internal quality evaluation can be divided into detection of internal structural features and detection of chemical composition. Internal structural features include interior voids, foreign material, and insects, internal solids such as pits or stones, and internal disorder and chemical compositions include water, sugar, and oil.

The objectives of this study are to review nondestructive quality evaluation methods in relationship to NMR based methods and to compare their advantages and disadvantages.

2. Detection of Internal Structural Features

Most nondestructive internal structural feature detection techniques are based on the principles of buoyant force, light interaction, X-ray, microwave, ultrasound, and NMR (ASAE, 1994). Researchers have investigated defect detection techniques using buoyant force, light interaction, and X-ray earlier than those using microwave, ultrasound, and NMR. Detection of internal structural features requires an imaging capability in most cases. Due to advances of modern computer technology and hardware cost reduction, researchers can utilize X-ray and NMR systems which have imaging capability and are widely used in medical radiology. Therefore to examine the applications of X-ray and NMR imaging methods and to compare their utilization are important research areas.

In the applications of X-ray systems, Lenker and Adrian (1970) used an X-ray system to determine the maturity of lettuce heads and Diener *et al.*(1970) applied this technique for detecting bruises in apples. Hollow heart in potatoes was investigated by Finney and Norris (1978) and now X-ray systems are commercially used for detecting hollow heart in potatoes (Rex and Mazza, 1989). Brecht *et al.* (1991) showed X-ray computed tomography images indicating the difference between mature and immature tomatoes and suggested this method could be used for a nondestructive maturity evaluation. Thomas *et al.* (1993) used an X-ray imaging system to detect an internal disorder called spongy tissue in mango fruits and demonstrated the high potential of an automated X-ray system for mangoes. In the citrus industry, commercial X-ray systems are installed and successfully used in detecting seeds and internal voids (Johnson, 1985).

Even though applications of magnetic resonance imaging (MRI) to agricultural products doesn't have a long research history like X-ray, many researchers have investigated this technique recently due to its potential in quality evaluation. Hinshaw *et al.* (1979) demonstrated the accurate measurement of the internal structure of intact fruits could be restored accurately using MRI methods. Wang *et al.* (1988) used MRI to study watercores and their distributions in Red Delicious apples from MR images. The difference between the normal and watercored tissues was clearly separated on the MR images as intensity differences. Chen *et al.* (1989) showed MRI was very effective in detecting most internal quality factors such as bruises, dry region, worm damage, stage of maturity, and presence of voids, seeds, and pits of agricultural products. Ishida *et al.* (1989) investigated physiological changes during maturation of a tomato using MRI and Williamson *et al.* (1993) used microscopic MRI of red raspberry with voxel dimensions of 70x70x50 μm to study the changes in spatial distribution of mobile protons. Clark and Forbes (1994) and Suzuki *et al* (1994) studied thermal injuries of persimmon and papaya caused by chilling or heating using a MRI based method. McCarthy *et al.* (1995) detected bruises in 2-D MR images of apples and analyzed the sources of image contrast caused by bruises. Most of former works were done from a biological point of

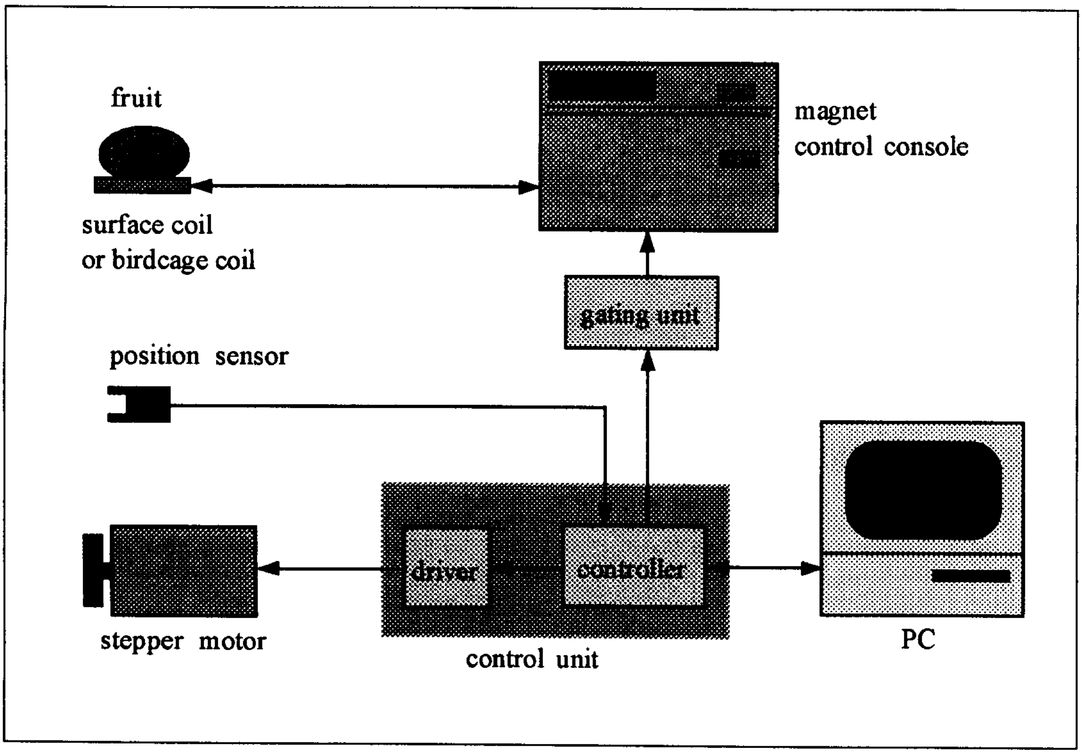

Figure 1. Schematic diagram of the on-line magnetic resonance sensor system.

view rather than an engineering point of view. Zion *et al.* (1994) detected pits in cherries from MRI 1-D profiles and demonstrated a potential for using this method as the basis of a high speed on-line sorting system. Zion *et al.* (1997) demonstrated the feasibility of on-line olive pit detecting sensor based on MRI technique. Figure 1 shows the schematic diagram of on-line MRI sensor used in the study.

X-ray and NMR imaging methods are widely used and will be more frequently used in quality uation research. The advantages of NMR imaging methods are that they are not harmful i.e. no ionizing radiation is used in forming images unlike X-ray imaging methods, NMR imaging is intrinsically a three dimensional technology while X-ray imaging is essentially a two dimensional technology, and image contrast factors are density, mobility, diffusivity, and susceptibility of NMR sensitive nuclei while X-ray image contrast is directly proportional to the electron density of the material. The disadvantage of NMR imaging methods against X-ray imaging methods is that no commercial system for quality detection is available.

3. Detection of Internal Composition

Three common components in agricultural products important in evaluating their quality are water, soluble solids, and oil. Many nondestructive techniques are being applied to detect these components in contrast to the detection of internal structural features. Mechanical, sonic, light interaction, dielectric, and microwave techniques have frequently been applied (Nattuvetty *et al.*, 1980; Kandala *et al.*, 1987; Nelson, 1987; Upchurch *et al.*, 1987; Zaltzman *et al.*, 1987; Mizrach *et al.*, 1989; Nelson and Lawrence, 1992; Nelson *et al.*, 1992; Huarng *et al.*, 1993; Sugiyama *et al.*, 1993). Among nondestructive composition detection techniques near-infrared (NIR) and NMR techniques can be applied to detect component composition and have a great potential for internal composition analysis.

NIR spectrum measurement can be divided into two methods, reflectance measurement and transmittance measurement, based on the placement of radiation and detector. Usually a transmittance measurement technique is preferred due to better prediction of internal composition because the NIR radiation passes through a larger region of the sample. For the last decade, NIR spectroscopy has been examined as a nondestructive internal quality evaluation tool for agricultural products by many researchers. Birth *et al.* (1985) showed NIR transmittance measurement for an intact sample could be used for determination of dry matter and carbohydrate concentration in onions, and Dull *et al.*

(1989) applied this technique to measure the dry matter of sliced and whole potatoes. For measuring soluble solids (SS) in the sample, Dull *et al.* (1989) applied a transmittance technique to cantaloupes, they obtained a lower correlation coefficient (r = 0.60) for intact samples which used a body transmittance technique than for slices which used a direct transmittance technique (r = 0.968). the rind of the sample fruit most likely disturbed the radiation resulting in a low correlation coefficient. Dull *et al.* (1992) experimented on honeydew melons using an improved NIR measurement system and obtained a better correlation coefficient for the intact sample. this technique may be applied to thicker rind fruits such as cantaloupe and watermelon. Professor Slaughter of UC Davis has worked intensively on nondestructive NIR quality evaluation. He has used a spectrometer, with a spectral span from visible to near-infrared range, equipped with a fiber optic probe to measure the soluble solids contents of peaches and nectarines and obtained a high correlation coefficient (r = 0.92). Simultaneously, other components such as sucrose and chlorophyll A were measured with high correlation values ranging from 0.87 for sucrose to 0.97 for chlorophyll A (Slaughter, 1995).

Nuclear magnetic resonance (NMR) techniques which have spectroscopic and imaging capability enable one to detect the internal composition of agricultural products. To predict internal composition using NMR, one usually measures relaxation time constants T_1 and T_2 from a free induction decay (FID) which is a time domain signal or the ratio of resonance peaks from a spectrum which is a frequency domain signal. Sugar and oil are two main maturity indexes for some agricultural products. NMR studies for nondestructive quality evaluation have concentrated on detecting sugar and oil. For sugar content measurement, Cho *et al.* (1991) used 200 Mhz high resolution NMR for acquiring the spectra of muskmelon tissue samples and correlated a sugar resonance peak with sugar content (r = 0.94). They suggested NMR spectroscopy could be used to predict sugar content in intact samples because their research actually was not done on samples of tissue. Cho *et al.* (1993) measured T_2 of grapes and cherries using a 10 Mhz low resolution NMR and correlated this time constant with sugar content of intact samples (r = 0.62). This study showed feasibility of NMR time domain signal analysis for estimation of sugar content of intact fruit samples. Ray *et al.* (1993) analyzed FIDs acquired from 5.35 Mhz low resolution magnet and showed better feasibility for the determination of sugar content of intact cherries using time domain data analysis (r = 0.95). Jordan and Eustrace (1993) evaluated an earth's field NMR system operating at 2.2 KHz for sugar content determination but they suggested this system didn't have a potential for a on-line sensor due to the long relaxation time constants at this field strength.

NMR spectrum analysis shows high potential for on-line high speed use. Zion *et al.* (1995) demonstrated the feasibility of an NMR on-line high speed sensor detecting sugar content of intact prunes. They used an 85.5 Mhz spectrometer, analyzed data in the frequency domain and calculated the ratio of peaks of soluble solids and water resonance. The ratio obtained from the NMR spectrum was well correlated with the soluble solids content of intact fruits (r = 0.907).

In oil detection, Barry *et al.* (1983) used a low-resolution NMR spectrometer for determining oil content of diced dried avocado flesh and the results compared very well with a chemical oil extraction method (Soxhlet extraction). Chen *et al.* (1989) demonstrated clear signal differences between mature and immature avocado NMR images and showed the potential of detecting oil content from intact avocados using an 85.5 Mhz NMR spectrometer. Chen *et al.* (1993) analyzed time and frequency domain signals and 2-D image data, i.e. measurement of T_1 and T_2, the ratio of oil and water resonance peaks, and image intensity. The results demonstrated that frequency domain data analysis was very well correlated with oil content of intact avocado fruits (r = 0.976) and this technique has a high potential for nondestructive on-line quality evaluation sensor. Chen *et al.* (1996) developed an on-line NMR sensor sensing maturity of avocados. It could acquire free induction decay (FID) spectra of avocados moving at speeds up to 25 cm/s. The oil/water resonance peak ratio, obtained from the spectrum, correlated very well(r^2=0.98) with the dry weight of the fruit. Figure 1 shows the schematic diagram of on-line NMR sensor developed in the study.

The advantage of an NMR sensor and an NIR sensor is that either method can determine the average quantity of specific compositions such as water or sugar from the entire or a localized section of a sample. NIR sensor systems have been used commercially since late 1980's. However NMR based sensor systems have been studied since beginning of 1990's.

4. Conclusions

Magnetic resonance techniques, magnetic resonance imaging and magnetic resonance spectroscopy, are becoming powerful experimental tools that provide chemical and internal physical information of agricultural products nondestructively without any noticeable hazards. Magnetic resonance techniques combined with external quality evaluation technique such as machine vision will suggest a perfect solution for nondestructive quality evaluation of agricultural and food products.

5. References

1. Abbot, J.A., G.S. Bachman, N.F. Childers, J.V. Fitzgerald , and F.J. Matuski. 1968. Sonic Techniques for Measuring Texture of Fruits and Vegetables. Food Tech. 22(5): 101-112.

2 ASAE. 1994. Nondestructive Technologies for Quality Evaluation of Fruits and Vegetables. ASAE. St. Joseph, Michigan.

3. Barry, G., B. Brown, and L. Barker. 1983. The Use of Low Resolution Nuclear Magnetic Resonance for Determining Avocado Maturity by Oil Content. J. Food Technology 18:401-410.

4. Birth, G.S. 1960. A Non-destructive Technique for Detecting Internal Discolorations in Potatoes. Am. Potato J. 37(2): 53-60.

5. Birth, G.S., and K.L. Olsen. 1964. Nondestructive Detection of Watercore in Delicious Apples. J. Amer. Soc. Hort Sci. 85: 74-84.

6. Birth, G.S., G.G. Dull, J.B. Magee, H.T. Chan, and C.B. Covaletto. 1983. An optical method for Estimating Papaya Maturity. J. Amer. Soc. Hort. Sci. 109(1): 62-66.

7. Birth, G.S., G.G. Dull, W.T. Renfroe, and S.J. Kays. 1985. Nondestructive spectrophotometric determination of dry matter in onions. J. Amer. Soc. Hort. Sci. 110(2): 297-303.

8. Brecht, J.K., R.L. Shewfelt, J.C. Garner, and E.W. Tollner. 1991. Using X-ray-computed tomography to nondestructively determine maturity of green tomatoes. HortScience Vol. 26(1): 45-47.

9. Chen, P., M.J. McCarthy, and R. Kauten. 1989. NMR for internal quality evaluation of fruits and vegetables. Transactions of the ASAE Vol. 32(5): 1747-1753.

10. Chen, P., and Z. Sun. 1991. A review of nondestructive methods for quality evaluation and sorting of agricultural products. J. Agri. Engng Res. 49: 85-98.

11. Chen, P., M.J. McCarthy, R. Kauten, Y. Sarig, and S. Han. 1993. Maturity Evaluation of Avocados by NMR Methods. J. Agric. Engng Res. 55: 177-187.

12. Chen, P., M.J. McCarthy, S.M. Kim, B. Zion. 1996. Development of a High-speed NMR Technique for Sensing Maturity of Avocados. Transactions of ASAE. Vol. 39(6): 2205-2209.

13. Cho, S.I., V. Bellon, T.M. Eads, R.L. Stroshine, and G.W. Krutz. 1991. Sugar Content Measurement in Fruit Tissue using Water Peak Suppression in High Resolution 1H Magnetic Resonance. J. Food Sci. 56(4): 1091-1094.

14. Cho, S.I., R.L. Stroshine, I.C. Baianu, and G.W. Krutz. 1993. Nondestructive Sugar Content Measurements of Intact Fruit using Spin-spin Relaxation Time (T_2) Measurements by Pulsed 1H Magnetic Resonance. Transactions of the ASAE Vol. 36(4): 1217-1221.
15. Clark, C.J., and S.K. Forbes. 1994. Nuclear Magnetic Resonance Imaging of the Development of Chilling Injury in 'Fuyu' Persimmon (Diospyros Kaki). New Zealand J. of Crop and Horticultural Science 22: 209-215.
16. Diener, R.G., J.P. Michell, and M.L. Rhoten. 1970. Using an X-ray Image Scan to Sort Bruised Apples. Agricultural Engineering 51: 356-361.
17. Dull, G.G. 1986. Nondestructive evaluation of quality of stored fruits and vegetables. Food Technology May 106-110.
18. Dull, G.G., G.S. Birth, and R.G. Leffler. 1989. Use of Near Infrared for Analysis of Dry material in Potatoes. Amer. Potato J. 66(4): 215-225.
19. Dull, G.G., G.S. Birth, D.A. Smittle, and R.G. Leffler. 1989. Near Infrared Analysis of Soluble Solids in Intact Cantaloupe. J. Food Sci. 54(2): 393-395.
20. Dull, G.G., R.G. Leffler, G.S. Birth, and D.A. Smittle. 1992. Instrument for nondestructive measurement of soluble solids in honeydew melons. Transactions of the ASAE Vol. 35(2): 735-737.
21. Finney, E.E., Jr. and Norris, K.H. 1978. X-ray Scans for Detecting Hollow Heart in Potatoes. American Potato Journal 55: 95-105.
22. Finney, E.E. 1972. Vibration Techniques for Testing Fruit Firmness. J. Texture Studies 3: 263-283.
23. Gunasekaran, S., M.R. Paulsen, and G.C. Shove. 1985. Optical methods for nondestructive quality evaluation of agricultural and biological materials. J. Agri. Engng Res. 32: 209-241.
24. Hinshaw, W.S., P.A. Bottomly, and G.N. Holland. 1979. A Demonstration of the Resolution of NMR Imaging in Biological Systems. Experientia 35: 1268-1269.
25. Huarng, L., P. Chen, and S. Upadhyaya. 1993. Determination of acoustic vibration modes in apples. Transactions of the ASAE Vol. 36(5): 1423-1429.
26. Ishida, N., T. Kobayashi, M. Koizumi, and H. Kano. 1989. 1H-NMR Imaging of Tomato Fruits. Agric. Biol. Chem. 53(9): 2363-2367.
27. Johnson, M. 1985. Automation in Citrus Sorting and Packing. Proc. Agri-Mation 1 Conf. and Expo. Feb. 25-28, Palmer House Hotel, Chicago, IL. 63-68.
28. Jordan, R., and C. Eustrace. 1993. Sugar Content Evaluation using Earth's Field NMR. ASAE Paper No. 933584.

29. Kandala, C.V.K., R.G. Leffler, S.O. Nelson, and K.C. Lawrence. 1987. Capacitive sensors for measuring single-kernel moisture content in corn. Transactions of the ASAE Vol. 30(3): 793-797.

30. Lenker, D.H., and P.A. Adrian. 1971. Use of X-ray for Selecting Mature Lettuce Heads. Transactions of the ASAE 14(5): 894-898.

31. McCarthy, M.J., B. Zion, P. Chen, S. Ablett, A.H. Darke, and P.J. Lillford. 1995. Diamagnetic susceptibility changes in apple tissue after bruising. J. Sci. Food Agric. 67:13-20.

32. Mizrach, A., N. Galili, and G. Rosenhouse. 1989. Determination of Fruit and Vegetable Properties by Ultrasonic Excitation. Transactions of the ASAE Vol. 32(6): 2053-2058.

33. Nattuvetty, V.R., and P. Chen. 1980. Maturity sorting of green tomatoes based on light transmittance through regions of the fruit. Transactions of the ASAE Vol. 23: 515-518.

34. Nelson, S.O. 1987. Potential agricultural applications for RF and microwave energy. Transactions of the ASAE Vol. 30(3): 818-822.

35. Nelson, S.O., and K.C. Lawrence. 1992. Sensing moisture content in dates by RF impedance measurements. Transactions of the ASAE Vol. 35(2): 591-596.

36. Nelson, S.O., K.C. Lawrence, and A.W. Kraszewski. 1992. Sensing moisture content of pecans by RF impedance and microwave measurements. Transactions of the ASAE Vol. 35(2): 617-623.

37. Ray, J.A., R.L. Stroshine, G.W. Krutz, and W.K. Wai. 1993. Quality Sorting of Sweet Cherries using Magnetic Resonance. ASAE Paper No. 936071.

38. Rex, B.L. and G. Mazza. 1989. Cause, Control and Detection of Hollow Heart in Potatoes: A review. American Potato Journal 66: 165-183.

39. Self, G., H. Wainwright, and M. Povey. 1993. Non-destructive quality determination for fruit and vegetables. Postharvest News and Information Vol. 4(1): 18-20.

40. Slaughter, D. 1995. Nondestructive determination of internal quality in peaches and nectarines. Transactions of the ASAE Vol. 38(2): 617-623.

41. Sugiyama, J., K. Otobe, S. Hayashi, and S. Usui. 1993. Quality evaluation of muskmelons by acoustic transmission images. ASAE Paper No. 93-3070.

42. Suzuki,K., T. Tajima, S. Takano, T. Asano, and T. Hasegawa. 1994. Nondestructive Methods for Identifying Injury to Vapor Heat-Treated Papaya. J. Food Science 59(4): 855-857.

43. Thomas, P., S.C. Saxena, R. Chandra, R. Rao, and C.R. Bhatia. 1993. X-ray Imaging

for Detecting Spongy Tissue, an Internal Disorder in Fruits of 'Alphonso' Mango. J. Horticultural Science 68(5): 803-806.

44. Upchurch, B.L., G.E. Miles, R.L. Stroshine, E.S. Furgason, and F.H. Emerson. 1987. Ultrasonic measurement for detecting apple bruises. Transactions of the ASAE Vol. 30(3): 803-809.
45. Wang, S.Y., P.C. Wang, and M. Faust. 1988. Non-destructive detection of watercore in apple with nuclear magnetic resonance imaging. Scientia Horticulture 35: 227-234.
46. Williamson, B., B.A. Goodman, and J.A. Chudek. 1992. Nuclear Magnetic Resonance (NMR) Micro-Imaging of Ripening Red Raspberry Fruits. New Phytologist 120: 21-28
47. Worthington, J.T., D.R. Massie, and K.H. Norris. 1976. Light Transmission Technique for Predicting Ripening Time for Intact Green Tomatoes. Quality Detection in Foods. Amer. Soc. Agric. Engr., St. Joseph, Mi. 46-49.
48. Yeatman, J.N., K.H. Norris. 1965. Evaluating Internal Quality of Apples with New Automatic Fruit Sorter. Food Tech. 19(3): 123-125.
49. Zion, B., M.J. McCarthy, and P. Chen. 1993. Real-time Detection of pits in processed cherries by magnetic resonance projections. Lebensmittel-Wissenschaft und-Technologie (Food Science and Technology) 27(5): 457-462.
50. Zion, B., P. Chen, and M. McCarthy. 1995. Nondestructive quality evaluation of fresh prunes by NMR spectroscopy. J. Sci. Food Agric. 67: 423-429.
51. Zion, B., S.M. Kim, P. Chen, M.J. McCarthy. 1997. Detection of Pits in Olives under Motion by Nuclear Magnetic Resonance. Journal of Science of Food and Agriculture. 75, 496-502.