Toward the implementation of mid-infrared spectroscopy along the processing chain to improve quality of the tomato based products

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Abstract

The mid-infrared spectroscopy (MIRS) was investigated as a tool to improve the quality of tomato products considering its implementation at different steps along the processing chain.

Models have been developed using partial least square (PLS) regression to predict the quality of raw and processed tomatoes. A relevant method (Multi-year Combining models) consisting in adding early-season tomatoes data within models developed using data of previous years, was shown as the most efficient and adapted to realistic industry conditions. MIRS predicted, in external validation, soluble solids content (R^2 0.95), titratable acidity (R^2 0.88) and dry matter content (R^2 0.81) with a high accuracy of 0.1°Brix, 2.8 mmol H^+/kg and 0.4% respectively.

Secondly, MIRS was used to classify tomato products depending on processing methods (hot- or cold-break) or varieties using factorial discriminant analysis (FDA) based only on spectral data. MIRS was assessed as an efficient tool to classify processed tomato purees according to process, year and variety, more accurately than the classification obtained with the reference data.

A possible implementation of MIRS was suggested at three strategic steps along the processing chain to i) characterize the incoming raw material, ii) monitor the matrix changes during processing and iii) control the final products.

Keywords: Industry-type tomato, quality, ATR-FTIR, prediction, classification.

Highlights:

- Strategies are setup to build robust models to predict tomato quality traits.
- MIRS allows an accurate classification of hot-break and cold-break tomato products.
- An efficient implementation of MIRS along the processing chain is proposed.

Introduction

Processed tomato trade is a competitive market, with a few major producers such as California (11 Mt/year), Italy (6 Mt/year) or China (5 Mt/year), and a number of smaller ones, such as France producing 180 000 t/year, but also importing more than 100 000 t/year. Tomatoes are processed into various base products such as raw juice, low concentrated 'passata', and up to highly concentrated tomato paste. Base products are then used as ingredients to generate various manufactured products such as soups, ketchup or sauces. To promote their products, most producers act on quality, leveraging on variety and local production, but also by developing specialties from juices directly concentrated at the right expected dry matter content. This avoids diluting highly concentrated tomato pastes as traditionally operated by many industrial tomato users. This trend results in an increased demand from the companies to sort and pay the raw material according to their quality. This includes not only the traditional soluble solids content (SSC expressed in degree Brix), but also the real dry matter content (DMC, including also insoluble component, more likely correlated to viscosity) and some new sorting criteria which should be developed. For example, the ability to process a viscous and colored product, or the ability to determine when the product reaches the expected quality according to guidelines during and after the manufacturing of products would be an achievement. The implementation of infrared tools throughout the production chain is therefore an issue for producers and processers to reach these objectives. This technique is already used in many other productions regarding quality targets. In the dairy industry, mid-infrared analyzers (MIRS) are used since 1964 and improved over years to provide a rapid determination of fat, protein and lactose content of milk (Barbano and Clark, 1989; Lynch et al., 2006). Today, MIRS assists most payment of milk and dairy products. Concerning cereals, MIRS is used to classify flours according to landraces or technological treatments (Cozzolino, 2014) and to determine their contents in proteins, lipids, ash and moisture (Sujka et al., 2017; Shi and Yu, 2017) and even further the intestinal digestibility of their proteins (Shi et al., 2019). Tomato industry still barely uses MIRS, despite strong needs for prediction tools associated to quality.

In the order of trade relevance, quality attributes of tomato products are their rheological properties (determining whether they are more or less viscous), their color (preferred as deep red as possible), and still to a lower extend, their taste and aroma. Viscosity mainly depends on processing methods. The critical steps are the breaking temperature (i.e. temperature at which fruits are crushed and initially heated) and the progressive juice concentration by thermal treatment under vacuum (Barrett et al., 1998; Page et al., 2012). Some cultivars were also selected for their ability to produce various levels of viscosity (Svelander et al., 2010; Ayvaz et al., 2016). However, the biochemical and physical factors driving puree viscosity remain not fully understood, and therefore viscosity is still empirically controlled in industry. Relationships between viscosity and microstructure (particle size and shape and serum viscosity), dry matter content (DMC) or pectin composition have been established (Barrett et al. 1998; Anthon et al., 2002; Moelants et al. 2014; Santiago et al. 2017), but no direct model taking into account those parameters allows an accurate prediction of puree viscosity from those biochemical data. As soluble solids content (SSC) has been partially correlated to DMC, the refraction index (which allows for a rapid evaluation of the SSC, expressed in Brix degree) is currently used all along the production chain as an evaluation of DMC, being often considered as an indirect indicator of the viscosity. Some companies are even using a price-increase according to SSC to encourage the incoming of high SSC tomatoes in the factory, expecting these tomatoes to also have a high DMC (Foolad, 2007). However, DMC corresponds not only to SSC (mainly sugars and acids) but also to insoluble solids (such as pectins and other cell wall components, proteins, lipids, pigments) and therefore DMC should be a more accurate marker of the rheological properties. On another side, titratable acidity (TA) affects the taste in balance with sugars. Measuring SSC together with DMC and TA is therefore relevant to follow tomato quality. But, as their measurement on fruit is time consuming, SSC is generally the only measurement, and its correlation to other traits is empirically expected. However, the relationships between SSC, dry matter content and puree viscosity become weak when a large variability of genotypes and various growing conditions are taken into account (Arbex de Castro Vilas Boas et al., 2017), and therefore, SSC is becoming of poor interest to predict DMC or viscosity. Color and taste mainly controlled by sugar, acid, volatile and lycopene content, are all strongly dependent on genetic factors as well as on the ripening stages at harvest (Saha et al., 2010; Figas et al., 2015). The processing treatments also affect the biochemical composition of puree (Svelander et al., 2010; Wilkerson et al., 2013; Lijima et al., 2016; Page et al., 2019). Still, neither global model nor easy-to-measure parameters are available to predict or measure their real influence.

Using MIRS coupled with the Attenuated Total Reflectance (ATR), provides a solution well adapted to aqueous samples such as juices and purees (Kemsley et al., 1996; Garrigues and Rambla, 1998). MIRS allows an accurate evaluation of dry matter content (DMC), soluble solids content (SSC) and titratable acidity (TA) based on one single spectrum acquired in a few seconds, compared to the time-consuming reference methods (Beullens et al., 2006; Scibisz et al., 2011). Such an efficiency is compatible with the cadency required for the grading of incoming raw tomatoes when trucks deliver them to factories. Quality traits such as sugar content, pH and viscosity are also predicted in hot-break cooked tomato juices by MIRS (Wilkerson et al., 2013; Ayvaz et al., 2016).

Despite those relevant results, strategies to adapt this technique to real industry conditions remain poorly documented. Therefore, the objective of this paper was to test several options to implement MIRS at three specific steps of the value chain of tomato products:

i) On fresh fruits, to develop accurate PLS models in order to predict, in a single run, a complete composition of the raw materials before processing such as dry matter content (DMC), soluble solids content (SSC) and titratable acidity (TA) instead of the only Brix degree actually measured as a biochemical quality trait of tomato. Here, strategies were compared to gain in efficiency to develop models taking into account industrial habits and constraints. (Figure 1).

ii) On fresh tomatoes and their corresponding purees, to verify if samples from an experimental design including genotypes x years x processing conditions can be discriminated using discriminant analysis (FDA). As the processed purees exhibit a large variability of quality traits, the objective was to evaluate if MIRS could detect puree variability according to the characteristics of the raw tomatoes.

iii) And on manufactured products, to assess the MIRS accuracy as a tool for assisting quality and traceability control. This was performed using both, data of our laboratory and data from the industry to measure whether correlations can be found between MIRS and quality measurement currently achieved by industry.

1. Material and methods

1.1. Plant materials and processed samples

1.1.1. Fresh tomatoes

Tomatoes were harvested over two years (2014-2015), all over the production area in France. In 2014, 102 samples from 30 varieties were collected in the South-East (Vaucluse and Bouches-du-Rhône Counties) as well as in the South-West (Lot-et-Garonne County) of France, from the 24th of July to the 10th of September at breaker, ripe and overripe ripening stages. In 2015, 144 samples from 45 cultivars were collected in the same areas, from the 20th of July to the 15th of September, but only at ripe and overripe stages. Samples included a core collection of 14 genotypes, namely Caladou, Delfo, H1293, H1301, H1311, H9036, Impact, Increase, ISI29714, JAG8810, Leader, Perfect Peel, Pietra Rossa and Terradou, which were planted every year in every location to measure the inter-annual and the local variability.

For each sample, 15 fruits were randomly harvested on three plants, cut into pieces of around 2 cm^3, quickly frozen and stored at -20°C. Before analysis, the tomato pieces were thawed and homogenized in a Waring blender. Fruit homogenates were used for the biochemical and spectral characterization.

1.1.2. Puree processing at the laboratory scale

In 2016 and 2017, four cultivars (Terradou, H1015, H1311 and Miceno) were cultivated in an experimental design including two irrigation levels and two blocks per treatment (Arbex de Castro Vilas Boas et al., 2017).

For each sample, about 1 kg of tomatoes was prepared as follow: a 1-cm slice was cut in the central part of each fruit and slices were directly stored at -20°C, representing the fresh tomatoes. The rest of the fruits were cut into 2-cm² pieces. All pieces were mixed and split into two similar samples dedicated to the hot break (HB) or cold break (CB) standard processing (Page et al., 2012). Both processing routes used the same heating and grinding energy, and only the order of each unit operation changed. Tomatoes for HB purees were first heated (microwave oven, 900 w, full power, 0.9 sec/g of tomato) and then grinded (30 seconds in a Waring blender) whereas the CB tomatoes were first grinded, macerated at room temperature for 30 seconds (allowing for intrinsic enzyme reactions) and then heated.

After cooking, purees were stored into 400-ml glass jars, pasteurized (100°C, 15 min) and stored at 4 °C until analyses. A total of 336 samples were characterized in 2016 and 2017, as fresh tomatoes, HB and CB cooked purees.

1.1.3. Industrial products

In 2015, 140 tomato-based products (juices, purees and pastes) were collected from two factories located in South-East (Tarascon) and South-West (Bergerac) of France. Their soluble solids content (SSC) and viscosity were measured in parallel by the quality control of the factories and by our laboratory.

1.2. Reference analyses

Soluble solids content (SSC) was determined with a digital refractometer (PR-101 ATAGO, Norfolk, VA) and expressed in °Brix at 20°C. Titratable acidity (TA) was determined by titration up to pH 8.1 with 0.1N NaOH and expressed in mmol H^+/kg of fresh weight using an autotitrator (Methrom, Herisau, Switzerland). The dry matter content (DMC) was determined by weighing and drying 3 g of samples in air oven at 7O°C to reach a constant weight. The viscosity was measured as described by Arbex de Castro Vilas Boas et al. (2017) using a viscosimeter (Anton Paar MCR 301, Graz, Austria). For the industrial products, consistency was measured using a Bostwick consistometer (CSC Scientific Company, Fairfaix, USA) and according to manufacturer's guidebook, results were expressed as arbitrary Bostwick unit (Bw). The lower the Bostwick value, the higher the consistency.

1.3. Mid-Infrared Spectroscopy analyses

Spectra were recorded as described by Bureau et al. (2009) at room temperature with 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. In the range between 4000 and 400 cm^{-1} light penetrates from about 0.4 to 4 µm (Bureau et al., 2019). The total optical path is therefore 2.4 µm at 4000 cm^{-1} and 24 µm at 400 cm^{-1} taking into account the six internal reflections.

1.4. Chemometrics

Spectral preprocessing and multivariate data analysis were performed as described by Bureau et al. (2013) with Matlab 7.5 (Mathworks Inc.Natick, MA) software using SAISIR package (Cordella & Bertrand, 2014). The absorption band around 2400 cm^{-1}, due to carbon dioxide, was discarded. Spectra were systematically pretreated with the standard normal variate correction (SNV).

1.4.1. PLS modelling

Models were developed by partial least squares (PLS) regression on the fresh tomatoes harvested in 2014 and 2015 (see § 1.1.1). In PLS, orthogonal latent variables are iteratively constructed by maximizing the covariance between the two matrices of data set, the spectral data (X) and the quality traits (Y, reference data) (Nicolaï et al., 2007). In a first step, models were calibrated and validated by randomly splitting the data set into a sub-set of calibration data (2/3 of the data) which was used to build the model, and a sub-set of validation data (1/3 of the data) for which the content was predicted by using the previous built model. The root mean square error (RMSE) between predicted and measured values was estimated to evaluate the accuracy of the prediction. The random selection of calibration/validation data was repeated 10 times for each quality trait and the RMSE value was recalculated in order to examine the stability of the model. In a second step, models were evaluated by an external validation, consisting in predicting the composition of an independent validation data set, not used for the internal validation.

The performance of models was evaluated by the determination coefficient of calibration and of validation (R_c^2 and R_v^2), determination coefficient of external validation (i.e. prediction) (R_p^2), root-mean-square error of calibration and of validation ($RMSE_C$ and $RMSE_V$) and root-mean square error of external validation ($RMSE_p$). Finally, the ratio of prediction to deviation (RPD) corresponding to the ratio of the standard deviation of the reference data to the RMSE was calculated. A RPD between 1.5 and 2 concerns a low performance model which can only discriminate low from high values; a value between 2 and 2.5 indicates a coarse quantitative prediction, and a value between 2.5 and 3 or above corresponds to good and excellent prediction accuracy, respectively (Nicolaï et al., 2007).

Three strategies were tested on the raw materials. The first one consisted in building models only based on one-year data in 2014 and 2015 (named YPY), the second one in building one global model combining total data of the two years (named GlC) and the third one in combining data of 2014 and a part of 2015 data corresponding to samples harvested during the early season of 2015 (before August, the 18th) (named MYC) (Figure 1). All models were compared using internal and external validations when possible.

1.4.2. Discriminant analysis

Factorial discriminant analysis (FDA) was performed to test the ability of MIRS to discriminate samples according to the known qualitative groups (genotypes, years and cooking procedures). FDA (Factorial Discriminant Analysis) was performed on samples characterized in 2016 and 2017, as fresh, HB or CB processed purees as described in § 1.1.2. It was carried out in two steps: 1) Principal Component Analysis (PCA) was calculated on the spectral data to visualize the samples distribution according to the most discriminating spectral ranges identified with the eigenvectors and 2) FDA was applied on the gravity centers of each qualitative group assessed on the normalized principal component scores (Bertrand et al., 1990).

2. Results and discussion

2.1. PLS models to predict quality traits of fresh tomatoes

2.1.1. Variability of the samples used to build models

To make our models as generic as possible, the sampling included 59 varieties harvested out of two regions of France, over two years and at three maturity stages (see § 1.1.1). The values ranged from 3.6 to 7.5°Brix for SSC, from 4.7 to 11.1% for DMC and from 30.2 to 81.7 mmol H^+/kg for TA (Table 1). Fruit quality varied for the reference data, and especially, a year effect was obvious on the relationship between SSC and DMC. The groups of points of each year, 2014 and 2015, are parallel indicating that the classification of varieties remained similar but, for a similar SSC, DMC revealed variations from 1 to 2% (Figure 2A). This was also the case for the core of 14 varieties present in the 2014 and 2015 data sets. The year effect was not so clear for the spectral data. On PCA plot calculated using spectra of the two years, the 2015 samples covered a larger variability than the 2014 ones. This was probably related to the higher number of genotypes in 2015 than in 2014 (respectively 45 and 30) (Figure 2B).

Our results were in accordance with data already reported for processing tomatoes grown in California counties between 2010 and 2014, and particularly for SSC which ranges from 3.2 to 7.2°Brix in (Wilkerson et al., 2013; Ayvaz et al., 2016). The set of samples covered a large range of the variability generally observed for industry-type tomatoes. This permits a standard robustness of calibration models, as robustness is directly related to the variability of the samples (Nicolai et al., 2007).

2.1.2. Comparison of strategies to build accurate and robust models

a) Model calibration and validation

Any of the three strategies (YPY, GlC or MYC) gave accurate results to predict SSC. Similar results were obtained for calibration and validation with R_c^2 and R_v^2 between 0.93 and 0.97 and $RMSE_{c\ and\ v}$ between 0.13 and 0.16°Brix, leading to a RPD equal or above to 3.6 corresponding to a highly accurate prediction. The MYC model obtained the highest RPD. Globally, RPD of models for SSC exhibited the highest RPD among the quality traits (Table 2). Our results were similar to those previously obtained on tomato fruits for the fresh market exhibiting SSC from 3.2 to 8.8 °Brix while our data exhibited no SSC above 7.5 °Brix (Scibisz et al., 2011). Similar results were obtained on industry-type tomatoes grown in California, as SSC is predicted with R_v^2 varying from 0.86 to 0.98 depending on the years, regions and varieties (Wilkerson et al., 2013; Ayvaz et al., 2016). Our data confirmed that SSC is extremely well predicted by MIRS.

For the DMC parameter, models still exhibited high performance although the values were not as good as for the SSC models. R_v^2 varied from 0.82 to 0.94 and RMSE from 0.24 to 0.49%. The RPD was in all cases higher than 2.5, and then within the highly accurate values for predicting models (Nicolaï et al, 2007). The YPY models exhibited RMSEv of 0.25% in 2014 and 0.41% in 2015. The higher variability of fruit DMC in 2015 than in 2014 could explain the results. The differences between min and max values were 5.4% in 2015 but only 3.1% in 2014 (Table 1). RPD values indicated some differences of model performances. The MYC model exhibited the highest values of R_v^2 (0.94) and RPD (3.9). Similar results with RPD of 4.8 are obtained on tomatoes for fresh market using a dataset including a large number of traditional varieties conferring a variability similar to that of our experiment (Scibisz et al., 2011).

As for DMC, models predicting TA did not present the same accuracy over the two years (Table 2). In 2015, models exhibited higher R_v^2 and RPD than in 2014, even if the $RMSE_v$ remained close around 2.2 mmol

H^+/kg. As for DMC, the range of TA was larger in 2015 (30.2-81.7 mmol H^+/kg) than in 2014 (45.3-76.8 mmol H^+/kg) (Table 1). This impacted the RPD values. However the prediction of TA remained within the excellent RPD values (≥ 2.5). For TA, our results were similar to those obtained on fresh tomatoes by Scibisz et al. (2011) and on industry-type tomatoes by Wilkerson et al. (2013).

So, combining data of different years in GlC models did not affect the model performance, except an increase of the $RMSE_v$ for TA, in comparison with the YPY strategy (Table 2). However, RPD remained acceptable for the three predicted quality traits with values ≥ 2.5. An interesting result came from the MYC strategy. By introducing new data every year, and especially the data of the early tomatoes, the MYC models were as accurate as the GlC models for SSC and DMC, despite less samples used to calculate the models. For TA, the MYC and GlC models did not much differ for their R_v^2 but $RMSE_v$ of MYC was the highest, giving a RPD of 2.2. The gain of the MYC strategy was not obvious on the validation results for TA.

b) External validation of models

The external validation constitutes the ultimate validation of predicting models as samples used for validation must differ from samples use for calibration belonging to another sample sets, and here to another year. In this case, the YPY and MYC strategies exhibited contrasted results (Table 3). Concerning the YPY models, predicting 2015 data with the 2014 models resulted in low R_p^2 and RPD and high $RMSE_p$ for the three quality traits, SSC, DMC and TA (Table 3). Predicting 2014 data with the 2015 models led to a better prediction of SSC (RPD of 2.7) but not for DMC and TA. For DMC, RPD was 0.1 due to the $RMSE_p$ of 2.54%, i.e. 5 times higher than the $RMSE_v$ (Tables 2 and 3). For TA, RPD was 0.3 in relation with the $RMSE_p$ of 53.44 mmolH^+/kg, i.e. 10 times higher than the $RMSE_v$ (Tables 2 and 3). These results can be explained by the difference of the fruit variability observed in the two years (Figure 2). The linear relationship between the quality traits, SSC and DMC, may be maintained but contents of DMC changed for a same SSC from one year to another.

The combination of data of several years significantly improved the models. The MYC models, which combined all data of the first year and data of the earliest tomatoes of the second year (2014 + early 2015 until August, 18th) accurately predicted SSC, DMC and TA of the late tomatoes of 2015 (from August, 18th) with similar RPD values (respectively 4.3, 2.8, 2.1) than those previously obtained (Tables 2 and 3). Adding the early data of 2015 within the 2014 data (MYC models) led to a more efficient prediction of the late tomatoes of 2015. Improving models by accumulating new data each year is an approach described by Thomas and Ge (2000) as a passive approach consisting in acquiring calibration data over a sufficiently long period. It tends to cover gradually the fruit variability by including variability such as seasons or years, varieties, orchards in the calibration data to improve the model accuracy as already suggested (Peiris et al., 1998; Peirs et al., 2003; Golic and Walsh, 2006; Bobelyn et al., 2010). Such approach is particularly relevant for the every-day work of the tomato processors. The earliest tomatoes may be used to calibrate and update models each year. The calibrated model can then be used for the rest of the season to accurately predict the quality of the incoming production. At the end of the season, models can be efficiently completed by the addition in the calibration of the most contrasted samples harvested during the running year. They can be identified using their infrared signature in comparison with those already placed on the cartography representing the tomato diversity, and only those samples can be analyzed by reference methods. This method is a way to minimize the quantity of analyses to the most relevant ones, and year after year, this approach leads to a progressive improvement of global models, by taking into account variability of early and late tomatoes as illustrated in this paper (Figure 3).

This demonstration was focused on building PLS models for predicting the quality of raw tomatoes. But one can assume that the same approach could be developed for the prediction of processed product quality as shown by Wilkerson et al. (2013) and Ayvaz et al. (2016). In this case, including variability due to the processing conditions should be considered in addition to all the other sources of variability.

2.2. Towards using MIRS to discriminate fresh fruits and processed products according to varieties, years and processing conditions.

Discriminant analysis only based on spectral data was performed on a set of samples issuing from an experimental design to evaluate the ability of MIRS to classify samples according to factors of interest, such as varieties, years and processing conditions. The experimental design included four varieties, two irrigation levels and was reproduced in 2016 and 2017 (see § 1.1.2). Samples were analyzed as fresh fruits and after a hot or a cold break processing, and all samples were evaluated for their SSC, TA and DMC using reference methods. Data exhibited a significant impact of the genotype (F=70, Prob>$5.3.10^{-34}$), water scarcity (F=70, Prob>$2.8.10^{-15}$) and processing (F=18.2, Prob>$3.7.10^{-8}$) but no significant impact of the year. However, the year affected standard deviations. In 2016, TA exhibited variations from 59.9 to 89.4 mmol H^+/kg FW while it ranged from 46.6 to 96.9 mmol H^+/kg FW in 2017. The same trends were also observed for DMC and SSC.

Factorial Discriminant Analysis (FDA) performed on spectral data classified the samples in their right classes with only few confusion concerning the processing. All the 144 fresh samples were well classified, 89 among the 96 HB and 94 among the 96 CB were well classified giving a performance of classification of 100% for fresh, 93% for HB and 98% for CB (Table 4). The results on genotype classification was more confused: for the two most contrasted genotypes, most samples were identified in their right classes (70% for H1311 and 90% for Terradou), but the classification was less accurate for the two other genotypes, as only 54% and 67% were well classified for H10 (H1015) and MIC (Miceno) respectively (Table 4). The classification according to varieties was good when FDA was performed separately on each year. On fresh tomatoes, for example, samples of Terradou in 2016 and H1311 in 2017 were 100% well classified whereas for the other varieties the classification was at least higher than 88%.

Nevertheless, when considering fresh and processed samples separately, the FDA gave accurate classifications of the genotypes. Each appeared as distinct and non-overlapped ellipses on the factorial maps (Figures 4A and 4B). Moreover, the classification was partially reproducible from one year to the other. When 2017 data were projected as illustrative data on the factorial map calculated with 2016 data, ellipses from 2017 data remained distinct from one genotype to the others. For two of the genotypes (H1311 and Terradou), 2016 and 2017 ellipses were in a very close area of the factorial map. The same trend was observed in the reverse situation. On this FDA space, the distances between ellipses of each year were greater for Miceno and H1015, but remained in the same region of the map, for fresh products as well as for processed ones (Figure 4). The most significant spectral area distinguishing varieties was between 1200 and 900 cm^{-1} corresponding to absorptions due to stretching and bending vibration modes of sugars (Talari et al., 2017).

Altogether, discriminations based only on spectral data indicated that MIR was a powerful tool to follow tomato quality during processing as it allowed a strict and accurate distinction of fresh, cold or hot break samples. However, the infrared sensors exhibited some limits for distinguishing samples according to the varieties when processed and fresh samples were considered altogether, and especially for those exhibiting similar qualities. This last result should be challenged to a larger range of varieties, as our set of data only contained four varieties, and to a high processing impact according to the genotype. Previous studies on fresh fruits indicated that accurate genotype discrimination is made possible over a larger set of varieties (Ibanez et al., 2019). To our knowledge, our studies was the first on tomato showing that the same kind of distinction remained after fruit processing.

2.3. Toward the use of MIR tools for quality control of manufactured products

The products exhibited a diversity including purees, sauces and pastes giving a large variation of quality traits. SSC varied from 5.3 to 36.5°Brix, pH from 3.9 to 4.7, TA from 44 to 319 mmol H^+/kg FW, DMC from 7 to 45 % and viscosity from 0 to 8 Bw unit (Table 5). SSC vs TA, SSC vs DMC and TA vs DMC exhibited correlations with determination coefficient R_v^2 higher than 0.95. SSC was measured both in the Lab and in the plants giving as expected similar values (R_v^2 = 0.99). TA and DMC were only measured in our laboratory, pH and viscosity only in factories.

A first set of PLS models were built to measure their efficiency for predicting the product composition taking into account their entire variability, from juice to paste (Table 5). SSC was extremely well predicted by MIRS with R_v^2 of 0.99 and error ranged between 0.73 and 0.98 °Brix in Laboratory and in the factories data respectively (Table 5). The RPD, higher than 12, confirmed that SSC can be predicted with a very weak error using MIRS. TA and DMC measured in the Lab exhibited similar levels of prediction with R_v^2 higher than 0.98 and RPD higher than 7.6, as we previously obtained in the other experimental assays. These results were also in accordance with the strong internal correlation measured between those traits in this set of samples. On the contrary, pH measured in the factories was predicted with a R_v^2 of only 0.51 and a RPD of 1.4 (Table 5). The quality of our prediction was lower than that already obtained on industry tomato (Ayvaz et al. 2016). This can be due to the lower size of our sample set (76 instead of 249 for the calculation of the model), and its lower variability (pH ranged from 3.98 to 4.6 instead of 3.8 to 4.6). The prediction of the viscosity (Bw) exhibited an apparent high accuracy. The R_v^2 of validation was 0.77 and the RPD 4.6. However, the high contrast of viscosity between juice and paste and the low quantity of intermediate samples were a concern regarding the statistical analysis. Therefore, in a second step, the models were built after removing pastes in order to have a more continuous and homogeneous set of samples. For all quality traits, RPD values decreased to values close to those obtained in our models on raw fruits (Table 5), assessing the accuracy of prediction on manufactured products.

With this restriction to juices and purees, models exhibited accuracy close to the models obtained by Ayvaz et al (2016), which were also dedicated to tomato juices and purees (between 11 and 25 Bw) and calculated with a large number of samples. Altogether, our results and those of Ayvaz et al. (2016) indicated that predicting consistency by MIRS was certainly possible but hardly in actual realistic industry conditions. Progress should be made in two directions. First, more universal and accurate measurements of the rheological properties should be used as comparing Bostwick values of contrasted products such as juices and purees should include specific corrections (Perona, 2005). Second, the rheology of tomato products does not enforce the same mechanical properties depending on their concentrations. Those properties depend upon biochemical and physical characteristics such as pectin dissolution and modification, particle size and shape and particle packing (Bayod et al., 2008). Each of those characteristics may have diverse MIRS signature, and this could explain why PLS models including pastes and less concentrated products gave less accurate results. For the prediction of consistency, models per classes of products, using a large variability within each class, should lead to models more accurate and adapted to the real industry activity. Combination of models may also rise to accurate results to predict intermediate products between purees and pastes, but require a more specific study.

Conclusions

Our results confirmed that MIRS is a powerful decision-making tool to assist the industry for the improvement of the quality of tomato-based products all along the processing chain. In the realistic industrial context, we demonstrated that MIRS could enhance industrial management at three strategical steps:

- For the incoming tomatoes: as, in a single measure, not only SSC but also TA and DMC can be predicted. MIRS gives a new framework for grading tomatoes regarding their quality.
- For assessing the processing: as Fresh, HB and CB samples can be discriminated, and considering that the sorting of fresh or processed samples was accurate, this indicates that MIRS is a powerful sensor to improve the product traceability before, during and after the processing step. Therefore, development of databases of MIRS spectra needs to be achieved in a large industrial context.
- For the post-processing quality and trade management, as most quality traits of manufactured products (SSC, DMC, acidity, viscosity) seemed to be predictable, MIRS could help for a more pragmatic and complete verification of the accordance of manufactured products regarding the specification books.

MIRS signature is easy and rapid to acquire on homogenous samples such as purees, liquids and pastes compared to the classical measurements by reference methods. MIRS coupled with chemometrics greatly increases the possibilities to enhance the quality, by a better management of raw materials and processed products at all steps of the production chain. Our results give strategies for an industrial development, including the accumulation of MIR data over years to integrate in calibration, and to gradually improve the accuracy and the robustness of prediction.

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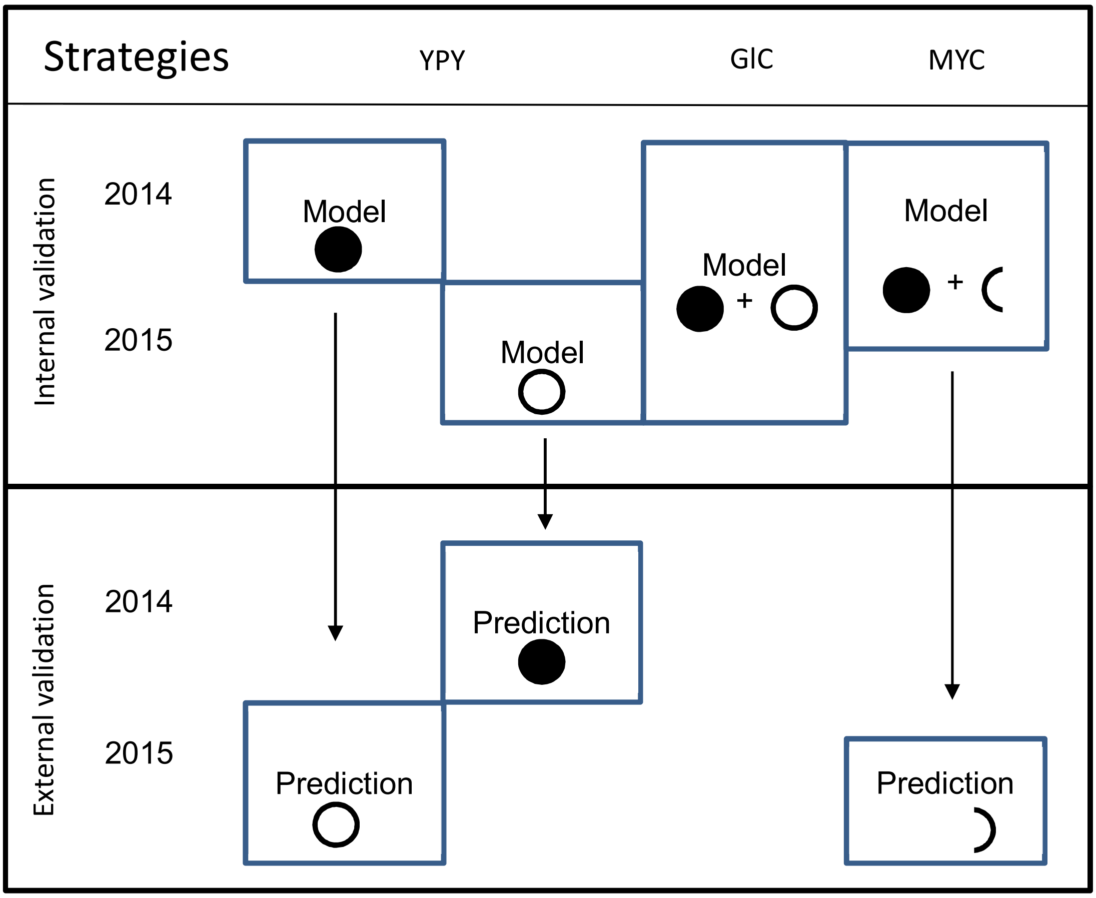
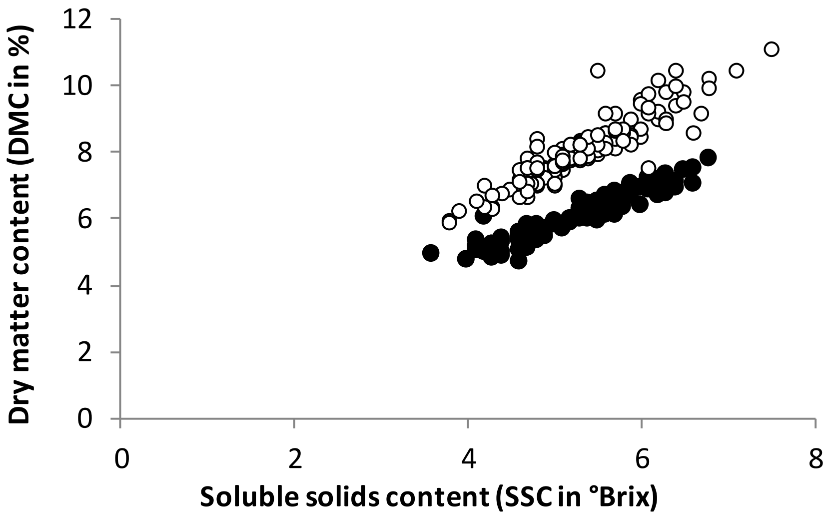


Figure 1. The three tested strategies to build models using both mid-infrared spectra and reference data of quality traits.

with YPY; Year per Year models, GIC: Global Combining models and MYC: Multi-Year Combining models.

A)



B)

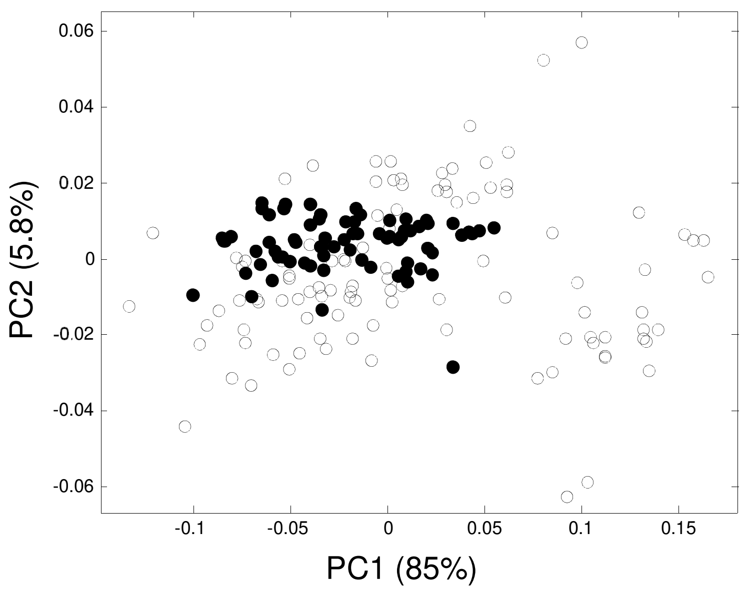


Figure 2. Variability of processing type tomatoes in France over two years. A) Biplot between soluble solids content (SSC) and dry matter content (DMC) and (B) Principal Component Analysis (PCA) performed on spectral data (2000-900 cm^{-1}) with tomatoes characterized in 2014 (●) and in 2015 (○).

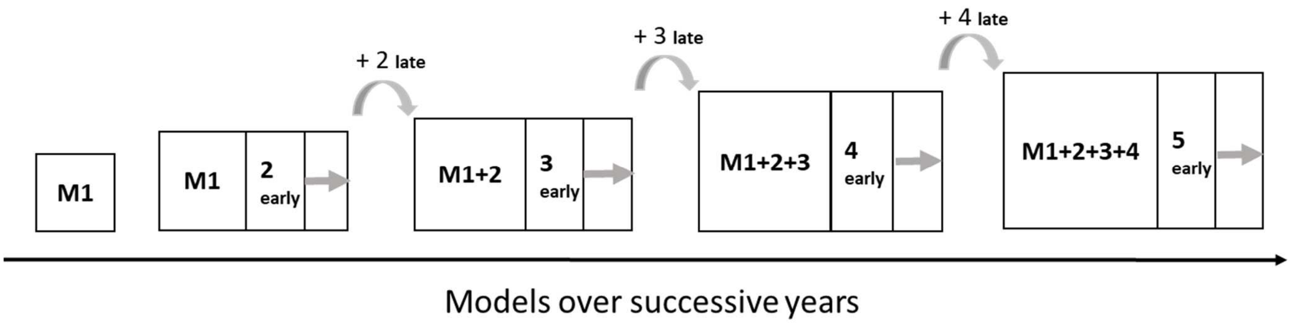
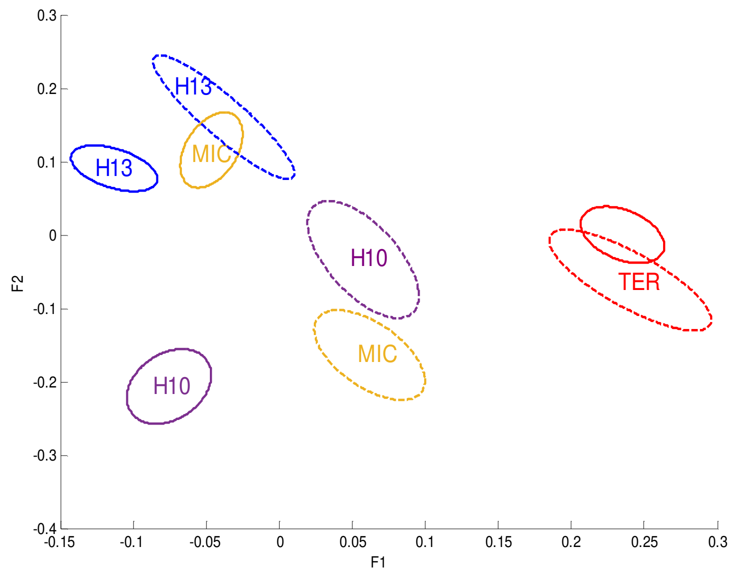


Figure 3. The best strategy to improve model ability over successive years.

With 2, 3, 4, 5: early and late data each year added in the previous models identified by M1+2+… and arrows simulating the model use to predict firstly the late tomato quality traits each year and then the tomatoes of next years.

A.



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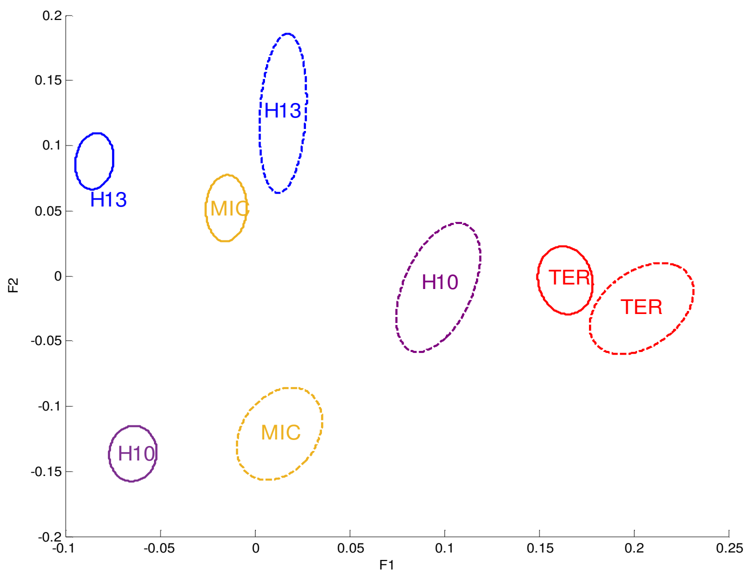

Figure 4. Factorial Discriminant Analysis (FDA) maps performed on mid-infrared spectral (MIRS) data (1200-900 cm^{-1}) of fresh tomato (A) and processed purees (B). Ellipses drawn with a P value of the confidence interval of 0.05, with continuous line (2016) and dotted line (2017). Terr: Terradou, H10: H1015, H13: H1311 and MIC: Miceno.

FDA was calculated on 2016 data. 2017 data were added as illustrated data.

Table 1. Soluble solids content (SSC), dry matter content (DMC) and titratable acidity (TA) of fresh tomatoes measured by reference methods over two successive years.

Quality traits	Year	Mean	SD	Min	Max
SSC (°Brix)	2014	5.2	0.7	3.6	6.8
	2015	5.4	0.7	3.8	7.5
DMC (%)	2014	6.0	0.7	4.7	7.8
	2015	7.9	1.1	5.7	11.1
TA (mmol H^+/Kg)	2014	59.1	6.7	45.3	76.8
	2015	55.6	10.6	30.2	81.7

SD: standard deviation, n=102 samples in 2014 and 144 in 2015 and each sample was a homogenate of 15 tomato fruits.

Table 2. Validation results to compare the performance of the models to predict SSC, DMC and TA depending on the strategies.

Quality trait	Sampling	LV	Calibration		Validation		RPD
			R_C^2	$RMSE_C$	R_V^2	$RMSE_V$	
SSC (°Brix)	YPY (2014)	7	0.95	0.16	0.95	0.16	4.3
	YPY (2015)	4	0.96	0.14	0.94	0.13	3.6
	GlC	8	0.95	0.15	0.93	0.17	3.9
	MYC	9	0.97	0.13	0.95	0.14	4.5
DMC (%)	YPY (2014)	7	0.89	0.24	0.87	0.25	2.6
	YPY (2015)	4	0.82	0.39	0.85	0.41	2.6
	GlC	6	0.86	0.48	0.85	0.49	2.5
	MYC	10	0.92	0.37	0.94	0.34	3.9
TA (mmol H^+/Kg)	YPY (2014)	10	0.89	2.33	0.84	2.19	2.5
	YPY (2015)	10	0.97	2.01	0.96	2.23	4.6
	GlC	9	0.84	3.74	0.90	3.47	3.1
	MYC	9	0.84	3.92	0.79	4.15	2.2

LV: latent variables, R^2: coefficient of determination, RMSE: root mean square error, with $_c$ for calibration and $_v$ for validation; RPD: ratio of the standard deviation (SD) of the response variable in the validation set to the $RMSE_v$; Strategies named: YPY for year-per-year models, GlC : global combining models, MYC : Multi-year combining models

Sample number was n=102 in 2014, n=144 in 2015, n=246 in 2014 + 2015 and n=181 in 2014 + 2015 early (all samples in 2014 and until August, 18th 2015).

With 2014 and 2015 from the Scenario1 (YPY models); 2014+2015 from the Scenario 2 (GlC) and 2014 + early 2015 from the Scenario 3 (MYC models combining all data of the first year 2014 and data of the beginning of the second year until August, 18th 2015).

Table 3. External validation results to compare the performance of the models to predict SSC, DMC and TA depending on the strategies

Quality trait	Models	Predicted samples	External validation		
			R_P^2	$RMSE_P$	RPD
SSC (°Brix)	YPY (2014)	2015	0.31	0.90	0.5
	YPY (2015)	2014	0.88	0.25	2.7
	MYC	end 2015	0.95	0.11	4.3
DMC (%)	YPY (2014)	2015	0.13	3.89	0.3
	YPY (2015)	2014	0.79	2.54	0.1
	MYC	end 2015	0.81	0.36	2.8
TA (mmol H^+/Kg)	YPY (2014)	2015	0.27	33.12	0.3
	YPY (2015)	2014	0.16	53.44	0.3
	MYC	end 2015	0.88	2.81	2.1

R_p^2: coefficient of determination of external validation, RMSEp: root mean square error of external validation.
With 2014 and 2015 from the Scenario1 (YPY models) with n=102 in 2014 and n=144 in 2015; 2014 + early 2015 from the Scenario 3 (MYC models) with n=181 in 2014 + 2015 early (all samples in 2014 and data of the beginning of the second year until August, 18th 2015) and n=65 in end 2015 (data from August, 18th 2015).

Table 4. Matrices of confusion given by the Factorial discriminant analysis (FDA) using PC scores of the PCA (Principal Component Analysis) performed on the spectral data (2000-900 cm^{-1}) of the fresh tomato homogenates and their corresponding cooked purees. Three factors were tested with A: years, B: type of samples and C: varieties.

A. Year

	2016	**2017**
2016	143	1
2017	0	192

B. Type of tomato-based products

	CB	**FR**	**HB**
CB	94	1	1
FR	0	144	0
HB	6	1	89

C. Variety

	H10	**H13**	**MIC**	**TER**
H10	45	9	24	6
H13	12	59	13	0
MIC	19	9	56	0
TER	3	1	4	76

The total number of samples for each condition being 2016: 144 samples; 2017: 192 samples; CB: 96 samples; HB: 96 samples and fresh: 144 samples; 84 samples for each of the H10, H13, MIC and TER varieties.

Table 5. Prediction of quality traits of industrial products using both reference data acquired by laboratory measurements and by plant control quality.

Samples	Quality traits	Reference data		LV	Calibration		Cross-validation		
		Mean	SD		R_C^2	$RMSE_C$	R_{CV}^2	$RMSE_{CV}$	RPD
All samples	SSC (°Brix)	17.4	8.4	5	0.99	0.73	1.00	0.66	12.7
	TA (mmol H^+/Kg)	131.2	71.6	7	0.99	8.79	0.98	9.47	7.6
	DMC (%)	20.5	9.4	5	0.99	1.01	0.99	0.99	9.4
Juices and purees	SSC (°Brix)	11.4	2.2	5	0.92	0.67	0.87	0.68	3.2
	TA (mmol H^+/Kg)	93.9	22.4	8	0.88	8.95	0.82	8.82	2.5
	DMC (%)	15.5	3.1	4	0.90	1.10	0.76	1.13	2.7
All samples	SSC (°Brix)	15.0	7.2	5	0.99	0.98	0.99	0.97	7.5
	pH	4.4	0.1	9	0.55	0.09	0.51	0.10	1.4
	Bw	6.0	5.0	5	0.80	1.02	0.77	1.08	4.6
Juices and purees	SSC (°Brix)	11.5	2.5	7	0.92	0.67	0.93	0.70	3.6
	pH	4.4	0.2	5	0.59	0.10	0.38	0.13	1.3
	Bw	2.8	1.5	6	0.46	1.07	0.35	1.22	1.2

When all samples (juices, purees and pastes) were used: n=76 in the calibration set and n=38 in the cross-validation set. When only juices and purees were used: n=57 in the calibration set and n=28 in the cross-validation set.

LV: latent variables, R^2: coefficient of determination, RMSE: root mean square error, with $_c$ for calibration and $_v$ for validation; RPD: ratio of the standard deviation (SD) of the response variable in the validation set to the $RMSE_v$. Bw: Bostwick.