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Classification of intact fresh plums according to sweetness using time-domain nuclear magnetic resonance and chemometrics

Fabíola Manhas Verbi Pereira *, André de Souza Carvalho, Luís Fernando Cabeça, Luiz Alberto Colnago

Embrapa Instrumentação, Rua Quinze de Novembro 1452, São Carlos, SP 13561-206, Brazil

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ABSTRACT

Time domain nuclear magnetic resonance (TD-NMR) and chemometric models were used to classify intact plums according to the total soluble solid content in percentage (% of SSC). The models were constructed using use Carr–Purcell–Meiboom–Gill (CPMG) decay (as independent variables) of intact plums. The reference values in % of SSC (as dependent variable) were obtained from the juice extracted from the same plums. The data sample was divided into two categories: class 1, up 9 to 12% of SSC and class 2, up 13 to 22% of SSC. The soft independent modeling of class analogy (SIMCA) of 171 plums correctly classified the class 1 plums approximately 89% of the total and the class 2 plums (sweeter) above 93% of the samples for both training and the validation data set, at 95% of confidence level. Therefore, the analysis of CPMG decay using SIMCA can be used to classify intact plums according to sweetness. This method is fast (seconds) and can easily be automated, allowing a better classification of each plum than the average SSC values of a lot.

1. Introduction

In fruits, the total soluble solid content (SSC) or Brix degree (°Bx) is one of the most important quality parameters for both the consumer and the industry. The standard method to measure SSC is refractometry, which measures the refractive index of a sample in Brix degrees, and it represents the percentage by mass of total soluble solids of a pure aqueous sucrose solution [1]. The SSC analysis must therefore be performed on the fruit juice. It is a destructive method that can be applied to a small set of representative samples to obtain an average Brix value [2].

As an alternative to refractometry, which is invasive and time-consuming, a few spectroscopic methods involving NMR and near-infrared spectroscopy (NIR) have been proposed to estimate sweetness in intact fruit relative to the fruit ripeness [3,4].

The SSC of intact fresh prunes has been estimated using a 2 Tesla (T) superconducting NMR spectrometer [5]. In this magnet, the resolution was sufficient to resolve the chemical shift of 100 Hz (1.2 ppm) between hydrogens in soluble solids (sucrose) and the water peak. The ratio between the heights of these two peaks shows a high correlation ($r = 0.907$) to the SSC of the prunes estimated with a refractometer. The NMR measurement time was approximately 1 s and, according to the authors, this time could be reduced to less than 100 ms.

Although this method is very promising, it has not been used commercially because the equipment is too delicate and expensive for use in packinghouses. In this study, we therefore propose the use of a low-cost time-domain nuclear magnetic resonance (TD-NMR) spectrometer, based on a permanent Halbach magnet, to classify plum samples according to SSC content.

The analytical technique TD-NMR is widely used for quantitative and qualitative analyses of food. These applications are motivated by low cost, ease of use of the instrumentation, preservation of sample integrity and the ability to perform direct analysis without sample preparation [3,4,6,7]. The additional advantages of an analytical method using TD-NMR are speed of analysis, which leads to an increase in the analytical frequency with low operating costs and equipment maintenance. These last two parameters are ten times lower than those same parameters observed for high field NMR [3]. Especially for food analysis, TD-NMR has been used to measure moisture and fat content and is currently also applied to evaluate shelf life, among other future possibilities [4].

The resolution of the TD-NMR spectrometer is normally insufficient to resolve the differences in chemical shift as used by Zion et al. [5]. In TD-NMR, the qualitative analyses are performed using the difference between the longitudinal (T_1) or transversal relaxation time (T_2) or self-diffusion coefficients (D) of the sample components. According to several studies, the elevation of T_2 values for vacuolar or cytoplasmic water can be associated with a decrease in the starch concentration during the ripening process [8]. Moreover, the decrease in the value for the self-diffusion coefficient is related to sugar accumulation as starch hydrolysis occurs [4].

* Corresponding author. Tel.: +55 16 2107 2821; fax: +55 16 2107 2902.
E-mail address: fmverbi@uol.com.br (F.M.V. Pereira).

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In this study, sugar content was determined using low field NMR on-line equipment according to the study of Marigheto et al. [2]. These authors developed a method to measure SSC on the intact cellular tissue of apples and strawberries. The suppression of the water signal using T_1-nulling and diffusion methods was necessary.

The purpose of the present study is to use Carr–Purcell–Meiboom–Gill (CPMG) decay, dependent on T_2, in a TD-NMR spectrometer, to classify intact plums by SSC (sweetness) using chemometric methods [9,10]. The main advantage of chemometric tools is the analysis of the whole decay profile without subjectivity when using exponential fitting procedures. The CPMG method can be performed more easily than the methods used by Marigheto et al. [2]. The classification models were constructed using reference values of % of SSC (dependent variable) for plums and TD-NMR spectra (independent variables).

2. Materials and methods

2.1. Samples

One hundred seventy-one plum samples were purchased at local markets (São Carlos–São Paulo State, Brazil) in three different lots separated by one week and from different cultivars. Care was taken with respect to the condition of the peels and the ripeness of the plums.

2.2. Signal acquisition

TD-NMR measurements of intact plums were carried out on an NMR spectrometer (Spinlock Magnetic Resonance Solution, Cordoba, Argentina) with a permanent Halbach magnet of 0.23 T (9 MHz for ^{1}H), 10 cm bore, 50 cm of analytical magnet and 120 cm of prepolarizer magnet. For CPMG sequence, the following parameters were applied: π/2 and π pulses 9.2 and 18.1 μs, respectively, echo times τ = 1000 μs and 2500 echoes. The analysis was performed with the sample at 22 °C.

2.3. Reference values

The total soluble solid content per 100 g (SSC) was measured on the plum juice using a RT-30ATC digital refractometer (Instrutherm, São Paulo, Brazil) with a 0–32% Brix scale [1].

2.4. Chemometric evaluation

The data were divided into 171 lines corresponding to the signals of TD-NMR relaxometry from plum samples and 1992 columns related to time (variables). The instrumental response for each time was the independent variables (**X** matrix). The Brix values were used as a parameter to separate the data within categories (or classes): category 1 with values up 9 to 12% of SSC-a total of 45 samples, and category 2 with values up to 13 to 22% of SSC—a total of 126 samples. The data were divided into two separate sets including samples of both categories, one for training the classification model with 137 samples (36 for class 1 and 101 for class 2) and another for validation with 34 samples (9 for class 1 and 25 for class 2). The chemometric tools performed are available on the Pirouette 4.0 rev. 2 software (Infometrix, Bothell, WA, USA).

3. Results and discussion

The raw TD-NMR CPMG signals of the intact plums were normalized to 1 at the maximum value of the amplitude to minimize differences within the amplitudes of the TD-NMR signals. Fig. 1 shows the CPMG decay, dependent on transverse relaxation time (T_2), of plums with low (9% of SSC, black line) and high Brix values (22% of SSC, gray line). In this same figure, it is possible to verify that the sample with high Brix (SSC) has faster decay than the sample with the lower sugar content [2].

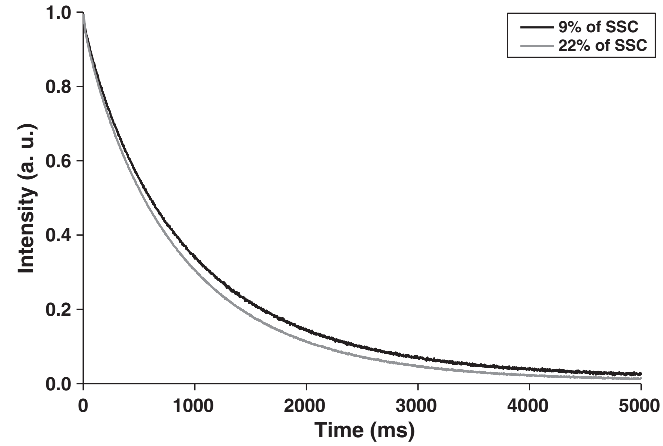

Fig. 1. Time-domain nuclear magnetic resonance signals obtained with CPMG pulse sequence for plums with 9% of soluble solid content (SSC) marked by black line and 22% of SSC marked by gray line.

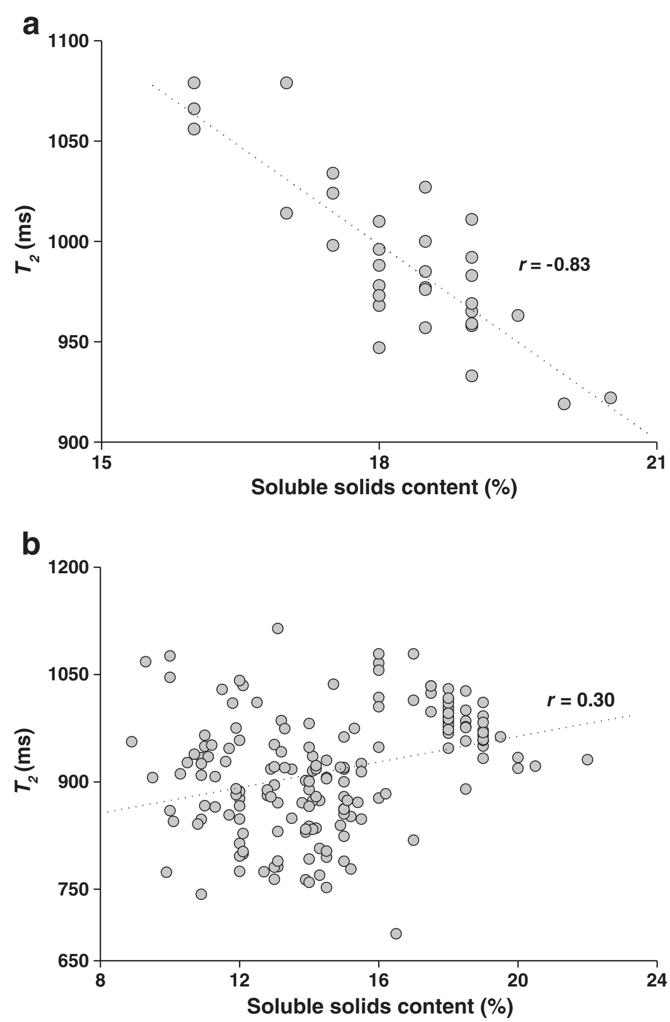

Fig. 2. Correlation between discrete values of transversal relaxation time (T_2) using mono-exponential fitting of a lot of 32 plums and % of soluble solid content (SSC) (a) and for 171 plum samples acquired in three consecutive weeks and from different sources (b).