Quality control of hazelnuts by means of NMR measurements

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Abstract. Hazelnuts are widely used in the confectionary industry for their flavour and taste. In order to guarantee a suitable level of quality, several standards have been defined by international organizations and producing countries. They define the minimum quality requirements of the fruits in terms of dimension, aspect, level of moisture, hidden defects. In this framework, our proposal is related to the set-up of an in-line classification system, based on low field NMR, able to detect the hidden defects of the hazelnuts. The proposed classification procedure is based on the CPMG sequence and the analysis of the transverse relaxation decay. The procedure includes three steps in which different features are detected: (i) moisture content, (ii) kernel development and (iii) healthy detection (presence of mould). Experimental results showed a very good capability to correctly detect the hidden defects, obtaining a sensitivity of 95%, with a specificity (correct detection of the healthy hazelnuts) around the 80%.

1. Main properties and hidden defects of the hazelnuts

Hazelnuts are widely used in the confectionary industry for their flavour and taste. They are characterized by a high nutritional value due to the presence of several components, mainly lipids (about 60% w/w), carbohydrates, proteins, sugar, and dietary fibres [1]. Both the yearly world production and the hazelnuts quality depend on the climate condition. In order to guarantee a suitable level of quality, several standards have been defined by the producing countries and regions. They define the minimum quality requirements of the fruits in terms of dimension, aspect, hidden defects. Other requirements, related to the quality of the hazelnuts and the place of production, can be found, for example, in the European Union certification like the Protected Geographical Indication (PGI). The most recent international standard has been set by the Organization for Economic Co-operation and Development [2]. It defines the quality requirements for the in-shell hazelnuts and hazelnut kernels intended for direct consumption or for food. The minimum requirements are described in the following. The shell must be:

- Intact; only slight superficial damages are allowed.
- Clean; free of any foreign matter.
- Free from blemishes and stains affecting more than 25% of the surface of the shell.
- Well formed.

The kernel must be:

- Free from rancidity.
- Sufficiently developed; kernels should fill at least 50% of the shell cavity.
- Not desiccated.
- Free from blemishes and stains affecting more than 25% of the surface of the shell.
- Well formed.

The whole nut must be:
Free from mould filaments.
- Free from living pests.
- Free from damage caused by pests.
- Free of any foreign smell or taste.
- Dried; moisture content not greater than 12% for the whole nut or 7% for the kernel.

The standard also defines the maximum allowed defects related to each requirement providing three quality classes: extra class, class I and class II. Figure 1 shows the aspect of healthy and unhealthy kernels.

2. Techniques to detect hazelnuts quality

The main technique used to detect the hidden defects of the hazelnuts is the visual inspection. A procedure to carry out this kind of test has been defined by the U.S. Food and Drug Administration in the Macroanalytical Procedures Manual (MPM) [3]. The document defines the test procedures for several food products, like fruits, vegetables, grain, dairy, cheese and seafood. It defines:
- Sample preparation.
- Sequential sampling plans.
- Visual and organoleptic examination.
- Classification of reject nuts.
- Report.

This method, being based on visual and organoleptic analysis, requires time and skilled personnel for a correct nut classification. Other techniques have been investigated in order to achieve automatic systems to check the quality parameters of the hazelnuts. The dimension of the shell and the blank nuts are detected by means of machines based on mechanical techniques. In particular, calibrator machines able to sort the whole hazelnuts on the basis of their diameter are available making use of sieves with different diameters. Air compressed-based machines can detect and separate some kinds of foreign body, like leaves or pieces of wood, from the whole hazelnuts. They can also detect blank nuts, even if they are not accurate. These kinds of equipment are useful for a pre-treatment of the product but they do not represent quality control systems. A different method to detect empty hazelnuts, based on the analysis of the acoustic signal generated by the impact of the nut on a steel plate, has been proposed [4]. It exploits both time-domain and frequency-domain analysis of the signal and can be used for a real-time detection. Using the same principle, a sorting method of cracked, hollow and regular shell has been developed for hazelnuts [5] and pistachio nuts [6], exploiting Frequency Domain (FD) signal processing techniques and Artificial Neural Network (ANNs).

Figure 1. Hazelnut kernels: (1) mould and pest damage; (2) desiccated and not well developed; (3) healthy
Several studies have been conducted related to the moisture content determination. This is an important quality parameter because a high level of moisture causes fungal diseases and mould formation, and then postharvest losses. Based on the weather condition around the harvest period, the moisture content of the hazelnuts can be more than 30%. They are dried using industrial dryer or, often, by means of sun drying techniques. After this process, farmers need instruments to verify that the moisture content is lower than the limits imposed by the quality standards. The most common method to evaluate the moisture content in food is based on oven drying in which the sample is heated under specified conditions and the amount of moisture is determined calculating the loss of weight:

\[
\% \text{Moisture} = \frac{\text{weight wet sample} - \text{weight dry sample}}{\text{weight wet sample}} \times 100 \quad (1)
\]

Other methods, related in particular to seeds and nuts, have been proposed. RF impedance measurement has been employed to determine the moisture in single grain and peanut kernels placed in a small parallel plate capacitor [7]. A similar method has been applied to determine the amount of moisture in in-shell hazelnuts placed in a probe with two vertical parallel-plate electrodes able to host a sample of 250 g of nuts [8]. More complex analytical techniques have been used to evaluate some quality characteristics of the hazelnuts. For example, a study for the identification of chemical markers of hazelnut roasting, based on Headspace Solid Phase Microextraction (HS-SPME) coupled with Gas Chromatography – Mass Spectrometric (GC-MS) detection has been proposed [9]. Near Infrared (NIR) Spectroscopy has also been used to detect flawed kernels and to estimate lipid oxidation [10]. These kinds of techniques allow extracting complex features in a non-destructive way, but are suitable for laboratory testing and cannot be used for industrial applications.

2.1 Using NMR in food quality control

NMR has been mainly used, in the past, in chemical analysis and medical diagnosis. The applications in food quality control have been developed progressively, thanks to the technical improvement in the instrumentation, the signal processing and especially the development of permanent magnets that allowed a significant cost reduction of the NMR equipment.

The NMR systems can be classified, on the basis of the technique used to carry out the analysis, in three main categories:

- NMR Spectrometry.
- NMR Relaxometry.
- MRI (Magnetic Resonance Imaging).

NMR Spectrometry, also named High Field NMR or Fourier Transform NMR (FT-NMR), makes use of superconducting magnets with a static magnetic field usually higher than 1 T. It is based on the frequency domain analysis of the NMR signals and it allows obtaining quantitative information related to the chemical composition of the samples under test.

Relaxometry mainly differs from the spectrometry for the use of permanent magnets that makes it the cheapest NMR technique and, for this reason, the most interesting to investigate industrial applications. It is also named Low Field NMR or Time Domain NMR (TD-NMR) because it employs magnets with a static magnetic field that is usually lower than 1 T and the signal analysis, differently from the spectrometry, is carried out in the time domain.

All of the above techniques have been investigated in food analysis. An overview of the food applications of the liquid state FT-NMR can be found in [11]. It presents a review of the NMR methodologies in food quality control, analysing several aspects as the sample preparation, which is an important step to obtain reproducible spectra, the spectral analysis and the statistical analysis. It also describes some applications to several products like alcoholic beverage, fruits and vegetables, milk and dairy products. An example of food authentication is described in [12], in which a bench-top spectrometer has been used for the analysis of olive oil with adulteration of hazelnut oil. A study on the compositional analysis of wine in a full intact bottle has been proposed in [13]. In the paper, the capability to detect acetic acid spoilage has been investigated using NMR spectrometry system. An overview of the potential applications of NMR and MRI for compositional and structural analysis, inspection of microbiological, physical and chemical quality, food authentication, on-line monitoring
of food processing is presented in [14]. A review focused on the development of TD-NMR and MRI based sensors for different food applications, can be found in [15].

Several studies have been carried out on methods and applications of Low Field NMR. A method for Solid Fat Content (SFC) and simultaneous oil and moisture determination has been described in [16]. Applications on quality control of different food products have been proposed: the evaluation of quality of oranges during storage [17]. Analysis of water dynamic states and age-related changes in mozzarella cheese [18]. The interest towards the industrial applications of the TD-NMR is constantly increasing. A study of the perspective of the use of the TD-NMR as in-line industrial sensor can be found in [19]. Among the proposed applications in in-line monitoring, Low Field NMR has been employed for the evaluation of the internal browning of whole apples [20]. Moreover, an automated system for oil and water content determination in corn seeds has been proposed in [21].

### 3. The adopted TD-NMR measurement system

The main applications of the TD-NMR in food quality control are related to the evaluation of the presence of water, moisture, oil, fat, that are well detected by this technique. The quality of the hazelnuts is strictly related to the presence of moisture and fatty acids and then, in this work, Low Field NMR has been taken into account as a suitable technique for the analysis of the hazelnuts quality [22]. The TD-NMR instrument used for the experimental work is composed by three main components (Fig. 2): (i) NMR console; (ii) Magnet and probe; (iii) Personal computer.

The NMR console is manufactured by Spincore Technologies Inc. It includes all the electronics to perform the generation and transmission of the excitation pulse sequences as well as the acquisition of the RF signals from the probe. It allows employing a resonance frequency up to 37.5 MHz.

These components have been designed for the specific application considering that the probe, placed in the magnet, has to be able to host a whole hazelnut. To this aim, the probe has a cylindrical coil characterized by height and diameter both equal to 25 mm.

Considering the value of the static magnetic field, the resonance frequency of the system is 21.8 MHz. The field homogeneity of the magnet is $10^{-4} \Delta B_0/B_0$. This value is only guaranteed in an area with 25 mm diameter at the centre of the magnet. For this reason, the coil of the probe must be placed at the centre of the magnet in order to work with the highest field homogeneity. The NMR console is connected to a personal computer and a Labview user interface has been implemented to send the setting commands to the NMR console and to carry out the signal processing and the classification algorithm on the received signals.

Permanent magnets have a coefficient of temperature in the order of $-1000 \text{ ppm/}^\circ\text{C}$, so the static magnetic field, and then the resonance frequency, changes when the temperature changes. In order to limit the resonance frequency variation due to the temperature variation, the magnet has been equipped with a temperature controller and insulated by means of sheets of extruded polystyrene. In this way, when the operating temperature is kept at 23.0 ± 0.1 °C the resonance frequency variation is lower than 5 kHz around the nominal value [23].
4. The classification algorithm
The proposed classification algorithm for the in-shell hazelnuts is composed by three steps (Fig.3)

1. Evaluation of the moisture content;
2. Evaluation of the kernel development;
3. Evaluation of the presence of mould.

In the first step, the hazelnuts with a moisture content greater than the limit imposed by the quality standards are discarded; the correctly dried hazelnuts are then evaluated on the basis of the kernel development. In this step, the following defects are detected and discarded:
- Empty hazelnuts;
- Not well developed kernels;
- Desiccated kernels.

Finally, in the third step, the presence of mould is evaluated and the healthy hazelnuts are selected.

The three steps are carried out on a single signal, acquired by means of the CPMG sequence, so for each sample, only one CPMG sequence is required [24], [25].

The tests were conducted on hazelnuts supplied by “Consorzio di Tutela Nocciola di Giffoni I.G.P.”. For each sample of hazelnut with shell, the following procedure was used to perform the test:
- Insertion of the hazelnut with shell inside the probe;
- Acquisition of the signal by means of CPMG sequence;
- Signal processing on the data acquired by the instrument and classification of the hazelnut by means of classification algorithm; extraction of the hazelnut from the probe;
- Breakage of the shell and classification of the hazelnut as healthy or unhealthy by means of vision inspection;
- Verification of the classification algorithm comparing the results with the vision inspection method.

The tests were carried out on 300 samples of hazelnuts, 220 dried samples and 80 fresh samples.

4.1. Moisture content evaluation
The moisture content evaluation is made analyzing the relationship between the amplitude of the FID signal ($A_{\text{FID}}$) and the amplitude of the 2nd echo, $A_{\text{echo}}$, of the CPMG sequence (Fig. 4) [26].
According to the threshold line defined in (eq. 2), the well-dried hazelnuts have to satisfy the following condition:

$$A_{echo} > (m - 3\sigma_m)A_{FID} + (b - 3\sigma_b) \quad (2)$$

The results obtained on 220 dried hazelnuts and 80 fresh hazelnuts are shown in Figs 5.

As can be seen from the figure one in 220 samples of dried hazelnuts has been mis-detected, while the 80 fresh hazelnuts have been correctly classified.

4.2. Kernel development evaluation

The analysis on the kernel development on the 219 hazelnuts correctly classified as dried in the previous step is described. It is made exploiting the threshold on the amplitude of the FID (Fig. 6). Three category of defects are considered: blank, insufficiently developed and desiccated have been included in the not well developed kernel. The well-formed hazelnuts have to satisfy the condition:

$$A_{FID} > threshold \quad (3)$$

In Fig. 6, the results related to the 219 samples selected from the previous step are shown.
Figure 6 Relation between the amplitude of the FID signal and weight of the kernel for 219 hazelnuts samples: fully developed kernels (in blue) and not well developed kernels (in red).

As can be seen, all the well-developed kernels have been detected and only one in 25 not well developed kernels has been not correctly classified.

4.3. Mould presence evaluation

The analysis of the mould presence is made on the dried and well-developed hazelnuts. Analysing the T$_2$ spectrum, calculated considering a model of the transverse relaxation curve with three exponential decay [22]:

$$y(t) = \sum_{j=1}^{3} x_j e^{-\frac{t}{T_{2j}}}$$

(4)

The healthy hazelnuts exhibited a greater value of the second time constant than the unhealthy ones, although the two categories are not well separated (Fig. 7).

Figure 7 T$_2$ spectrum for healthy (blue) and unhealthy (green) hazelnuts

Starting from this consideration, a healthy condition has been defined to detect the healthy hazelnuts:

$$T_{2,2} > T_{2,2}^{THR}$$

(5)

The threshold has been determined considering an approach based on ROC curves [27]. The analysis has been carried out considering two classes:

- Unhealthy hazelnuts: positive test;
- Healthy hazelnuts: negative test.

The parameters used to evaluate the classification errors are described in Table I.
Table I  Classification parameters and indexes

| Classification parameter | Description                  | Index                  | Description                      |
|--------------------------|------------------------------|------------------------|----------------------------------|
| True positive, TP        | Unhealthy sample correctly classified | True positive rate TPR | $TPR = \frac{TP}{TP + FN}$       |
| False positive, FP       | Healthy sample classified as unhealthy | False positive rate FPR | $FPR = \frac{FP}{FP + TN}$       |
| True negative, TN        | Healthy sample correctly classified | True negative rate TNR | $TNR = \frac{TN}{TP + TN}$       |
| False negative, FN       | Unhealthy sample classified as healthy |                           |                                  |

The true positive rate (TPR), also named sensitivity or recall, represents the capability of the system to detect the unhealthy samples. The false positive rate (FPR) is a measure of the false alarms, namely the healthy samples wrongly classified as unhealthy. The true negative rate (TNR) is the specificity, which represents the capability of the system to detect the healthy hazelnuts.

The ROC curve is a two-dimensional graph in which the y-axis is represented by the TPR and x-axis is represented by the FPR; each point of the ROC curve is related to a value of the threshold to set, and it is obtained calculating the TPR and FPR using that value of the threshold.

Figure 8 shows the ROC curve related to the classification of the hazelnuts obtained varying the threshold THR

![ROC curve related to the threshold $T_{2,2}^{THR}$](image)

Analysing the curve, it can be observed a linear behaviour until a TPR value around 0.80 and FPR around 0.20, then the slope drastically decreases. It means that from that point, the FPR increases faster than the TPR, causing a performance degradation. The threshold $T_{2,2}^{THR} = 0.058$ s has been selected.

Considering the global performance of classification algorithm, a sensitivity (TPR) of 95.0% and a specificity (TNR) of 80.0% has been obtained. The classification algorithm exhibited a high sensitivity, so a high capability to detect the unhealthy hazelnuts.

5. Conclusions

In this work, a method for the quality detection of the in-shell hazelnuts has been proposed. It is based on the low field NMR, which is a non-destructive technique employed in the quality control of food, especially in offline laboratory applications. This research project focuses on an in-line industrial application of the NMR system that has to be able to detect the hidden defects of the hazelnuts in order to help the farmers and the producers to meet the quality requirements imposed by the international standards and rules. A permanent magnet and probe specifically designed for this application have been used in order to be able to host a whole nut. The proposed classification algorithm is based on the analysis of the transverse relaxation decay, which is obtained with the CPMG sequence. In particular, three different steps of the algorithm have been defined. In each step a single quality property of the hazelnuts is analysed: the moisture content, which is responsible of the mould development, is
evaluated analysing the relation between the maximum amplitude of the CPMG signal and the second echo peak. The kernel development, that allows detecting the empty, not well developed and desiccated nuts, is evaluated considering the maximum amplitude of the acquired signal. Finally, the mould presence is evaluated analysing the $T_2$ spectrum of the CPMG signal, which consists of the amplitudes and the time constants related to the multi-exponential decomposition of the transverse relaxation decay. The first two features can be detected in a very fast way, only 12 ms are needed to obtain the results, because the information are contained in the first part of the acquired signal; for the third feature, the total acquisition time is needed, which is around 245 ms.

The classification algorithm showed a high sensitivity (95%) with a specificity around the 80%, so it is capable detecting the unhealthy hazelnuts but with a relatively high number of discarded healthy hazelnuts. The loss of specificity is mainly due to the third step of the algorithm, while in first two steps this value is similar to the sensitivity. This does not represent a limit because the defects related to the kernel development are well detected and they outnumber other kinds of defects. Moreover, the moisture content is also well detected by the classification algorithm, and this allows discarding the hazelnuts that contain a high level of moisture, that causes the mould development during the storage. Finally, the study has been carried out on the hazelnuts, but it can be easily extended to other kinds of fruit in shell, as well as the measurement algorithms can be applied in other kinds of NMR applications.

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