Accepted Manuscript

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PII: S0023-6438(16)30489-3

DOI: [10.1016/j.lwt.2016.08.003](https://doi.org/10.1016/j.lwt.2016.08.003)

Reference: YFSTL 5652

To appear in: *LWT - Food Science and Technology*

Received Date: 19 May 2016

Revised Date: 4 August 2016

Accepted Date: 7 August 2016

Please cite this article as: Bureau, S., Georgé, S., Perrin, A., Renard, C.M.G.C., Use of mid-infrared spectroscopy to monitor shelf-life of ready-made meals, *LWT - Food Science and Technology* (2016), doi: 10.1016/j.lwt.2016.08.003.

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Comment citer ce document :

Bureau, S. (Auteur de correspondance), Georgé, S., Perrin, A., Renard, C.M.G.C. (2017). Use of mid-infrared spectroscopy to monitor shelf-life of ready-made meals. *LWT - Food Science and Technology*, 85, 474-478. DOI : 10.1016/j.lwt.2016.08.003

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

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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 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 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

1. Introduction

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

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

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

2. Materials and methods

2.1. Materials

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

plastic bags (recipes given in complementary data). Two plastic packagings, Alu and Alox, provided by Amcor Flexibles Moreuil (Zone Industrielle, 80110 Moreuil, France) were compared. They corresponded to stand-up bags made of:

- (PET/PET SiOx/PP) (Polyethylene terephthalate/Silicon oxide/Polypropylene), 12 μ printed material [green flatness + white flatness] / SiO x 12 μ PET / 70 μ PP OB with aliphatic glue, standardized size (for canned goods of 200-250 g) 130 mm x 140 mm with half a bellows 35mm (named in this study the bag "Alox"),
- PET/Alu/PP (Polyethylene terephthalate/Aluminium/Polypropylene), 12 μ material, all solid color white / ALU 8/70 PP, standardized size 130 mm x 160 mm with half a bellows 35 mm (named in this study the bag "Alu").

Their permeability was declared to be less than $1.14 \cdot 10^{-16} \text{ m.s}^{-1}.\text{Pa}^{-1}$ at 23 °C and 50% relative humidity for material before heat treatment.

2.2. Accelerated aging

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

2.3. MIR spectral acquisition

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

2.4. Data treatment

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

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

2.5. *Informal sensory analysis*

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

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

3. Results and discussion

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

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

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

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

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

The eigenvectors of PCA indicate the spectral regions that play an important role to create principal components. As the first components of the two PCA above (Figure 2 and 3) explained around 98% of the total variance, the first eigenvectors allowed to identify markers characterized by the following clear absorption bands: 2918 cm^{-1} , 2850 cm^{-1} , 1741 cm^{-1} , 1463 cm^{-1} and 1164 cm^{-1} , which increased particularly in both, meals such as Bolognaise and mashed potatoes with cheese over storage and packaging such as Alox bags at equivalent 18 months (Figure 4). These absorption bands could be attributed to fats, which thus appeared to have a major effect in sample discrimination (Guillen and Cabo, 1997). Indeed these characteristic bands correspond to aliphatic hydrocarbons with -C-H stretching vibrations of CH_2 functional groups between 3000 and 2800 cm^{-1} , -C-H bending vibrations of CH_2 and/or CH_3 groups between 1465 and 1319 cm^{-1} and rocking vibrations of $-(\text{CH}_2)-$ at 723 cm^{-1} . The bands are also specific of esters with the ester carbonyl C=O stretching vibrations at 1741 cm^{-1} and the stretching/bending vibrations of acyl -C-O ester bond occurring between 1300 and 1000 cm^{-1} and particularly a strong band at 1168 cm^{-1} . The identification of markers presenting spectra similar to those of oil or fat (Guillen and Cabo, 1997) in Bolognaise sauce and mashed potatoes with cheese was in relation with their composition containing respectively 43% of pork and 16 % of cheese. However, in the same way, potato chips and the corresponding extracted chip oil present similar MIR profiles indicating the importance of signals due to oil (Shiroma and Rodriguez-Saona, 2009). In our study, these bands specific of oil or fat increased over time in Bolognese sauce and mashed potatoes with cheese.

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

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

4. Conclusion

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

Acknowledgments

This study was supported by the UMT Qualiveg and FranceAgriMer.

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Captions to figures:

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

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

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

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

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⁻¹).
 3 ¹).

	0 month	3 months	6 months	9 months	12 months	18 months
0 month	5	0	0	0	0	0
3 months	0	5	0	0	0	0
6 months	0	0	5	0	0	0
9 months	0	0	0	5	0	0
12 months	0	0	0	0	5	0
18 months	0	0	0	0	0	5

4
 5 8 latent variables.
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1 **Figures**

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5 **Figure 1.**

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Figure 2.

Figure 3.

Figure 4.

Highlights

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

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