Ultrasonic Spectroscopy – a rheological tool?

Henrik Kragh

Danisco A/S, Edwin Rahrs Vej 38, DK-8220 Brabrand, Denmark.

ABSTRACT

37 samples of drinking yoghurt were examined by ultrasonic spectroscopy, sensory analysis, rheology and several other physical measurements. Correlations were made between the different measurements. Among other things very good correlations were found between the ultrasonic results and texture parameters obtained from the sensory evaluation. Furthermore it was shown that ultrasonic results correlated to the mouth feeling called mouth coating. A parameter that is often very difficult to predict from traditional rheological measurements. The correlations to the product compositions seemed to be very strong. Besides dry matter content, fat content etc. it was also revealed that the choice of sweetener had a strong influence on the textural properties. The influence of sugar as an ingredient was not seen in traditional rheology. Surprisingly the correlations between rheology, exemplified by flow curves, and ultrasonic measurements were not particularly good. The results are visualised using Principal Component Analysis (PCA) and Partial Least Square plots (PLS).

INTRODUCTION

The main purpose of this work has been to obtain a better understanding of the strengths and weaknesses of ultrasonic spectrometry (US) as tool for characterisation of food products.

The characterisation of drinking yoghurt by US was also made to obtain an understanding of the influence of different combinations of pectin on the physical properties of drinking yoghurt. To support the understanding, designed experiments with different composition of both ingredients (pectin, starch, culture, etc.) as well as raw materials (fat, protein, water, etc.) were set up.

The yoghurts were characterised by sensory analysis, particle size distribution, confocal laser scanning microscopy (CLSM), sub-surface reflections, viscosity (Brookfield single value and StressTech flow curve), sedimentation (Turbiscan MA2000) and ultrasonic spectroscopy.

However the focus in this paper has not been set on the influence of pectin but on the understanding of US as a tool in food characterisation. Therefore the effort has been aimed at the correlations between the US data and the other disciplines. Special attention has been paid to the correlations between ultrasonic measurements and sensory analysis, rheology and Turbiscan measurements. The main purpose is to obtain an improved understanding of the information that can be extracted from an ultrasonic spectrometer.

MATERIALS AND METHODS

The drinking yoghurt was analysed by a high-resolution ultrasonic resonance spectrometer, HR-US 102, from Ultrasonic Scientific, Ireland. The instrument was

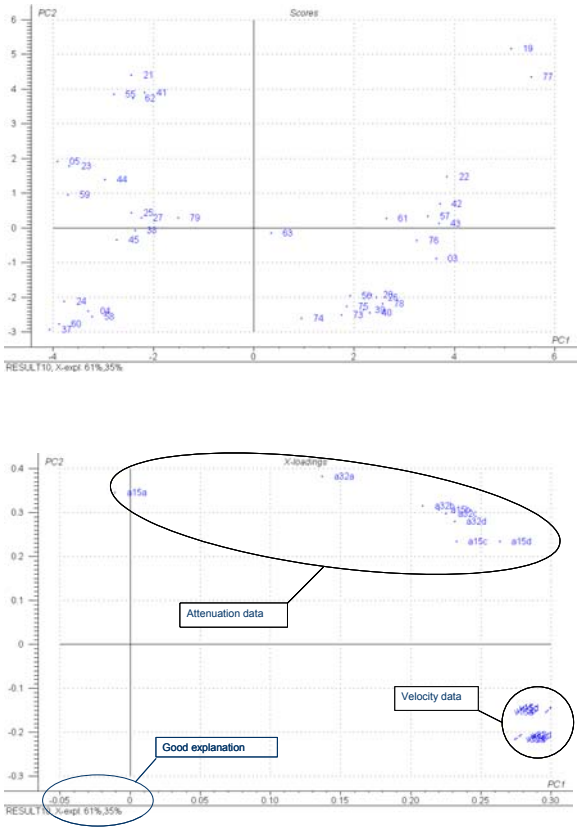
equipped with two 1 ml measuring cells and the temperature was maintained at appropriate values by an external ThermoHaake water bath with a precision of 0.01°C. No stirring was applied during the analysis.

The samples were characterised by their ultrasonic velocity, u [m/s], and the corresponding attenuation, α [Np/m], at four different frequencies and two different temperatures. The frequencies were: 2.5 MHz, 5.0 MHz, 8.0 MHz and 12.0 MHz, and the temperatures were 15°C and 32°C. The velocity and the attenuation values were recorded relatively to the values of water. The absolute values are obtained by adding the recorded values to the values of water at the appropriate temperatures. In this study the relative values were used due to the fact that they only differ from the absolute values by a constant.

Each of the sixteen US values that characterises a sample is the average of values recorded over a 30 minutes period. Approximately 60 data points were included in each average. All measurements were performed in duplicate. The results were named according to a four letter code starting with either v (velocity) or a (attenuation). A two-digit number (15 or 32) is following the first letter. It reflects the temperature of the measurement. Finally a single letter is indicating the frequency used (a: 2.5 MHz; b: 5.0 MHz, c: 8.0 MHz or d: 12.0 MHz). The variable name for the velocity measured at 15°C and 2.5 MHz would be: v15a; the attenuation measured at 32°C and 12 MHz would be: a32d and so forth.

The explorative data analysis was made using The Unscrambler® v8.0 from CAMO Process AS, Norway. The values used for Principal Component Analysis, PCA, and Partial Least Square Regression, PLS-R (usually just called PLS), are the averages of the duplicates. All PCA and PLS analyses were carried out using centred and weighted (1/Std) data.

EXPLORATION OF ULTRASONIC DATA



Figures 1a & 1b. Scores and loadings plots from PCA of ultrasonic data.

Figures 1a and 1b illustrate the PCA results from the ultrasonic analysis of the 37 yoghurts. The two first principal components describe 96% of the validated variance in the data set.

It can bee seen from the loadings plot that all the velocities at each temperature are contributing with the same information and that the velocities at the two temperatures are contributing with approximately the same type of information. In contrast the attenuation provides different contributions at the two different temperatures as well as at the four different frequencies. The largest difference is seen at the lowest frequency (a15a and a32a).

In the scores plot, Fig. 1a, a clear grouping of the samples is seen.

Samples 20, 39, and 78 represent a reference that was included in the weekly production of samples. It can bee seen that the samples are grouped together indicating a good reproducibility both in production and in the ultrasonic analysis.

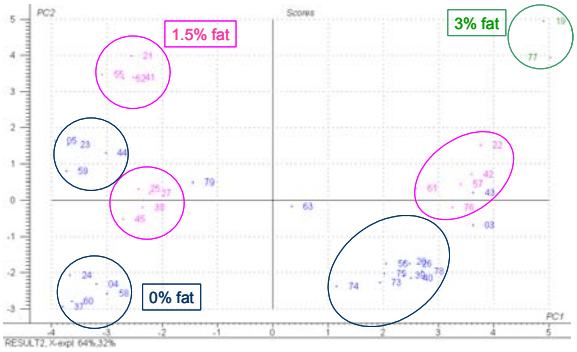


Figure 2. PCA illustrating the grouping based on fat content of the products.

Fig. 2 illustrates the influence of the fat content of the products. As shown in the figure, the fats shift the texture in the same direction going from high fat content in the upper right corner to no fat in the lower left corner. As will be discussed later, this indicates that the lower the fat content is the more watery and the less mouthfeel there is.

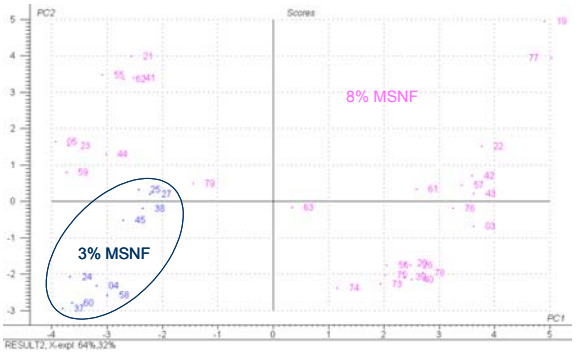


Figure 3. Scores plot from PCA illustrating the grouping based on milk solid non-fat (MSNF) content of the products.

As seen from Fig. 3 the influence of the MSNF is also clearly defined by the ultrasonic results.

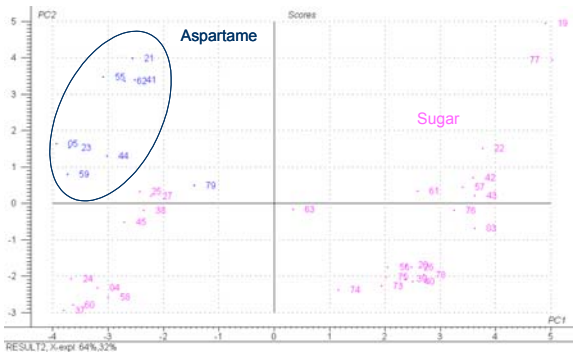


Figure 4. Scores plot from PCA illustrating the grouping based on type of sweeteners used in the yoghurts.

Fig. 4 illustrates the influence of sweeteners on the ultrasonic results. It is believed that the result more likely reflects a difference in concentration of the two types of sweeteners rather than a difference in textural properties. As it will be shown later, the correlation between textural properties and US data were not convincing for these experiments.

CORRELATIONS BETWEEN SENSORY AND ULTRASONIC DATA

The 37 samples have been characterised by 16 sensory parameters. Parameters can be seen in Table 1.

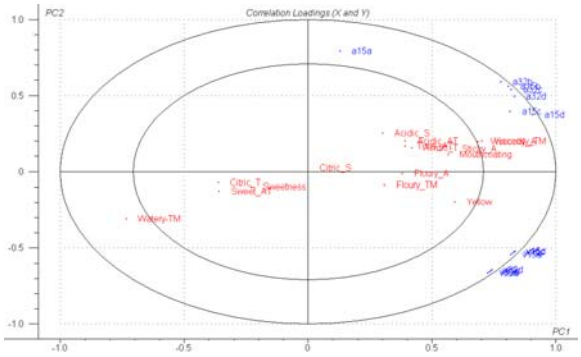


Figure 5. Correlation loadings from a PLS2 analysis with US data as the x-matrix and sensory data as the y-matrix.

As seen in Fig. 5, the best correlations are found between the US data and sensory data that describe physical properties such

as viscosity and mouth coating. Table 1 gives the correlation coefficients of the separate PLS1 correlations between US data and the respective sensory value. Values followed by A indicate a visual characterisation (A = apparent). Values followed by M indicate that the samples have been evaluated in the mouth, S if evaluated by smell, T if evaluated by taste, TM defines texture in the mouth and AT the aftertaste.

Table 1. Correlation coefficients from PLS1 predictions of sensory parameters based on US data.

Sensory parameters	Corr.
Viscosity_A	0.84
Watery_TM	0.83
Viscosity_TM	0.81
Yellow	0.78
Mouthcoating	0.75
Sticky_A	0.73
Time_AT	0.68
Acidic_S	0.56
Acidic_T	0.55
Floury_A	0.54
Floury_TM	0.53
Citric_T	0.42
Acidic_AT	0.36
Sweetness	0.29
Sweet_AT	0.27
Citric_S	0.21

Table 1 shows that the physical parameters such as apparent viscosity, watery mouthfeel and oral viscosity have the highest correlation coefficients whereas the parameters relating to smell and taste are found at the bottom. This relates well to the understanding of the ultrasonic spectrometer as an instrument that belongs in the physical characterisation of products.

CORRELATIONS BETWEEN ULTRASONIC DATA AND RHEOLOGY

The yoghurts were subjected to viscosity measurements. Traditional one-point measurements were made on a Brookfield instrument from Brookfield Viscometers Ltd., United Kingdom, and flow curves were made on a StressTech Rheometer from Rheologica AB, Sweden. The flow curves were fitted to a Power Law model and the consistency index, K, and flow index, n, was used as representatives for the entire flow curve. The correlation coefficients can be seen in Table 2.

Remarkably, the correlations between ultrasonic data and the rheological data are not as strong as expected. Even though it can be argued that US measurements at high frequencies and flow curves are not obviously related, some correlation would be expected based on the previous results from the sensory evaluation.

Table 2. Correlation coefficients from PLS1 predictions of viscosity parameters based on US data.

Rheology parameters	Corr.
Viscosity	0.62
K	0.68
n	0.29

CORRELATIONS BETWEEN ULTRASONIC AND TURBISCAN DATA

A Turbiscan MA200, Formulaction, France, was used to analyse the samples. Only the Mean and the Span have been used for making correlations to US data. The Mean value represents an average of the back scattering of light from each sample. High values of Mean could indicate increased solid content in the samples or a decrease in particle size. The Span represents the variation in the backscattering. High values of Span indicate an inhomogeneous sample. Inhomogenity is related to variation in the samples such as inhomogeneous fillings, roughed surface due to graininess etc. The correlation coefficients are shown in Table 3.

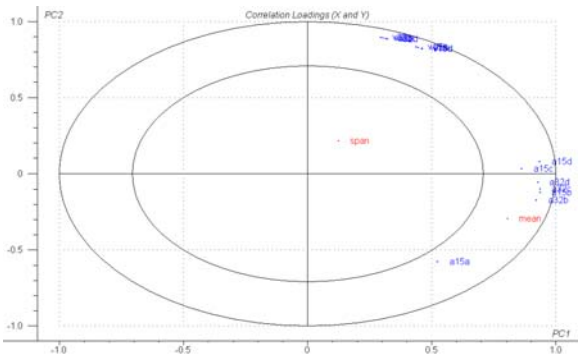


Figure 6. Correlation loadings from a PLS2 analysis with US data as the x-matrix and Turbiscan data as the y-matrix

Table 3. Correlation coefficients from PLS1 predictions of Turbiscan parameters based on US data.

Turbiscan parameters	Corr.
Mean	0.87
Span	0.01

The correlation at 0.87 between the Mean value and the US data indicates that the two types of measurements are both sensitive to product composition; whereas the correlation for Span illustrates that the inhomogenity that could exist due to large particles is not seen. The Mean value from the Turbiscan is a function of particle size and concentration of MSNF. The mean value is mainly influenced by small particles (0.3 – 20 µm) whereas the Turbiscan span value is believed to relate to large particles (>120µm). The particle size of the drinking yoghurt is expected to be in the range of 1 µm, and it is therefore in good agreement that the Span does not catch differences in particle size. It is expected that the US data does contain information relating to particle size and therefore the missing correlation between the span and the US data is not surprising.

CONCLUSION

Ultrasonic measurements on drinking yoghurt have shown that the instrument provides information relating to the composition of the products such as fat content, protein content etc. as well as the concentration of sweetener. Correlations are also found for some sensory parameters such as visual viscosity and mouth coating. In contrast no clear correlation between rheological data such as viscosity and flow curve parameters was found.

It was furthermore indicated that the attenuation was a stronger tool in differentiating between the physical properties than the velocity.

ACKNOWLEDGEMENT

Thank you for analytical contributions as well as fruitful discussions to my colleagues Kirsten Lauridsen, Stine Møller, Hanne Thorsøe and Flemming Møller.