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***MULTIVARIATE CURVE RESOLUTION APPLIED TO NEAR
INFRARED SPECTROSCOPIC DATA ACQUIRED THROUGHOUT
THE COOKING PROCESS TO MONITOR THE EVOLVING
BÉCHAMEL SAUCES***

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Abstract

This study presents an exploratory analysis of the kinetics and mechanisms involved in the cooking process of 27 béchamel sauces. The evolving béchamel sauces during their elaboration were investigated using a hand-held near infrared spectroscopy (NIRS) sensor in combination with multivariate curve resolution - alternating least-squares (MCR-ALS) approach. MCR-ALS under hybrid hard- and soft- constraints as well as other active constraints within the ALS optimization phase was applied to elucidate the mechanism of the cooking process of evolving béchamel sauces aiming to resolve kinetic profiles and pure spectral signatures of the monitored products, being the rate constants outputted as additional information. The evolving béchamel sauces could be described with a kinetic model based on a first-order reaction ($A \xrightarrow{k} B$). These two species (A and B) involved on the process were related to changes in the scattering and in the nature and state of the water. Differences in the kinetic constants between béchamel sauces were found, which were associated with differences in the initial temperature of the cooking

process. The obtained results were coherent with the images observed using a scanning electron microscopy (SEM).

The methodology presented in this work offers a new strategy to study the elaboration of béchamel sauces in a non-destructive way, with the aim to give industrial producers a better understanding of their manufacturing process in a rapid and real time manner.

Keywords: White sauce, near infrared spectroscopy, multivariate curve resolution alternative least squares, scanning electron microscope, chemometrics, process monitoring.

1. Introduction

The béchamel sauce, also known as white sauce, is a traditional recipe used in many food preparations in the French cuisine, which has also been adopted by other countries. This sauce is made of milk, flour (usually coming from wheat) fat, salt and spices (Heyman et al., 2010). It is considered an oil-in-water emulsion, whose disperse phase is formed by oil droplets and the continuous phase by the rest of the ingredients (Herranz et al., 2019).

The control of the process in the elaboration of béchamel sauces is crucial, because small changes will be reflected in the quality of the final product. During the cooking process the evolving béchamel sauces go from a liquid mixture to a sauce with the consistency of a gel. This occurs due to the gelatinization of the starch. Starch is a carbohydrate composed of amylose and amylopectin. When starch granules are in the presence of excess liquid and heat, they undergo the process of gelatinization, an irreversible phase transition where their ordered structure and the molecular organization are disrupted. The hydrogen bonds collapse, producing irreversible changes. These changes follow the swelling of the starch granules, which, under mixing conditions and with enough liquid in the system, will lead to an increase of the viscosity of the medium (Ratnayake & Jackson, 2008; Tako et al., 2014; Thebaudin et al., 1998; Wang & Copeland, 2013). The development of tools enabling an objective monitoring and control of the

process is of great interest for the food industry, since it will allow not only to ensure that the cooking process is correctly executed but also to make corrections at real time (i.e. changes in temperature, ingredients, mixing time) if sauces are not behaving as expected.

Nowadays, non-destructive monitoring analytical techniques have arisen as an alternative to perform the control of processes in the food industry. They are rapid and allow the inspection of all or almost all the production (McCarthy & McCarthy, 2013). In particular, near infrared spectroscopy (NIRS) is one of the most used analytical techniques in process analytical technology (PAT), for monitoring and modelling different food processes (Grassi & Alamprese, 2018). This analytical technique usually requires the use of chemometrics to extract the useful information, since it is contained in broad and overlapped bands of the spectra (Blanco & Villarroya, 2002). Multivariate curve resolution (MCR) encompasses a group of chemometric models that have been applied successfully to NIRS to understand physico-chemical changes related with data coming from processes (Grassi et al., 2014; Mas et al., 2015; Babaei Rouchi et al., 2019; Grassi et al., 2019; Cavaglia et al., 2022). They try to solve mixture analysis problems, providing meaningful models with components that can be interpreted. They are used for analysing data coming from a process or an analytical measurement (de Juan et al., 2000; de Juan et al., 2014). Multivariate curve resolution-alternating least squares (MCR-ALS) was selected, in the present report, as a proper advanced chemometric model to uniquely extract pure concentration profiles and spectral signatures of each involved responsive species contained in the evolving experimental data. This chemometric model relies on the variation of the measured data to describe the evolution of the system under study. Previous studies have already shown the capability of MCR-ALS to make exploratory studies of processes (Mas et al., 2008; de Juan & Tauler, 2021; Mas Garcia et al., 2021). However, MCR-ALS approaches have never been reported to study evolving béchamel sauces during cooking, which will help to improve the knowledge about the mechanisms involved.

Despite the importance of béchamel sauce in gastronomy, few works have been carried out to gain a better understanding of this product. Most of the studies have been focused on the substitution of the wheat starch, using starches of different botanical origins (Arocas et al., 2010), different ingredients such as hydrocolloids (Heyman et al., 2010) or gluten free béchamel sauces (Guardeño et al., 2013). Several phenomena were studied in some works, such as the one by (Martinez-Padilla & Hardy, 1989), in which the aim was to observe the thixotropy of the sauces, or the study of their stability when freezing / thawing made by Herranz et al., (2019). Other studies have made progress in the control and optimization of a béchamel production line, proposing a methodology for their computer-based control and optimization (Xiaoyan et al., 2007). However, up to authors knowledge, there are no works that monitor and explore the behaviour and kinetics of evolving béchamel sauces during the cooking process, to better understand the chemistry behind.

Considering all this information, this study was carried out with the aim of monitoring the cooking process of evolving béchamel sauces using NIRS coupled with MCR-ALS. To explain the results obtained, some béchamel samples were observed using a Scanning Electron Microscopy (SEM). All this knowledge will allow industrial producers to gain a better understanding and control over their manufacturing process.

2. Materials and methods

2.1 Elaboration of the béchamel sauces

In this study 27 different béchamel sauces have been prepared. They were elaborated in all the cases using the same recipe and following the same procedure. The ingredients used in the preparation, in all the cases, were the following: pre-gelatinized wheat flour, milk, olive oil, butter and salt. For the elaboration of the sauces, first, the fatty ingredients (butter and oil), were incorporated in the frying pan until the mix was boiling. Then, the flour and salt were added

and cooked for 2 minutes. Once the mixture was cooked, the 80 % of the milk was added, and the sauce was mixed until obtaining a homogeneous paste. Then, the rest of the milk was added. The moment when all the ingredients were in the frying pan was considered as time 0 minutes of the cooking process, and the data was recorded since that point.

2.2 NIRS analysis

NIRS measurements were taken during the cooking process of the sauces. For that purpose, a handheld NIR spectrometer (MicroNIR OnSite from VIAVI Solutions Inc., Italy) was used, with a spectral range from 900 nm to 1650 nm and a resolution of 6 nm. Each spectrum taken resulted from an average of 100 spectral acquisitions. The sampling was designed to cover a wide range of spatial and temporal variability of the sauce during the cooking process. In order to take a wide range of the spatial variability, spectra were acquired directly in the sauce while cooking at 4 different points distributed randomly in the frying pan. One spectrum was acquired at one location and three replicates were performed in other three spots. Each spectrum was taken in duplicate. For the data analysis, these duplicates were averaged, and each repetition was used for creating a different model (so that each experiment had 4 different MCR-ALS replicates). The temperature of the sauce was recorded when the first spectrum was measured. To cover the temporal variability during the process, the NIR spectra of the evolving béchamel sauces were measured at different cooking times. Samples were measured since minute 6.5 every minute until minute 16.5 in 16 sauces and until minute 20.5 in 3 sauces. The other 8 sauce samples were recorded since minute 8.5 until minute 32.5 every two minutes. All spectral acquisition started at 6.5 minutes since that was the time of the cooking process when all the ingredients were integrated. Figure 1 shows a scheme of the cooking process and the sampling.

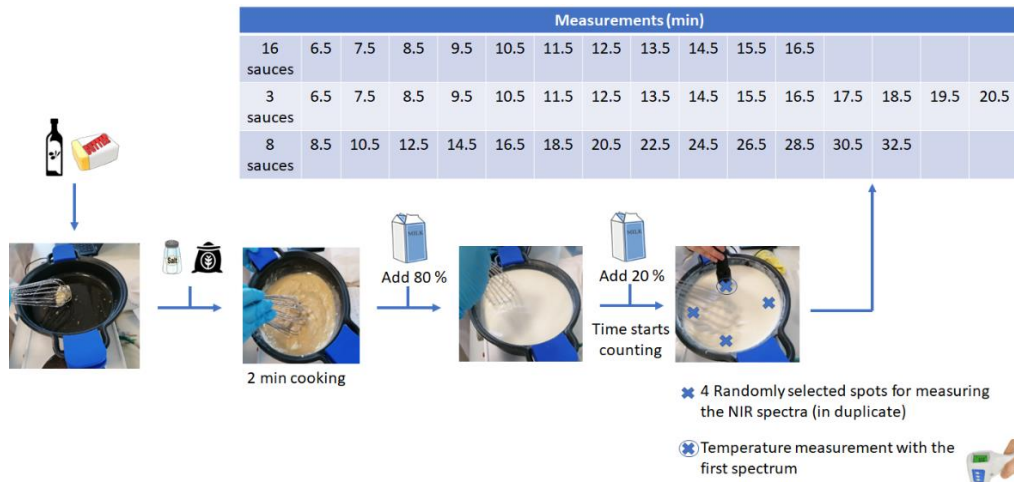


Figure 1. Scheme of the cooking process and the data collection.

The shape and the main absorption peaks of the recorded NIR spectra were studied and identified to interpret the bands that had the greatest influence.

2.3 Multivariate curve resolution-alternating least squares (MCR-ALS)

Every K th béchamel elaborated, measured by NIRS, produces a data matrix, \mathbf{D}_k . This data matrix can be described with the bilinear model of Equation 1:

$$\mathbf{D}_k = \mathbf{C}_k \mathbf{S}^T + \mathbf{E}_k \tag{Equation 1}$$

where \mathbf{D} is an $K \times J$ matrix containing K samples individually acquired in a vectorial signal at J measured variables of different wavelengths. The rows of the matrix \mathbf{D}_k describe the NIR spectra acquired at different timesteps of the process and the columns the kinetic traces recorded at different wavelengths. \mathbf{C}_k is an $K \times N$ matrix which contains the concentration evolution of N species in the K samples, and \mathbf{S}^T is a $N \times J$ matrix that contains the spectral signatures of N species at J measured variables of different wavenumbers (Mazivila & Santos, 2022). Finally, \mathbf{E}_k is the matrix of the residuals which includes the data not modelled from the \mathbf{D}_k dataset (Figure 2).

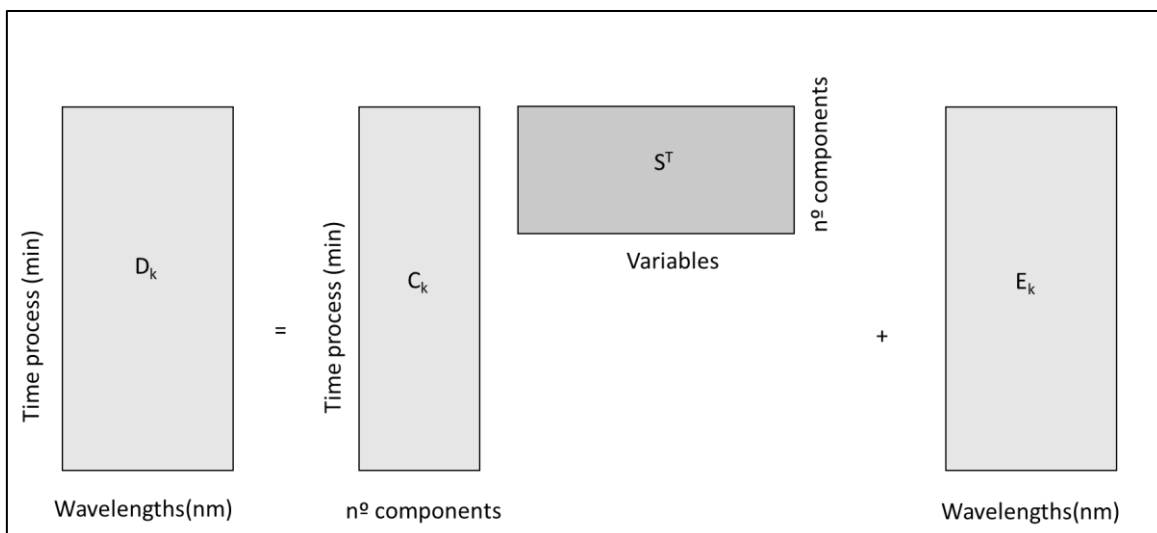


Figure 2. MCR-ALS bilinear model of a single matrix (one cooking experiment).

The goal of the MCR-ALS algorithm is to recover the underlying bilinear model expressed in Equation 1 using only the information of the data matrix \mathbf{D}_k . To do so, an ALS procedure under constraints is used, in order to optimize both \mathbf{C}_k and \mathbf{S}^T matrices in an iteratively way, until the convergence is achieved (Tauler, 1995; de Juan et al., 2009). In this work, the convergence was achieved when the fitting error, measured as the sum of the squares of the residuals of the reconstructed matrix with respect to the original one, increased or decreased less than 1 % or the process reached a maximum of 100 iterations.

In order to start the iterative procedure, previous determination of number of contributions in the \mathbf{D}_k and the generation of \mathbf{C}_k or \mathbf{S}^T estimates are needed. In this work, the determination of number of contributions were carried out by singular value decomposition (SVD) (Henry & Hofrichter, 1992) and initial estimates of \mathbf{S}^T were obtained using SIMPLISMA (Windig & Guilment, 1991).

As mentioned before, in MCR-ALS analysis both \mathbf{C}_k and \mathbf{S}^T matrices are optimized under constraints. The use of these constraints allows obtaining chemically meaningful and more accurate spectral signatures and concentration evolutions (Tauler, 1995; de Juan et al., 2009). In this work, the constraints used were: unimodality (the kinetic profiles in the elaboration of a béchamel sauce present one maximum per profile), normalization of the pure spectral

signatures and non-negativity (the kinetic profiles and the pure spectral signatures of the resolved components are forced to be positive). A hard-modelling constraint was also used. This constraint forces the concentration profiles to be fitted by a parametric physicochemical model, and the parameters of the model are obtained as an additional output (de Juan et al., 2014). To do so, a kinetic model was imposed into the resolution, so that the concentration profiles are forced to obey the shapes described by this specific kinetic model. Furthermore, the kinetic rate constants are outputted as additional information (de Juan et al., 2000). It is worth to mention that the use of constraints in MCR-ALS are optional and very flexible (i.e. species can be constrained in different way within of both \mathbf{C}_k and \mathbf{S}^T matrices).

An outstanding advantage of the MCR-ALS algorithm relies in the possibility of analysing simultaneously kinetic experiments, in a single multiset structure, in order to obtain more reliable results (Tauler, 1995; de Juan et al., 2009). In this work, this multiset structure was obtained forming a column-wise data matrix by setting all data matrices, \mathbf{D}_k , one on top of each other. The bilinear model explained in Equation 1 was extended, as it can be seen in Equation 2, to the augmented data set:

$$\mathbf{D}_{\text{aug}} = \begin{bmatrix} \mathbf{D1} \\ \mathbf{D2} \\ \dots \\ \mathbf{Dn} \end{bmatrix} = \begin{bmatrix} \mathbf{C1} \\ \mathbf{C2} \\ \dots \\ \mathbf{Cn} \end{bmatrix} \mathbf{S}^T + \begin{bmatrix} \mathbf{E1} \\ \mathbf{E2} \\ \dots \\ \mathbf{En} \end{bmatrix} = \mathbf{C}_{\text{aug}} \mathbf{S}^T + \mathbf{E}_{\text{aug}} \quad \text{Equation 2}$$

where \mathbf{C}_{aug} is a column-wise augmented matrix formed by the \mathbf{C}_k submatrices which contain the resolved kinetic profiles in the different cooking experiments, and \mathbf{S}^T is a single data matrix of pure NIR spectra, assumed to be valid and common for all experiments (Figure 3).

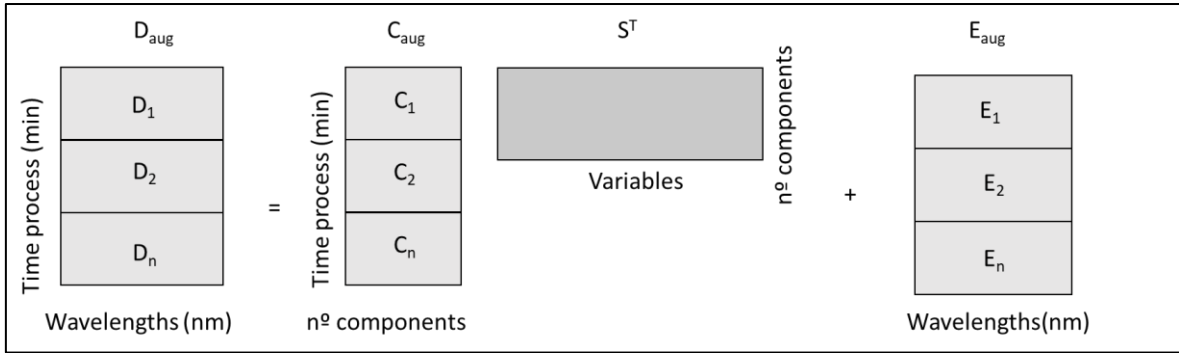


Figure 3. MCR-ALS Bilinear model of an augmented matrix.

In this case, the application of constraints in the MCR-ALS algorithm is also very flexible, i.e., each submatrix of concentration profiles can be constrained independently. In this work, different kinetic models were used for each cooking experiment.

The quality of the MCR-ALS results is described by the percentage of lack of fit (% LOF) and the explained variance (% r^2), which were calculated according to Equations 3 and 4:

$$\% \text{ LOF} = 100 \times \sqrt{\frac{\sum e_{ij}^2}{\sum d_{ij}^2}} \quad \text{Equation 3}$$

$$\% r^2 = 100 \times \left(1 - \frac{\sum e_{ij}^2}{\sum d_{ij}^2} \right) \quad \text{Equation 4}$$

where e_{ij} is equal to $d_{ij} - d_{ij}^*$, d_{ij}^* are the values of the data set reproduced by the bilinear model and d_{ij} the values in the original data set \mathbf{D}_k . To consider the results adequate, the % r^2 must be sufficiently high, the % LOF sufficiently low, and the obtained concentration profiles and spectra must show shapes consistent with the variation in the original data sets and be chemically meaningful.

More information about the chemometric model can be obtained in Tauler, 1995; Jaumot et al., 2015 and a GUI to use the algorithm is freely available at: <http://mcral.info>.

2.4 Projections of the pure spectral signatures

To interpret the pure spectral signatures obtained with the MCR-ALS analysis (S_1 and S_2), two projections were created (X_1 and X_2). X_1 represents the common part between both S_1 and S_2 . It was obtained projecting the first spectra (S_1) onto the second (S_2). X_2 , which represents the differences between both spectra, was created subtracting X_1 from S_1 . Both X_1 and X_2 were normalized before they were represented.

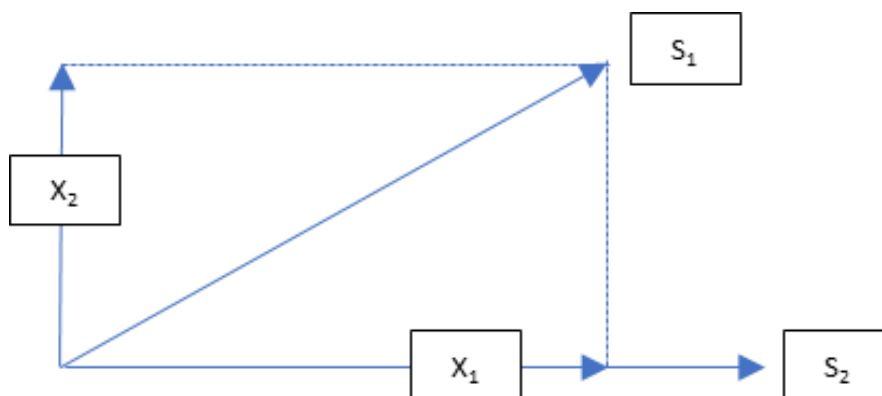


Figure 4. Creation of the orthogonal projections to interpret the pure components obtained in MCR-ALS analysis

2.5 Scanning electron microscope images

With the aim to see the possible structure differences during the cooking process, and to better interpretate the results obtained with NIRS and the MCR-ALS analysis, three samples were observed using SEM. For this purpose, a new béchamel sauce was elaborated with the same recipe and procedure, and samples were collected when the sauce was (1) at minute 6.5, (2) at minute 16.5 and (3) at minute 26.5. Then, samples were lyophilised to remove the water and placed in a sample holder using conductive double sided adhesive carbon tape. Samples were coated with Au (40 nm) using a Q150T S/E/ES Sample Preparation System (Quorum Technologies). Also, Cu tape was placed on the edges of the sample holder to avoid any excess of charging. The SEM used was a JEOL JSM-6400 with W filament. Images were acquired with a beam current of 0.5 nA at 20kV, working distance of 10 mm and magnifications of up to $\times 2,000$.

3. Results and discussion

3.1 NIR spectra

The NIR spectra obtained from the measurement of the evolving béchamel sauces during the cooking process are shown in Figure 4.

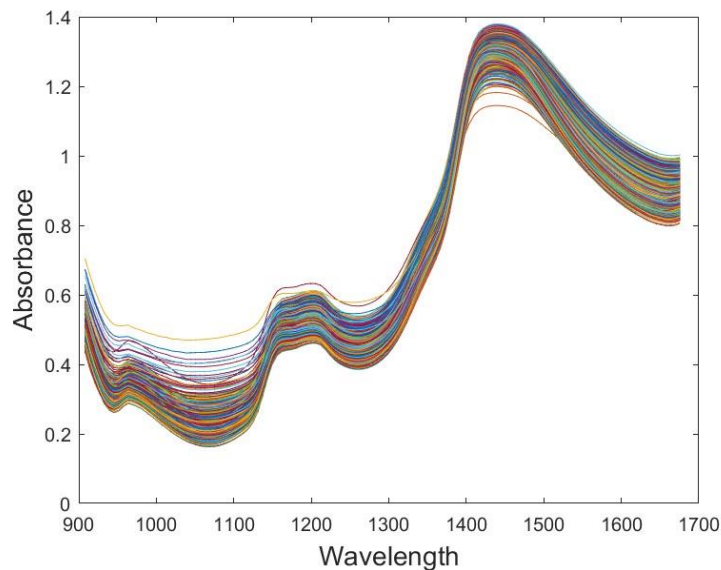


Figure 4. Raw NIR spectra of the evolving béchamel sauces

In the NIR raw spectra (Figure 4), three main absorption bands are observed. The first one, located at 960 nm, corresponds with the second overtone of the -OH stretching, and it is specific and characteristic of water (Otal et al., 2003). The second one, which is placed between 1100 nm and 1250 nm, seems to be composed of two peaks: one at 1150 nm and another one around 1200 nm. The NIR peak located at 1150 nm is related with water, specifically with the first overtone of the O-H stretching band and the O-H bending band (Salgó & Gergely, 2012). Regarding the second, some studies have attributed this part of the spectra with the second overtone of the stretching of C-H molecular bonds, related with fat (Downey et al., 2002; Garrido-Varo et al., 2017). This interpretation is coherent, considering that three of the main ingredients of the béchamel sauce are milk, oil and butter, which are made by a mix of water and fat. The big peak located between 1400 nm and 1500 nm has been associated with the -OH first overtone of the water molecule and with wheat starch (Kaddour et al., 2007). When starch is mixed with aqueous liquid (milk in this case) and warmed up, it starts to hydrate and swell, taking place the gelatinization process, where amyloses form a continuous network, making the solution more viscous (Santos et al., 2002).

It can also be seen in Figure 4 that the spectra are vertically shifted. That is due to the scattering effect, since it is related with structural and physical changes that occur, in this case, when the evolving béchamel sauces pass from a liquid to a paste (Xie & Guo et al., 2020).

3.2 MCR-ALS analysis for a particular cooking process

The MCR-ALS bilinear model of one béchamel sauce can be seen in Figure 5. The concentration profiles (\mathbf{C}) and the pure signals (\mathbf{S}^T) of the first béchamel elaborated are shown as an example. \mathbf{D}_k shows the spectra recorded at different times of the cooking process. \mathbf{C} represents the evolution of the concentration of the two components extracted by MCR during the cooking process of the béchamel sauce, while \mathbf{S}^T are their pure spectral signatures.

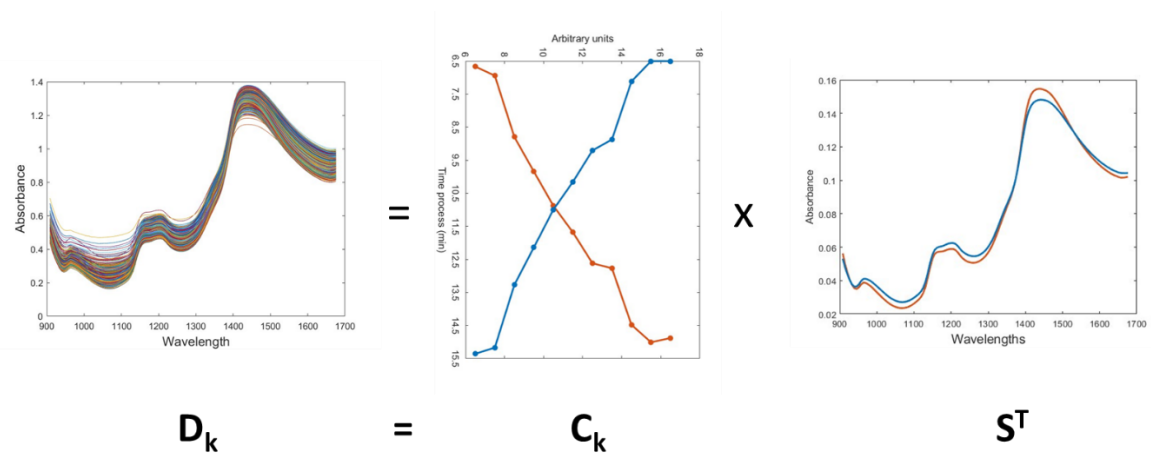


Figure 5. MCR-ALS bilinear model of the first elaborated béchamel sauce.

\mathbf{C} and \mathbf{S}^T of both components for the first béchamel elaborated are better shown in Figure 6. Figure 6a shows the concentration profiles (\mathbf{C}) and Figure 6b the pure spectral signatures (\mathbf{S}^T). Resolution of two species was achieved with the lack of fit (LOF %) equal to 0.37 % and the explained variance (r^2 %) equal to 99.9 %. A different number of components (1 and 3) gave worse data fits or unreliable spectra or concentration profiles.

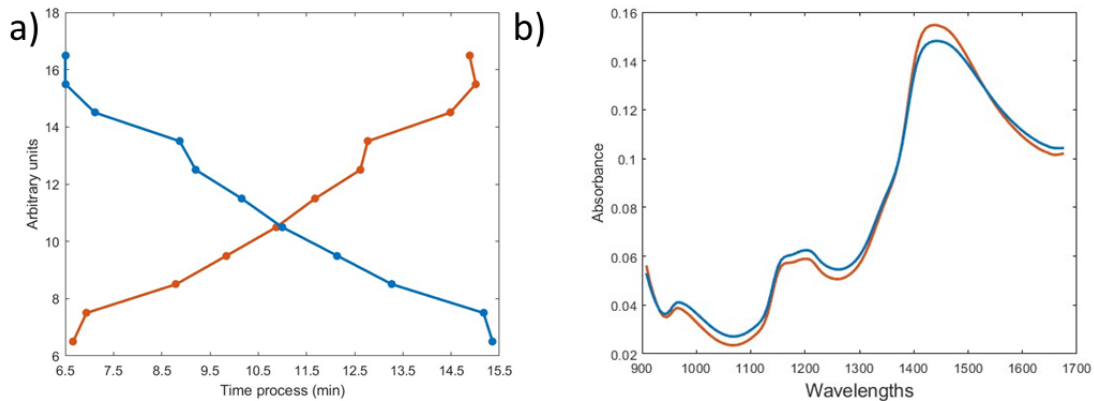


Figure 6. MCR-ALS results from the elaboration process of the first béchamel sauce with soft-modelling constraints. a) kinetic profiles (**C**); b) pure spectral signatures (**S^T**). Blue curve represents component A and red curve component B.

The shape of the resolved concentration profiles suggests a simple kinetic model based on a first order reaction ($A \xrightarrow{k} B$), where A (blue curve) decreases while B (red curve) increases. Therefore, the postulated model was introduced as a hard-modelling constraint. Now, the concentration profiles (**C**) (Figure 7a) and the pure spectral signatures (**S^T**) (Figure 7b) obtained resemble in shape to the latest results using soft-modelling constraint and similar good data fit was achieved (LOF = 0.94 % and $r^2 = 99.9$ %), indicating that the hypothesis of the selected kinetic model was correct. Moreover, a kinetic rate constant was obtained as additional information ($k = 0.019 \text{ min}^{-1}$).

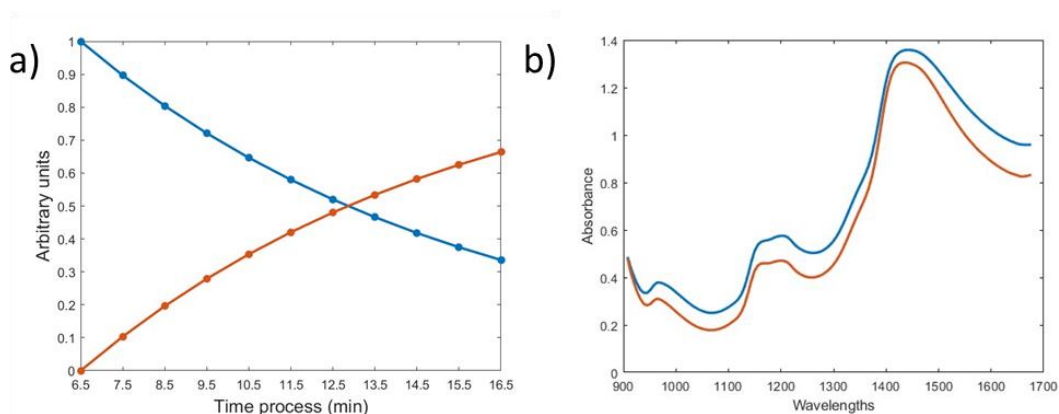
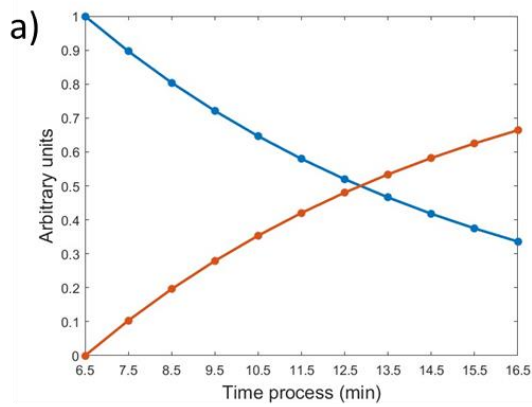


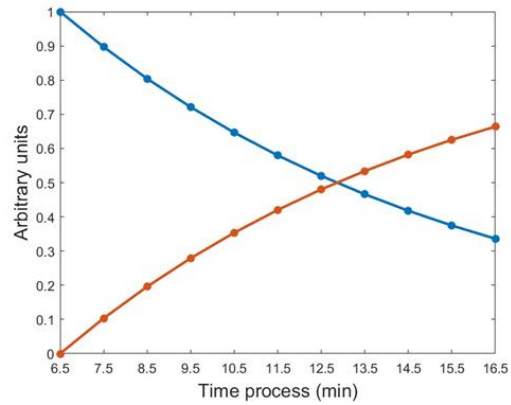
Figure 7. MCR-ALS results from the elaboration process of the first béchamel sauce with hard-modelling constraints. a) kinetic profiles (**C**); b) pure spectral signatures (**S^T**). Blue curve represents component A and red curve component B.

Simultaneous analysis by MCR-ALS can be extended to the four replicates elaborated in the first béchamel sauce. After checking the repeatability of the replicates and fitting each replicate individually to the proposed kinetic model (data not shown), more reliable results could be

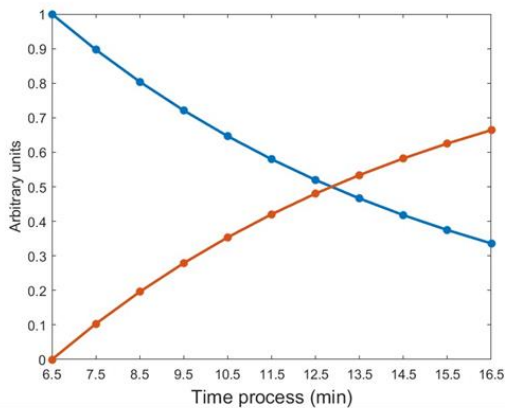
obtained when fitting the set of replicates to a single global model. This means that a global model ($A \xrightarrow{k} B$) was fitted in the simultaneous analysis. Consequently, the concentration profiles and related rate constants were estimated in a more accurate and robust way. Figure 8 shows the resolved augmented concentration matrix (**C**) (Figure 8a) and the pure spectral signatures (**S^T**) (Figure 8b) of the simultaneous analysis of the four replicates elaborated for the first béchamel. The pattern of two species, which follows the kinetic model based on a first-order reaction ($A \xrightarrow{k} B$) was again observed. Good data fit (LOF = 0.89 % and $r^2 = 99.9$ %) and a more reliable rate constant were also obtained ($k = 0.093 \text{ min}^{-1}$).



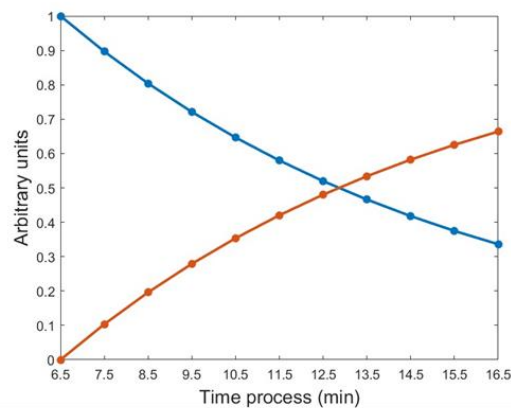
1st replicate



2nd replicate



3rd replicate



4th replicate

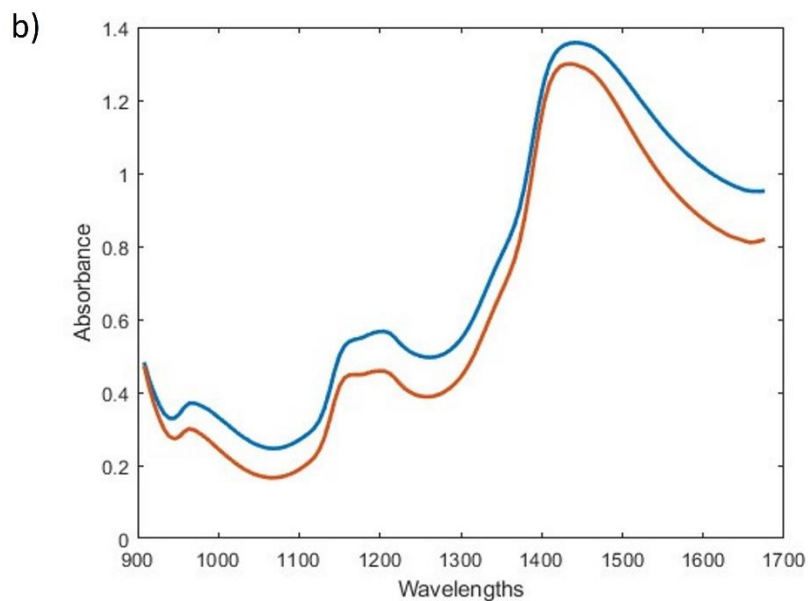


Figure 8. Simultaneous analysis by MCR-ALS of the four replicates elaborated in the first béchamel sauce with hard-modelling constraints. a) kinetic profiles (**C**); b) pure spectral signatures (**S^T**). Blue curve represents component A and red curve component B.

Taking into account the chemical changes that should occur during the cooking of the evolving béchamel sauces, the first species shown in Figure 8 (blue line, **C₁** and **S₁**) could be related to the free water in the process, which decreases as it evolves to bounded water due to the process of gelatinization of the starch. The second species (**C₂** and **S₂**), the red curve, could be associated with the evolution of the scattering of the NIR signal, which increases during the cooking process. However, due to the similarities between the obtained pure spectral signatures (Figure 8b) and in order to better appreciate the subtle differences between **S₁** and **S₂**, the two projections **X₁** and **X₂** were calculated, with **X₁** representing the common part while **X₂** the difference (Figure 9).

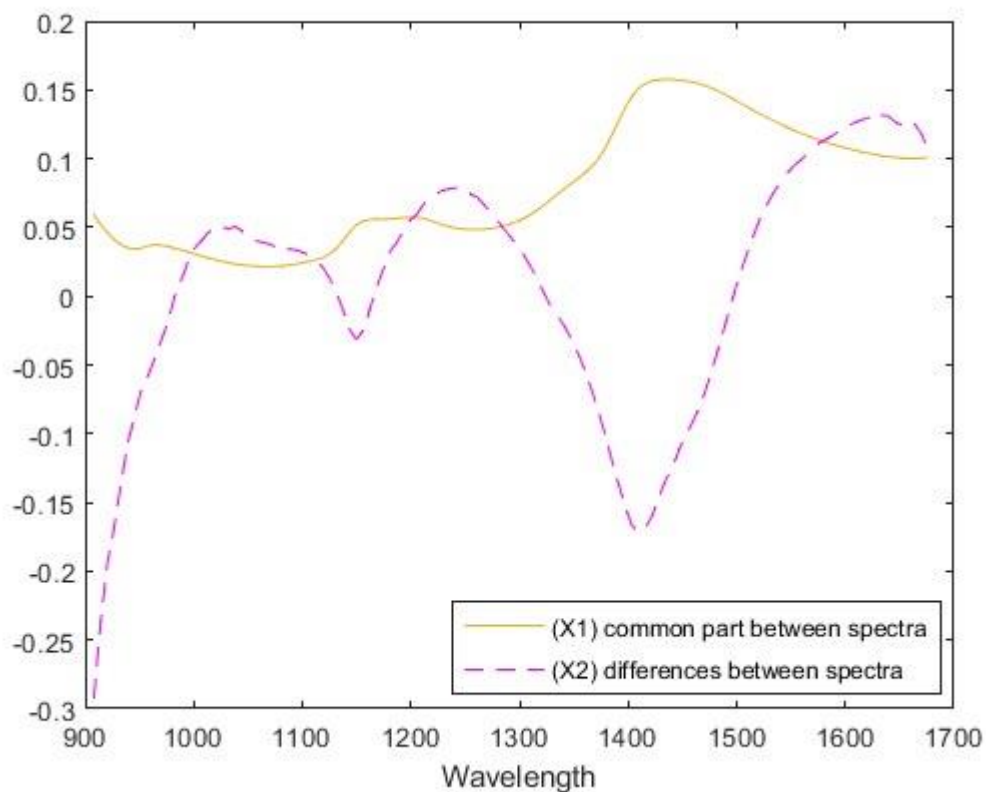


Figure 9. Projections X_1 and X_2

X_2 shows that the differences between the two components are located in the left part of the spectra (around 900 nm) and at two different peaks: 1150 nm and 1400 nm. The left part of X_2 is related to scattering, which is present in the model since samples have not been pre-processed. Indeed, scattering adds baselines to the NIRS absorption spectra which, to a first approximation, are slopes. The higher the scattering, the steeper the baseline slope. Since S_2 (red line on Figure 8) has a steeper slope and is higher than S_1 (blue line on Figure 8) in the 900 - 950 nm region, and since the concentration of S_2 increases over time, it can be inferred that scattering increases during the preparation. At the beginning of the preparation, the mixture appears as a liquid, in which the NIRS radiation can penetrate quite freely. Although light scattering is significant, it is only due to the presence of the milk micelles and the flour grains suspended in the water. As the starch gel forms, the medium becomes structured into a network. The whole material becomes diffusive and the scattering increases.

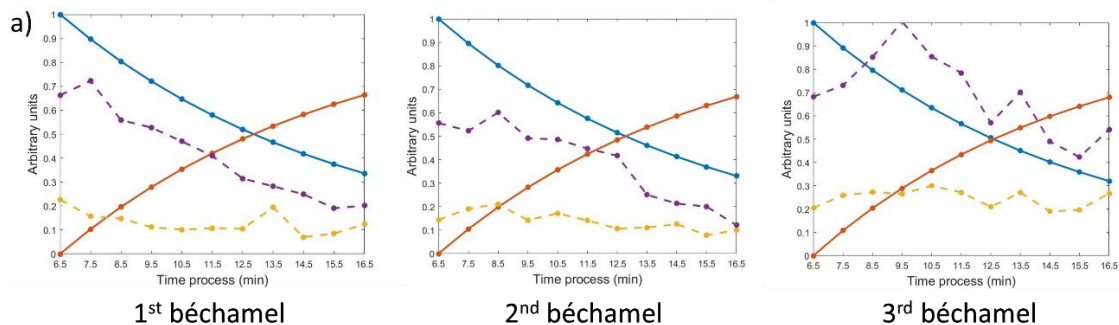
The other two structures that appear in X_2 are two peaks at 1150 nm and 1400 nm, both related to water. Since the amount of water in the sauce does not change, it is inferred that X_2 is related to a change in the binding of the water. In the measured spectra (Figure 4), peaks were observed in the same areas, but much broader. The peak at 1150 nm was related with water (Salgó & Gergely, 2012). In the 1400 – 1490 nm region, several water-related peaks can be observed, the wavelength of which depends on the binding state of the water molecules (Williams, 2009). The fact that the X_2 peaks are negative and, given that the C_1 concentration is decreasing, tells us that the free water decreases during the preparation.

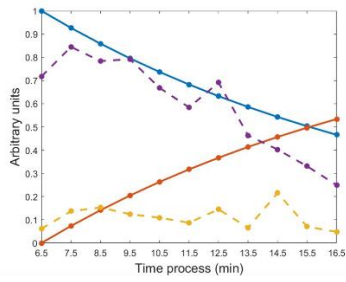
3.3 Simultaneous MCR-ALS analysis of all experiments.

An advantage of analysing several experiments simultaneously is that the results are more reliable and the extracted features are common to all experiments. Thus, we can expect to extract more information about the béchamel trait variability. To extend MCR-ALS to the simultaneous analysis of all the evolving béchamel sauces, it is required that the pure spectral signatures of all species involved in the process do not change among experiments. No significant differences between resolved pure spectral signatures of all 27 béchamels were found (Figure not shown) and, hence, performance of the simultaneous treatment of all experiments can be attempted.

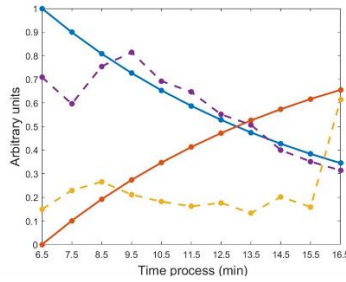
Firstly, a simultaneous analysis by MCR-ALS with soft-modelling constraints was performed, obtaining a LOF = 1.51 % and a $r^2 = 99.9$ %. Now, in contrast to analysis of a particular experiment, resolution of four species is proposed. As in individual analysis, the two species process pattern is observed (Figure not shown). These two species suggest again the underlying kinetic model $(A \xrightarrow{k} B)$. However, two new species (C and D) not involved in the proposed kinetic model were needed to achieve a complete description of the measurements. These new contributions could be originated to fit the slight spectral differences among experiments.

Afterwards, simultaneous analysis of the different experiments were performed using a hard-modelling constraint, forcing the concentration profiles involved in the kinetic process to obey the shapes described by this kinetic model. As mentioned before, it is possible to constrain in a different way the concentration profiles in \mathbf{C}_k , i.e., the hard-modelling constraint can be applied to some or to all concentration profiles in \mathbf{C}_k . Taking into consideration the assumption that species C and D are not involved in the kinetic process, these species were modelled using only soft-modelling constraints. On the contrary, species A and B were fitted to the proposed kinetic model. Once the repeatability of replicate experiments was checked and the possible outlying experiments were eliminated, each béchamel and its replicates were fitted to a single global model. This means that 27 global models incorporating species A and B, each related to a different béchamel, were fitted in the simultaneous analysis. Therefore, the differences between the evolving béchamel sauces could be more easily interpreted. C and D species were left out of the kinetic model. The resolved augmented concentration matrix (\mathbf{C}_{aug}) and the pure spectral signatures (\mathbf{S}^T) of the simultaneous analysis of the 27 evolving béchamel sauces (only the first replicate as an example) are shown in Figure 10. \mathbf{C}_{aug} and \mathbf{S}^T of the four replicates of the simultaneous analysis of the 27 béchamel sauces can be seen in Figure 1 of the supplementary material. A good data fit (LOF = 5.4 % and $r^2 = 99.7$ %) was achieved. Also, the kinetic rate constants, k , were outputted as additional information (Table 1 of the supplementary material).

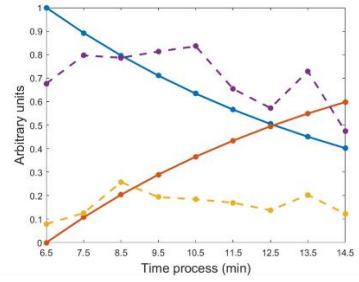




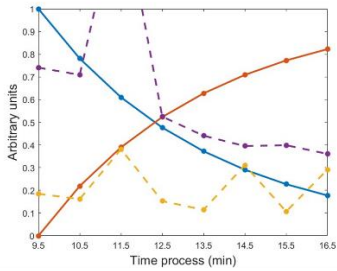
4th béchamel



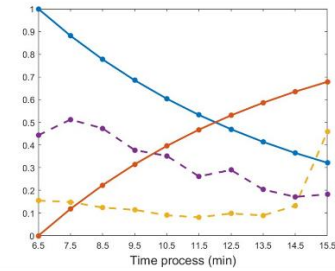
5th béchamel



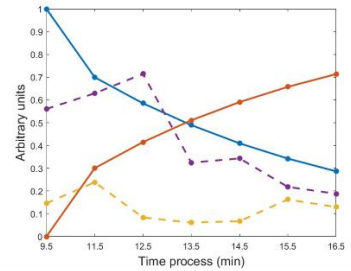
6th béchamel



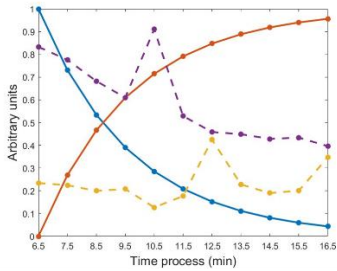
7th béchamel



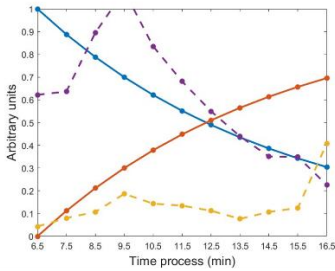
8th béchamel



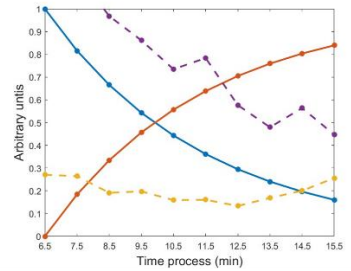
9th béchamel



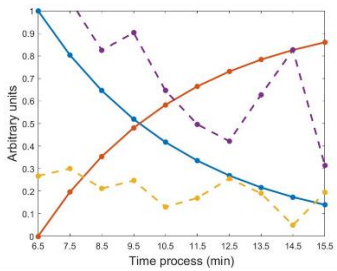
10th béchamel



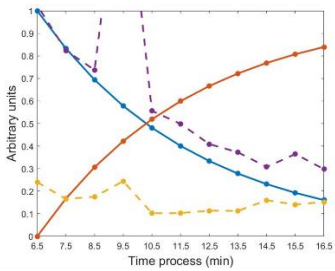
11th béchamel



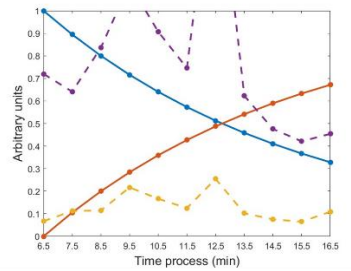
12th béchamel



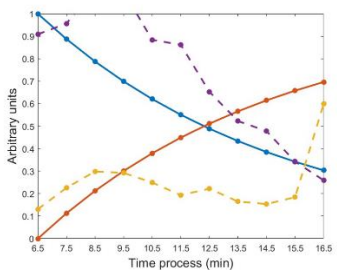
13th béchamel



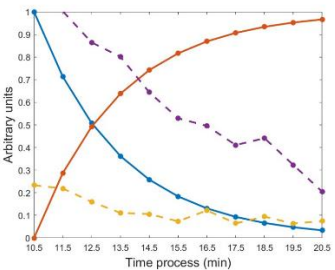
14th béchamel



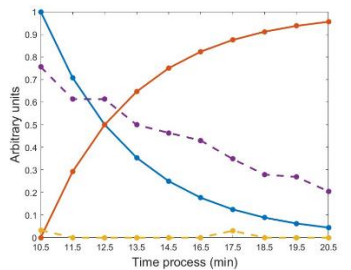
15th béchamel



16th béchamel



17th béchamel



18th béchamel

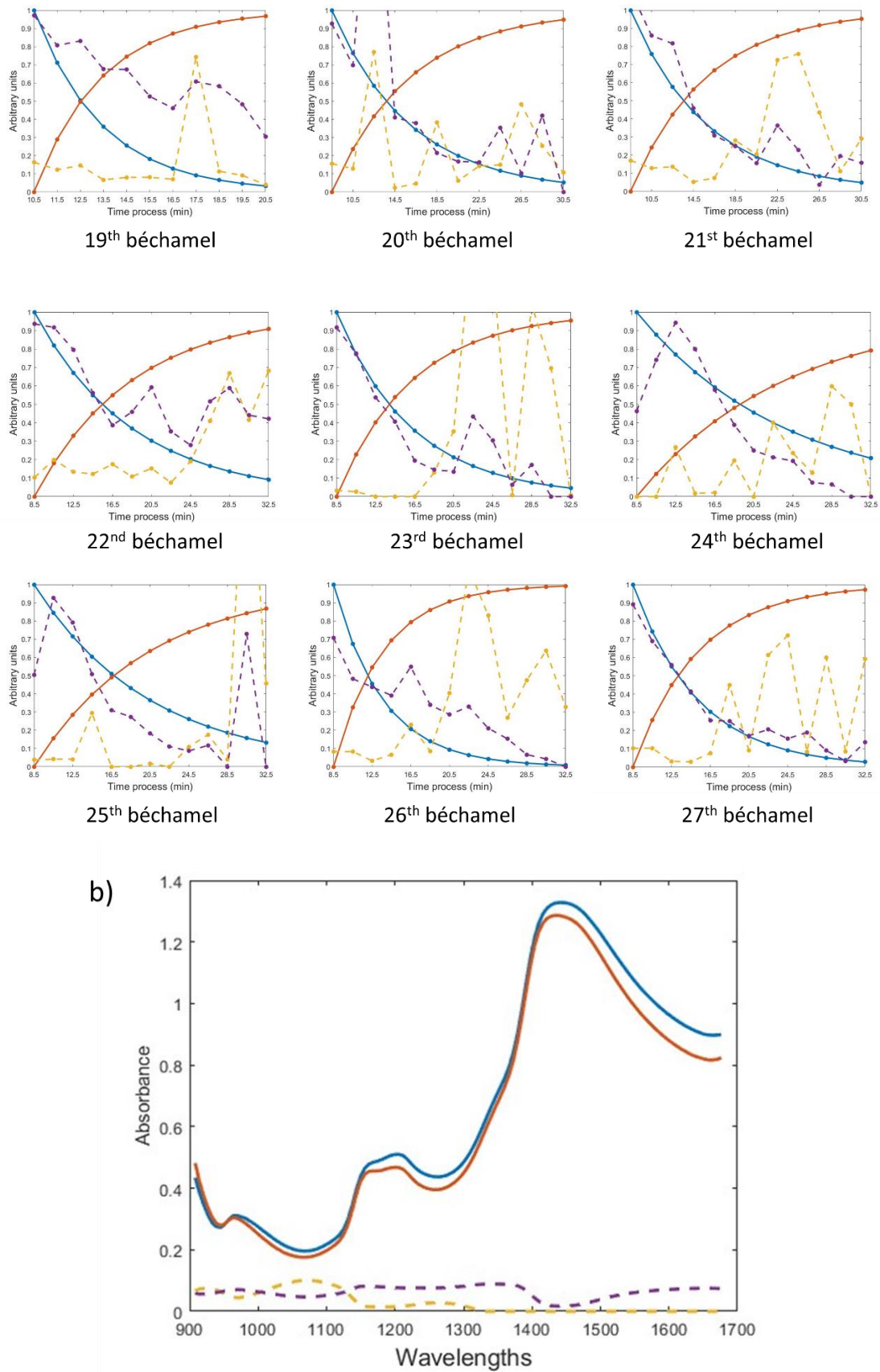


Figure 10. MCR-ALS results for the multiset analysis of the 27 experiments (only the first replicate is shown): a) kinetic profiles of each experiment from the augmented concentration matrix (C_{aug}); b) related pure spectral signatures. Continuous lines correspond with species A (blue) and B (red). Discontinuous lines are C and D, the species left out of the kinetic model

As it can be seen in Figure 10, the resolved concentration profiles are consistent with the reference kinetic model and with the pure spectral signatures obtained in the individual and in the simultaneous analysis. In all the cases two resolved concentration profiles are obtained, which suggests a kinetic model based on a first order reaction ($A \xrightarrow{k} B$), where A decreases while B increases, and the spectral contributions of species C and D were also needed to perform the complete description of the data set.

At some time during the cooking process the two concentration profiles cross, and the time when this occurs seems to be related with the value of k. As an example, 4th and 24th béchamel sauces, where the crossing of the curves take place later (around 16 and 19 minutes), present the smallest value of k (0.08 min⁻¹ and 0.06 min⁻¹). On the other hand, 18th and 19th béchamel sauces, whose concentration profiles cross before, around 12 minutes, have the biggest value of k (0.35 min⁻¹ and 0.34 min⁻¹). To better understand these differences, Figure 11 shows a representation of the constants k versus temperature recorded at the beginning of the elaboration of each sauce (6.5 min).

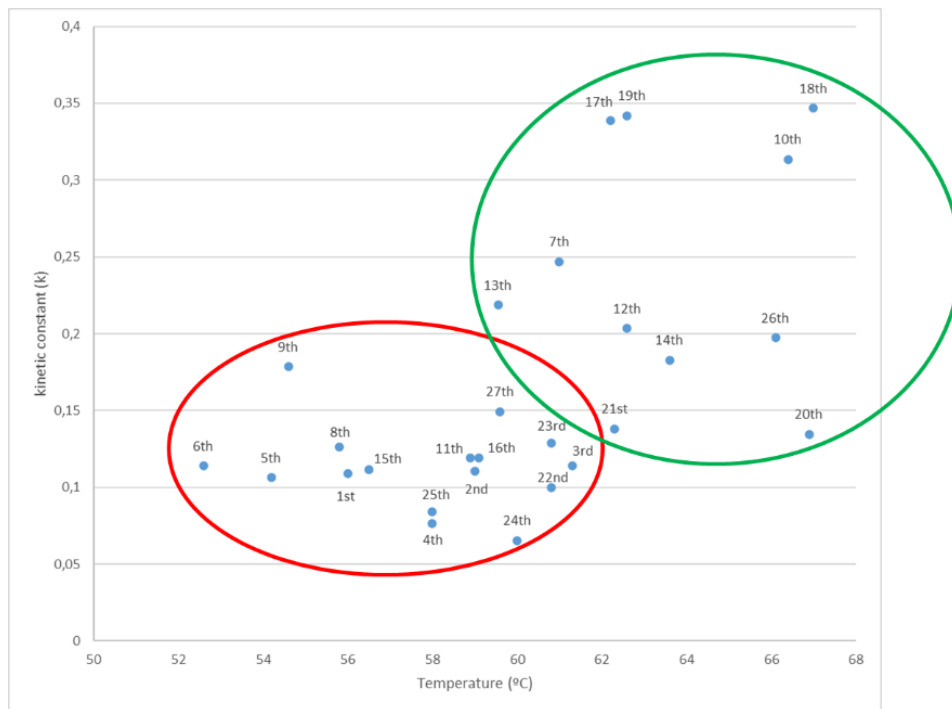


Figure 11. Representation of the kinetic constant (k) of the 27 experiments vs their initial temperature. The ordinal numbers in the graphic correspond with the number of the experiment. The red and green circles correspond to the classification of the experiments according to their k and initial temperature.

The differences observed on the kinetic constants extracted from the MCR-ALS analysis, as it can be seen in Figure 11, are related with the initial temperature of the cooking process. This makes sense considering that heat is one of the variables related with the gelatinization of starch (Ratnayake & Jackson, 2008). Although all the experiments were conducted following the same procedure, differences in the heating of the electric cooker can change the initial temperature of the sauces, making involuntary changes in the kinetics of the cooking process.

Observing Figure 11, the sauces elaborated can be classified in two different groups, according to their k value and the initial temperature of the process. The first group, composed by the béchamel sauces in the red circle, is made of the sauces with the lowest k value. The kinetic constants are a measure of the speed of the process (the higher the k value, the faster occurs the reaction $A \xrightarrow{k} B$), so these béchamel sauces can be described as the slowest, since the reaction takes longer to occur. The initial temperature in all the cases is below 62 °C. The second group is composed of the béchamel sauces in the green circle. In this group the k values are highest, meaning that the reaction in these sauces occurs faster. The initial temperature is in most of the cases higher than 62 °C.

The differences between the two groups can be explained by the differences in the initial temperature. The peak temperature in wheat starch (the temperature of the beginning of gelatinization process, where the crystal melting starts) is around 61.6 °C (Ratnayake & Jackson, 2008). In the first group, this temperature had not yet been reached when the initial temperature was recorded, so that these sauces needed more time to start the gelatinization process, thus being slower. On the contrary, the sauces of the second group had reached the peak temperature, so that the gelatinization process had already started when the initial temperature was recorded, being therefore faster.

However, some atypical béchamel sauces which do not follow exactly that pattern are found. For example, the 20th béchamel has one of the highest initial temperatures, but the kinetic

constant is lower than 0.15. On the other hand, the 9th béchamel, with an initial temperature around 54°C has a kinetic constant around 0.17. In these cooking process it is possible that the temperature was recorded in a different point of the frying pan, since only one measurement of temperature was done in each stage and the temperature of the frying pan was not the same in all the surface.

3.4 SEM images

The SEM images obtained during the different stages of the cooking process of the béchamel are shown in Figure 12.

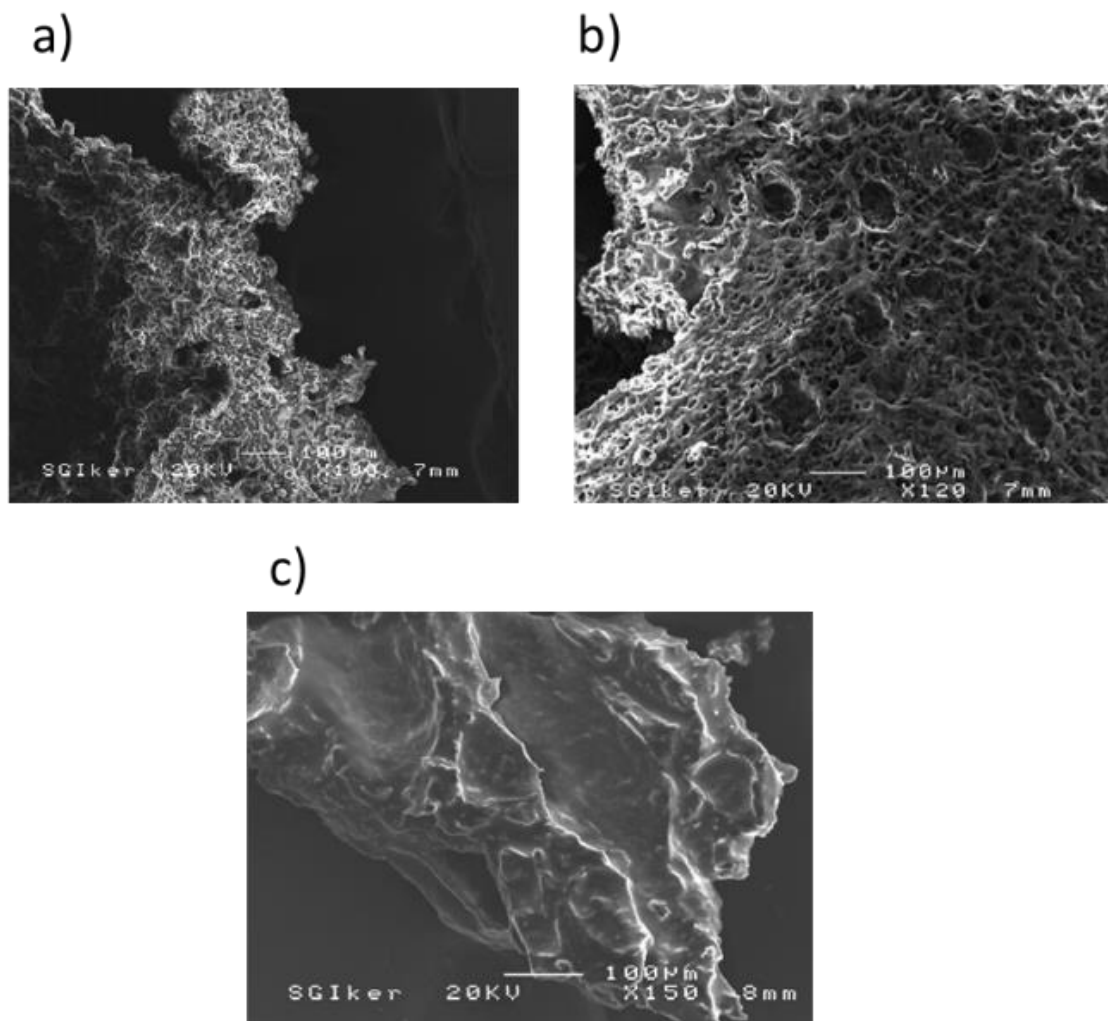


Figure 12. SEM images of the process of the bechamel cooking. A) Béchamel extracted at minute 6.5; b) béchamel extracted at minute 16.5; c) béchamel extracted at minute 26.5.

In Figure 12 three images of fragments of the lyophilised sauce can be observed, where the evolution during the cooking process is shown. Specifically, the evolving béchamel sauces go from a structure full of holes (Figure 12a, béchamel extracted at minute 6.5), going through a structure slightly more compacted (Figure 12b, béchamel extracted at minute 16.5) to a compact matrix (Figure 12c, bechamel extracted at minute 26.5). Similar structures can be found in other studies, where SEM was used to analyse freeze-drying starch samples which have undergone a heating process (Ratnayake & Jackson, 2006).

This evolution is related with the results obtained by MCR-ALS, specifically with the concentration profile which is decreasing (C_1). As it was explained in 3.2, component A is related with the diminution of the free water, which during the cooking process is gradually enclosed in the starch network, being transformed into water bounded to the starch by hydrogen bounds (Tako et al., 2014). Before the SEM analysis, samples were lyophilized, so that the free water was removed. However, bounded water is difficult to remove only with lyophilization (Joardder et al., 2019a; Joardder et al., 2019b). The first two images (Figure 12a and 12b), where the béchamel is still undergoing the cooking process, present big holes, which may be caused by the removal of the free water. The third image (Figure 12c) shows a massive structure without any holes. At this point of the cooking process the water is possibly bounded to the starch due to the gelatinization process, which is the reason why it was not removed during the lyophilization.

4. Conclusions

This work shows the potential of the combination of NIRS and MCR-ALS for studying the cooking process of béchamel sauces. In particular, the usefulness of NIRS coupled with MCR-ALS for the observation of the underlying processes that take place during the elaboration of the sauce was demonstrated.

The individual analysis has allowed to relate the concentration profiles with a kinetic model based on a first order reaction, where the concentration profile of the first species decreases while the second increases at a constant rate, k . The analysis of the obtained pure spectral signatures allowed to relate both species with the increasing of the scattering and the evolution from free to bounded water, which was also observed by a SEM analysis. While analysing simultaneously the different béchamel elaborated in a single multiset structure this kinetic model could be seen again ($A \xrightarrow{k} B$), although two more species (C and D) were needed to describe the whole dataset. The kinetic constant, k , was influenced by the initial temperature of the process, achieving the crossing of the concentration profiles before in the experiments with a higher constant value.

More studies must be done with the objective of controlling the elaboration of béchamel sauces using smart sensors. However, this study present as a first step an exploratory analysis, which will allow to understand the kinetics and the chemistry behind the process. Since the behaviour of béchamel sauces during their elaboration has been stablished, industrial producers would benefit from its use to control if the cooking process of the sauces is behaving as expected, and if not, try to make corrections on real time.

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Declarations

- Conflict of Interest: The authors declare no competing interests

Author contributions

Conceptualization, Sonia Nieto-Ortega, Silvia Mas García, Jean-Michel Roger; Methodology, all authors participated in the methodology; Validation, Silvia Mas García; Formal Analysis, Sonia Nieto-Ortega, Silvia Mas García, Jean-Michel Roger; Investigation, all authors participated in the investigation; Data Curation, Sonia Nieto-Ortega, Silvia Mas García, Jean-Michel Roger; Writing – Original Draft Preparation, all authors participated in the original draft preparation; Writing – Review & Editing, all authors participated in the review and editing process; Visualization, Sonia Nieto-Ortega, Silvia Mas García, Idoia Olabarrieta; Supervision, Jean-Michel Roger; Project Administration, Idoia Olabarrieta; Funding Acquisition, Ángela Melado-Herreros, Giuseppe Foti, Idoia Olabarrieta.

Data Availability Statement: The datasets generated during and/or analysed during the current study are not publicly available due to confidential reasons.

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