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1 **Use of mid-infrared spectroscopy to monitor shelf-life of ready-made meals.**

2

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## 15 Abstract

16 The objective of this work was to use mid-infrared spectroscopy as a rapid analytical method to  
17 monitor the change in stored ready-made meals over time. Six ready-made meals were  
18 packaged in two plastic bags, Alu and Alox, and stored at 23°C at a partial oxygen pressure of 96  
19 kPa. After thawing, samples were directly measured in attenuated total reflectance mid-infrared  
20 spectroscopy between 4000 and 650  $\text{cm}^{-1}$ . Multivariate analyses applied on spectral data  
21 highlighted some changes in the global profile, particularly in Bolognese soup and in mashed  
22 potatoes with cheese. Indeed, the Bolognese sauce samples were clearly discriminated (i)  
23 according to the storage time and (ii) according to the packaging type presenting a greater  
24 oxidation in the Alox packaging. The eigenvectors allowed for the identification of clear  
25 absorption bands at 2918, 2850, 1741 and 1164  $\text{cm}^{-1}$  which increased over storage. These  
26 absorption bands could be attributed to fats, which thus appeared to have a major effect in  
27 sample discrimination. Mid-infrared spectroscopy was shown to be a relevant tool for  
28 discriminating the oxidation state of canned ready-made meals and might be used to determine  
29 their shelf-life.

30

31 Keywords: FTIR-ATR, multivariate analyses, oxidation, plastic packaging

## 32 1. Introduction

33 Mid-infrared spectroscopy (MIR) is largely used for food analysis insofar as food are mainly  
34 composed of lipids, carbohydrates, proteins and water which present characteristic absorption  
35 bands in this electromagnetic range ( $4000\text{-}400\text{ cm}^{-1}$ ). Rapid MIR quality-control methods have  
36 been described on a large variability of food with the quantitative prediction of quality traits  
37 such as moisture and fat in potato chips (Shiroma and Rodriguez-Saona, 2009) or in butter (Van  
38 de Voort, Sedman, Emo, and Ismail, 1992), fat and proteins in meat (Dion, Ruzbie, Van de Voort,  
39 Ismail, and Blais, 1994), refraction index and relative density in edible oils (Luna, da Silva, Ferré,  
40 and Boqué, 2013), sugars and organic acids in fruits and vegetables (Scibisz, Reich, Bureau,  
41 Gouble, Causse, Bertrand, et al., 2011; Bureau, Quilot-Turion, Signoret, Renaud, Maucourt,  
42 Bancel, et al., 2013). The prediction of these quality traits in food products needs development  
43 of calibration models established by correlating reference classical data with spectral data. This  
44 step is time consuming and probably limits the development of MIR method in the food field.  
45 However MIR coupled with multivariate data analysis could be used qualitatively for grouping,  
46 separating or classifying unknown samples based only on similarity or differences of spectral  
47 characteristics, i.e. using fingerprinting techniques. Applications have been described to monitor  
48 food authenticity and adulteration, particularly to discriminate control from adulterated milk  
49 (Santos, Pereira-Filho, and Rodriguez-Saona, 2013), to classify sparkling wines according to both  
50 style and production method (Culbert, Cozzolino, Ristic, and Wilkinson, 2015) or to discriminate  
51 defective and high quality olive oils (Borràs, Mestres, Aceña, Busto, Ferré, Boqué, and Calvo,  
52 2015). As MIR is known for its ability to analyze quickly and easily samples with little or no  
53 sample preparation, it offers the possibility to monitor sample changes over time specially the

54 oxidation processes in oils and fats (Guillen and Cabo, 1997; Le Dréau, Dupuy, Gaydou, Joachim,  
55 and Kister, 2009). Oxidation phenomena result in some undesirable chemical changes leading to  
56 a degradation of the food quality (organoleptic, nutritional...). They particularly occur in ready-  
57 made meals in plastic packaging during storage time and therefore it is imperative to manage  
58 these products and to check their quality over time. Shelf-life is defined for these products to  
59 determine the length of time for which a food remains usable for consumption. In this work, a  
60 system was used to accelerate aging under pressurized oxygen which increased the oxygen  
61 concentration in the product (to accelerate the oxidation reactions) by increasing the input of  
62 oxygen rate through the plastic film, which is done by applying a high partial pressure of oxygen  
63 outside the package. Food sample were stored in these conditions for accelerated oxidative  
64 aging (all the oxygen passing through the packaging being consumed by oxidative reactions).  
65 Aging is then accelerated, 4 to 8 times faster depending on the packaging material permeability  
66 to oxygen. For example, 40 days of storage under oxygen may be equivalent to 6 months in  
67 ambient conditions.

68 The objective in this work was to evaluate the possibility of mid-infrared spectroscopy as a rapid  
69 analytical method to monitor the change over time in six ready-made meals packaged in two  
70 different plastic bags.

## 72 2. Materials and methods

### 73 2.1. *Materials*

74 Six ready-made meals (lentils, mashed potatoes, mashed potatoes with cheese, béchamel  
75 sauce, vegetable soup, Bolognese sauce) were prepared at CTCPA Avignon and packaged in

76 plastic bags (recipes given in complementary data). Two plastic packagings, Alu and Alox,  
77 provided by Amcor Flexibles Moreuil (Zone Industrielle, 80110 Moreuil, France) were  
78 compared. They corresponded to stand-up bags made of:  
79 - (PET/PET SiOx/PP) (Polyethylene terephthalate/Silicon oxide/Polypropylene), 12  $\mu$  printed  
80 material [green flatness + white flatness] / SiO x 12  $\mu$  PET / 70  $\mu$  PP OB with aliphatic glue,  
81 standardized size (for canned goods of 200-250 g) 130 mm x 140 mm with half a bellows 35mm  
82 (named in this study the bag "Alox"),  
83 - PET/Alu/PP (Polyethylene terephthalate/Aluminium/Polypropylene), 12  $\mu$  material, all solid  
84 color white / ALU 8/70 PP, standardized size 130 mm x 160 mm with half a bellows 35 mm  
85 (named in this study the bag "Alu").  
86 Their permeability was declared to be less than  $1.14 \cdot 10^{-16} \text{ m}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$  at 23 °C and 50% relative  
87 humidity for material before heat treatment.

## 89 2.2. Accelerated aging

90 The six meals in the packaging Alu and Alox bags were stored at 23°C at a partial oxygen  
91 pressure of 96 kPa to accelerate oxidation phenomena. In our experimental conditions, these  
92 Alu and Alox bags presented an oxygen permeability of respectively 0.028 and 0.040  
93  $\text{cm}^3/(\text{packaging}\cdot\text{day})$ . Three bags of each ready-meal x plastic packaging combination were  
94 sampled at 6 different times: T0 the start of the experiment, 20 days (equivalent to 3 months),  
95 40 days (equivalent to 6 months), 59 days (equivalent to 9 months), 79 days (equivalent to 12  
96 months) and 119 days (equivalent to 18 months). Samples were then frozen at -20°C until  
97 measurements. After thawing, samples were directly measured in mid-infrared spectroscopy.

98 *2.3. MIR spectral acquisition*

99 Spectra were acquired on each sample corresponding to meals x packaging type x storage time.  
100 Samples were analyzed directly without homogenization but to take into account their  
101 heterogeneity, five spectra were acquired for each sample. Fourier transform mid-infrared  
102 (FTIR) spectra were recorded as described by Bureau, Ruiz, Reich, Gouble, Bertrand, Audergon,  
103 et al. (2009) at room temperature on a Tensor 27 spectrometer (Bruker Optics, Wissembourg,  
104 France) equipped with a horizontal attenuated total reflectance (ATR) sampling accessory  
105 composed of a zinc selenide (ZnSe) crystal with six internal reflections and with a deuterated  
106 triglycine sulfate (DTGS) detector. Spectra were acquired between 4000-650  $\text{cm}^{-1}$ , with scanner  
107 velocity of 10 kHz, a background of 32 scans, and a resolution of 4  $\text{cm}^{-1}$ . The reference spectra  
108 were recorded using a blank ATR crystal every twenty samples. Between measurements the  
109 crystal was carefully cleaned using distilled water and dried with filter paper.

110 *2.4. Data treatment*

111 Spectral pre-processing and data treatment were performed with Matlab 7.5 (Mathworks Inc.  
112 Natick, MA) software using SAISIR package (Cordella and Bertrand, 2008). The MIR data were  
113 systematically transformed with standard normal variate (SNV) to correct multiplicative  
114 interferences and variations in baseline shift. Multivariate analyses and Principal Component  
115 Analyses (PCA) in particular were achieved on spectral data to test if mid-infrared signatures  
116 make possible sample discrimination according to different parameters such as storage time  
117 and packaging.



118 PLS Discriminant Analysis (PLS-DA) was used to test the ability of MIR to classify samples. It is a  
119 classical PLS regression but where the response variable indicates the classes or the categories  
120 of the samples.

### 121 2.5. *Informal sensory analysis*

122 Six sessions of tasting were organized for all products in which 4 or 5 examiners of a home  
123 trained panel participated. Each session was dedicated to a meal and the 5 dates of storage (3,  
124 6, 9, 12 and 18 months) were compared to the control (same product stored at 4 °C and  
125 stabilized under nitrogen).

126 For the tasting, the products were prepared as follows: meal was put in a glass and heated in  
127 microwave. Four global characteristic were evaluated: appearance, texture, smell and taste.

128

## 129 3. Results and discussion

130 Multivariate analyses and precisely Principal Component Analysis (PCA) applied on spectral  
131 data of all samples enabled to highlight changes in the global profile. Whereas samples  
132 measured at different times for lentils, soup, mashed potatoes and Béchamel sauce remained  
133 grouped and did not change over time, Bolognese sauce and mashed potatoes with cheese  
134 began to change at equivalent 12 months and were well discriminated at equivalent 18 months  
135 (results not shown).

136 In comparison with the informal sensory analysis performed on the same meals (results not  
137 shown), in Béchamel and soup, no unpleasant smell and taste appeared in the two packaging  
138 bag during storage. These two meals are acceptable during all the tested 18 months. In lentils  
139 and mashed potatoes, parasite taste appeared respectively at 3 and 9 months but meals

140 remained acceptable until 12 months. Mashed potato with cheese was not acceptable beyond  
141 12 months and different flavors were noticed in the two packaging bags: old potatoes and low  
142 cheese flavor for Alox and acid odor and high cheese flavor for Alu. The difference between Alu  
143 and Alox was not found in Bolognese but from 12 months its quality was deteriorated with a  
144 taste classified as fatty, acid and tasteless. Some trends observed by MIR and by sensory  
145 analysis were in agreement but a future work will be necessary to calibrate MIR with the  
146 sensory descriptors. The objective will be to replace the sensory analysis, money and time  
147 consuming, by the fast and simple MIR.

148 In the two meals, in which spectral changes were observed, several interesting spectral  
149 bands have been identified with an increase of absorption over time (Figure 1).

150 PCA were then carried out using spectral data of Bolognese sauce samples to illustrate the  
151 change occurring over time and in the two packaging bags. Samples were discriminated  
152 according to duration of storage (Figure 2). The first component explained 98.9% of the total  
153 variance and separated samples at equivalent 18 months from the others. The signal changes  
154 began at equivalent 12 months and were drastic at equivalent 18 months. In a second PCA,  
155 samples were also discriminated according to the types of plastic packaging at equivalent 18  
156 months (Figure 3). The first component explained 97.8% of the total variance and separated, at  
157 equivalent 18 months after storage, samples in Alox packaging (g for green bags) from the other  
158 samples such as samples in Alu packaging (w for white bags) and samples at the other times  
159 between 0 and equivalent 12 months. As expected, the Alox packaging, presenting the highest  
160 oxygen permeability, led to a greater oxidation of samples.

161 The eigenvectors of PCA indicate the spectral regions that play an important role to create  
162 principal components. As the first components of the two PCA above (Figure 2 and 3) explained  
163 around 98% of the total variance, the first eigenvectors allowed to identify markers  
164 characterized by the following clear absorption bands: 2918  $\text{cm}^{-1}$ , 2850  $\text{cm}^{-1}$ , 1741  $\text{cm}^{-1}$ , 1463  
165  $\text{cm}^{-1}$  and 1164  $\text{cm}^{-1}$ , which increased particularly in both, meals such as Bolognaise and mashed  
166 potatoes with cheese over storage and packaging such as Alox bags at equivalent 18 months  
167 (Figure 4). These absorption bands could be attributed to fats, which thus appeared to have a  
168 major effect in sample discrimination (Guillen and Cabo, 1997). Indeed these characteristic  
169 bands correspond to aliphatic hydrocarbons with -C-H stretching vibrations of  $\text{CH}_2$  functional  
170 groups between 3000 and 2800  $\text{cm}^{-1}$ , -C-H bending vibrations of  $\text{CH}_2$  and/or  $\text{CH}_3$  groups  
171 between 1465 and 1319  $\text{cm}^{-1}$  and rocking vibrations of  $-(\text{CH}_2)-$  at 723  $\text{cm}^{-1}$ . The bands are also  
172 specific of esters with the ester carbonyl C=O stretching vibrations at 1741  $\text{cm}^{-1}$  and the  
173 stretching/bending vibrations of acyl -C-O ester bond occurring between 1300 and 1000  $\text{cm}^{-1}$   
174 and particularly a strong band at 1168  $\text{cm}^{-1}$ . The identification of markers presenting spectra  
175 similar to those of oil or fat (Guillen and Cabo, 1997) in Bolognaise sauce and mashed potatoes  
176 with cheese was in relation with their composition containing respectively 43% of pork and 16 %  
177 of cheese. However, in the same way, potato chips and the corresponding extracted chip oil  
178 present similar MIR profiles indicating the importance of signals due to oil (Shiroma and  
179 Rodriguez-Saona, 2009). In our study, these bands specific of oil or fat increased over time in  
180 Bolognese sauce and mashed potatoes with cheese.

181 MIR spectral data were then used for a classification data treatment employing the PLS-DA  
182 method (Table 1). All Bolognaise samples were well-classified according to their storage

183 duration. This confirmed the relevance of using the couple, MIR and chemometrics , to classify  
184 meals according to their shelf-life.

185

#### 186 4. Conclusion

187 MIR coupled with chemometrics proved to be a simple and rapid method to discriminate  
188 and classify samples according to the storage and packaging. Four of the six samples showed  
189 identical spectra throughout storage, whereas two of these samples (Bolognese and potato with  
190 cheese) had noticeable change over time. Moreover, the evolution was more marked for the  
191 most oxygen-permeable packaging, and PCA revealed apparition of distinct bands in the MIR  
192 spectra, which appear to be from fat degradation. This method could be very relevant and  
193 useful for food industry to check the shelf-life of their products. In parallel, an informal sensory  
194 analysis highlighted changes of smell and taste during storage. Some of the results obtained by  
195 these two approaches, sensory and MIR, were consistent and must be explored. Further studies  
196 will be needed to better understand changes in meals over time in relation to spectral data and  
197 human perception.

198

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201

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- 237
- 238

239 **Captions to figures:**

240 Figure 1. MIR spectral data ( $4000\text{-}650\text{ cm}^{-1}$ ) of ready-meals in plastic packaging over a simulated  
241 shelf-life of 18 months. The ready-meals were: lentils, mashed potatoes, mashed potatoes with  
242 cheese, béchamel sauce, vegetable soup, Bolognese sauce.

243

244 Figure 2. PCA (Principal Component Analysis) performed on spectral data ( $4000\text{-}650\text{ cm}^{-1}$ ) of  
245 Bolognese sauce samples acquired over time from 0 to equivalent 18 months in Alox packaging

246

247 Figure 3. PCA (Principal Component Analysis) performed on spectral data ( $4000\text{-}650\text{ cm}^{-1}$ ) of  
248 Bolognese sauce samples acquired over time from 0 to equivalent 18 months, in two types of  
249 packaging, Alu (w) and Alox (g).

250

251 Figure 4. First eigenvectors of PCA carried out on the MIR spectra ( $4000\text{ - }650\text{ cm}^{-1}$ ) of  
252 Bolognese sauce in two different plastic packaging stored for up to equivalent 18 months.

253

1 Table 1. Confusion matrix (PLS-DA) of MIR spectra of Bolognese sauce samples during storage for up to  
 2 equivalent 18 months. Five spectra were recorded for each date (spectral data in the range 4000-650 cm<sup>-1</sup>).  
 3 <sup>1</sup>).

	<b>0 month</b>	<b>3 months</b>	<b>6 months</b>	<b>9 months</b>	<b>12 months</b>	<b>18 months</b>
<b>0 month</b>	5	0	0	0	0	0
<b>3 months</b>	0	5	0	0	0	0
<b>6 months</b>	0	0	5	0	0	0
<b>9 months</b>	0	0	0	5	0	0
<b>12 months</b>	0	0	0	0	5	0
<b>18 months</b>	0	0	0	0	0	5

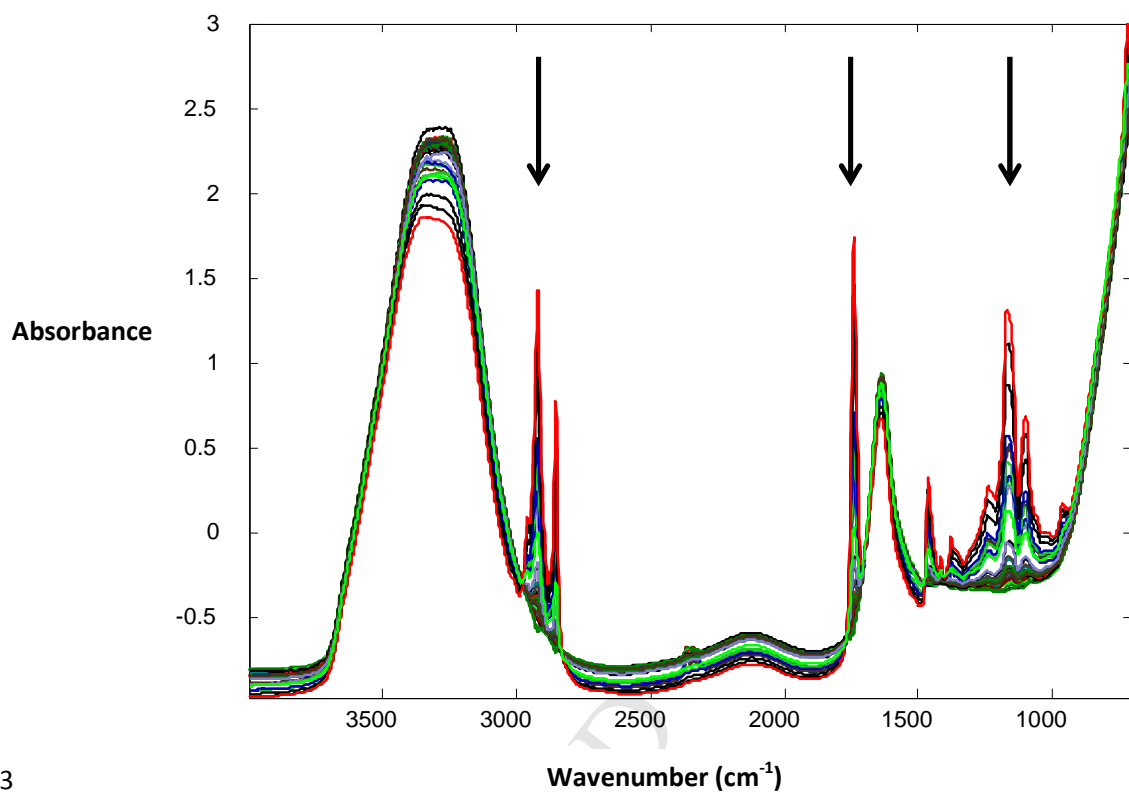
4  
 5 8 latent variables.

6



1 **Figures**

2



3

4

5 **Figure 1.**

6

7

8

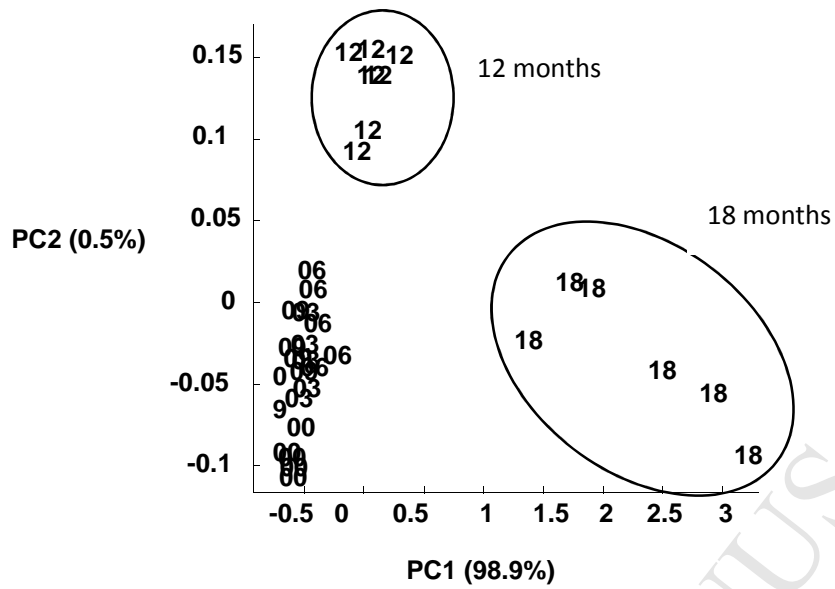


Figure 2.

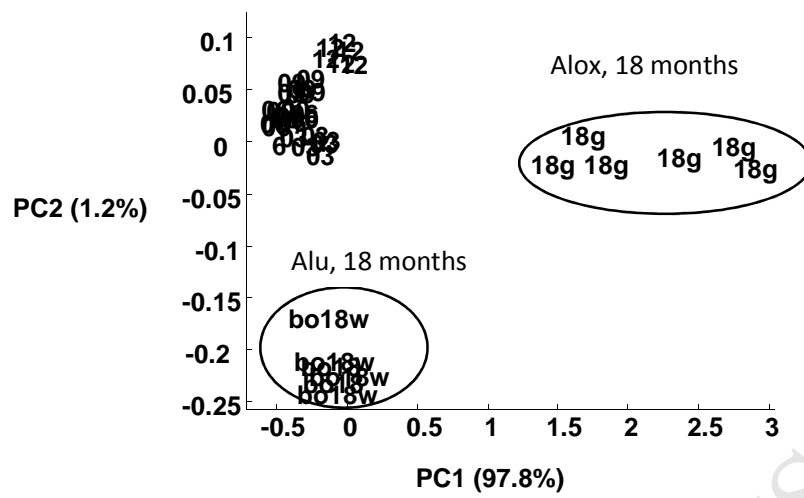


Figure 3.

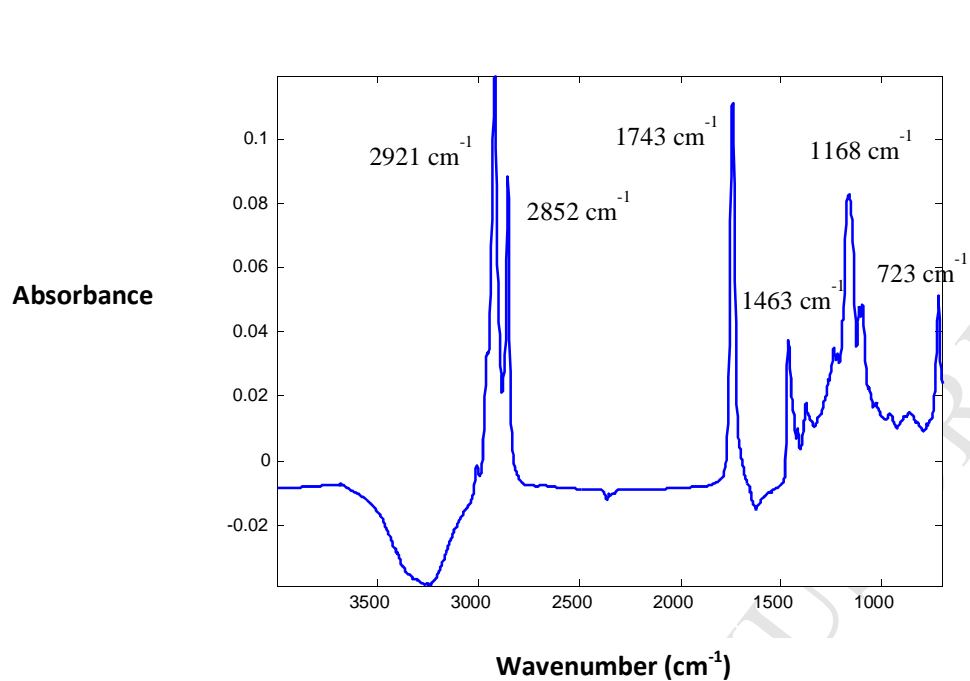


Figure 4.

47

### Highlights

- Mid-Infrared Spectroscopy coupled with chemometrics
- Changes observed in Bolognese sauce and mashed potatoes with cheese
- Apparition of bands between 4000 and 650  $\text{cm}^{-1}$  related to fats
- Classification of meals according to their shelf-life

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