# Changes of ultrasound characteristics of mango juice during fruit ripening

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Abstract

Attenuation and propagation velocity of ultrasound signals at 25 MHz were measured on clear mango juice samples using a pulse echo method. Ultrasound characteristics were determined with other physico-chemical characteristics on juice samples extracted from fruits undergoing ripening for three weeks at 23 °C and 80 % RH and periodically removed every two or three days. During fruit ripening, the changes of biochemical composition induced more effect on velocity than attenuation. Velocity were positively correlated to soluble solids content ($R = 0.98$), to sucrose content ($R = 0.80$) and negatively correlated to titratable acidity ($R = -0.59$) and fruit firmness ($R = -0.76$). A linear model based on soluble solids content and a PLS model based on all the physico-chemical characteristics were built to predict ultrasound velocity. Finally, the results obtained in this study showed that velocity is a relevant parameter linked to the major biochemical changes occurring during controlled fruit ripening. Due to high attenuation of ultrasound waves in mango peel and pulp tissues, confirmation of these results for whole fruit will be a challenge.

Keywords: ultrasonic waves, mango juice, ripening, fruit quality.

## 1. Introduction

Products quality management is of prime importance to promote fresh fruits and vegetables consumption and to deliver high quality products. For climacteric fruit such as mango, identification of optimal fruit maturity at picking and control of fruit ripening and softening are crucial for delivering products of premium quality.

During fruit ripening, sugars composition, organic acids, aromatic compounds and firmness change rapidly and extensively, modifying significantly fruit quality perception by consumers. Monitoring the evolution of the ripening of fruit batches can lead to increase biochemical analysis that are costly and time-consuming. Hence, there is a need to develop rapid, cheap and robust methods for fruit on- line quality assessment or to integrate them into automatic grading robotic devices for quality control of fruit samples representative of commercial batches.

As ultrasound techniques match these specific criteria, this technology has been widely investigated during the past decades to non-destructively assess maturity or fruit quality for various fruit species (apple, avocado, kiwifruit, mango, melon, orange, plum, tomato). However, due to their peel, to their internal heterogeneity, and to the presence of intercellular air spaces in their pulp tissues, which act as resonant structures, whole fruit are strong attenuating and scattering materials in the frequency domain ranging from 100 kHz to 100 MHz. As a result, ultrasonic waves cannot propagate easily inside their tissues by transmission impeding propagation properties measurements. To overcome this problem, many research studies have been oriented toward the use of frequencies lower than 100 kHz and to the use of the reflection mode instead of the transmission mode (Mizrach, 2008). As a consequence, ultrasounds are increasingly seen as efficient research tools rather than commercial solutions for on-line fruit quality sorting (Mizrach, 2008). According to the same author, this outcome could result from the need to specifically determine for each fruit species the appropriate frequency and the power requirement for the ultrasonic excitation. The other challenge consists of adapting existing ultrasound systems or designing new devices.

Implementation of ultrasound techniques for characterizing fruit juice quality seems less challenging firstly in terms of attenuation, even if cellular debris and fibers present in juices may impact ultrasound wave propagation. More generally, applications on liquid food materials have concerned quantification of oil content in aqueous milling waste (Benedito et al., 2004), ethanol in fermented sugar mixtures (Resa et al., 2004), sugars in fruit juices (Contreras et al., 1992; Kuo et al., 2008).

Concerning the fruit juices, impact of the nature of sugars (glucose, fructose, sucrose) and their respective concentrations on their ultrasound properties has already been investigated for velocity (Contreras et al., 1992) and attenuation (Asmani et al., 1992). By contrast, the effects of non-sugar compounds of fruit juices such as organic acids and soluble pectic compounds have only been quoted without thereby being quantified.

The present research work aims at studying the ultrasound properties changes of mango juice extracted from fruit undergoing ripening and softening under controlled conditions. The second objective is to find relationships between these parameters and some major physico-chemical quality parameters relevant for mango fruit. Finally, we will try to propose a PLS prediction model for ultrasound velocity based on sugars composition and to quantify the effects of the non sugar compounds on velocity.

## 2. Material and methods

### 2.1. Material

Experiments were performed on two commercial mango cultivars, Kent and Keitt. Two batches of Kent mangoes (respectively 42 and 25 fruits) and one of Keitt (42 fruits) were purchased from a mango producer in the province of Andalusia, Spain. Fruits were harvested at two harvesting periods (early and late) at hard green maturity stage. Refrigerated vehicles were used for transporting fruits from the fruit grower to the lab.

Once received, each fruit batch was kept at 22°C and 80% RH for the two or three weeks that necessitated the complete softening of all the fruits. Five to six fruits were periodically drawn at random every two or three days and analyzed to monitor physiochemical changes during storage. Fruit texture was measured on whole fruit (hardness) and on the pulp (penetrometry). Fruits were then juiced using a juicer (Whole Fruit Juicer LTK7189) and the resulting juice was centrifuged, frozen, and kept at -20°C to be later analyzed. Juice measurements concerned their refractive index, ultrasound properties, sugars composition and titratable acidity.

### 2.2. Methods

#### 2.2.1. Ultrasonic measurements on juice

The innovative pulse echo method implemented in this study has already been used for characterizing aqueous sorbitol solutions (Laux et al., 2009). Starting from an arbitrary distance along the vertical axis called z (typically a few millimeters) between an ultrasonic plane transducer (central frequency at 25 MHz) and the bottom of a tank containing the

mango juice, the distance between the sensor and the bottom of the container was gradually reduced step by step (fig.1). At each step, the ultrasonic echo reflected from the bottom of the container after propagation in the juice was acquired via an USB-GPIB interface. At the end of acquisition, the plot the arrival time of each echo versus z position gave a straight line (fig.1). The ultrasound velocity was calculated from the slope (a) of the linear regression equation by using the expression V = 2/*a*.
In the same way, if A represents the echo amplitude for a given value of z and if 20.Log (A) is plotted versus z, the ultrasonic attenuation dB, in decibel, can be deduced. Indeed, the slope of 20.Log (A) versus z is equal to "-2dB".
Concerning the apparatus, the excitation was achieved by a Sofranel Panametrics 5800 pulse generator and the echoes were displayed on a LT374M Lecroy© oscilloscope before acquisition on personal computer. All the displacements were made with a Microcontrol© stepper motor controlled by a MM4005 MicroControler with an accuracy of $\pm$ 1 μm. Signal processing was performed with softwares written with Labview. Ultrasound properties being temperature-dependant, all the measurement system (juice - container - sensor- motor) was put in a Binder KB 53 cooled incubator at a controlled temperature of 20°C ±0.1 °C.

2.2.2. Physico-chemical analysis of mango fruits and juices

Whole fruit firmness and pulp texture were respectively measured by a durometer and a texturometer (Valente et al., 2011). The durometer (Durofel$^{TM}$, Setop Giraud Technologie, France) equipped with a flat tip cylindrical probe (D10, contact area of 0.1 $cm^2$) measured fruit hardness (H). This quality-parameter ranged from 22 (over ripe fruit) to 96 (rock hard green fruit) on a 0 – 100 scale. Penetrometry firmness (Wa), expressed in N.mm, corresponded to the work required to penetrate the flesh at 1 $mm.s^{-1}$ to the maximum penetration depth (10 mm).

Soluble solids content (SSC) was measured by refractometry at 20°C by using a handheld digital refractometer, Atago (Tokyo, Japan) ranging from 0.0 to 33.0 ° Brix.
Soluble sugars i.e. fructose (Fru), glucose (Glu) and sucrose (Suc), were separated by high performance ionic chromatography using a DX600 system (Dionex Corp., Sunnyvale, CA, USA), equipped with a Carbopac MA-1 Column (250 x 4 mm) in combination with a Carbopac MA1 guard column (25 x 4 mm) and coupled to a Dionex ED50 pulsed amperometric detector (Gibert et al., 2009). Glucose, fructose and sucrose contents were given in grams per liter. Titratable acidity (TA), expressed in milli-equivalents per 100 grams, was determined with an automatic titrator (Titroline easy, Schott Instruments GmbH, Germany) to pH 8.1 by using a 0.1 M NaOH solution.

2.2.3. Statistical analysis

Principal Component Analysis (PCA) and Partial Least Squares Regression (PLSR) were achieved by using The Unscrambler v.9.7 (Camo, Norway). The PLS model for predicting ultrasound velocity from biochemical composition was built by using calibration data set (73 data) and validated by using the prediction data set (36 data). Calibration and prediction data sets were selected in such a way that they were both representative of the initial samples population and they covered the entire range of variation of velocity. Calibration and prediction performances were assessed by coefficients of determination ($R^2$), the root mean square error of cross validation (RMSECV) and the standard error of prediction (SEP).

## 3. Results and discussion

3.1. Changes of US characteristics with fruit ripening
Figure 2 (left) showed a linear increase of US velocity during the first seven ripening days for the early fruits (kent, Keitt) in conjunction with an increase of sucrose content and a decrease in titratable acidity during the same period (fig. 3). From seven until twenty days of ripening,

velocity maintained the same level. For early fruits, attenuation reached a maximum between 7 and 14 days of ripening and then decreased steadily (fig. 2 right). For late fruits, velocity and attenuation displayed higher values resulting from higher sugars and faster ripening. This could be explained by the impact of the harvesting period which was greater than the variety factor.

3.2. Relationship between US parameters and fruit characteristics

The principal component analysis of data showed that three groups of variables could be identified for explaining 80.8 % of the total variance (fig.4). Velocity and attenuation were positively correlated to the degree of ripeness of the mangoes in terms of soluble solids content ($R = 0.98$, *respectively* $R = 0.81$) and sucrose content ($R = 0.80$, *respectively* $R = 0.66$) and negatively correlated to titratable acidity ($R = -0.59$, *respectively* $R = -0.52$) and fruit firmness ($R = -0.76$, *respectively* $R = -0.67$). Glucose and fructose variables were both independent of SSC and sucrose content. Moreover, the two variables TA and H were highly correlated ($R = 0.89$).

3.3. Prediction models

As velocity was better correlated than attenuation to physico-chemical characteristics of mango fruits, two models were built for its prediction: a linear model with SSC and a PLS model based on the seven physico-chemical parameters (Wa, H, TA, Fru, Glu, SSC, Suc). This later model was optimized by using the Martens' uncertainty test (Esbensen, 2002) that allowed the selection of three significant variables (SSC, Fru, TA) having model coefficients significantly different from zero. Small differences were observed between the two models (fig. 5). This was confirmed by a similar coefficient of determination ($R^2$= 0.95). However, the standard error of prediction gave a better performance of the PLS model (SEP= 1.5 $m.s^{-1}$) compared the linear model (SEP= 2.3 $m.s^{-1}$).

## 4. Conclusion

Ultrasound velocity and attenuation were strongly linked to the changes of biochemical composition of mango fruits during ripening, mainly in terms of sucrose and organic acids contents. These last two parameters also depended on the stage of fruit maturity at picking that was found to have a greater impact on the ultrasound parameters than the variety factor.

Due to the fact that velocity was not frequency dependent, better correlated than attenuation to physic chemical characteristics and more accurately measured than attenuation, this parameter was selected for monitoring fruit ripening. However, these results will have to be confirmed on mango flesh pulp samples. In particular, the effect of flesh tissue structure on ultrasound transmission velocity will have to be specified. This represents a big challenge because of the strong attenuating and scattering properties of intact mango pulp tissues in the frequency domain ranging from 100 kHz to 100 MHz.

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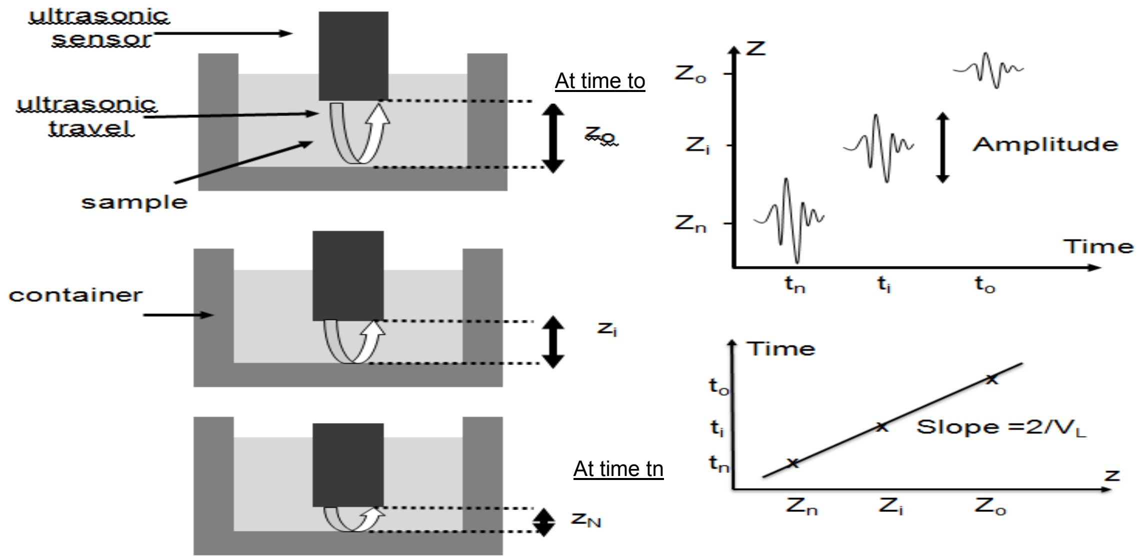


Figure 1: Principle of the ultrasound pulse echo method implemented.

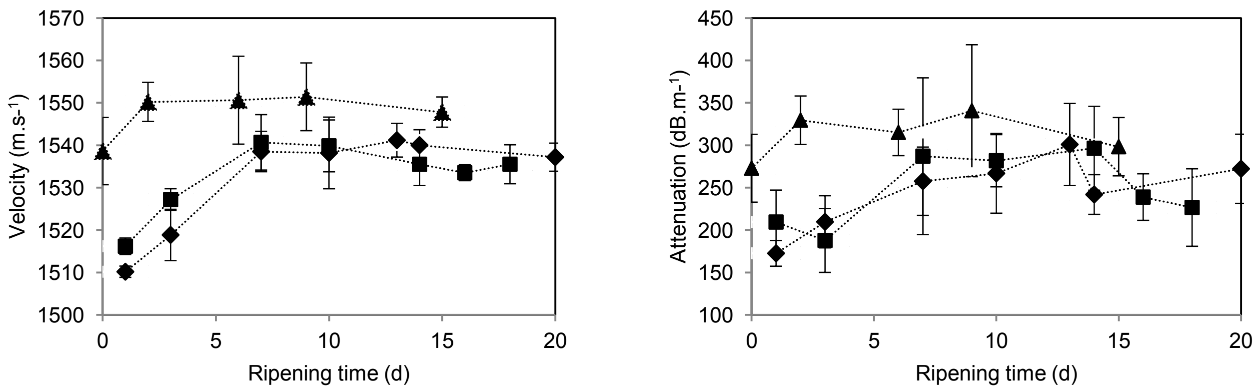


Figure 2: Changes of velocity (left) and attenuation (right) with fruit ripening
(■ Kent early, ▲ Kent late, and ♦ Keitt early)

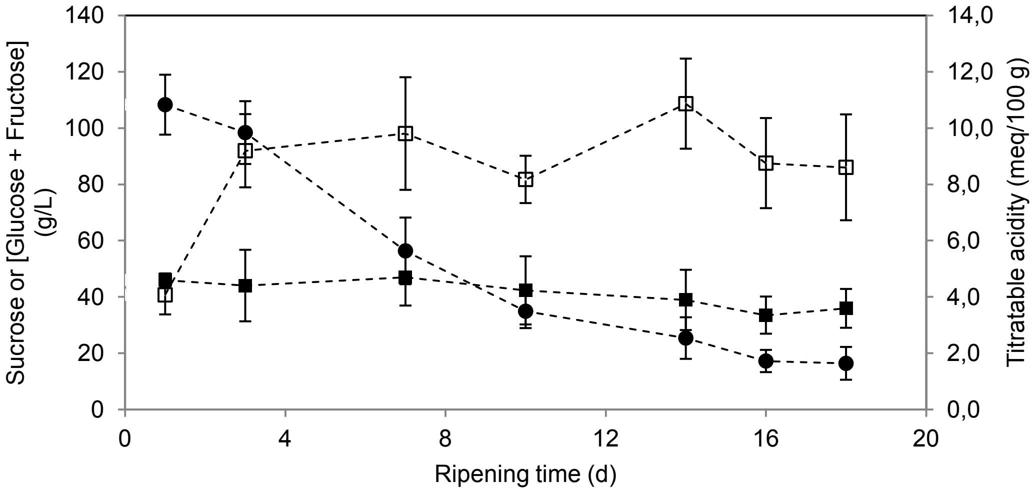


Figure 3: Changes of soluble sugars and titratable acidity with fruit ripening for Kent early (■ fructose + glucose, □ sucrose, and ● titratable acidity)

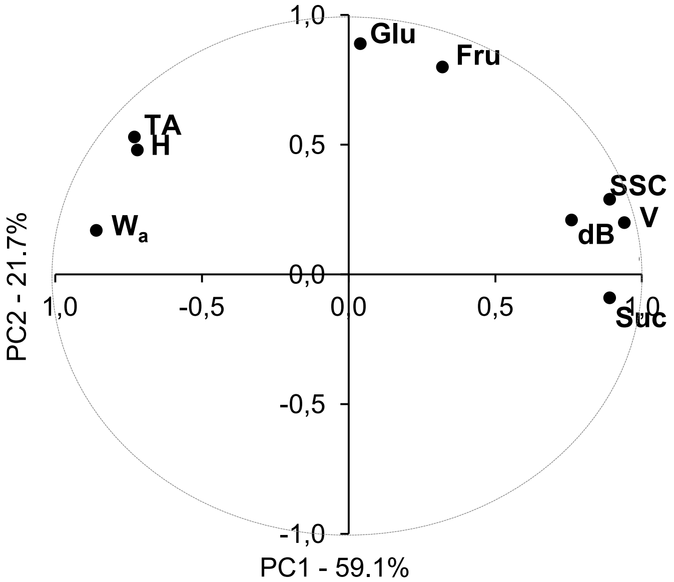


Figure 4: Plot of the x-loadings for the nine physico-chemical variables

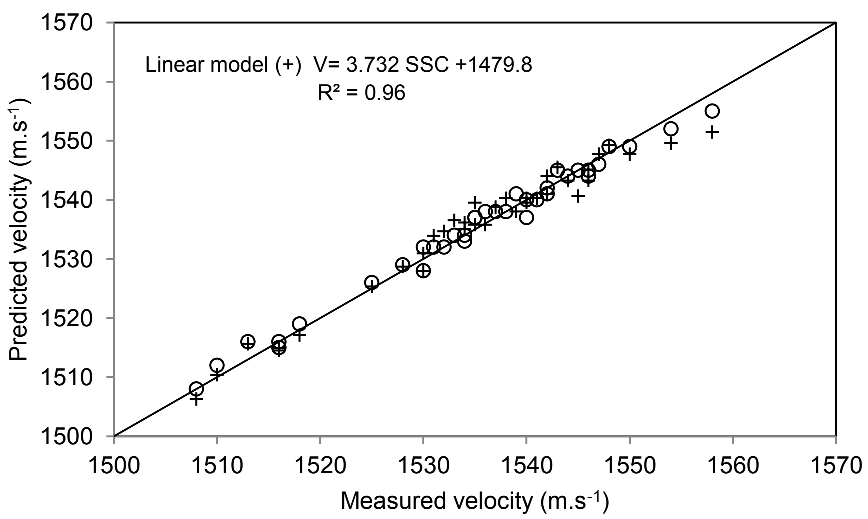


Figure 5: Predicted vs measured velocity for the PLS model (o) and the linear model (+).