Chemical modifications of Tonda Gentile Trilobata hazelnut and derived processing products under different infrared and hot-air roasting conditions: a combined analytical study

Chemical modifications of Tonda Gentile Trilobata hazelnut and derived processing products under different IR and hot-air roasting conditions – a combined analytical study

Arianna Binello[a], Marta Giorgis[a], Clara Cena[a], Giancarlo Cravotto[a], Laura Rotolo[a], Paolo Oliveri[b], Cristina Malegori[b], Maria Chiara Cavallero[c], Stefania Buso[d], Monica Casale[b*]

[a]*Dipartimento di Scienza e Tecnologia del Farmaco, University of Turin, Via P. Giuria 9, 10125, Turin, Italy*

[b]*Department of Pharmacy, University of Genoa, Viale Cembrano 4, 16148 Genoa, Italy*

[c]*POLO AGRIFOOD Regione Piemonte, MIAC Scpa c/o Tecnogranda, Via G.B. Conte 19 Dronero, Italy*

[d]*F.lli Ruata Spa, Frazione Baroli 107 Baldissero d'Alba*

* Corresponding author:
Dr. Monica Casale, Ph.D.
Department of Pharmacy
University of Genoa
Viale Cembrano, 4
16148 GENOA
Tel: +39-010-3532633
fax: +39-010-3532684
e-mail: casale@difar.unige.it

BACKGROUD

For the processing industry, it is crucial to know what effect the roasting process and conditions have on hazelnut quality. The present study investigates, for the first time, on the effects of hot-air and infrared (IR) roasting at different time-temperature combinations on Tonda Gentile Trilobata hazelnut: whole kernels and derived processing products (paste and oil).

RESULTS

Nutritional and physical characteristics of hazelnuts and processing products were determined to study the influence of the different roasting conditions as a function of the intended use. The antioxidant profile (DPPH, ORAC and total phenolic content) were analyzed on roasted hazelnut and paste extracts. For a comprehensive understanding of the complex bio-chemical phenomena occurring during roasting, E-nose and near-infrared spectroscopy were also applied. All analytical data were processed using univariate (ANOVA) and multivariate data analyses (PCA) .

Hazelnuts derived from IR roasting at higher temperatures (195°C) showed a richer antioxidant profile and a more intense flavour. On the other hand, the yield associated to the oil extraction under the same conditions was unsatisfactory making this process completely inadequate for oil production. Oil obtained by hot-air roasting and IR roasting at lower temperature (135°C) resulted to be of good quality, showing rather similar acidity grade, peroxide number and acidic composition. In particular, a slightly but significantly lower acidity was related to lower roasting temperatures (0.21-0.22% vs 0.27 % for higher temperatures).

All roasting conditions tested, allow to quantitatively obtain homogeneous hazelnut paste and from a rheological point of view, higher roasting temperatures gave pastes characterised by higher density and viscosity values.

CONCLUSION

IR proved to be a promising alternative method for hazelnut roasting, thanks to its capability in preserving nutritional values and enhancing organoleptic quality.

50 Keywords: Tonda Gentile Trilobata (TGT) hazelnut, Infrared (IR) roasting, hot-air roasting, Near
51 Infrared (NIR) spectroscopy, E-nose, Principal Component Analysis (PCA)

52

Introduction

From an economic point of view, the European hazelnut (*Corylus avellana* L.) is the most important nut species in the *Betulaceae* family. There is general agreement on the fact that hazelnuts from Piedmont (Italy) are among the most renowned, and the "Tonda Gentile Trilobata" (TGT) variety (as covered by IGP designation) is particularly prized. Due to the intensity of its sweetness, the cooked-bread aroma and the low intensity of the burnt aroma, TGT is widely recognised as the best-suited hazelnut for industrial processing into roasted kernels[1].

Although hazelnuts can be consumed raw, the characteristics of the roasted nuts are more desirable in terms of both taste and texture[2-3].

Roasting can be defined as the dry heat treatment of seeds and nuts which not only brings about dehydration but also leads to the development of the flavour, colour and crunchy texture[4]. A number of chemical modifications and non-enzymatic browning lead to the peculiar characteristics responsible for the pleasantness of roasted hazelnuts[5-6]. Roasting allows to reduce moisture content in shelled hazelnuts, up to values ranging from 3.0-4.5% to 1.0-2.5%, contributing to the reduction of possible microbial contaminations and of the activity of enzymes involved in lipid peroxidation.

It is crucial for the processing industry to know what effect the roasting process and conditions (e.g. time and temperature) will have on hazelnut quality. The various roasting methods available have been found to yield significant differences in phenolic and antioxidant activities[7], humidity, protein concentration as well as other nutritional and technological values[8-10].

A common method for nut roasting is the convective heat transfer process, performed in hot-air roasters working either in continuous or in batch systems[11]. The conventional roasting of hazelnuts is currently carried out in commercial electrical ovens at 100-180°C for 10-60 min, according to shell thickness. It is well known that temperature modulation is an important parameter as it significantly affects hazelnut product quality[12]. However, long processing times, high energy consumption and low heating efficiency are its main disadvantages[13]. Other alternative roasting methods have been

proposed: for example, Rakesh Kumar Raigar *et al.*[14] compared the microwave roasting of peanuts with conventional drum roasting. FTIR, SEM and E-nose results showed that the microwave roasting can be effectively controlled by selecting an appropriate combination of time and microwave power levels.

IR (infrared) heating has successfully been used for the dry-roasting and pasteurization of almonds[15]. By contrast to conventional heating mechanisms, in which heat is usually transferred from the surface to the interior, the main advantage of IR treatment is that roasting proceeds from the inside of the hazelnut outwards without ventilation, meaning that the loss of aroma is minimised. However, the effects of IR roasting on hazelnuts have only recently been investigated and, then, only partially studied. Belvisio *et al.*[16] monitored the changes in two different hazelnut cultivars caused by both hot air and infrared roasting over nine months of storage.

In the present study, the effects of hot-air and IR roasting methods on TGT from Piedmont on the hazelnut processing products (paste and oil) have been investigated for the first time. In particular, two different time and temperature combinations have been considered for each roasting method.

Chemical, nutritional (fatty acids, peroxide value, total phenolic content, antioxidant capacity) and physical (viscosity, density) characteristics of hazelnuts and processing products (pastes and oils) were determined to study the influence of the different roasting conditions as a function of the intended use. For the antioxidant profile, hazelnut and paste extracts were considered. Moreover, for a comprehensive understanding of the complex bio-chemical phenomena occurring during roasting, E-nose and near-infrared spectroscopy were applied in order to provide rapid and non-destructive fingerprinting analyses to characterise physico-chemical and sensory attributes. There are, in fact, numerous studies that highlight the potential of using NIRS on fruit and vegetables and that promote it as an analytical technique for determining internal and external qualitative characteristics[17]. Furthermore, the E-nose has recently received considerable attention as an aroma-technology tool for the chemical and sensory characterisation of odorant products[3,18]. As an example, the stability of shelled peanuts during storage was assessed using a hybrid electronic nose with 18 MOS sensors by

Rakesh Kumar Raigar *et al.*[19]*:* the predictability of storage time using the sensors data closely matched with conventional rancidity indices advocating the applicability of E-nose as an eco-friendly alternative for rapid, non-destructive, and global analysis of shelled peanuts during post-harvest operations.

Materials and methods

Material

Hazelnuts TGT from organic farming were supplied by "Lurgo Flavio" (Corneliano d'Alba, Cuneo, Italy), stocked at controlled temperature (4° C) and shelled at roasting time.

Solvents and reagents, used to determine extraction and antioxidant profiles, were purchased from Sigma-Aldrich (Darmstadt, Germany), diethyl ether and phenolphthalein were acquired from Panreac Quimica S.A.U. (Barcelona, Spain). Ethyl alcohol, sodium hydroxide 0.1 mol/l in aqueous solution, acetic acid 100%, potassium iodide and sodium thiosulphate 0.01 mol/l in aqueous solution were acquired from VWR (Milan, Italy), while chloroform RPE for analysis and soluble starch RPE were acquired from CARLO ERBA reagents (Milan, Italy). *n*-heptane, potassium hydroxide and methanol were acquired from Merck (Darmstadt, Germany).

Hazelnut Roasting

The hot-air and IR roasting processes were performed by DSC Srl (Bernezzo, Cuneo, Italy).

The hot-air roasting device is created by DSC and is equipped with an internal transport tape, which can be adapted to processed dry fruits, and a number of roasting compartments to manage temperature conditions and optimise the process over its three steps: drying, roasting and cooling. Two different time and temperature conditions were chosen, on the basis of preliminary hazelnut browning tests. To understand the influence of temperature and time on hazelnut quality, treatments at lower temperatures and longer times were compared with treatments at higher temperature for shorter times. For hot air (HA) roasting, time and temperature were set at:

- 45 minutes at 135°C (HA-Lot1);

- 27 minutes at 195°C (HA-Lot2).

IR roasting was carried out in an infrared roaster (RI/700LAB, DSC) equipped with a cooling bath. Roasting takes place in a controlled and uniform manner thanks to the direct monitoring of temperature via specific probes. For infrared (IR) roasting, time and temperature were set at:

- 40 minutes at 135°C (IR-Lot1);
- 20 minutes at 195°C (IR-Lot2).

Each roasting condition was applied to two batches (referred to as 'a' and 'b') of 25 kg of hazelnuts. Roasted hazelnuts were stored at room temperature in vacuum packaging.

Hazelnut paste

A total of eight pastes were produced from roasted hazelnut batches (four conditions for two batches). Hazelnut paste was produced in a ball mill refiner (Easy Cream, DSC) with a power of 3 kW working at room temperature in continuous mode without the need for compressed air. Samples were obtained in one step (10 min from the whole hazelnut to the final paste) without significant heating during the process. The yield was around 100% for all hazelnut types tested and about 7 kg of paste, with a particle size of about 20 μm, was produced for each batch.

Hazelnut oil

An IBC (Monforts, Oekotec) cold press, equipped with a screw and 4 loading hoppers, was used for oil extraction.

The process starts with the loading of hazelnuts that move into an internal chamber where the extraction starts. Rotation speed of the screw was 40 rpm and press head temperature was set at 70°C. The outlet oil temperature did not exceed 45°C. Oil was collected in a duct, carried into a bin and then stored in a dry place. Two oil samples (one for each batch, 'a' and 'b') were collected starting from 5 kg of roasted hazelnuts; due to technical hurdles, for IR-Lot2, a low yield was achieved and, therefore, only one replicate sample was produced.

Antioxidant profile (whole hazelnut and paste)

156 *Extraction of phenolic compounds*

157 5 g of roasted hazelnut kernels, finely ground and previously defatted with hexane (1:10 w/v), were
158 extracted with 50 mL of 80% acetone – 20% water at 50 °C for 30 min under magnetic stirring[9] . The
159 procedure was repeated three times for a total extraction time of 1.5 h and the three extracts were
160 collected, dried under vacuum and then lyophilized.

161 5 g of each hazelnut paste were extracted with 50 mL of 80% acetone – 20% water according to the
162 same protocol described for hazelnut kernels. Each sample of hazelnuts and pastes was extracted in
163 triplicate and the yields obtained are reported in Table 1.

164 *Antioxidant activity: DPPH and ORAC assays*

165 The radical scavenging properties of each extract were determined via reactivity with the stable 2.2-
166 diphenyl-1-picrylhydrazyl radical (DPPH)[20]. The absorbance decay of ethanolic DPPH solutions,
167 after the addition of the various dimethyl sulfoxide (DMSO) extract solutions, was followed for 30
168 min. Percentages of residual DPPH concentrations were calculated and radical absorbance values
169 were interpolated with a DPPH standard curve and correlated *vs* extracts concentrations, giving an
170 exponential decay curve analysed with non-linear regression to obtain EC_{50} values.

171 The Oxygen Radical Absorbance Capacity (ORAC) test was also performed, using a PerkinElmer
172 2030 Multilabel Reader with 96-well black plates according to the ORAC assay described by Zeppa
173 *et al.*[21]. The Trolox equivalent molar concentrations were calculated using a linear regression model
174 between Trolox concentration and the net area under the fluorescein decay curve (delta AUC). Data
175 are expressed as ORAC values, defined as micromole Trolox equivalents present in 1 g of dried
176 extract. Results are reported in Table 1 as a mean of at least three measures.

177 *Total phenols determination*

178 Total phenols were determined using Folin-Ciocalteu's phenol reagent. Extracts were dissolved in
179 ethanol and analyses were performed as described by Singleton[22]. The phenolic content was
180 calculated using a standard curve for catechin and results were expressed as mg of catechin
181 equivalents per g of dried extract. Results are reported in Table 1 as a mean of at least three measures.

182

183 ***Viscosity and density (paste)***

184 Paste viscosity was determined using a steady-stress rheometer (Brookfield DV-II, LV Viscometer,
185 Brookfield Engineering Laboratories, Middleboro, MA, USA) equipped with a SC4-18/13R small
186 sample adapter. All measurements were carried out at 25.0 ± 0.1 °C, ensured by means of a controlled
187 fluid bath unit and an external thermostatic bath. Samples were allowed to equilibrate for 300 s to
188 establish a baseline shear history. Flow experiments were performed over a 0.4–80 s-1 range of shear
189 rates in duplicate. Viscosity was designated in units of Centipoise (Cp) (Table 2).
190 Density determinations were performed in a sealed boron-silicate glass pycnometer of approximately
191 10 mL capacity (Duran Group, model BlauBrand). Measurements were carried out at room
192 temperature. Density unit was g/mL. Results are reported in Table 2 as a mean of at least three
193 measures.

194

195 ***Oil analysis***

196 Oil was analysed according to Annex II of European Regulation 2568/1991[23], which refers to
197 characteristics modifications of olive oil and olive-residue oil and on the relevant methods of analysis.
198 Oil samples were analysed in triplicate and results are reported in Table 3.
199 *Acidity*
200 Acidity, measured by acid-base titration with a standardised sodium hydroxide 0.1 mol/l aqueous
201 solution, was expressed as a percentage (weight/weight) of oleic acid (Table 3).
202 *Peroxide value*
203 Peroxides were determined by iodometric titration in which the obtained triiodide ion solution is
204 titrated against a standard sodium thiosulfate solution 0.01 M in water. The peroxide values were
205 expressed in milliequivalents of active oxygen per kg (Table 3).
206 *Acidic composition*

6 mL of heptane were mixed with 0.3 g of hazelnut oil and 0.6 mL of a methanolic solution of KOH 2 N for acidic composition determination and the mixture was shacked for 30 s and centrifuged for 5 min at 3500 rpm. The obtained heptane solution was directly analysed by gas chromatography carried out on a HRGC 5300 Mega Series Carlo Erba equipped with a capillary column (Supelco Phase SP^{tm} 2340, 60 m length and 0.25 mm internal diameter, df 0.20 μm) and with a flame ionization detector (FID) EL 580. The carrier gas was hydrogen (1 mL/min) and the temperature program was from 160°C to 205°C, with a rate of 5°C/min.

Acid identification was performed using an external standard method while quantitative data were reported as normalised percentages (Table 3).

Fingerprinting techniques

Electronic nose

An electronic olfactory system (EOS 507, Sacmi Imola S.C., Imola, Italy) equipped with a measuring chamber with six metal oxide sensors was used. During the analyses, sensors were maintained in the temperature range of 350–450 °C. The EOS 507 was controlled by an integrated Personal Digital Assistant and was connected to an automatic sampling apparatus (Model HT500H). Samples were located in a chamber equipped with a system that removes humidity from the surrounding environment and incubated at 37 °C for 7 min before injection. Ambient air, filtered with activated silica and charcoal, was used as the reference gas.

15 whole hazelnuts, for each lot, and 10 g, for each paste, and 20 mL, for each oil, were analysed in duplicate.

NIR spectroscopy

NIR measurements were performed on an FT-NIR spectrometer (Buchi NIRFLEX N-500) in the 4000–10,000 cm^{-1} range at 8 cm^{-1} resolution and using 64 scans on whole hazelnuts, pastes and oils. The diameter of the circular surface analysed was reduced to 3.0 mm using a specific adaptor for whole hazelnut spectra acquisition; spectra were recorded in the reflectance mode.

A total of 368 whole hazelnuts were analysed by NIR spectroscopy producing 368 spectra; 64 from HA-Lot1 and HA-Lot2, 120 from IR-Lot1 and IR-Lot2.

Considering the variability among hazelnut kernels from the same batch, the average spectrum of four replicated signals was calculated, obtaining 92 mean spectra.

Analyses were performed in duplicate and oil spectra were recorded in the transmittance mode.

Data Processing

Univariate statistical analysis

All measurements were done in triplicate and results were expressed as mean ± standard deviation (SD). One-way ANOVA[24] was performed to evaluate the significance of differences among different roasting conditions. Differences were considered to be significant at $p \leq 0.05$. All analysis were performed with GraphPad Prism 7.00 software (San Diego, CA, USA).

Multivariate analysis

In this study, Principal Component Analysis (PCA)[25] was performed on the NIR, E-nose, viscosity, density and antioxidant activity data.

Before PCA, NIR data were pre-treated using the Standard Normal Variate (SNV) transformation[26] in order to eliminate unwanted variations, such as global intensity effects and baseline shifts.

Results and discussion

Hazelnuts

Results relative to DPPH, ORAC and total phenolic compounds assays on roasted hazelnut extracts are reported in Table 1. They underline as IR-Lot2 roasting conditions allow to better preserve the antioxidant activity, data are always significantly different from ones belonging to other lots (ANOVA, $p < 0.05$) . Considering literature data, there are a lot of differences due to type of cultivar, harvest period, roasting conditions and antioxidant performed assays, nevertheless our values

regarding air roasted hazelnut extracts are in general agreement [27,10]. To our knowledge, studies about hazelnuts roasted by IR are still limited in number. However our results are similar to those reported by Belviso *et al.*[16], who found that this method of roasting at 170°C for 20 min resulted in total phenolic content higher than those obtained with hot air at 120°C for 40 min.

Results derived from PCA performed on the **antioxidant data** confirm that IR radiation is less destructive for antioxidant phenols overall, when applied for shorter time, even at higher temperature. Figure 1 shows the PC1-PC2 biplot of the autoscaled data which describe 94% of the total variance. Sample pattern, explained by score distribution, displays that the antioxidant profile of IR-Lot2 is very different to the others, while the variable pattern, shown by loading distribution, reveals that IR-Lot2 is characterised by a richer antioxidant profile.

Regarding PCA performed on the **E-nose data**, the first PC principally explains the variation in the data due to the day of analysis (*data not shown*). The score plot on PC2-PC3 (Figure 2a), which explains 47% of the total variance, shows that hazelnuts differ according to the roasting method, while slight differences are highlighted between time and temperature levels. In particular, samples roasted with hot air are found at positive scores on PC2 while samples roasted with IR at negative scores. These results might be ascribable to the fact that hazelnuts roasted with IR can be more appreciable thanks to a more intense flavour due to a lower aroma loss.

Concerning PCA on **NIR data**, the score plot on PC1-PC2 (Figure 3a), explaining 87% of the total variance, shows four different groups that correspond to the four different roasting conditions. In particular, it is possible to see the influence of both roasting method and temperature. In fact, samples treated by IR are mainly found towards the right-bottom corner, while samples treated by hot air are towards the left-top corner. Focusing on the temperature effect, it is possible to notice that samples treated at higher temperatures are mainly located towards the right-top corner, while samples treated at lower temperatures are grouped in the opposite direction.

Furthermore, the average NIR reflectance spectra of the four different lots (HA-Lot1, HA-Lot2, IR-Lot1, IR-Lot2) were compared (Figure 4) in order to understand the changes that occur in the NIR

region due to hot air and IR roasting. By a visual inspection, the spectral regions in which major changes occur can be easily detected. Many compounds may have chemical bonds with absorptions in such spectral regions, but only few of them can be related with chemical changes due to roasting. The bands at 8200 cm^{-1} and 7200 cm^{-1} may be related to absorptions of fats: in particular, to C-H stretching second overtone and a combination between C-H stretching and C-H bending, respectively. Both the broad band around 6900 cm^{-1} (first overtone of O-H stretching) and the band at 5150 cm^{-1} (O-H combination bands) are related to water, whose decrease is highly influenced by the roasting process.

The region around 4250 – 4300 cm^{-1} may be ascribable to compounds formed in the Maillard reaction[28] which naturally occurs during hazelnut roasting. Since hazelnuts contain high amounts of oxidisable lipids, lipid oxidation may also occur, contributing to the formation of reactive carbonyl compounds which may promote the Maillard reaction[2]. Such chemical changes are reflected in absorptions of C-H and C-O stretching combination bands, and C-H stretching and C-H deformation modes.

Paste

The conditions used to produce hazenult paste do not affect antioxidant profiles, as showed in Table 1. Results from the PCA performed on these data are very similar to those obtained from the whole hazelnuts themselves; pastes from IR-Lot2 have a richer antioxidant profile, thanks to the shorter treatment time.

The processing of **E-nose data** is reported in Figure 2b. PC1, which explains 84% of the total variance, clearly separates pastes obtained from IR-Lot2 from the others, due to a more intense flavour originated by the higher temperatures in combination with the IR technology.

Figure 3b shows that the PCA outcomes of **NIR data** explains the temperature effect. In fact, temperatures at which pastes were roasted are positively correlated with PC1 scores: lower temperatures are associated with negative score values, while higher temperatures are associated with

positive score values. Since the chemical composition of the pastes is similar to that of hazelnuts, a comparison between the various NIR spectra profiles gave the same information as reported in the previous session for hazelnuts **Viscosity and density data** of the eight pastes, whose values are reported in Table 2, were analysed in triplicate, but one replicate of HA-Lot1 was eliminated as an outlier due to the aberrant values measured. The score plot in Figure 5a shows that the pastes obtained from hazelnuts roasted at higher temperature are characterised by higher density and viscosity, as indicated by a joint examination of loadings (Figure 5b). The significant difference between rheological parameter obtained with higher and lower roasting temperatures is also confirmed by ANOVA test.

Oil

Oils derived from the cold pressing procedure still contain solid particles in suspension, which were separated by natural decantation in order to determine the final yield of clear oil. The part named "pressing lost" was formed by hazelnuts which remained on the press surface during the pressing process. **Yields** are reported in Table 3 and results show that the best oil yields were obtained for HA-Lot1 roasted hazelnuts for which, furthermore, **pressing lost** values are the lowest.

IR-Lot1 roasted hazelnuts yields are slightly lower than HA-Lot1 yields, while pressing lost values are slightly larger. HA-Lot2 pressing presented many problems; oil yield was low and pressing lost values very high. Moreover, roasting conditions for IR Lot-2 made hazelnuts too friable for the screw oil press and it was not possible to effectively separate the oil phase from the solid particles in suspension. Nevertheless, a sufficient amount of oil to perform E-nose and NIR analyses was obtained; conversely, yield associated to such an extraction makes this process completely inadequate from an industrial point of view.

Produced oils were stored in a cold and dry place and then analysed for the determination of **acidity, peroxide number and acidic composition** (Table 3). Values, that are in according with those previously reported in literature [27, 16], resulted very similar across all samples, indeed there aren't

significant differences in peroxide number and acidic composition. It may be just noted that lower roasting temperatures implicate slightly lower acidity, with a significant ANOVA difference. Noteworthy, acidity and peroxide number of roasted hazelnut oils are lower than extra-virgin olive oils [29] this indicating their good quality.

E-nose data were analysed with PCA (Figure 2c): PC1, which explains 78% of the total variance, seems to be associated to the temperature effect, while PC2 clearly differentiates oils obtained from HA-Lot1 hazelnuts from all of the others. In more detail, oils obtained from hazelnuts roasted at higher temperature (195°C) have positive scores lengthwise PC1.

The differences between the oil samples were highlighted by PCA applied to the **NIR spectra**, where the score plot on PC1-PC2 (Figure 3c) explains 97% of the total variance. In particular, PC2 evidently differentiates the roasting methods, IR and hot air.

Average NIR spectra of the four oils (HA-Lot1, HA-Lot2, IR-Lot1 and IR-Lot2) are reported in Figure 6. Comparison of the spectral profiles reveals that the spectral region in which the most noticeable changes in absorption intensity occur is 5600–5800 cm^{-1}, ascribable to the first overtone of C-H stretching vibrations of methylene and ethylene groups, involved in degradation processes of triglycerides. Triacylglycerols, in fact, account for 95-98% of hazelnut oils and their composition can be considered as fingerprints of oils.

Conclusions

The analytical and chemometric investigations carried out in this work demonstrate that the roasting method and the conditions used for the roasting process affect not only the physico-chemical and sensory properties of hazelnuts but also their nutritional profile. Whole kernels, pastes and oils derived from hazelnuts were analysed by E-nose, NIRS and conventional analytical methods, highlighting interesting differences between the two roasting methods (IR and hot air) and also between temperature and time combinations. The advantage of combining information from different analytical sources – including non-selective fingerprinting methods – is reflected in the possibility to

provide a comprehensive evaluation of the complex bio-chemical phenomena that occur in the final products depending on process parameters.

It is not possible to define the best roasting process in general terms, because a key factor is the intended use of the raw kernels and of their derived processing products.

As for as the whole hazelnuts are concerned, both the roasting method and the time-temperature combination strongly affect the kernel characteristics, with an interestingly preserved content of antioxidant compounds for those treated with IR radiation.

Concerning pastes, hazelnuts treated with IR process at 195°C are considerably differentiated from the others, also from a rheological point of view, being characterised by higher viscosity and density, besides by a stronger aroma. A potential intended use of such pastes is the preparation of creams, chocolate and ice cream – products in which availability of an ingredient with higher concentration of aroma and better spreadability is convenient from an economical point of view.

Considering oil, the yield associated to an extraction under the same conditions (IR process at 195°C) is unsatisfactory, making this roasting process completely inadequate from an industrial point of view.

As a conclusion, IR roasting proved to be a promising alternative method for hazelnut roasting, considering its capability in preserving nutritional values.

Obviously, when designing a hazelnut roasting process, not only the effects of the different roasting conditions on kernels, but also the final use of the roasted products should be considered.

Acknowledgements

The Authors are grateful to the Corylox project (Innovazione e Transizione Produttiva PAR-FSC 2013, Fondo Europeo di Sviluppo Regionale – Regione Piemonte).

References

1. Zeppa G, Rolle L, Gerbi V, Valentini N, Me G, Application of sensory analysis to characterize

388 new selections of hazelnut [Corylus avellana L,]. *Ind Aliment (Italy)* (2000).
389 2. Alasalvar C, Pelvan E, Bahar B, Korel F, Ölmez H, Flavour of natural and roasted Turkish
390 hazelnut varieties (Corylus avellana L,) by descriptive sensory analysis electronic nose and
391 chemometrics. *Int J Food Sci Technol* ***47*****(1):** 122–131 (2012),
392 http://dx.doi.org/10.1111/j.1365-2621.2011.02817.
393 3. Langourieux S, Perren R, Escher F, in Weurman flavour research symposium. *Front Flavour Sci*
394 527-535 (2000) by Deutsche Forsc. Lebens. Garching.
395 4. Alamprese C, Ratti S, Rossi M, Effects of roasting conditions on hazelnut characteristics in a
396 two-step process. *J Food Eng* **95:** 272–279 (2009). doi:10.1016/j.jfoodeng.2009.05.001.
397 5. Kiefl J, Cordero C, Nicolotti L, Schieberle P, Reichenbach SE, Bicchi C, Performance evaluation
398 of non-targeted peak-based cross-sample analysis for comprehensive two-dimensional gas
399 chromatography–mass spectrometry data and application to processed hazelnut profiling. *J*
400 *Chromatogr A* **1243:** 81–90 (2012). http://dx.doi.org/10.1016/j.chroma.2012.04.048.
401 6. Krishnamurthy K, Khurana H K, Soojin J, Irudayaraj J, Demirci A, Infrared Heating in Food
402 Processing: An Overview. *Compr Rev Food Sci Food Saf.* ***7*****(1):** 2-13 (2008).
403 http://dx.doi.org/10.1111/j.1541-4337.2007.00024.x.
404 7. Chang SK, Alasalvar C, Bolling BW, Shahidi F, Nuts and their co-products: The impact of
405 processing (roasting) on phenolics bioavailability and health benefits – A comprehensive
406 review. *J Funct Foods* **26**: 88–122 (2016) https://doi.org/10.1016/j.jff.2016.06.029.
407 8. Locatelli M, Coïsson JD, Travaglia F, Bordiga M, Arlorio M, Impact of Roasting on
408 Identification of Hazelnut (Corylus avellana L.) Origin: A Chemometric Approach. *J Agric*
409 *Food Chem.* ***63*****(32):** 7294–303 (2015). http://dx.doi.org/10.1021/acs.jafc.5b03201.
410 9. Pelvan E, Alasalvar C, Heyla Uzman S, Effects of Roasting on the Antioxidant Status and
411 Phenolic Profiles of Commercial Turkish Hazelnut Varieties (Corylus avellana L.). *J Agric*
412 *Food Chem* ***60*****(5):** 1218–23 (2012). http://dx.doi.org/10.1021/jf204893x.
413 10. Pelvan E, Olgun EÖ, Karadağ A, Alasalvar C, Phenolic profiles and antioxidant activity of

Turkish Tombul hazelnut samples (natural roasted and roasted hazelnut skin). *Food Chem.* **244**: 102-108 (2018). http://dx.doi.org/10.1016/j.foodchem.2017.10.011.

11. Perren R, Escher F, Nut roasting technology and product quality. *The Manufacturing Confectioner* ***87*****(6)**: 65–75 (2007).

12. Donno D, Beccaro GL, Mellano G, M. Di Prima S, Cavicchioli M, Cerutti AK, Bounous G, Setting a Protocol for Hazelnut Roasting using Sensory and Colorimetric Analysis: Influence of the Roasting Temperature on the Quality of Tonda Gentile delle Langhe Cv. Hazelnut. *Czech J. Food Sci* ***31*****(4):** 390–400 (2013).

13. Ceylan İ, Aktaş M, Modeling of a hazelnut dryer assisted heat pump by using artificial neural networks. *Appl Energy* **85(9)**: 841–854 (2008). http://dx.doi.org/ 10.1016/j.apenergy.2007.10.013.

14. Raigar R K, Upadhyay R, Mishra H N, Optimization of microwave roasting of peanuts and evaluation of its physicochemical and sensory attributes. *J Food Sci Technol* **54:** 2145-2155 (2017). https://doi.org/10.1007/s13197-017-2654-0

15. Yang J, Bingol G, Pan Z, Brandl MT, McHugh TH, Wang H, Infrared heating for dry-roasting and pasteurization of almonds. *J. Food Eng* ***101*****(3)**: 273–280 (2010). http://dx.doi.org/10.1016/j.jfoodeng.2010.07.007.

16. Belviso S, Dal Bello B, Giacosa S, Bertolino M, Ghirardello D, Giordano M, Rolle L, Gerbi V, Zeppa G, Chemical mechanical and sensory monitoring of hot air- and infrared-roasted hazelnuts (Corylus avellana L.) during nine months of storage. *Food Chem*. **217**:398-408 (2017). doi: 10.1016/j.foodchem.2016.08.103.

17.Malegori C, José E, Marques N, Tonetto De Freitas S, Pimentel MF, Pasquini C, Casiraghi E, Comparing the analytical performances of Micro-NIR and FT-NIR spectrometers in the evaluation of acerola fruit quality using PLS and SVM regression algorithms. *Talanta* **165**: 112–116 (2017). http://dx.doi.org/10.1016/j.talanta.2016.12.035.

18. Wilson AD, Baietto M, Applications and advances in electronic-nose technologies. *Sensors*

(Basel Switzerland) 9(7) 5099–148 (2009). http://dx.doi.org/10.3390/s90705099.

19. Raigar R K, Upadhyay R, Mishra H N, Storage quality assessment of shelled peanuts using non-destructive electronic nose combined with fuzzy logic approach. *Postharvest Biol Technol* **132:** 43-50 (2017).

20. Mantegna S, Binello A, Boffa L, Giorgis M, Cena C, Cravotto G, A one-pot ultrasound-assisted water extraction/cyclodextrin encapsulation of resveratrol from Polygonum cuspidatum. *Food Chem* **130**: 746–750 (2012). http://dx.doi.org/10.1016/j.foodchem.2011.07.038

21. Zeppa G, Belviso S, Bertolino M, Cavallero MC, Dal Bello B, Ghirardello D, Giordano M, Giorgis M, Grosso A, Rolle L, Gerbi V, The effect of hazelnut roasted skin from different cultivars on the quality attributes polyphenol content and texture of fresh egg pasta. *J Sci Food Agric 95*(8) 1678–1688 (2015). http://dx.doi.org/10.1002/jsfa.6871.

22. Singleton VL, Orthofer R, Lamuela-Raventós RM, Analysis of total phenols and other oxidation substrates and antioxidants by means of folin-ciocalteu reagent *Methods Enzymol*. **299**: 152–178 (1999). doi:10.1016/S0076-6879(99)99017-1.

23. Commission Regulation (EEC) No 2568/91 of 11 July 1991 on the characteristics of olive oil and olive-residue oil and on the relevant methods of analysis.

24. St»hle L, Wold S, Analysis of variance (ANOVA). *Chem Intel Lab Syst* **6:** 259-272 (1989) https://doi.org/10.1016/0169-7439(89)80095-4.

25. Massart DL,Vandeginste BGM, Buydens LMC, De Jong S, Lewi PL, Smeyers-Verbeke J, In B. G. M. Vandeginste & S. C. Rutan (Eds.) *Handbook of Chemometrics and Qaulimetrics: Part B* (pp. 88–103) (1998). Elsevier.

26. Barnes R J, Dhanoa M S, Lister S J, Standard Normal Variate Transformation and De-trending of Near-Infrared Diffuse Reflectance Spectra. *Appl Spectrosc* **43:** 772-777 (1989).

27. Özcan M M, Al Juhaimi F, Uslu N, The effect of heat treatment on phenolic compounds and fatty acid composition of Brazilian nut and hazelnut. *J Food Sci Technol* **55**(1): 376-380 (2018).

466 28. Mauer L J, Chernyshova A A, Hiatt A, Deering A, Davis R, Melamine detection in infant
467 formula powder using near-and mid-infrared spectroscopy. *J Agric Food Chem* **57**: 3974–3980
468 (2009). http://dx.doi.org/10.1021/acs.jafc.7b02083.
469 29. Méndez A I, Falqué E, Effect of storage time and container type on the quality of extra-virgin
470 olive oil. *Food Control* **18**: 521-529 (2007)].
471

Figure Captions:

Figure 1: PCA biplot of hazelnut antioxidant profile data. The scores are shown using 4 different colors that correspond to the 4 different roasting conditions. Loadings are written in black italics.

Figure 2: PCA score plots of E-nose data of whole hazelnuts (a), hazelnut pastes (b) and hazelnut oils (c). The scores are shown using 4 different colors that correspond to the 4 different roasting conditions.

Figure 3: PCA score plots of NIR data of whole hazelnuts (a), hazelnut pastes (b) and hazelnut oils (c). The scores are shown using 4 different colors that correspond to the 4 different roasting conditions.

Figure 4: Profiles of the NIR data of whole hazelnuts. The 4 profiles are shown using 4 different colors that correspond to the 4 different roasting conditions.

Figures 5: (a) PCA score plot of hazelnut paste viscosity and density data; the scores are shown using 4 different colors that correspond to the 4 different roasting conditions. (b) PCA loading plot: the 3 loadings represent the 3 original variables in the orthogonal space of the Principal Components.

Figure 6: Profiles of the NIR data of hazelnut oils. The 4 profiles are shown using 4 different colors that correspond to the 4 different roasting conditions.

Table 1

Yields and antioxidant profile of hazelnut kernel and paste extractions expressed as a mean ± SD (n = 3).

* Values within each column followed by different letters are significantly different ($p \leq 0.05$)

roasting conditions	Yields % ± SD		DPPH EC_{50} ± SD (µg/mL)		ORAC µmol Trolox/g extract ± SD		Total Phenols mg catechin/g extract ± SD	
	kernel	paste	kernel	paste	kernel	paste	kernel	paste
HA-Lot1 (45 min 135 °C)	12.6 ± 1.3*	7.3 ± 1.7	657 ± 16 [a]	525 ± 28 [a]	168 ± 19 [a]	182 ± 20 [a]	6.2 ± 0.7 [a]	4.2 ± 1.1 [a]
HA-Lot2 (27 min 195 °C)	10.2 ± 1.6	18.7 ±2.1	553 ± 22[b]	405 ± 18 [b]	219 ± 8 [a]	192 ± 65 [a]	7.0 ± 0.7 [a]	8.4 ± 1.0[b]
IR-Lot1 (40 min 135 °C)	6.3 ± 1.0	5.3 ± 1.4	620 ± 19 [a]	471 ± 14[c]	208 ± 9 [a]	192 ± 20 [a]	6.5 ± 0.6 [a]	6.8 ± 0.9 [a]
IR-Lot2 (20 min 195 °C)	9.9 ± 0.5	16.7 ± 1.8	371 ± 14[c]	226 ± 20[d]	286 ± 15 [b]	224 ± 12 [a]	11.7 ± 1.5[b]	13.6 ± 1.4[c]

Table 2

Rheological profile of hazelnut pastes expressed as a mean ± SD (n = 3).

roasting conditions	Viscosity (Cp)	Density (g/mL)
HA-Lot1 (45 min 135 °C)	1615 ± 48[a]	1.029 ± 0.004[a]
HA-Lot2 (27 min 195 °C)	4467 ± 51[b]	1.076 ± 0.003[b]
IR-Lot1 (40 min 135 °C)	2271 ± 14[a]	1.027 ± 0.005[a]
IR-Lot2 (20 min 195 °C)	3657 ± 10[b]	1.063 ± 0.002[c]

* Values within each column followed by different letters are significantly different ($p \leq 0.05$)

505 **Table 3**

506 Yields, pressing lost, acidity, peroxide number and acidic composition of roasted hazelnut oils (the
507 quantity of oil obtained from IR_Lot2 was very low and it was used only for E-nose and NIR
508 analyses). Values are reported as a mean of batch a and b analyses ± SD (n = 3).
509

Parameter	HA-Lot1 (45 min 135 °C)	HA-Lot2 (27 min 195 °C)	IR-Lot1 (40 min 135 °C)
Yield oil %	51.8 ± 7.60	17.8 ± 0.40	46.5 ± 1.50
Pressing lost %	6.6 ± 1.80	19.8 ± 1.80	11.8 ± 0.40
Acidity (% of oleic acid)	0.2 ± 0.01[a]	0.3 ± 0.01[b]	0.2 ± 0.05[a]
peroxide number (millieq. O_2 /kg)	1.5 ± 0.02 [a]	1.5 ± 0.20 [a]	1.5 ± 0.10 [a]
miristic acid %	N.D.[**]	N.D.	N.D.
palmitic acid %	6.2 ± 0.20 [a]	6.2 ± 0.10 [a]	6.1 ± 0.20 [a]
palmitoleic acid %	0.2 ± 0.04 [a]	0.2 ± 0.06 [a]	0.3 ± 0.03 [a]
stearic acid %	2.8 ± 0.10 [a]	2.8 ± 0.10 [a]	2.8 ± 0.10 [a]
oleic acid %	83.7 ± 0.30 [a]	83.5 ± 0.70 [a]	83.5 ± 0.80 [a]
linoleic acid %	6.8 ± 0.20 [a]	7.0 ± 0.40 [a]	7.0 ± 0.20 [a]
linolenic acid %	0.1 ± 0.02 [a]	0.1 ± 0.02 [a]	0.1 ± 0.03 [a]
arachidic acid %	0.1 ± 0.01 [a]	0.1 ± 0.01 [a]	0.1 ± 0.02 [a]
eicosenoic acid %	0.1 ± 0.02 [a]	0.1 ± 0.03 [a]	0.1 ± 0.01 [a]
behenic acid %	N.D.	N.D.	N.D.

510 [*]Values within each row followed by different letters are significantly different ($p \leq 0.05$).
511 [**] N.D.: not detected.
512
513
514
515

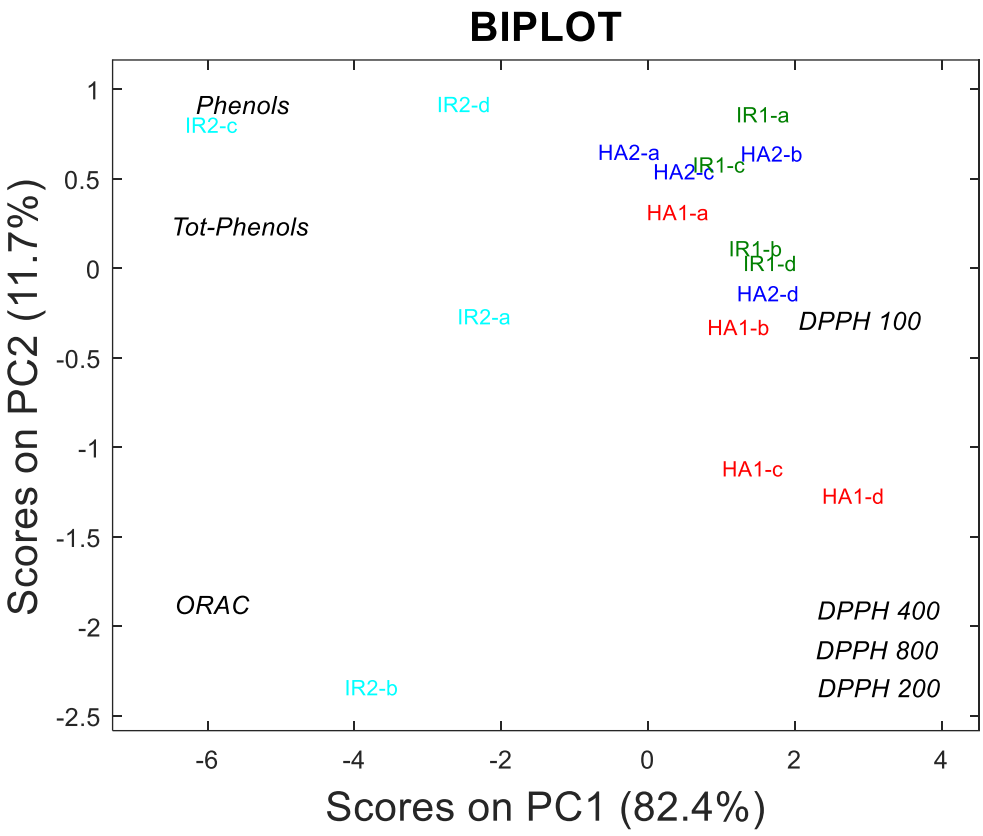

BIPLOT
Phenols
IR2-c
IR2-d
IR1-a
HA2-a
HA2-b
HA2-c
IR1-c
HA1-a
Tot-Phenols
IR1-b
IR1-d
HA2-d
IR2-a
HA1-b
DPPH 100
HA1-c
HA1-d
ORAC
DPPH 400
DPPH 800
DPPH 200
IR2-b
Scores on PC2 (11.7%)
Scores on PC1 (82.4%)
1
0.5
0
-0.5
-1
-1.5
-2
-2.5
-6
-4
-2
0
2
4

Figure 1

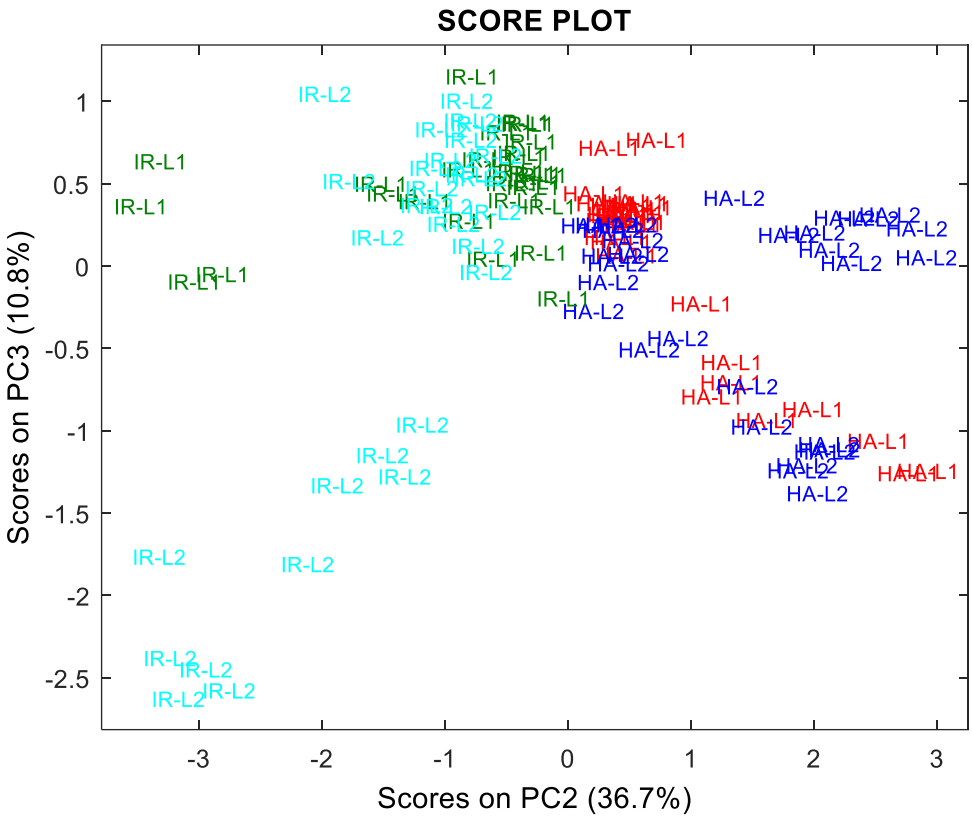

SCORE PLOT
Scores on PC3 (10.8%)
Scores on PC2 (36.7%)
IR-L1
IR-L2
HA-L1
HA-L2

Figure 2a

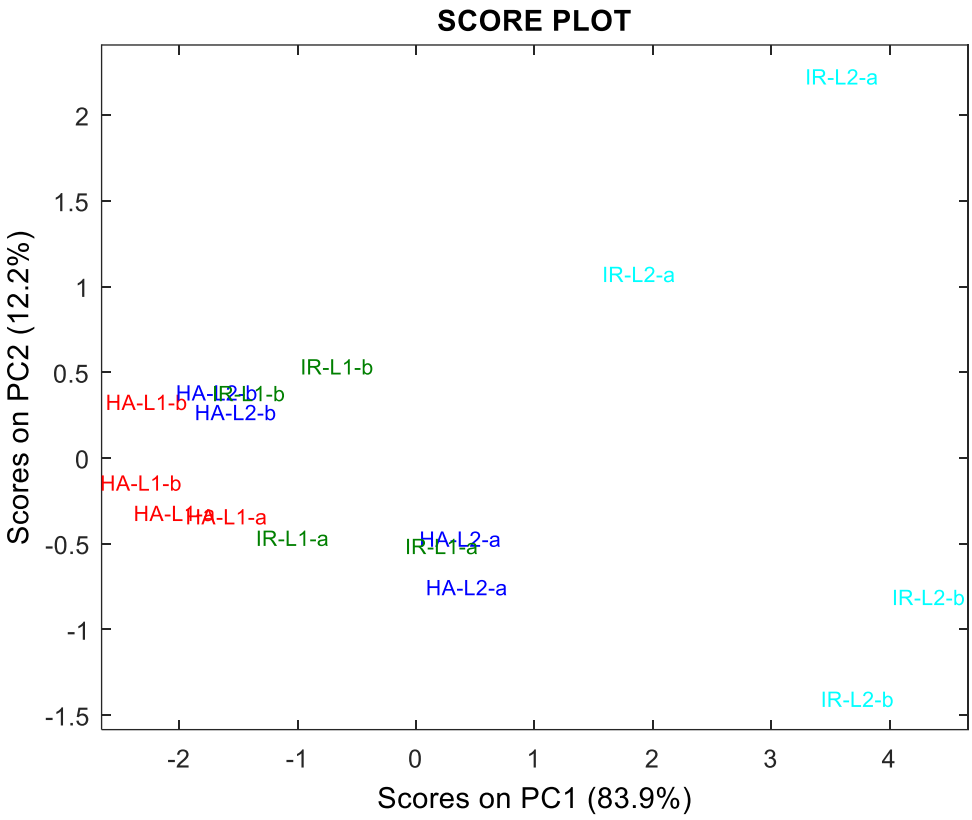
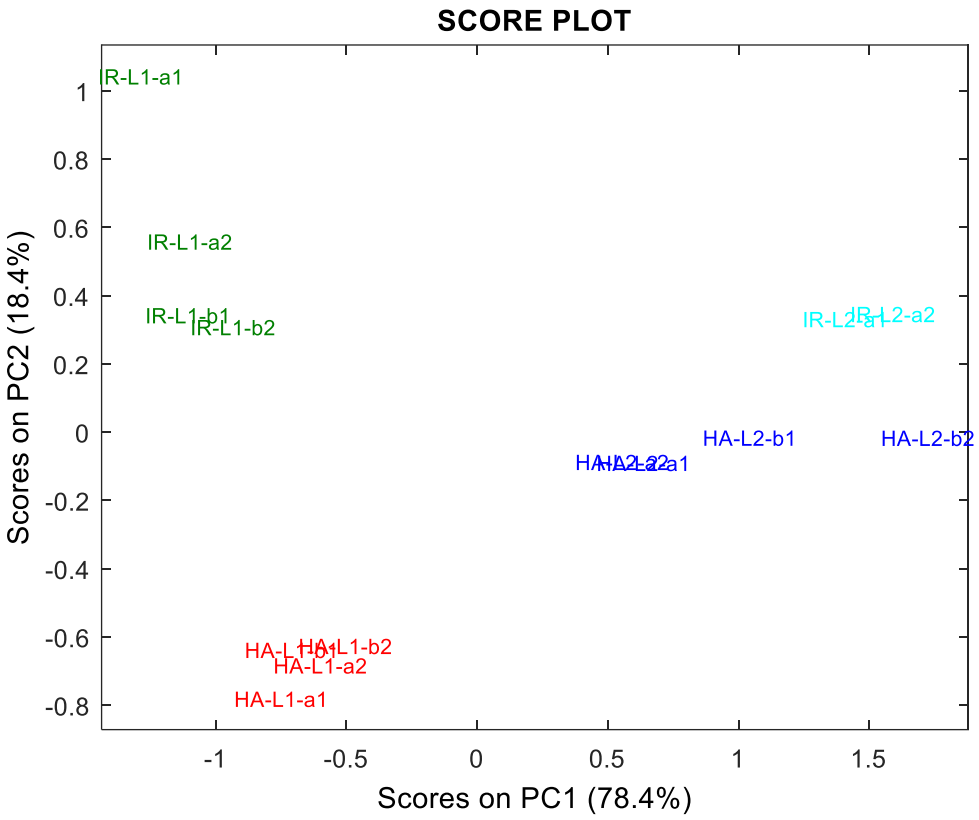

SCORE PLOT
IR-L2-a
IR-L2-a
IR-L1-b
HA-L1-b
HA-L2-b
HA-L1-b
HA-L1-a
IR-L1-a
HA-L2-a
HA-L2-a
IR-L2-b
IR-L2-b
Scores on PC2 (12.2%)
Scores on PC1 (83.9%)
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
-1
0
1
2
3
4

Figure 2 b



529

530 Figure 2c

531

532

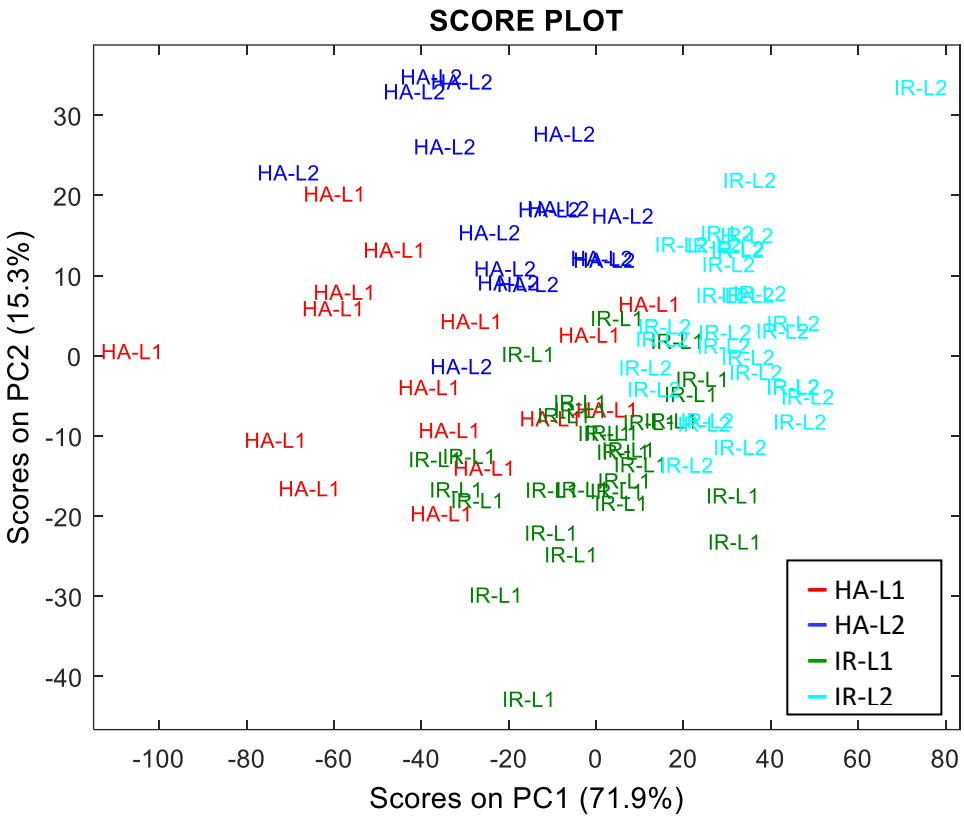

SCORE PLOT
Scores on PC2 (15.3%)
Scores on PC1 (71.9%)
HA-L1
HA-L2
IR-L1
IR-L2

Figure 3a

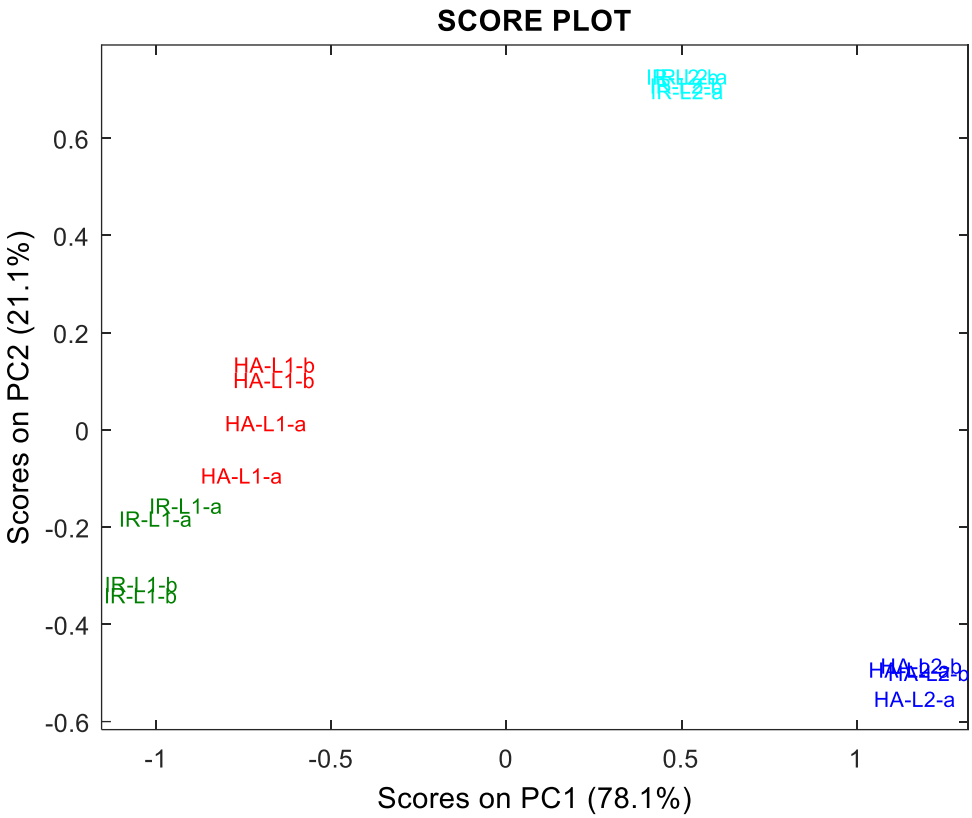

SCORE PLOT
Scores on PC2 (21.1%)
Scores on PC1 (78.1%)
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-1
-0.5
0
0.5
1
HA-L1-b
HA-L1-b
HA-L1-a
HA-L1-a
IR-L1-a
IR-L1-a
IR-L1-b
IR-L1-b
HA-L2-a

Figure 3b

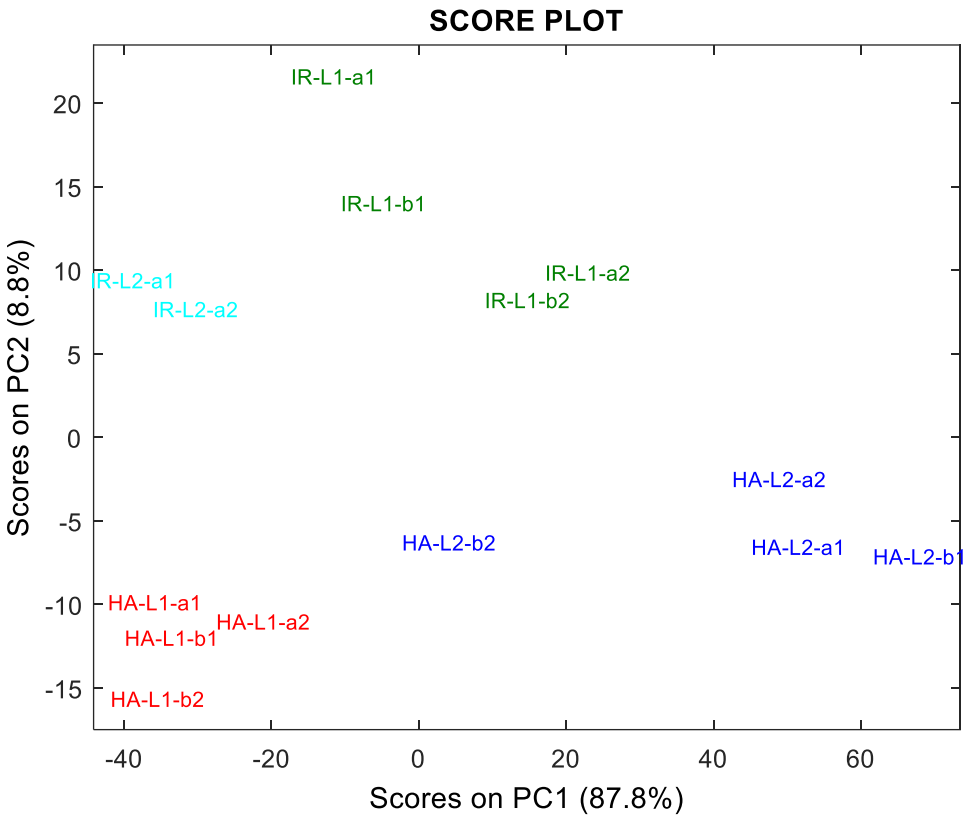
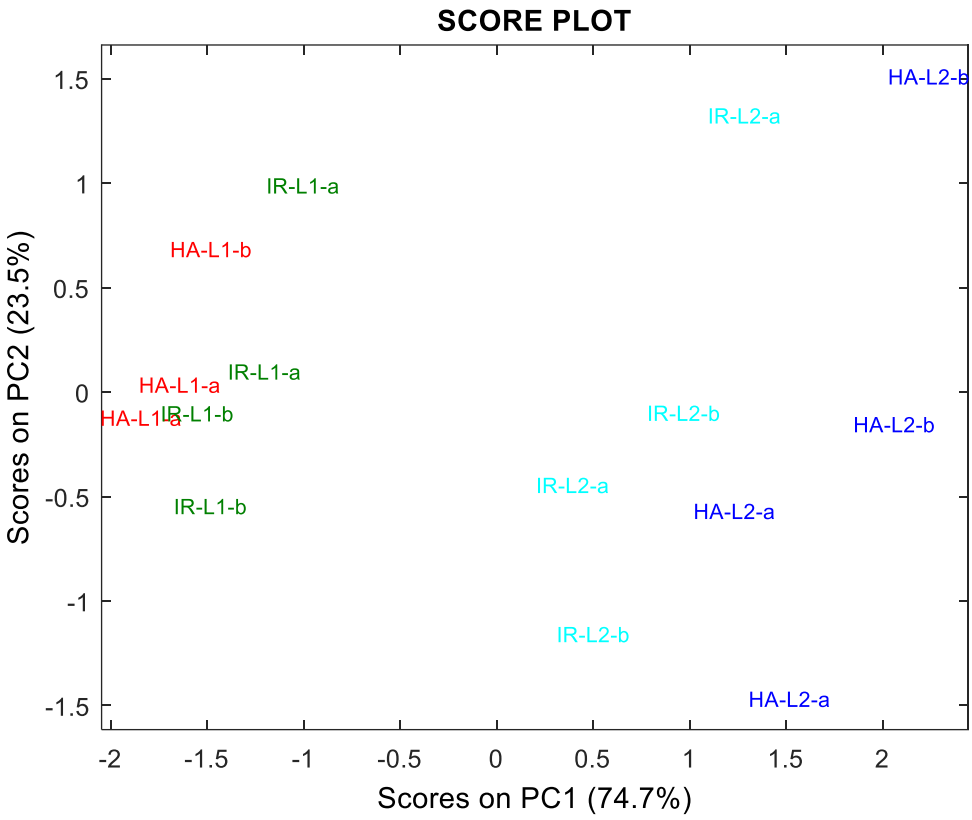

SCORE PLOT
IR-L1-a1
IR-L1-b1
IR-L2-a1
IR-L2-a2
IR-L1-a2
IR-L1-b2
HA-L2-a2
HA-L2-b2
HA-L2-a1
HA-L2-b1
HA-L1-a1
HA-L1-a2
HA-L1-b1
HA-L1-b2
Scores on PC2 (8.8%)
Scores on PC1 (87.8%)
20
15
10
5
0
-5
-10
-15
-40
-20
0
20
40
60

Figure 3c

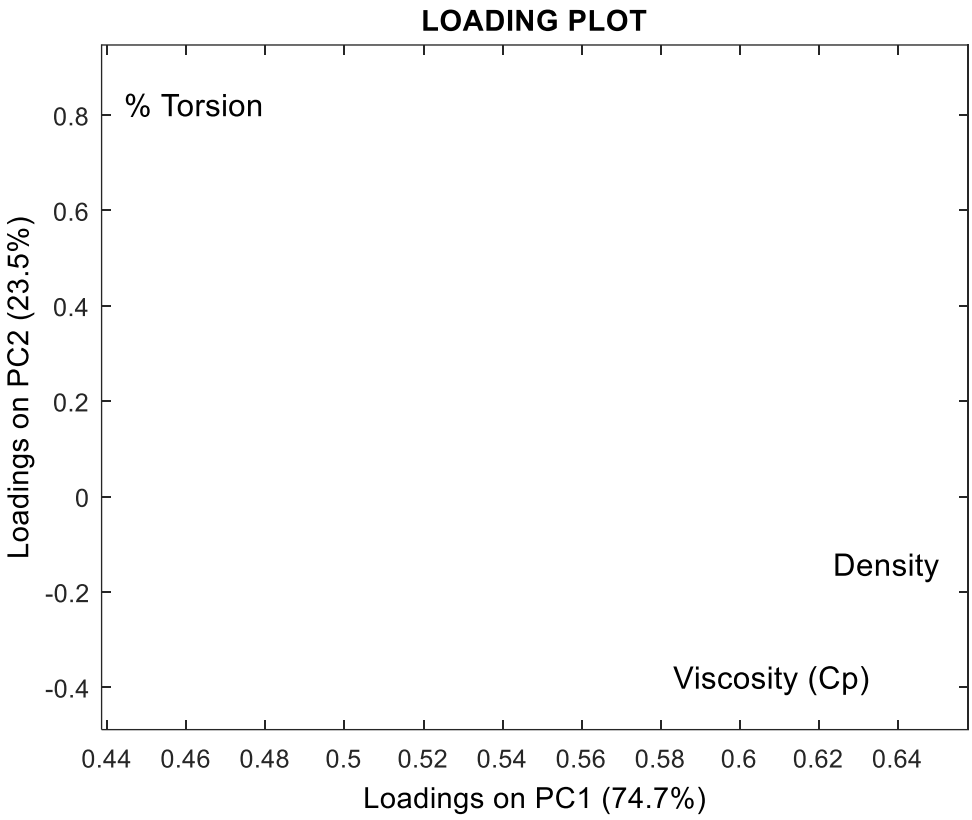


546

547 Figure 5a

548

549



550

551 Figure 5b

552