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Differential mobility spectrometry coupled to mass spectrometry (DMS–MS) for the classification of Spanish PDO paprika

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ABSTRACT

Ion mobility spectrometry (IMS) has proved its huge potential in many research areas, especially when hyphenated with chromatographic techniques or mass spectrometry (MS). However, focusing on food analysis, and particularly in classification and authentication issues, very few applications have been reported. In this study, differential mobility spectrometry coupled to mass spectrometry (DMS–MS) is presented for the first time as an alternative and high-throughput technique for food classification and authentication purposes using a fingerprinting strategy. As a study case, 70 Spanish paprika samples (from *La Vera*, *Murcia*, and *Mallorca*) were analyzed by DMS–MS to address their classification —using partial least squares regression-discriminant analysis (PLS-DA)— and authentication —through soft independent modeling of class analogy (SIMCA). As a result, after external validation, complete sample classification according to their geographical origin and excellent *La Vera* and *Mallorca* sample authentication were reached.

1. Introduction

In the early 20th century, the first studies using ion mobility spectrometry (IMS) were conducted. However, it was not until the 1970s that Cohen and Karasek introduced it as an analytical tool (Cohen & Karasek, 1970; Karasek, 1974). Since then, and especially in the last two decades, this platform has attracted the interest of scientists as a powerful separation technique, owing to its capacity of separating strongly related compounds. In IMS, ions are separated in the gas phase based on their mobility, which depends on their charge, size, and shape (D'Atri et al., 2018; Dodds & Baker, 2019; Eiceman, Karpas, & Hill, 2013; Gabelica & Marklund, 2018; Kirk, 2019). However, the specific separation mechanism differs among the different platforms (manufacturer), being possible to establish three different categories. (i) Time-dispersive techniques, which encompass drift-time ion mobility spectrometry (DTIMS) and traveling wave ion mobility spectrometry (TWIMS), separate ions based on the time they require to go through the same pathway. (ii) Space-dispersive techniques, such as field asymmetric waveform ion mobility spectrometry (FAIMS), differential mobility spectrometry (DMS), and differential mobility analysis (DMA), rely on the different trajectories that ions describe based on their mobility. (iii) In ion-trapping with selective release techniques, such as trapped ion mobility spectrometry (TIMS), the ions are trapped in a pressurized region and are selectively ejected based on their mobilities (D'Atri et al., 2018).

In the last years, the interest in the hyphenation of IMS with other techniques has spectacularly grown. In this line, ion mobility spectrometry coupled to mass spectrometry (IMS–MS) combines the separation capacity based on the mobility of ions with the structural information provided by mass spectrometry. Beyond that, the addition of a third separation dimension, such as liquid chromatography (LC), opens excellent possibilities for analyzing complex samples. Indeed, IMS, as a standalone technique as well as coupled to LC and MS, has been extensively used in a wide range of research areas, from biomedical or pharmaceutical applications to environmental and security fields (Armenta, Esteve-Turrillas, & Alcalà, 2020; Cossoul et al., 2015; Hernández-Mesa, Escourrou, Monteau, Le Bizec, & Dervilly-Pinel, 2017; Odenkirk & Baker, 2084; To, Ben-Jaber, & Parkin, 2020).

In food analysis, where chromatographic techniques (often hyphenated to MS) are still the gold standard for determining a wide range

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of compounds, from natural components to additives or contaminants, IMS begins to be seen as an alternative. Although it can be used as a standalone technique, its combination with LC, gas chromatography (GC), or MS is usually preferred (Alikord, Mohammadi, Kamankesh, & Shariatifar, 2021; Domínguez, Frenich, & Romero-González, 2020; Hernández-Mesa et al., 2019). Until now, IMS has been mainly focused on the determination of specific compounds (targeted analysis) (Rue, Glinski, Glinski, & van Breemen, 2020; Wang, Harrington, Chang, Wu, & Chen, 2020; Will, Behrens, Macke, Quarles, & Karst, 2021), and fewer applications have been reported following a fingerprinting approach (non-targeted analysis) (Burnum-Johnson et al., 2019; Freire et al., 2021; Paglia, Smith, & Astarita, 2021). In this regard, the -omics strategy has been used basically for authentication and food integrity assessment, being DTIMS the preferred mode of IMS (Martín-Gómez & Arce, 2021). However, other separation mechanisms, such as space-dispersive methods, can also be exploited for fingerprinting analysis (Piñero et al., 2020).

DMS separates the ions based on their differential mobility under the influence of a high asymmetric radiofrequency. Under these conditions, only those ions with the proper mobility can describe the correct trajectory to traverse the DMS cell while interferences are deviated into the cell walls. A compensation voltage (CoV) is then applied to correct the trajectory of the ions letting only target ions enter the mass spectrometer. The main application of this technique deals with improving the method sensitivity by reducing background noise and removing isobaric interferences (Bravo-Veyrat & Hopfgartner, 2018; Dempsey, Moeller, & Poklis, 2018; Su et al., 2021). However, to our knowledge, DMS, or more specifically differential mobility spectrometry coupled to mass spectrometry (DMS–MS), has not been previously used for non-targeted analysis in food research. The good reproducibility, speed, and high separation capacity of this technique offer an attractive alternative not only to those well-established chromatographic methods but also to direct MS techniques, such as flow injection analysis coupled to high-resolution mass spectrometry (FIA–HRMS) or ambient mass spectrometry (AMS) (Campmajó, Saurina, & Núñez, 2021; Ibáñez, Simó, García-Cañas, Acunha, & Cifuentes, 2015).

This manuscript aimed at evaluating the applicability of direct infusion DMS–MS fingerprinting for food classification and authentication purposes, using Spanish paprika samples as a case study. In this regard, paprika is a red powdered spice, obtained from red pepper fruits of the genus *Capsicum* (Solanaceae family), widely used because of its characteristic organoleptic properties. Currently, only three paprika products are registered in Spain with the protected designation of origin (PDO) status: *Pimentón de La Vera*, *Pimentón de Murcia*, and *Pebre bord de Mallorca*. Although it ensures high-quality products, it also leads to higher prices, making them vulnerable to food fraud practices. To date, several fingerprinting methods based on LC, with spectroscopic detection or coupled to HRMS, have been developed to address paprika classification (Barbosa, Saurina, Puignou, & Núñez, 2020; Campmajó, Rodríguez-Javier, Saurina, & Núñez, 2021). In this study, the DMS–MS fingerprints of 70 paprika samples from *La Vera*, *Murcia*, and *Mallorca* PDOs, were used for the first time to classify and authenticate them through partial least squares regression-discriminant analysis (PLS-DA) and soft independent modeling of class analogy (SIMCA), respectively.

2. Materials and methods

2.1. Reagents and solutions

Regarding the sample treatment, water was purified using an Elix® 3 coupled to a Milli-Q® system (Millipore Corporation, Bedford, MA, USA) and filtered through a 0.22-μm nylon membrane, while UHPLC-supergradient acetonitrile was purchased from Panreac (Castellar del Vallès, Spain). For DMS optimization, technical grade acetone and UHPLC-supergradient acetonitrile and methanol obtained from Panreac and 2-propanol obtained from Merck (Darmstadt, Germany) were used. Phenolic compounds used in the DMS optimization were purchased from different suppliers: quercetin dihydrate from Riedel-de-Haën (Seelze, Germany); chlorogenic acid from HWI Analytik GMBH (Ruelzheim, Germany); gallic, homogentisic, and ferulic acids, and vanillin from Fluka (Steinheim, Germany); and D-(−)-quinic, caffeic, homovanillic, *p*-coumaric, sinapic, and betulinic acids, syringaldehyde, protocatechuic aldehyde, and rutin from Merck.

2.2. Instrumentation

A 5500 Qtrap (AB Sciex, Framingham, MA, USA) mass spectrometer with an electrospray ion source (ESI) and the SelexION differential mobility separation device (DMS, AB Sciex, Framingham, MA, USA), installed between the ionization source and the vacuum interface, was used for the analysis of samples. Paprika extracts were directly introduced for 1.6 min by infusion to the ionizations source at a rate of 5 $\mu L \cdot min^{-1}$ using the integrated syringe pump.

Regarding DMS conditions, the temperature was fixed at 225 °C (medium), the separation voltage (SV) and DMS offset (DMO) were set at 2500 V and 3 V, respectively, and the high DMS resolution enhancement option was selected. Under these conditions, a CoV ramp (from −10 to 7 V) was performed. MS detection in negative full-scan MS mode (Enhance MS, EMS) was used from 100 to 650 *m/z* at a scan rate of 1000 $Da \cdot s^{-1}$. Nitrogen, used as nebulizer and auxiliary gas, was set at 20, 15, and 0 arbitrary units for the curtain gas, the ion source gas 1, and the ion source gas 2, respectively. Besides, the ion spray voltage (IS) was set at −4500 V without heating the ion source, and the declustering potential (DP) and the entrance potential (EP) were fixed at −100 V and −10 V, respectively. Analyst software (version 1.6.2) from AB Sciex was used for instrument control and data acquisition.

2.3. Samples, sample treatment, and sample analysis

In this study, 70 paprika samples belonging to the three Spanish regions with the PDO label were analyzed. In this line, 30 *La Vera* samples (10 of each paprika type: hot, sweet, and bittersweet) were directly purchased from paprika production companies, and 20 *Murcia* and 20 *Mallorca* samples (containing half hot and half sweet types, each one) were bought in Spanish commercial markets.

Samples were subjected to an ultrasound-assisted solid–liquid extraction (USLE) method, previously described by Cetó et al. (2018), using water:acetonitrile (20:80, *v/v*) as extracting solvent.

Samples were randomly analyzed to reduce the impact of any potential instrumental drift on the chemometric results. Moreover, a quality control (QC) sample, prepared by mixing 50 μL of each paprika sample extract, was also analyzed (at the beginning and every ten samples) to check for systematic errors along the analysis.

2.4. Data analysis

2.4.1. Data matrix construction

Raw data were converted to mzXML format using the MSConvertGUI software (Chambers et al., 2012). Then, aiming at constructing a data matrix containing DMS–MS fingerprints, data were processed using the mzMine 2.53 software (Pluskal, Castillo, Villar-Briones, & Orešič, 2010). Firstly, nominal mass detection centroided each mass spectrum acquired for a sample, through the "Wavelet transform" algorithm (establishing a noise level of 2.0×10^4, a scale level of 3, and a wavelet window size of 30%), particularly suitable for noisy low-resolution mass spectrometry (LRMS) data. Secondly, using the option of chromatogram builder, nominal mass signals found in at least 5 contiguous scans for a sample were connected, with a group intensity threshold of 3.0×10^4, a minimum highest intensity of 7.0×10^4, and an *m/z* tolerance of 800 ppm. Thirdly, each ionogram was then deconvoluted into individual peaks, using the "Baseline cut-off" algorithm that recognized peaks with a CoV duration range between 0.4 and 2.0 V and fulfilling the peak intensity

conditions established in the previous step. Fourthly, isotopes were removed, considering the most intense isotope as the most representative and setting an *m/z* tolerance of 800 ppm. Finally, the random sample consensus (RANSAC) aligner matched *m/z* signals detected across samples, establishing a mass tolerance of 1000 ppm, peak CoV tolerances of 1.5 and 0.5 V (before and after correction, respectively), and a minimum number of points of 80%. In the end, an X-data matrix containing DMS–MS fingerprints (ion peak area matrix in which each row corresponds to a sample (78 samples) and each column corresponds to a variable (203), being a variable a specific ion (specific *m/z*) migrating at a specific CoV) of the studied samples was obtained (Table S1).

2.4.2. Chemometric analysis

Principal component analysis (PCA), PLS-DA, and SIMCA were carried out using Solo 8.6 chemometrics software from Eigenvector Research (Manson, WA, USA). Details of the theoretical background of these chemometric methods are given elsewhere (Massart et al., 1997; Wold, 1976). In this paper, we will only make a brief description of the most relevant aspects related to our study.

Independently of the chemometric method employed, an X-data matrix was required, consisting of DMS–MS fingerprints. Moreover, data were autoscaled before the chemometric analysis to suppress differences in each variable's magnitude and amplitude scales. For such a purpose, data were mean-centered and subsequently divided by the standard deviation of the corresponding variable according to the following expression:

$$x_{iautoscaled} = \frac{x_i - \overline{x}}{s}$$

where $x_{i\ autoscaled}$ is the value for variable *i* after autoscaling, x_i is the original value for variable *i*, and $\overline{X}$ and *s* are the mean value and standard deviation, respectively.

A preliminary exploration of DMS-MS fingerprints by PCA assessed the behavior of samples and variables. PCA concentrates the relevant information of the X-matrix, contained in a large number of experimental variables, into a reduced number of mathematical variables called principal components (PCs). PCA relies on decomposing the experimental data matrix into two smaller submatrices of scores (T, with coordinates of the samples) and loadings (P^T, with the eigenvectors or coordinates of the variables). As a result, the scatter plot of scores on PC space depicts the sample layout which may reveal similarities and differences among sample characteristics such as origins and varieties. The loadings' plots may figure out the most descriptive variables and their correlations.

The supervised sample classification (according to geographical origin and type) was studied through PLS-DA and evaluated after external validation through sensitivity, specificity, and accuracy. The experimental X-matrix is correlated with the class matrix that encodes the sample membership to its class. The classification model is established to obtain the minimum error in the sample assignation to the corresponding classes. Here, the optimal number of latent variables (LVs) used in each PLS-DA model was established at the first significant minimum point of cross-validation (CV) error using the Venetian blinds method. Subsequently, the classification performance was assessed by external validation using independent test samples.

SIMCA was proposed for paprika sample authentication. SIMCA relies on a PCA model constructed using only samples belonging to a given class. Hence, a PCA model is obtained, for instance, with la Vera, Murcia, or Mallorca samples. Reduced Q residuals and Hotelling T^2 values, normalized to a 95% confidence limit, were used to calculate the distance between a new projected sample and the established PCA submodel. The number of PCs used in the PCA submodel, as well as the decision threshold, were optimized in each SIMCA model by maximizing the calibration step performance. Then, both the distance and the decision threshold assessed the sample class membership. Moreover, considering that SIMCA calibration models were built with less than 20 samples, the leave-one-out method was proposed for CV. Finally, as with PLS-DA, SIMCA models' performance was assessed by external validation.

3. Results and discussion

3.1. Selection of the DMS–MS conditions

A mixture of 15 phenolic compounds (namely chlorogenic, gallic, homogentisic, ferulic, D-(−)-quinic, caffeic, homovanillic, p-coumaric, sinapic, and betulinic acids, vanillin, quercetin, syringaldehyde, protocatechuic aldehyde, and rutin), previously identified as possible key components for the classification of paprika samples (Barbosa, Campmajó, Saurina, Puignou, & Núñez, 2020), was used to set DMS–MS conditions. As commented before, this work was not focused on optimizing the polyphenol separation but on the untargeted analysis of paprika samples to obtain characteristic sample fingerprints to discriminate samples according to geographical origin and type.

With this in mind, the polyphenol standard solution (10 $mg{\cdot}L^{-1}$ each compound) was introduced by infusion to the mass spectrometer through the SelexION differential mobility separation device to establish the DMS–MS parameters. Then, a negative full-scan using Q3 in ion trap mode (EMS) was recorded from 100 to 650 *m/z*. Total ion intensity was monitored to evaluate MS parameters such as DP and IS, obtaining the maximum signal intensity at −100 V and −4500 V, respectively. Following the same criterion, DMS temperature was fixed at 225 °C (medium).

The separation of the polyphenols included in the standard mixture was studied to choose the most appropriate SV. Hence, a ramp of the CoV was performed at different SV (from 1000 V to 4000 V, in steps of 500 V). As a result, the higher the SV, the higher degree of separation was observed. However, the signal intensity was strongly affected (Fig. S1), and therefore, as a compromise, an SV of 2500 V was selected to analyze paprika samples.

Additionally, several gas modifiers —namely methanol, acetonitrile, 2-propanol, and acetone— were evaluated. Volatile reagents introduced into the gas flow may interact differently with the ions to form clusters, thus modifying their mobility and affecting both separation and signal intensity. Hence, the effect of each modifier on the DMS separation of the selected polyphenols was studied at low (1.5%) and high (3.0%) modifier concentrations. However, no significant improvement was observed in any case. Therefore, and considering that this study aimed to use a simple method to generate discriminating sample DMS–MS fingerprints, the addition of a gas modifier was discarded.

Fig. 1 shows representative DMS–MS fingerprints for a hot *La Vera*, *Murcia*, and *Mallorca* PDO paprika sample. Several qualitative differences in the ionograms regarding compounds detected and their peak intensity can be observed. In this context, *Mallorca* paprika samples presented the most distinctive DMS–MS fingerprints. However, remarkable dissimilarities were encountered among *La Vera* and *Murcia* samples. Therefore, the DMS–MS fingerprints were proposed as chemical descriptors for further multivariate chemometric analysis.

3.2. Non-supervised and supervised chemometric analysis

After the visual inspection of the DMS–MS raw data, a 78 × 203 (samples × variables) data matrix was constructed following the procedure described in Section 2.4.1. Then, PCA was used for an exploratory assessment of the behavior of samples and QCs. Fig. S2 presents the PCA scatter plot of scores on the PC2-PC1 (describing 28.06% of the variance), where QC samples were in a compact cluster, discarding the presence of a systematic error (e.g., a shift in the analytical system) and, thus validating the subsequent chemometric results. *Mallorca* paprika samples were located on the top of the plot, displaying positive PC2

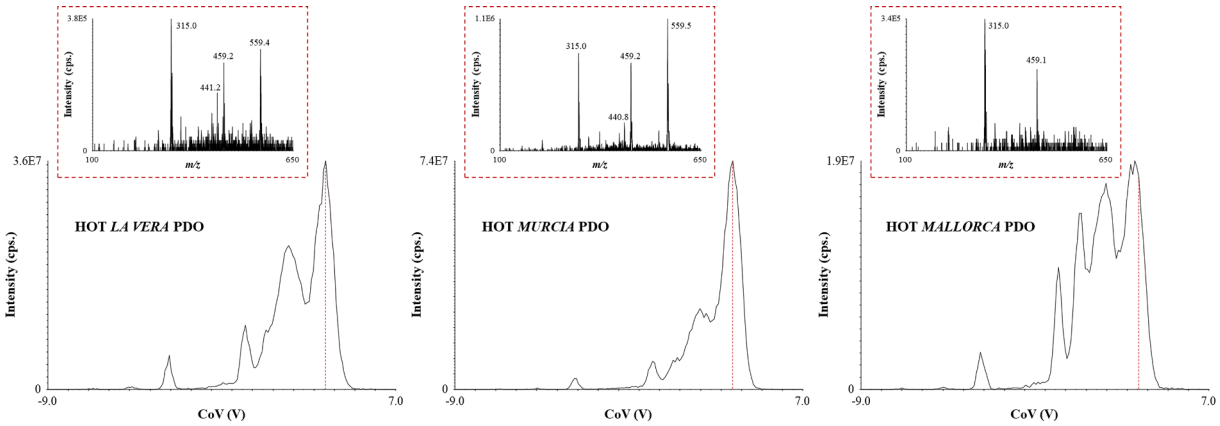

Fig. 1. DMS–MS fingerprints obtained for a hot La Vera, Murcia, and Mallorca PDO paprika sample at SV 2500 V, and MS full-scan spectra at CoV 3.58 V.

values, while *La Vera* and *Murcia* ones appeared jointly (Fig. S2A). Moreover, the PCA score plot noticed no sample distribution according to paprika type (Fig. S2B).

Once demonstrated the good performance of the analysis, QC samples were removed from the DMS–MS data matrix for the supervised chemometric classification carried out through PLS-DA, resulting in a dimension of 70 × 203 (samples × variables). Firstly, sample classification according to the geographical origin (*La Vera*, *Murcia*, and *Mallorca*) was studied. In this context, a PLS-DA model built with two LVs (explaining a Y-variance of 58.51%) allowed an apparent distinction between the three Spanish regions under study, thus improving the non-supervised chemometric results given above. Hence, in the obtained scores plot of LV1 *vs*. LV2, LV2 values allowed the isolation of *Murcia* samples, located at the bottom of the diagram, while the separation of *La Vera* and *Mallorca* samples (placed on the top of the diagram, displaying positive LV2 values) was mainly attributed to LV1 values (Fig. 2A).

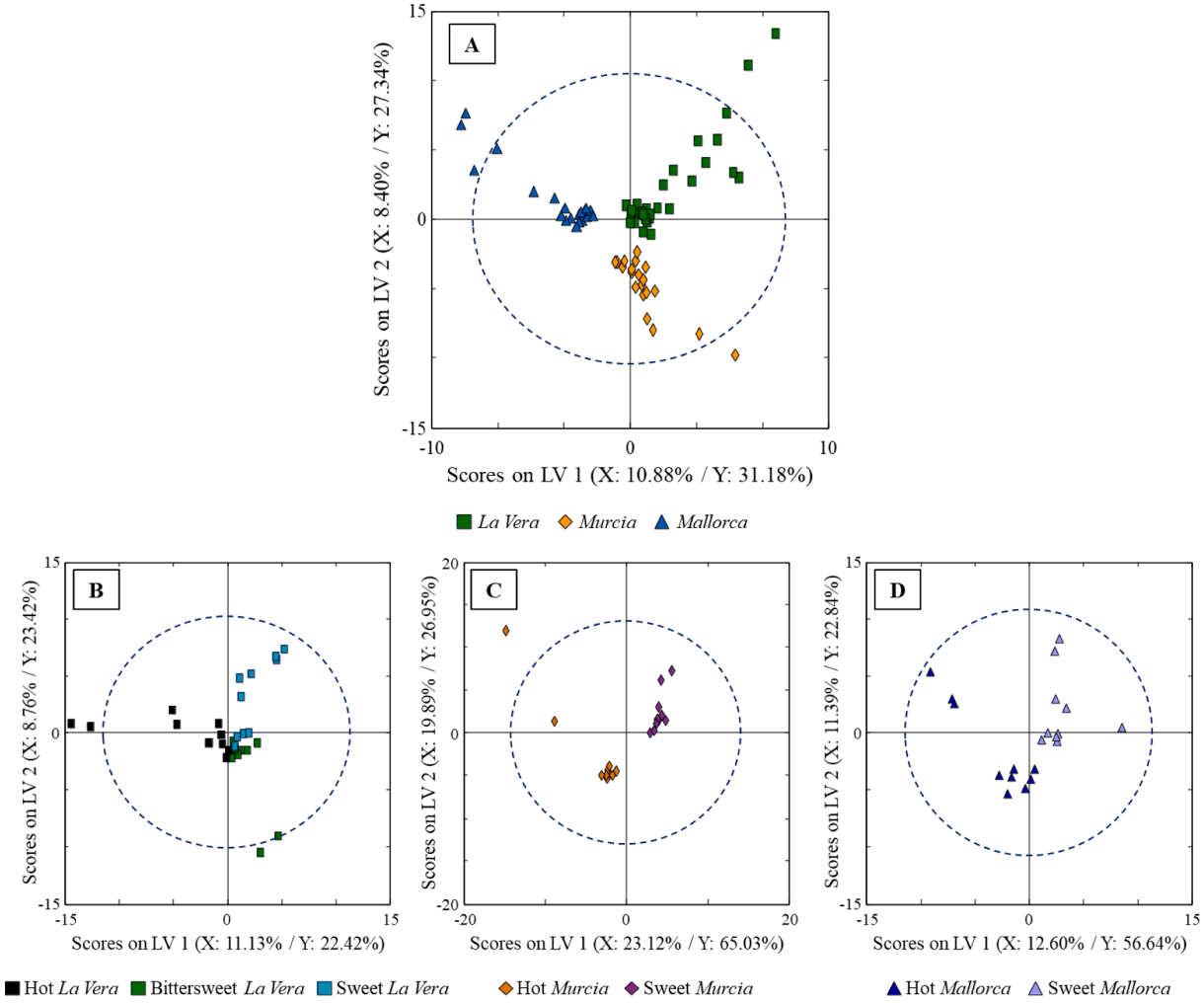

Fig. 2. PLS-DA scores plot of LV1 *vs*. LV2 obtained for the analyzed paprika samples according to their geographical origin, using DMS–MS fingerprints (A) and individual *La Vera* (B), *Murcia* (C), and *Mallorca* (D) PLS-DA models to classify samples according to their type.

External validation was carried out to evaluate the ability of the PLS-DA model established to classify paprika samples from the three Spanish regions distinguished with the PDO label. Thus, 60% of samples were randomly stratified and used as the calibration set, while the remaining 40% were used as the external validation set. As a result, a classification rate of 100% was achieved, being [12, 0, 0; 0, 8, 0; 0, 0, 8] the confusion matrix for the established PLS-DA model. Please note that rows in the confusion matrix correspond to *La Vera*, *Murcia*, and *Mallorca* classes, respectively, and columns are given in this same order. Hence, the 12 *La Vera*, the 8 Murcia, and the 8 *Mallorca* samples were correctly classified into their respective classes.

Additionally, sample classification regarding paprika's type (hot, bittersweet, or sweet) was also evaluated by PLS-DA. In this line, Fig. S3 contains the plot of scores of LV1 *vs.* LV2 obtained after assigning each sample to its class, considering both geographical origin and type. As can be seen, although *Murcia* and *Mallorca* paprika samples seemed to follow a trend related to the sample type (*La Vera* samples appeared jointly in the plot), the similarities due to the geographical origin prevailed. Therefore, to better analyze sample grouping depending on the product type, individual PLS-DA models were built for each region under study. As a result, as shown in Fig. 2B, DMS–MS fingerprints allowed *La Vera* samples separation according to their type. To our knowledge, this separation has only been previously achieved using an untargeted ultra-high-performance liquid chromatography coupled to high-resolution mass spectrometry (UHPLC–HRMS) method (Barbosa et al., 2020). However, the UHPLC-HRMS method required more expensive and complex instrumentation than the method proposed here. In addition, 30 min were needed for analyzing each sample, while only 1.6 min were required using the DMS-MS method. Both PLS-DA scatter plots of scores of *Murcia* (Fig. 2C) and *Mallorca* (Fig. 2D) samples also discriminate between their hot and sweet type. However, in this case, no external validation could be performed because of the scarcity of samples for each class.

Finally, considering the excellent classificatory results obtained with PLS-DA, SIMCA was proposed as a one-class modeling chemometric technique to assess the authenticity of the Spanish paprika samples according to their geographical origin based on DMS–MS fingerprints. Again, as in the PLS-DA study, DMS–MS data was split into the calibration set (42 × 203, samples × variables) and the validation set (28 × 203, samples × variables). Table 1 shows the number of PCs and the decision threshold selected in each SIMCA model, as well as the authentication performance in terms of sensitivity, specificity, and accuracy after the external validation. The developed *La Vera* and *Mallorca* SIMCA models provided good accuracy results, although specificity and sensitivity were more limited. Instead, assignation results were poorer with the *Murcia* SIMCA model.

A variable selection strategy was applied to improve these results, given that the first PCs of the SIMCA model do not necessarily contain discriminant information. Thus, a new data matrix was constructed, containing only the 10 variables with the highest selectivity ratio among the 20 ones with the highest variable importance in projection (VIP) values obtained for each paprika geographical origin class in the previous PLS-DA model. As a result, considering that some variables were simultaneously relevant for two of the studied classes, 42 × 25 (samples × variables) and 28 × 25 (samples × variables) calibration and external validation data matrices were built, respectively. As observed in Table 1, the applied variable selection strategy remarkably improved the assignation accuracy of the SIMCA models in all the cases. In this context, excellent results were obtained for *La Vera* (assignation rate of 92.9%) and *Mallorca* (assignation rate of 100.0%) authentication because of an enhancement in the specificity and sensitivity results, respectively, when using the reduced data matrix. Instead, although better assignation performance was achieved in the *Murcia* SIMCA model due to good specificity values, poor sensitivity values were obtained.

4. Conclusions

As commented before, LC or GC, often coupled to MS, is the preferred separation technique when dealing with classification or authentication in food analysis. The separation capacity of IMS to separate closely related compounds is well-known; however, not much research has been done using this technique for dealing with food classification or authentication issues. In fact, from our point of view, considering the separation potential of this technique, there is still a long way to go. Separations by IMS, and more specifically by DMS, offer faster and greener alternatives to the widely used LC counterpart. With this in mind, the applicability of DMS–MS was evaluated in this manuscript. It is worth highlighting the short analysis time required for sample analysis (1.6 min per sample). From the results obtained, we conclude that this technique was satisfactorily applied for the first time to a food classification and authentication issue through a fingerprinting approach combined with chemometrics. With such a purpose, 70 paprika samples from the three Spanish regions distinguished with the PDO label (*La Vera*, *Murcia*, and *Mallorca*) were used as a case study. Sample classification according to geographical origin and type was achieved by subjecting DMS–MS fingerprints to PLS-DA. In this context, in the first case, a classification accuracy of 100% was reached after external validation. Moreover, SIMCA results proved the ability of DMS–MS fingerprinting to authenticate *La Vera* and *Mallorca* paprika samples, especially after applying a previous variable selection strategy. Therefore, with this study, DMS–MS has been demonstrated to be a reliable high-throughput alternative to other currently applied techniques.

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CRediT authorship contribution statement

Guillem Campmajó: Methodology, Formal analysis, Investigation, Writing – original draft. **Javier Saurina:** Formal analysis, Writing – review & editing. **Oscar Núñez:** Conceptualization, Writing – review & editing. **Sonia Sentellas:** Conceptualization, Writing – original draft, Writing – review & editing.

Table 1
Calibration model parameters —number of PCs and established decision threshold— and external validation results —class sensitivity (%), class specificity (%), and global accuracy (%)— for each of the SIMCA models built.

	LA VERA					*MURCIA*					*MALLORCA*				
	Calibration model		External validation			Calibration model		External validation			Calibration model		External validation		
	PCs	Threshold	Sens.	Spec.	Accuracy	PCs	Threshold	Sens.	Spec.	Accuracy	PCs	Threshold	Sens.	Spec.	Accuracy
Non-reduced matrix	3	0.5	83.33	68.75	75.00	1	0.5	50.00	55.00	53.57	5	0.5	62.50	100.0	89.29
Reduced matrix	2	0.5	83.33	100.0	92.86	6	0.5	25.00	85.00	67.86	3	0.5	100.0	100.0	100.0

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodchem.2022.133141.

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