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Development of a Dielectric Spectroscopy Technique for Determining Key Chemical Components of Apple Maturity

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Dielectric measurements (from 500 MHz to 20 GHz) on different standard solutions (K^+, malic acid) with different sugar contents were assayed simulating concentrations of these substances during apple ripening. These assays were performed for considering the potential use of dielectric spectra (500 MHz to 20 GHz) to determine the optimal time for eating the fruit. Good correlations between a newly defined dielectric maturity index and the Thiault index were found. This work presents prospective data of dielectric spectra for certain apple key chemical components in order to consider its potential application as a nondestructive control sensor for the prediction of climacteric fruit maturity.

KEYWORDS: Dielectric spectroscopy; dielectric spectra; dielectric properties; apple ripening; climacteric fruits; Thiault index

INTRODUCTION

The physiological pathways that take part in fruit ripening, which are controlled and/or modified in the confection processes of postharvesting lines, mark the sensorial quality and the shelf life of the fruit. During the ripening, a series of chemical and biochemical changes occur, and mainly affect sugar, organic acids and pectines composition, among others (*1*). Thus, sugar content and acid concentration are the properties generally utilized to determine fruit maturity, but currently they require destructive and tedious measurements that cannot be implemented in postharvest lines (*2*). In this context, dielectric spectroscopy appears as an interesting technique for controlling the basic aspects of fruit quality in a rapid and nondestructive way; moreover, it can be directly applied in postharvesting lines.

Cells are the functional units of parenchimatic apple tissue, and their state determines mainly the chemical and biochemical transformation of apple during the maturation process. Cell volume is constituted by a big central vacuole, formed by aqueous solutions of amino acids, organic acids (malic acid), some saccharides (fructose), and inorganic ions (potassium). Mean chemical composition of Granny Smith apple is shown in **Table 1**. A detailed chemical composition of apple juice is also shown (**Table 2**).

In **Table 1**, it can be observed that carbohydrates are, except for water, the major components. Glucose, fructose and sucrose are the main sugars (**Table 2**). It is important to highlight the importance of organic acids in apple composition, malic acid being the most important. Of the inorganic fraction, the main mineral is potassium (*4*).

There is an increasing interest in determining fruit maturity in a rapid and nondestructive way. In recent years, dielectric spectroscopy is a novel technique which is being employed for determining numerous quality attributes in food products (*5*). More concretely, it has been employed in determining fruit maturity based on soluble solids content in honeydew melons (*6*, *7*) and watermelons (*8*) with promising results. It was also employed to study the dielectric properties of apples during storage, but no high correlations were found between the dielectric properties and soluble solids content (*9*).

Complex permittivity (ε_r) (eq **1**) is the dielectric property that describes food behavior under an electromagnetic field (*10*, *11*). The real part of complex permittivity is called the dielectric constant (ε'), and the imaginary part is called loss factor (ε'').

Table 1. Mean Chemical Composition and Standard Deviation of Granny Smith Apple (*3*)[a]

energy content (kcal)	58 ± 4
water content (g)	84 ± 1
proteins (g)	0.3 ± 0.1
lipids (g)	0.6 ± 0.2
carbohydrates (g)	15 ± 2

[a] Composition per 100 g.

Table 2. Mean Chemical Composition and Standard Deviation of Apple Juice (*4*)

water (g/100 g)	85.8 ± 1.8
carbohydrates (g/100 mL)	
sucrose	2.16 ± 0.73
glucose	2.01 ± 0.53
fructose	5.7 ± 0.8
minerals (ppm)	
potassium	1511 ± 267
calcium	41.9 ± 13.6
magnesium	64.9 ± 9.9
phosphates	252 ± 73
organic acids (mg/100 mL)	
malic	847 ± 280
citric	11.9 ± 5.4
quinic	42 ± 24

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Table 3. Standard Solutions of Water, Malic Acid and K^+ at Different °Brix Used in the Present Research

°Brix	potassium D-gluconate (g/100 mL)	malic acid (g/100 mL)	K^+ (g/100 mL)
0	0.100	0.000	0.017
0	0.100	0.500	0.017
0	0.100	0.700	0.017
0	0.100	1.000	0.017
0	0.150	0.000	0.025
0	0.150	0.500	0.025
0	0.150	0.700	0.025
0	0.150	1.000	0.025
0	0.200	0.000	0.033
0	0.200	0.500	0.033
0	0.200	0.700	0.033
0	0.200	1.000	0.033
0	0.250	0.000	0.042
0	0.250	0.500	0.042
0	0.250	0.700	0.042
0	0.250	1.000	0.042
13	0.100	0.000	0.017
13	0.100	0.500	0.017
13	0.100	0.700	0.017
13	0.100	1.000	0.017
13	0.150	0.000	0.025
13	0.150	0.500	0.025
13	0.150	0.700	0.025
13	0.150	1.000	0.025
13	0.200	0.000	0.033
13	0.200	0.500	0.033
13	0.200	0.700	0.033
13	0.200	1.000	0.033
13	0.250	0.000	0.042
13	0.250	0.500	0.042
13	0.250	0.700	0.042
13	0.250	1.000	0.042

The subscript r indicates that values are relative to air, and therefore the variable is dimensionless.

$$\varepsilon_r = \varepsilon' - j \cdot \varepsilon'' \quad (1)$$

The dielectric constant reports the ability of the food to store the electromagnetic energy. Only a perfect dielectric can store and release wave energy without absorbing it. Loss factor is related to absorption and dissipation of electromagnetic energy from the field (*12*). Such energy absorptions are caused by different factors that depend on structure, composition and measurement frequency (*5*).

At microwave frequencies the main mechanisms that contribute to the loss factor spectra are the ion conductivity and the dipole polarization (mainly free water molecules). Moreover, sugar content also contributes to dielectric spectra of fruits. Sugars can form hydrogen bonds to water molecules which produce the reduction of water mobility and the displacement of the relaxation frequency of free water to lower frequencies (*13*). This phenomenon is higher when the concentration of solute is higher (*14−16*).

The aim of this research was to analyze the viability of using dielectric spectra (500 MHz to 20 GHz) for determining the content of specific key molecules of apple maturity (soluble solid content and organic acid concentration) for a subsequent online quality control of this product by using dielectric spectroscopy.

MATERIALS AND METHODS

Standard Solutions. Standard solutions were prepared with Brix values of 0, 7, 9, 11, 13, and 15 and malic acid concentrations of 0 and

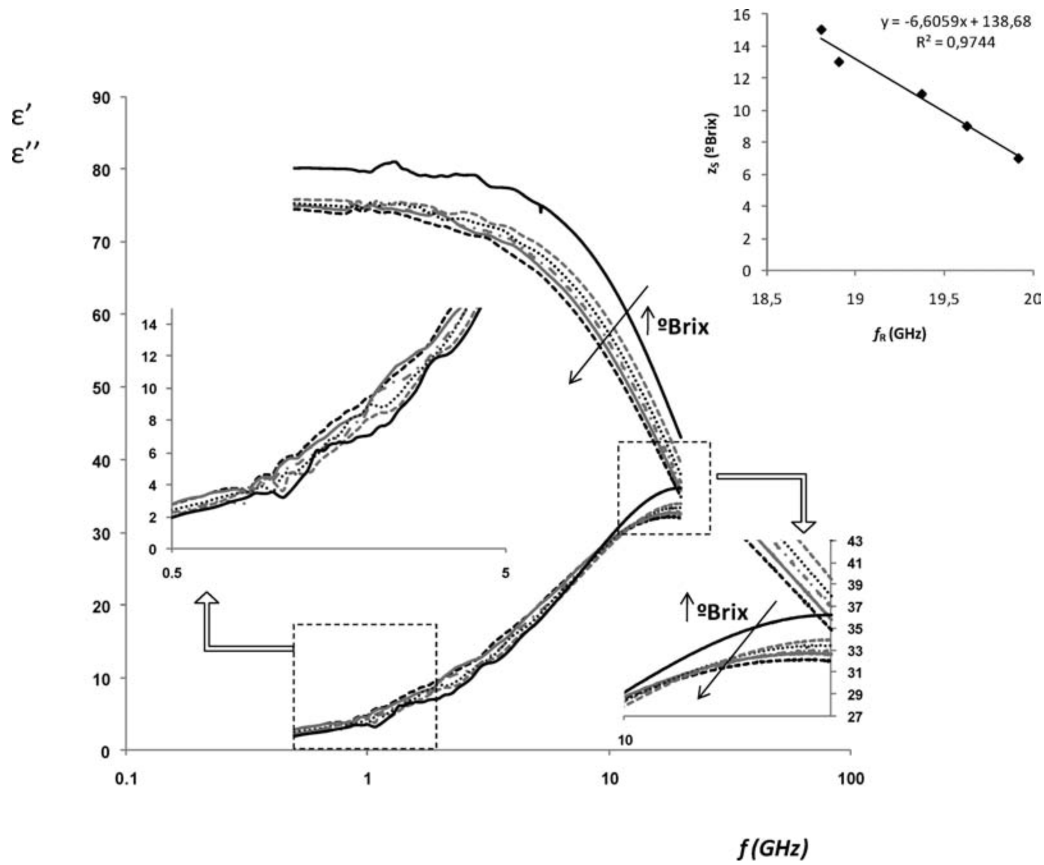

Figure 1. Dielectric spectra of water and sugar (glucose, fructose and sucrose at 1:1:3 proportions) with different concentrations: water (—), 7 °Brix (gray — — —), 9 °Brix (· · ·), 11 °Brix (gray — · —), 13 °Brix (gray —), 15 °Brix (— — —). At the lower right side, loss factor spectra at frequencies near the dipolar relaxation frequency could be observed in detail. At the upper right side, the relation between sugar concentration and the relaxation frequency can be observed. On the left side, loss factor spectra at low frequencies are shown in detail.

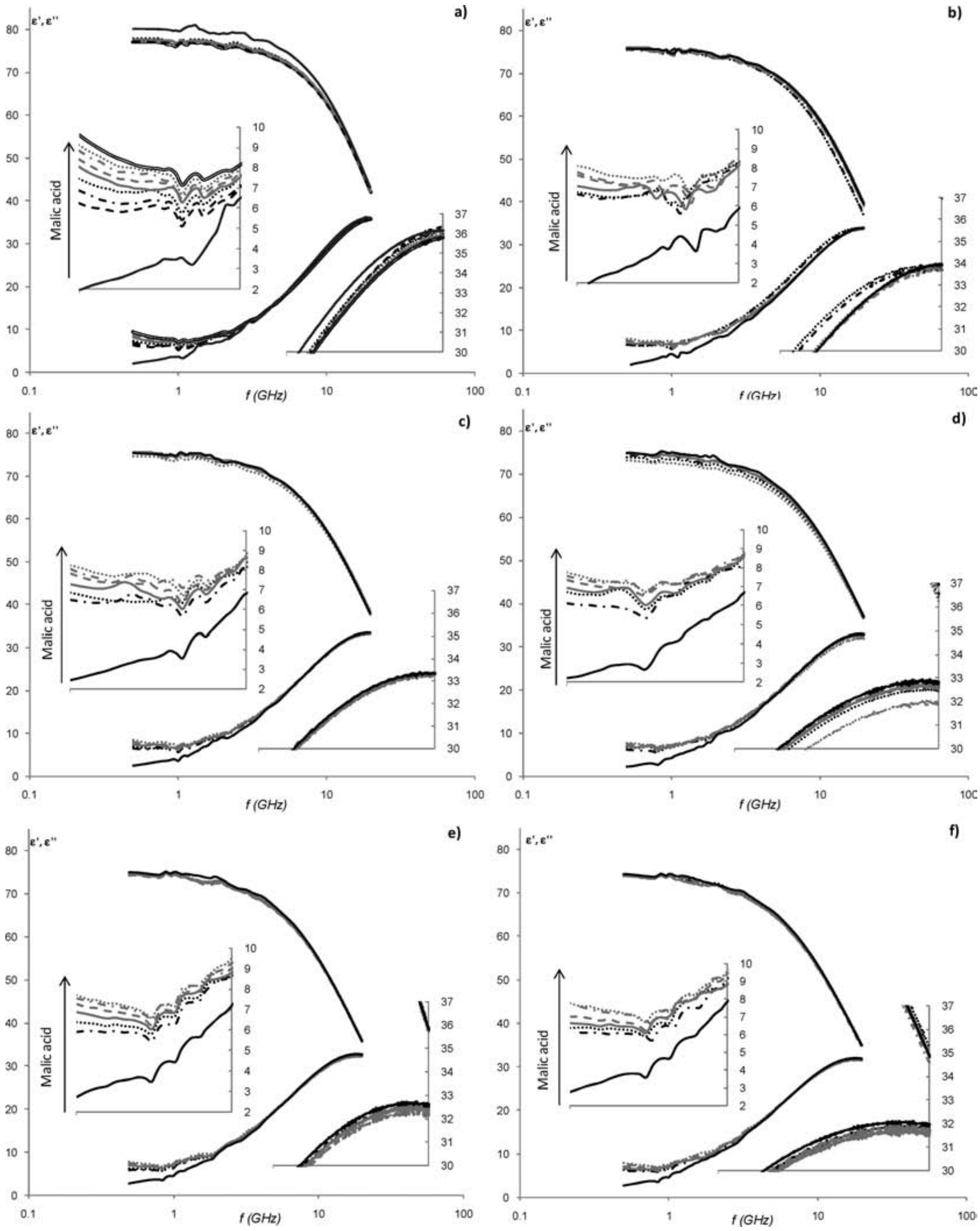

Figure 2. Dielectric spectra of experimental standard solutions at different malic acid concentrations (g/mL), 0 (—), 0.4 (— — —), 0.5 (— · —), 0.6 (· · ·), 0.7 (gray —), 0.8 (gray — — —), 0.9 (gray — · —), 1 (gray · · ·), 1.1 (═): (**a**) distilled water and malic acid, (**b**) 7 °Brix sugar solution with malic acid, (**c**) 9 °Brix sugar solution with malic acid, (**d**) 11 °Brix sugar solution with malic acid, (**e**) 13 °Brix sugar solution with malic acid, (**f**) 15 °Brix sugar solution with malic acid. In all graphs: on the right side, a detail of loss factor variations around the dipolar relaxation frequency; on the left side, a detail of the solutions' ionic behavior at low frequencies (0.5−1.5 GHz).

0.5 to 1.0 g/100 mL in increments of 0.1 g/100 mL. Also prepared were standard solutions of water, malic acid, and K^+ with different Brix values of 0 and 13 (**Table 3**). The composition of the standard solutions was based in bibliographic sources (*3*, *4*) trying to simulate the apple liquid phase. Moreover, sugar composition was obtained mixing sucrose, glucose and fructose taking into account that the relationship among these three main apple sugars is 1:1:3, respectively (*4*) (**Table 2**).

The additives used for preparing standard solutions were DL-malic acid (E-296, F.C.C.), aditio quality (Panreac Quimica S.A.U., Barcelona, Spain); potassium D-gluconate, aditio quality, puriss p.a. ≥ 99.0% (NT) (Sigma-Aldrich, Germany). Standard solutions were prepared with distilled water.

The water activity and °Brix of the standard solutions were determined. All the measurements were made at controlled temperature of 30 °C.

Dielectric Property Measurement. The system used to measure dielectric properties consisted of an Agilent 85070E open-ended coaxial probe connected to an Agilent E8362B Vector Network Analyzer. The software of the network analyzer calculates the dielectric constant and loss factor as a reflected signal function. For these measurements the probe was fixed to a stainless steel support, and an elevation platform brought the sample near the probe to avoid possible phase changes due to cable movements after calibration.

The system was calibrated by using three different types of loads: air, short-circuit and 25 °C Milli-Q water. Once the calibration was made, 25 °C Milli-Q water was measured again to check calibration suitability.

The dielectric properties were measured by introducing the open-ended probe at least 5 mm deep in the aqueous solutions. The mean values of three replicates of each solution are reported in this article. The dielectric properties were measured from 500 MHz to 20 GHz.

Physical−Chemical Analysis. The water activity of standard solutions was determined by using a dew point hygrometer Aqualab series 3 TE (Decagon Devices, Inc., Pullman, Washington). Sugar content was determined by a refractometer (ABBE, ATAGO model 3-T, Japan).

RESULTS AND DISCUSSION

In **Figure 1**, the dielectric constant and loss factor spectra (500 MHz to 20 GHz) of solutions of water and sugar at different concentrations can be observed. In **Figure 1** it can be observed that sugar molecules produce a decrease in dielectric constant and loss factor spectra with regard to dielectric spectra of pure water at dipolar dispersion frequencies. This effect is due to the fact that sugar molecules can form hydrogen bonds with water dipoles, limiting its movement and decreasing its polarization capacity. For this reason, dipolar dispersion is displaced to minor frequencies of the spectrum, decreasing dipolar relaxation frequency as can be appreciated in **Figure 1**. On the other hand, due to the fact that there existed no ions in the prepared standard solutions, any effect cannot be appreciated at low frequencies due to ionic losses, only the effect of the displacement of dipolar dispersion to lower frequencies produced by sugars can be observed also at low frequencies, being the higher sugar content the higher loss factor.

Dielectric spectra (500 MHz to 20 GHz) of malic acid standard solutions at different °Brix are shown in **Figure 2**.

Figure 2 shows that the effect of malic acid can be detected at low frequencies. At these frequencies of the spectrum, the ionic conductivity phenomenon is the main contribution to loss factor; for this reason, it is possible to affirm that malic acid is in malate form, a strongly anionic molecule which markedly increases ionic losses. This effect can be clearly appreciated in **Figure 2a**, in which distilled water and malic acid solutions spectra are represented with no sugar presence. The sugar addition to the solution produces an increase of solution viscosity with the subsequent decrease of loss factor spectra due to the dipolar and ionic

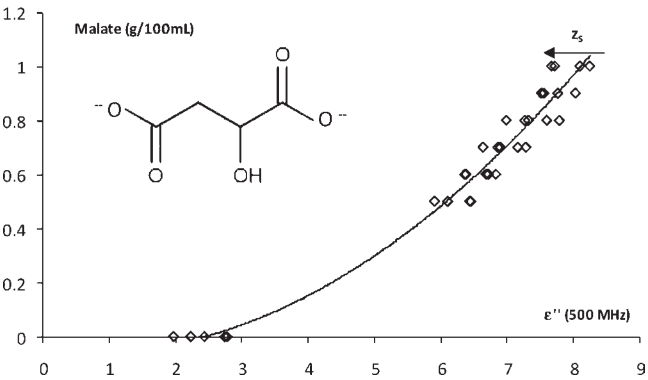

Figure 3. Malate (g/100 mL) and sugar content effect (z_S, °Brix) on the loss factor at the punctual frequency of 500 MHz.

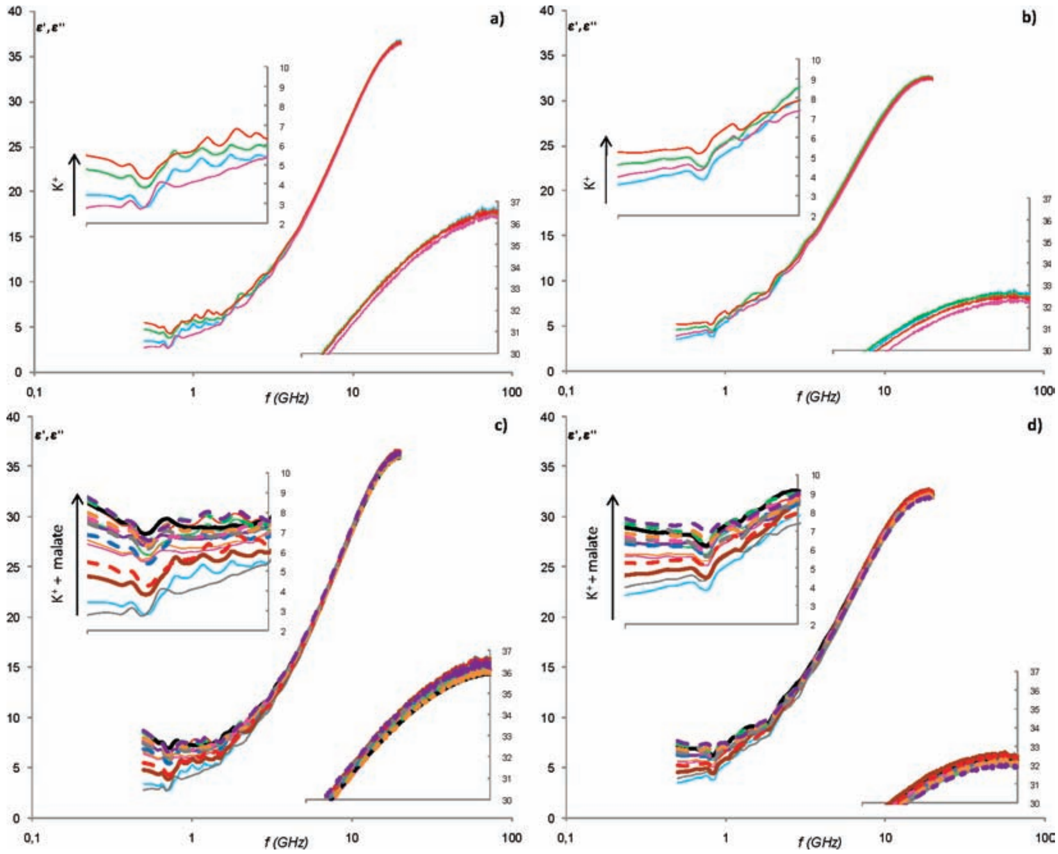

Figure 4. Loss factor spectra of standard solutions at different concentrations of malic acid (g/100 mL), potassium (g/100 mL) and sugars (°Brix). (**a**) Distilled water and K^+ at different concentrations: 0.017 (blue), 0.025 (pink), 0.033 (green), 0.042 (red). (**b**) 13 °Brix solution with K^+ at the same concentrations as in preceding case. (**c**) Solutions of malic acid and K^+: 0 malic acid and 0.017 K^+ (blue), 0.5 malic acid and 0.017 K^+ (pink), 0.7 malic acid and 0.017 K^+ (green), 1 malic acid and 0.017 K^+ (red), 0 malic acid and 0.025 K^+ (gray), 0.5 malic acid and K^+ (orange), 0.7 malic acid and 0.025 K^+ (purple), 1 malic acid and 0.025 K^+ (black), 0 malic acid and 0.033 K^+ (brown), 0.5 malic acid and 0.033 K^+ (blue − − −), 0.7 malic acid and 0.033 K^+ (pink − − −), 1 malic acid and 0.033 K^+ (green − − −),0 malic acid and 0.042 K^+ (red − − −), 0.5 malic acid and 0.042 K^+ (gray − − −), 0.7 malic acid and 0.042 K^+ (orange − − −), 1 malic acid and 0.042 K^+ (purple − − −). (**d**) 13 °Brix solution with malic acid and K^+ at the same concentrations as in preceding case.

mobility reduction. This decrease can be appreciated in **Figures 2b−2f** which have an increasing sugar concentration.

Figure 3 represents the malate and sugar content effect on the loss factor at 500 MHz frequency. In the same figure, malate chemical structure can be also appreciated.

Figure 3 shows that malate molecule has two negative electrical charges which generate a strong ionic behavior when the molecule is subjected to electromagnetic radiation. Higher malate content produces higher loss factor at 500 MHz. The sugar content effect on the loss factor at this frequency can also be observed. For equal malate content, loss factor value is minor when sugar content is increased. This phenomenon is due to the reduction of malate mobility when sugar concentration increase.

The effect of K^+ on the dielectric spectrum, in frequency range from 500 MHz to 20 GHz, was also studied because of its importance in apple composition (*4*) (**Figure 4**). Potassium ion generates an increase in loss factor spectrum at low frequencies (**Figure 4a**). This effect is lower when sugar is added to the standard solution (**Figure 4b**). Moreover, sugar produces also a decrease in loss factor on dipolar zone (frequencies near 10 GHz). On the other hand, malate ion effect is shown in **Figures 4c** and **4d**, where, at low frequencies, an increase in loss factor can be appreciated due to the addition of malate to the potassium ion losses. The effect of sugars in loss factor spectrum can also be observed, which produces an increase in viscosity and a reduction in molecules' mobility, decreasing both ionic and dipolar losses.

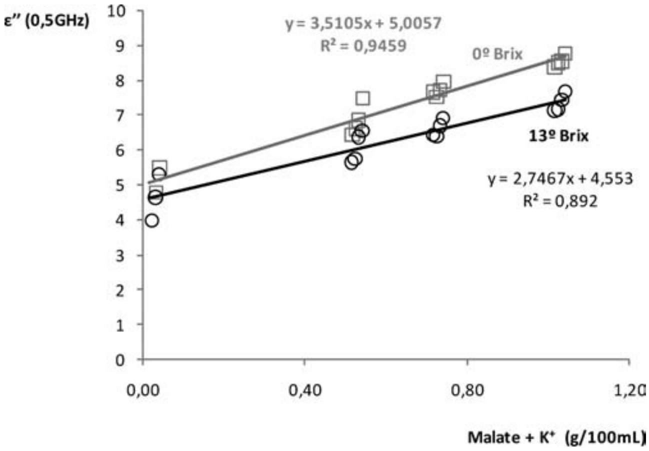

Figure 5. Malate and potassium ions (g/100 mL) versus loss factor at 500 MHz for pure water and 13 °Brix solution.

In **Figure 5** the additive effects of malate and potassium ions on loss factor at 500 MHz are presented for water and 13 °Brix solutions.

Figure 5 corroborate that both ions have an additive effect on loss factor at 500 MHz, increasing its value when both ions increase. Moreover, the effect of sugars on loss factor at low frequencies of the spectrum can be observed again, provoking a decrease in ion mobility due to the presence of these macromolecules.

Maturity Index. Thiault index (TI) was used as an indicator of apple maturity. The Thiault index is defined by eq **2** (*17*).

$$\mathrm{TI} = c_s + 10\mathrm{Ac} \quad (2)$$

where c_s represents the sugar concentration (g/L) measured by refractometry, and Ac represents the NaOH estimated acidity (expressed as g/L). The Lewis expression of sugar solution density (*18*) was used to transform the sugar mass fraction (g/g) to sugar concentration (g/L) (eq **3**).

$$c_s = z_s \rho_{ss} \quad (3)$$

In apple, if TI is equal to 170, it is the minimum for acceptable fruit quality; if TI is equal to 180, it is recommended to harvest the fruit; if TI is more than 180, the fruit quality is excellent (*19*, *20*).

As it can be observed in eq **2**, Thiault index is an indicator of soluble solid content and acid concentration. Both soluble solid content and acidity are quantified in the same order; for this reason the acidity is multiplied by 10.

Due to the fact that malic acid concentration is positively related to loss factor at 500 MHz, and the concentration in soluble solids is negatively related to loss factor at relaxation frequency, it

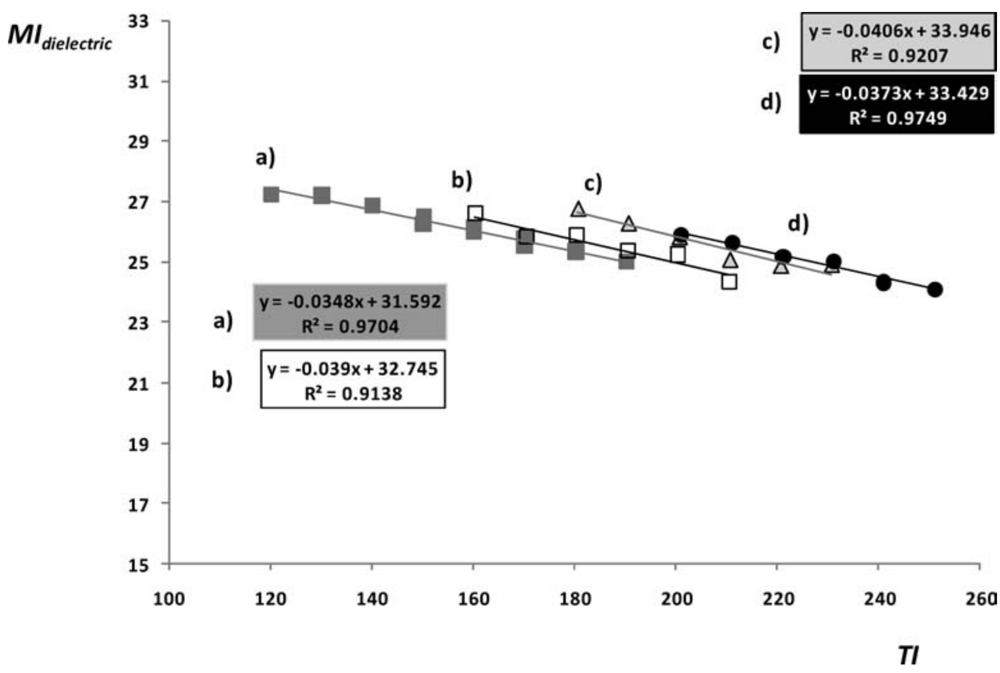

Figure 6. Maturity index obtained from dielectric properties versus Thiault index from standard solutions of different malic acid concentrations (0.5, 0.6, 0.7, 0.8, 0.9, 1 g/100 mL) at different sugar concentrations of (gray ■) 7 and 9 °Brix, (□) 11 °Brix, (gray ▲) 13 °Brix, (●) 15 °Brix.

could be possible to define a new maturity index based on dielectric properties (eq **4**).

$$MI_{dielectric} = \varepsilon''(f_{relaxation}) - \varepsilon''(f_{0.5GHz}) \qquad (4)$$

It is important to highlight that the loss factor at 500 MHz is directly related to malic acid concentration and an increase in malic acid produces an increase in loss factor at this frequency; on the contrary, an increment in sugar content produces a decrease in the loss factor at relaxation frequency. As it was explained above, Thiault index quantifies both soluble solid content and acid concentration; for this reason, to define a dielectric maturity index it is necessary to subtract the loss factor at relaxation frequency from loss factor at 500 MHz. It could be interesting to remark that loss factor at relaxation frequency is higher than loss factor at 500 MHz, and for this reason and to avoid negative signs the subtraction was defined as specified in eq **3**. Moreover, it is also important to denote that an increase in Thiault index will produce a decrease in dielectric maturity index; thus, when dielectric maturity index takes lower values, more quality is present in the fruit.

Figure 6 represents the dielectric maturity index from standard solutions of different malic acid and sugar concentrations as a function of the Thiault index, where good correlation coefficients obtained for each sugar concentration are shown.

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