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NON-DESTRUCTIVE RIPENESS SENSING

BY USING PROTON NMR

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INTRODUCTION

More than 80 kinds of fruits and vegetables are available in the United States. But only about 6 of them have their quality standards (Dull, 1986). In the 1990 Fresh Trends survey (Zind, 1990), consumers were asked to rate 16 characteristics important to their decision to purchase fresh produce. The four top ranking factors were ripeness/freshness, taste/flavor, appearance/condition and nutritional value. Of those surveyed, 96% rated ripeness/freshness as extremely important or very important. Therefore, the development of reliable grading or sorting techniques for fresh commodities is essential. By using the proper sensors, improved monitoring of ripeness of fruit and vegetables from production to distribution can create a value added product.

Consumers want fruit that looks and tastes good. The good taste is based on a combination of sugar, acid and other flavor components. In most fruit good taste is highly correlated to soluble solids, largely sugars. Thus, nondestructive evaluation of soluble solids will give an indication of sweetness. Sweetness is an important indicator of fruit quality and highly correlated with ripeness in most fruit. Ripe fruit have high sugar contents. Sweetness is considered a function of sugar concentration or content.

Determination of fruit quality often involves cutting and tasting. Non-destructive quality control in fruit and vegetables is a goal of growers and distributors, as well as the food processing industry. Many nondestructive techniques have been evaluated including soft x-ray, optical transmission, near infrared radiation, and machine vision. However, there are few reports of successful non-destructive measurement of sugar content directly in fruit. Higher quality fruit could be harvested and available to consumers if a nondestructive sensor that detects ripeness level directly by measuring sugar content were available. Using proton Nuclear Magnetic Resonance (NMR) principle is the possibility.

NMR is based on the resonant absorption and emission of very low magnetic energy by a certain atomic nucleus when subjected to two perpendicular magnetic fields as shown in Figure 1. The NMR

spectroscopy is recognized as one of the most powerful techniques for chemical analysis. NMR can be used to develop sensors which give electrical signals proportional not only to the total concentration of selected nuclei, but also to the amounts of particular components or molecules in the sample being measured. Because of its nondestructive and noncontacting (or non-toxic) treatment, NMR has many potential applications in biological, agricultural and food engineering problems.

OBJECTIVES

A nondestructive ripeness (or sweetness) sensor for fruit quality control can be developed with the proton NMR principle (Cho, 1989). Several feasibility studies were necessary for the ripeness sensor development. Main objectives in this paper was to investigate the feasibilities (1) to detect ripeness (or sweetness level) of raw fruit tissue with an high resolution proton NMR spectroscopy (200 MHz) and (2) to measure sugar content of intact fruit with a low resolution proton NMR spectroscopy (10 MHz).

MATERIALS AND METHODS

(1) Test with 200 MHz NMR

Instruments and test materials

A Chemagnetics A-200 proton FT NMR manufactured by Hemenway Corporation was used to test fruit tissue in a sample tube with 5 mm diameter. Temperature in the NMR laboratory was maintained at 23 ± 1 °C. The NMR had a 46 KGauss magnetic field and a 200 MHZ radio-frequency transmitter.

Bananas were chosen by color: yellow, less yellow and green. Yellow banana was well ripened and green banana was not ripened yet. Banana sample was cored with the sample tube and were inserted gently into the tube. Original structure of the banana tissue was kept as closely as possible. It was important to the test that the sample should be made and tested as soon as possible (within 5 minutes) to

reduce the enzymatic effects that breakdown sugar.

Sugar content of banana sample was measured destructively with a portable refractometer (Atago N_1, Brix 0-32%). An IEC Clinical Centrifuge separated *supernatant* and sludge from smashed banana samples. The separated supernatant was used for the sugar content measurement.

Sugar Peak in NMR Spectra

A simple single pulse (90° and 24 μs pulse width) was used. After the 90° RF pulse was supplied, magnetized proton nuclei induced an electrical signal in an adjacent receiver coil. This signal is called *free induction decay* (FID) signal. 16K number of data points were used to store a FID signal. Sixteen FID signals of each test sample were accumulated and processed through the Fourier transformation to get a NMR spectrum shown in Figure 2. There is a big water peak around 4.6 ppm and a small sugar peak around 3.5 ppm. The water peak was used as a reference signal at 4.608 ppm chemical shift. A parameter for line broadening was set to 0.1 Hz, but this function did not work at all because the banana sample was semi-solid. Total measurement time for one spectrum was about 2 to 3 minutes. Each banana was tested 4 times with four different samples.

(2) Test with 10 MHz NMR

Instruments and test materials

A Bruker 10 MHz Pulsed ^1H NMR spectrometer (Model PC-10) was used to measure sugar content in intact California sweet cherries. The size of sample tube was 20 mm diameter. The 10 sweet cherries were tested and were almost the same size in the range of 18 to 20 mm diameter. The weight distribution of and the cherries was 5.652 ± 0.459 gram.

The identical refractometer was also used to measure sugar content of cherries destructively. Free sugar juices for the refractometer measurement were obtained by squeezing the samples by hand. The

sugar content was measured three times from the same sample and an average value was used.

T₂ Measurements

T_2 is called *spin-spin* relaxation time and is the time constant of the FID signal. T_2 values were measured with the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence (Martin et al, 1980). T_2 measurements were carried out at $25 \pm 1°C$. The observed, transverse magnetization decays were close, in most cases, to a single exponential. The errors in T_2 measured from the exponential decays are, in principle, affected if the decay is multi-exponential. The CPMG pulse sequence which we employed can be specified as:

$$[90°-\tau] - [180°-2\tau-180°-\tau-A_{cq}-\tau]_n$$

Total experiment time was about 19 seconds for one T_2 measurement. The measurement time includes a delay time of 12 seconds and a time for 100 echoes with $\tau = 16$ ms. If τ is decreased, the solid components also contribute to the decay and the T_2 error increases. If the number of echoes is decreased, the T_2 error is increased. T_2 errors of less than 5% were considered to be satisfactory. T_2 time was measured twice and average values were used.

RESULTS AND DISCUSSION

Correlation of Sugar Content to Sugar Peak Intensity

Because of their high water contents, fruit represent a less concentrated source of carbohydrates. The sugar available from carbohydrate may range from 6 to 25% in fresh fruit (Lapedes, 1977). Most of the sugar in raw fruit consists of sucrose, fructose and glucose. One sucrose molecule has 22 chemically different hydrogen protons. Therefore, theoretically there would be 22 peaks in the sucrose NMR spectrum. The 21 sugar peaks are located between 3 and 4 ppm. Because the banana sample was in a semi-solid phase, the sugar peaks were gathered together and made one broad peak as shown in Figure 2.

Sugar peak from an unripe banana was not detected because the strong water peak masked the weak sugar peaks. Sugar content of the unripe banana was measured with the refractometer and was around 8%. Sugar peaks intensity is proportional to the sugar concentration or total number of sugar molecules. The intensity is represented as area under the sugar peak. The area under 0.5 ppm width was referred to the sugar peak intensity. Instead of using electronic integration, the area was roughly calculated by multiplying 0.5 ppm width by sugar peak height measured from the base line. Therefore, the sugar peak height was measured to get a correlation between ripeness (or sweetness) level and sugar peak intensity. Sugar peak height corresponding to the banana ripeness was plotted in Figure 3. Sugar peak height was linearly correlated to ripeness (or sweetness) level and the correlation coefficient r was 0.94.

Correlation between Sugar Content and Measured T_2

Figure 4 shows the correlations between measured T_2 and sugar content in the sweet cherries. The T_2 was linearly correlated to sugar content which was measured with the refractometer. The correlation coefficient r was 0.85. Measured T_2 was assumed to be the decaying time constant of liquid (water and sugar juice) resonance in the cherries. Shorter T_2 was corresponded to higher sugar content, because of its higher viscosity. Temperature effect on T_2 measurement was not significant (up to 8.6 ms per °C) compared to the measurement error (usually around ±15 ms). Care must be taken when cherry samples were chosen. The size and weight of the cherries should be maintain as closely as possible. Damaged or bruised samples should not to be taken, because they can increase the T_2 value regardless of its sugar content or ripeness level.

CONCLUSIONS

The following conclusions were drawn:

1. Sugar and water peak were observed in NMR spectra of banana tissue samples with a 200 MHz

high resolution NMR spectroscopy.

2. Sugar peak intensity was linearly correlated to ripeness level or sweetness of banana samples. The correlation coefficient r was 0.94.

3. Measured T_2 of intact cherries with a 10 MHz low resolution NMR spectroscopy was linearly correlated to sugar content measured with a refractometer. The correlation coefficient r was 0.85.

4. Sweetness or sugar content of intact sweet cherries can be estimated nondestructively according to their measured T_2 value with the NMR spectroscopy. Therefore, the quality of intact cherries can be sorted nondestructively according to their estimated sweetness.

5. The 10 MHz NMR spectroscopy had a 2,300 gauss magnetic field. Therefore, a fruit ripeness sensor based on the NMR principle can be developed using a low magnetic field which can be obtained from permanent magnets.

ACKNOWLEDGEMENT

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FIGURES
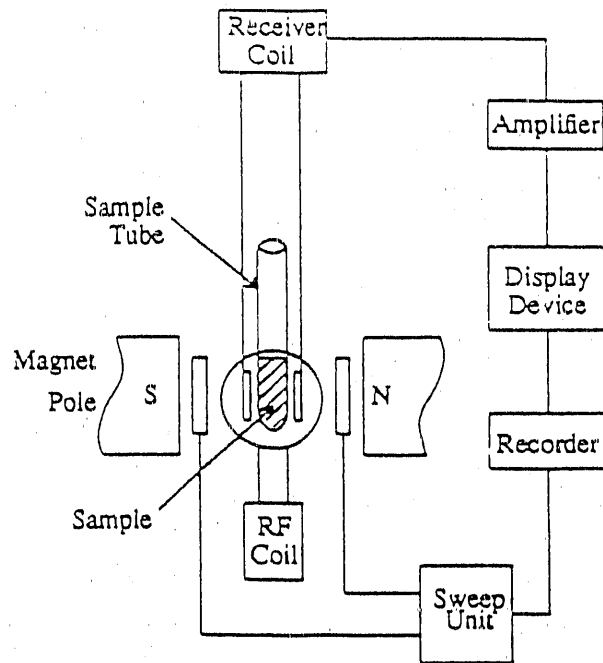
Figure 1. Block Diagram of a Typical NMR Spectrometer
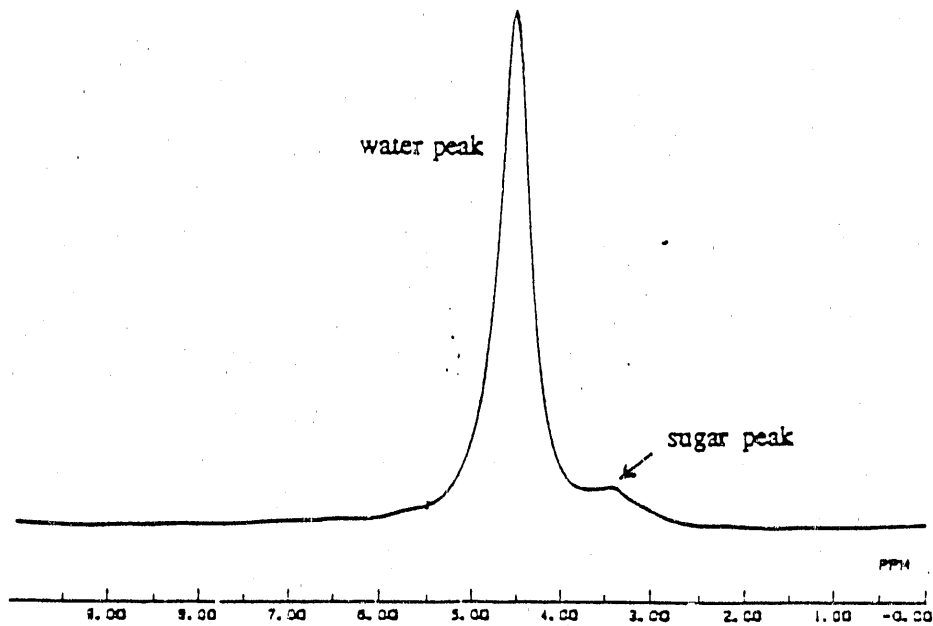
Figure 2. Proton NMR Spectrum of a Ripe Banana Sample
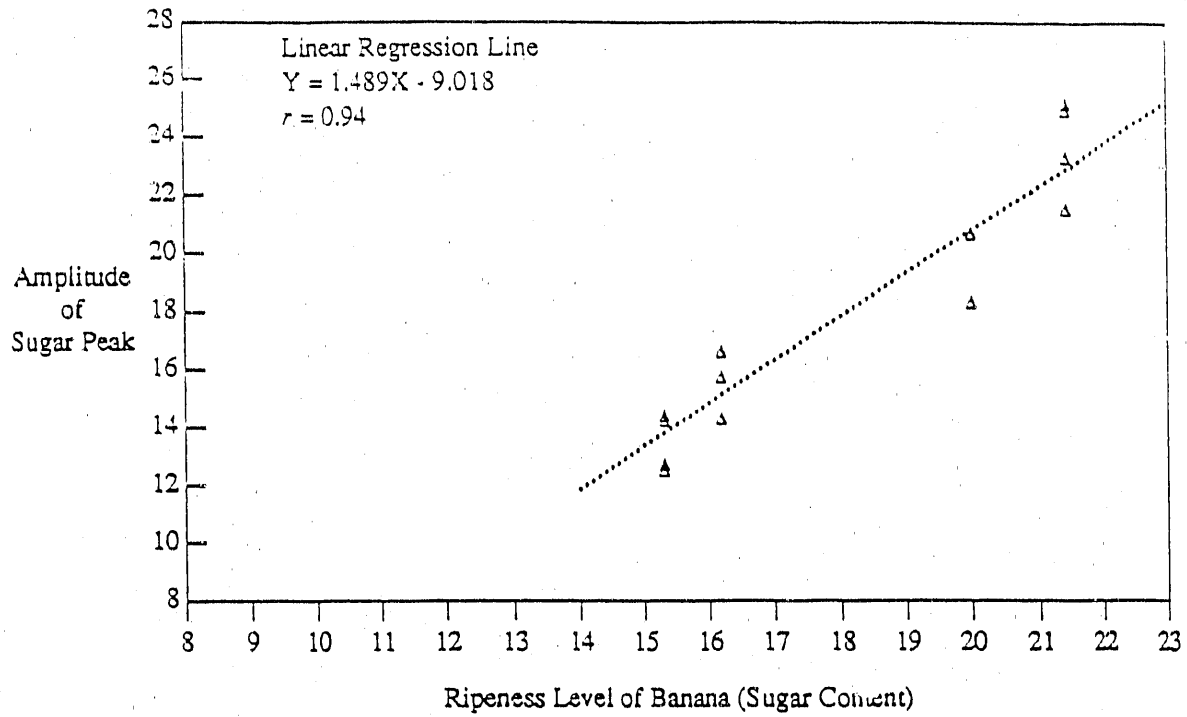
Figure 3. The Correlation between Ripeness Level of a Banana and Amplitude of Sugar Peaks
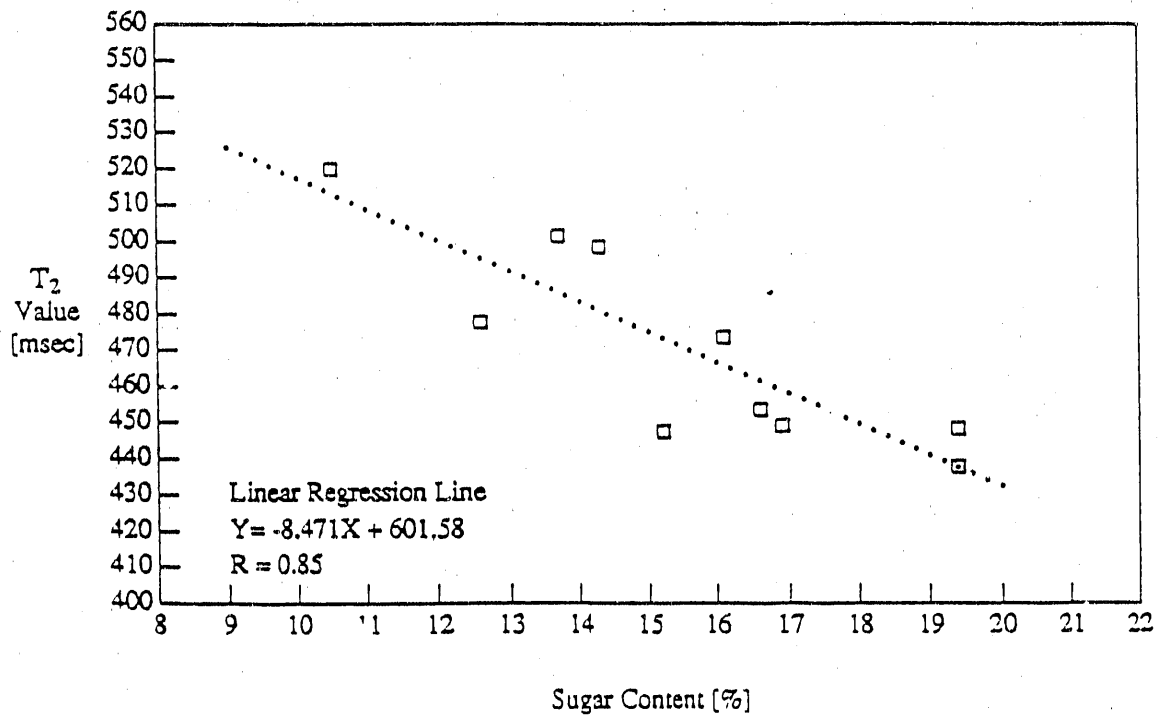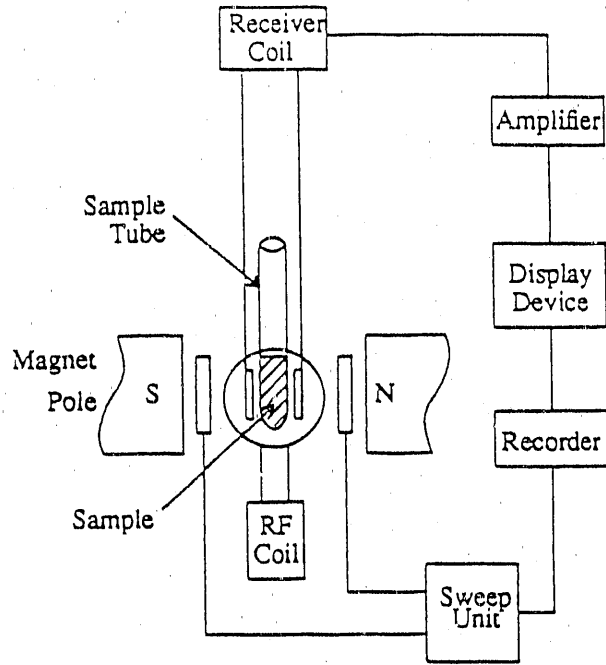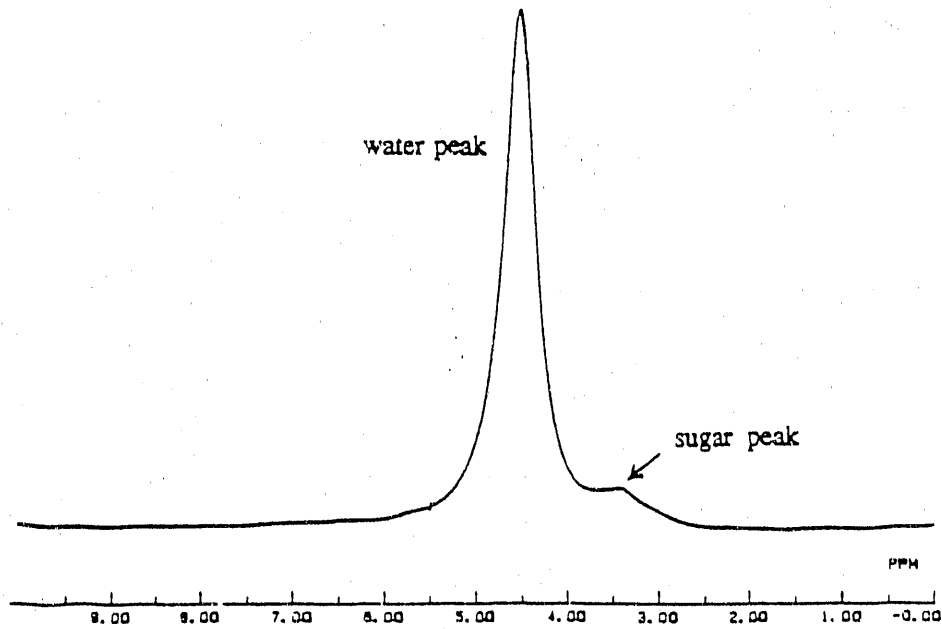

Figure 4. The Correlation of Sugar Content with T_2 Relaxation Times for Intact Sweet Cherries

FIGURES

Figure 1. Block Diagram of a Typical NMR Spectrometer

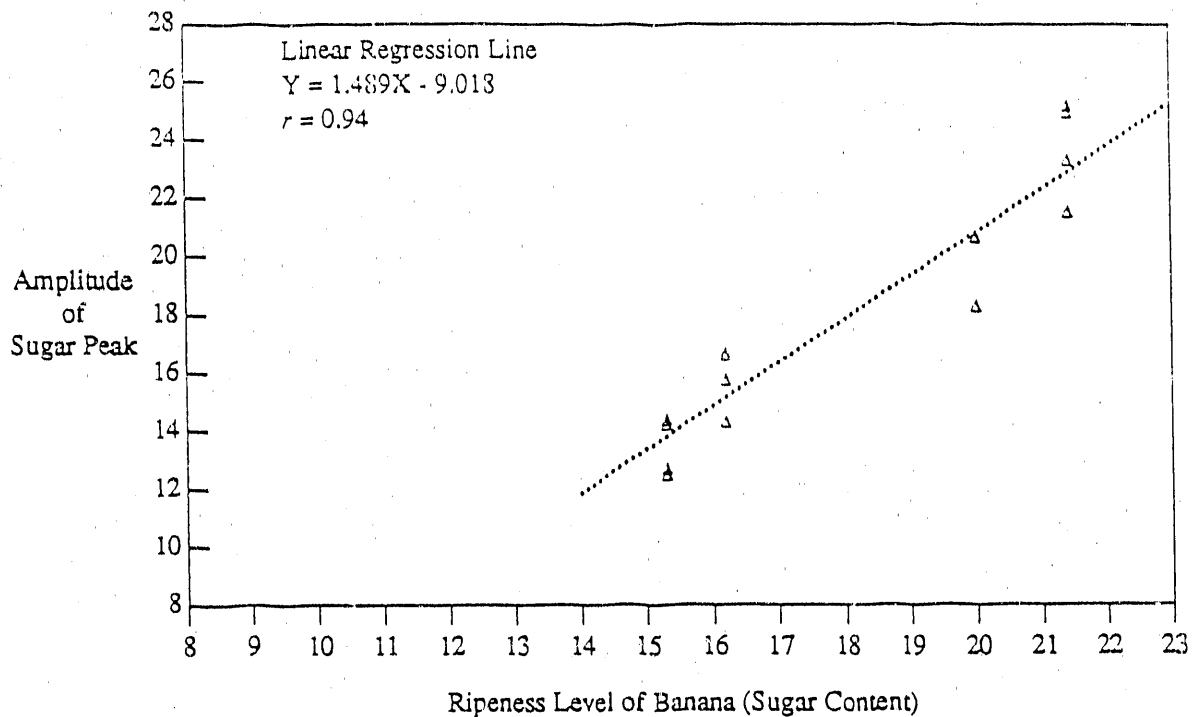Figure 2. Proton NMR Spectrum of a Ripe Banana Sample

Figure 3. The Correlation between Ripeness Level of a Banana and Amplitude of Sugar Peaks
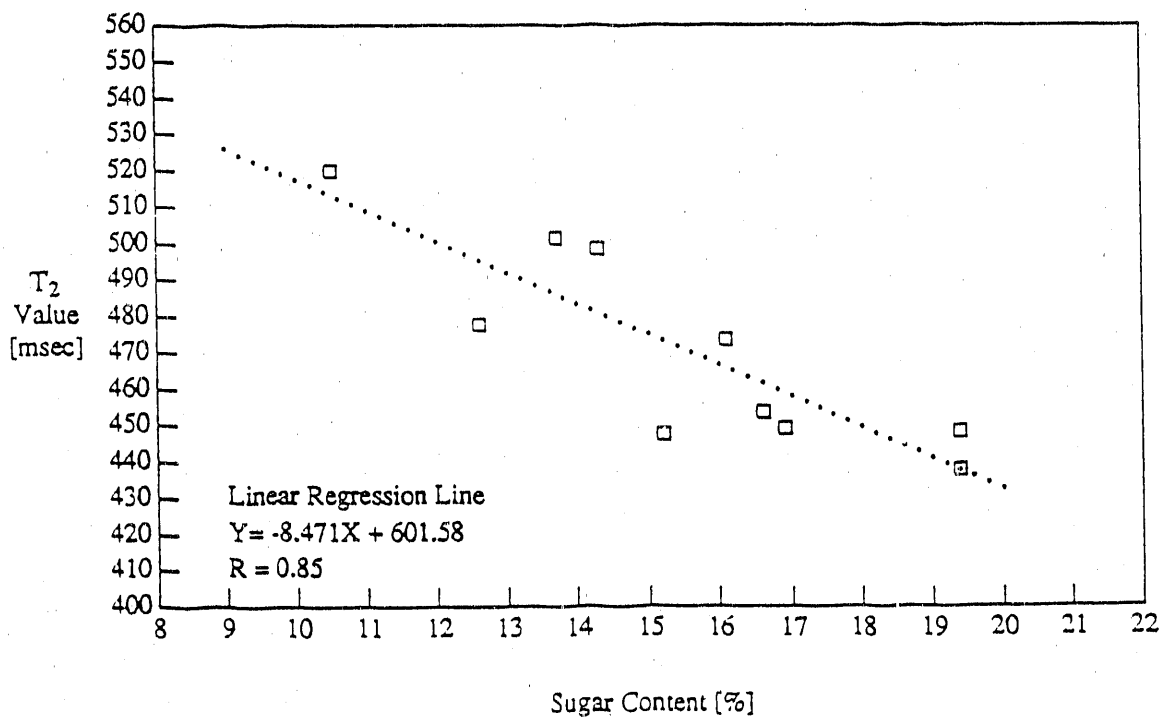

Figure 4. The Correlation of Sugar Content with T_2 Relaxation Times for Intact Sweet Cherries

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