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Characterization of dried and freeze-dried sea fennel (*Crithmum maritimum* L.) samples with headspace gas-chromatography/mass spectrometry and evaluation of an electronic nose discrimination potential

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Abstract

Processed samples (air-dried @ 40 and @ 60°C and freeze-dried) of sea fennel (*Crithmum maritimum* L.), an autochthonous spice with interesting market potential, were analyzed by headspace gas-chromatography/mass spectrometry and classification capabilities of an electronic nose in discriminating between samples with stepwise forward statistics were evaluated as well. Freeze-drying process was the most preservative in terms of limiting darkening without compromising appearance of the final product, providing weight loss of about 85% and water activity below the limit for mold growth issues. Headspace analysis of samples highlighted the presence of 35 volatiles grouped as terpene hydrocarbons, oxygenated terpenes, sesquiterpen hydrocarbons, phenyl propanoids, not-terpenic aldehydes and not-terpenic ketones. Correlations emerged between selected sensors and some detected volatile organic compounds. Stepwise linear discriminant analysis and simple K-nearest neighbors obtained a 100% overall correct classification rate in cross-validation of the electronic nose in classifying samples, whereas stepwise K-means and Naive-Bayes gave 93.3%. The sea fennel could be a new interesting spice to launch in the food market and the electronic nose showed the potential to be used in monitoring the industrial process aimed at extending its shelf-life.

Keywords: sea fennel, *Crithmum maritimum* L., color, water activity, gas-chromatography/mass spectrometry, electronic nose, stepwise selection of predictors

1. Introduction

Interest on wild species of Italian flora is increasing for the greater attention people pay toward a healthy diet, the needs to restore a link with nature and old gastronomic traditions. Wild Edible Plants (WEPs) (leaves, buds, stalks etc.) use in culinary nutrition was sometimes named herbophilia (Łuczaj, ZovkoKončić, Miličević, Dolina, & Pandža, 2013). Among WEPs sea fennel (*Crithmum maritimum* L.), a facultative halophyte also known as crest marine, marine fennel, sampier and rock samphire, may be one of the most appealing (Petropoulos, Karkanis, Martins, & Ferreira, 2018). It belongs to the Apiaceae botanical family, the same of parsley and celery and grows on maritime rocks, breakwaters, piers, and sandy beaches along Mediterranean, Black sea, Atlantic coast of Portugal, South and South-West England, Wales and Southern Ireland. It was used as an appetizer, tonic, carminative, diuretic or for treating obesity due to its richness of biologically active compounds such as vitamin C, iodine, carotenoids, flavonoids, minerals (basically calcium), organic acids and phenolics. As nutraceutical, sea fennel can be a source of molecules for the food industry with antioxidant properties and minerals in the form of innovative health-promoting herbal beverages (Pereira et al., 2017). For its slightly salty taste and some notes of celery, followed from light notes of common fennel and peel of green citrus with a pungency aftertaste, sea fennel has numerous culinary uses in many European countries. Leaves are used crude, for salads served with a dressing of mixed juice and olive oil (Bianco et al., 2009), otherwise they are kept like capers in vinegar (Atia, Barhoumi, Mokded, Abdelly, & Smaoui, 2011) or used to prepare soups, sauces or seasonings (Bianco, Mariani, & Santamaria, 2009). A new spice-colorant can be obtained from fresh leaves of sea fennel through different drying processes (Renna & Gonnella, 2012). Air-drying, microwave-drying, microwave-assisted air-drying and freeze-drying are optimal for preserving organoleptic properties of sea fennel for food use other than as spice colorant (Renna, Gonnella, Caretto, Mita, & Serio, 2017). Odor notes of sea fennel are due to volatile organic compounds (VOCs), mainly produced for plants-plants interactions, symbiotic organism's signals and as insect

attractants or repellents. Pistelli et al. (Pistelli, Nocchioli, D'Angiolillo, & Pistelli, 2013), by using a headspace solid phase micro-extraction gas-chromatography/mass spectrometry (HS-SPME-GC/MS) technique, reported as main constituents of the odor profile of sea fennel: γ -terpinene, methyl carvacrol, α -pinene, p-cymene, sabinene, myrcene, α -thujene, camphene, β -thujene, α -terpinene, (Z)- β -ocimene, terpinolene. Authenticity of food products is a subject of ongoing concern, since it allows producers to obtain market recognition and premium prices (Berna, Trowell, Clifford, Cynkar, & Cozzolino, 2009; Giannetti, Mariani, & Mannino, 2016). Among monitoring devices, electronic nose is emerging as a simple, fast, high time-resolved and cheap tool that is attracting the scientific community, although it suffers some limitations. It requires a multivariate, robust and tailored statistical approach, is influenced by environmental conditions (i.e., humidity, temperature) and a robust training as well. Numerous applications of electronic noses in food products are reported in literature and, selecting only those dealing with spices, we can report that canonical discriminant function analysis on onion (head-space of allinase inactivated samples) analyzed with a MOS (Metal Oxide Semiconductor)-based electronic nose showed a clear separation among four onion groups with an overall correct classification rate of 97.5% (Russo et al., 2013). An electronic nose based on eight MOS sensors used for discriminating cultivated and wild black caraway and cumin seeds revealed a correct classification rate of 87.1% for parallel factor analysis-LDA (linear discriminant analysis) and 100% for two-dimensional-LDA and unfolded-partial least square discriminant analysis (Ghasemi-Varnamkhasti et al., 2018). An overall of 94.44% of the accuracy in the recognition and classification of adulterated cumin samples with coriander was obtained with a five sensor array of an electronic nose (Tahri, Tiebe, El Bari, Hübner, & Bouchikhi, 2016). A six MOS-based sensor array in an electronic nose was able to discriminate between black, white, and green ground pepper powders, and between samples with different grinding techniques (Liu et al., 2013). Three grounded spices, basil (*Ocimum basilicum*), cinnamon (*Cinnamomum cassia*), and garlic (*Allium sativum*), were blended and the composition of the mixtures was predicted by using a 12 conducting polymer-based sensor array in an electronic nose

using three different neural networks with an average absolute prediction error on weight fraction ranging from 0.031 to 0.076 (Zhang, Balaban, Portier, & Sims, 2005). Combination of e-nose data with color measurements was applied successfully with a stepwise forward selection of predictors in evaluating the roasting degree of coffee beans by an electronic-nose (Giungato, Elisabetta, & Cervone, 2010; Giungato, Laiola, & Nicolardi, 2017). Recently, in-house manufactured electronic noses have been successfully tested in discriminating wines with both different ageing time and tank (type of oak barrel) with a classification success rate of 97% and 84% (Lozano, Arroyo, Santos, Cabellos, & Horrillo, 2008), also using dimensionality reduction technique achieving classification success ratios higher than 87% (Aguilera, Lozano, Paredes, Álvarez, & Suárez, 2012). A MOS-based electronic nose combined with an autosampler has been tested in detecting and discriminating synthetic wine samples doped with acetic acid in concentrations equal or greater than 2 g/L (Macías et al., 2012). A portable and wireless connected sensor array has been used for the recognition and classification of musts coming from both different grape ripening times and grape varieties (Aleixandre et al., 2015). Poultry meat shelf-life, rapeseed oil degree of thermal degradation and olive oil adulteration with administration of rapeseed oil, were successfully evaluated with accuracies of 100-100-82% respectively, by using an electrochemical-based array of a portable electronic nose (Wojnowski, Majchrzak, Dymerski, Gębicki, & Namieśnik, 2017). Considering the prior art found in literature, the present work has been focused on the chemical characterization of processed samples (air-dried @40°C, air-dried @60°C and freeze-dried) of an autochthonous sea fennel with headspace analysis and on the assessment of the classification capabilities of an electronic nose in discriminating between them. Headspace analysis of processed samples will be carried out with a technique not previously reported in literature for sea fennel and appositely tested in this work for the first time. The correlation between chemical and electronic nose data could be useful to understand the selectivity of the sensors in the array to the VOCs emitted by the samples. Different classification models in the electronic nose were used,

individuating the most performing ones and selection of best discriminating sensors will be made on the basis of a stepwise approach.

2. Materials and methods

2.1 Sample collection and processing

Aerial parts of sea fennel were collected along the shoreline of “Mola” in the province of Bari Southern Italy (41°03’01’’N - 17°06’45’’E) figure 1, above. After removing of inedible parts, the samples were washed with tap water and blotted dry with paper towels. The samples were homogenized and divided into three portions. One portion was retained fresh, while the others were dried by using two different drying methods. Three replicates of each sample (about 300 g of fresh vegetable) were prepared for each drying treatment. One of them was used for electronic nose sampling of the head-space volatiles; the second one for color, water activity and weight analysis; the third for chemical analysis. Conventional air-drying was performed in a forced-ventilated oven (Model M40-VF, MPM Instruments s.r.l., Bernareggio, Italy) on fresh samples at 60 °C for 48 h. The second dried sample was obtained at 40 °C for 72 h. Freeze-drying was performed in a freeze-dryer (Labconco FreeZone® Freeze Dry System, model 7754030, Kansas City, USA) equipped with a stoppering tray dryer (Labconco FreeZone® Stoppering Tray Dryer, model 7948030, Kansas City, USA) for 72 h. Pictures of samples are reported below in figure 1. Drying times were tailored to obtain a final product with a water activity (aw) value < 0.6 to prevent mold growth and extend the shelf-life (Darriet 2007; Muggeridg et al. 2000). After each drying treatment, the dehydrated material was grounded and passed through a fine-mesh sieve to obtain a powder with a diameter ≤ 1 mm. The powdered sample was then packed in glass jars closed with an air-tight cap and stored at -20°C in absence of light.

2.2 Color, weight and water activity measurements

The analysis of color in the CIE $L^*a^*b^*$ coordinates represents one approach widely used in the literature, in which the parameter a^* ranges from positive values for reddish colors to negative values for the greenish ones whereas b^* ranges from positive values for yellowish colors to negative values for the bluish ones. L^* the brightness measures the luminosity, in a scale in which the color can be considered between black and white (0-100) of a greyscale (Pathare, Opara, & Al-Said, 2013). Color measurements were performed on the processed sea fennel samples equilibrated at room temperature, with a colorimeter (CR-400, Konica Minolta, Osaka, Japan) equipped with a D65 illuminant, working in reflectance mode and with the CIE L^* (lightness) a^* (redness) b^* (yellowness) colour scale. Before the readings were performed, the colorimeter was calibrated with a standard reference with L^* , a^* and b^* values reported in table 2. Coordinates in the CIEL $^*a^*b^*$ space, were obtained from the average results on three replicates, mixing the powder at every measure. Water activity was measured at 25 °C with a water activity meter (AquaLab Series 3, Decagon Devices Inc., USA) on three replicates. Weight was measured with a 1 mg precision balance (Mettler Toledo S.p.A, model XS403S, Novate Milanese, Milan, Italy) on three replicates of about 100 g.

2.3 Head Space-Solid Phase Micro Extraction-Gas Chromatography/Mass Spectrometry (HS-SPME-GC/MS)

0.5 g of sample of processed sea fennel (dried @ 40°C, dried @ 60°C and freeze-dried) were placed in a 20 mL vial crimp-sealed with a PTFE septum cap. The sample was allowed to equilibrate at 40°C for 2 min at 250 rpm using the automatic sampling system Gerstel MPS2-Twister (Gerstel GmbH & Co., Mülheim, Germany). The analysis was conducted by a GC/MS system (Agilent 6890/5973 Inert, Agilent, Santa Clara, CA, United States) equipped with the abovementioned

autosampler with helium as carrier gas (1.5 ml min^{-1}). A coated Divinylbenzene/Carboxen/Polydimethylsiloxane (DVB/CAR/PDMS) fiber (Sigma-Aldrich S.r.l., Milan, Italy) was exposed to the headspace of the sample for 15 min maintaining the sample at 40°C . The fiber was desorbed for 5.00 min at 250°C in the injection unit, in split-less mode. The separation was carried out in an Agilent DB-5 capillary column (30 m x 0.25 mm i.d. x 0.25 μm film thickness). The GC oven temperature program started at 35°C for 5 min, then was ramped to 150°C at 5°C/min and to 260°C at 15°C/min . The mass spectrometer operated with ion source at 230°C , quadrupole temperature of 170°C , 70 eV electron energy, acquiring in TIC mode from m/z 30 to 300 uma . Identification of the constituents was based on software matching against commercial (NIST 09 MS) library mass spectra, considering compounds as identified when the match quality was above 90%. The SPME fiber was thermally cleaned prior to each analysis at 265°C for 15 min. Analysis were conducted on three replicates.

2.4 Electronic nose sampling

Electronic nose used was the model PEN3 (Airsense Analytics GmbH, Schwerin, Germany) composed of 10 MOS sensors having different selectivity to volatiles, due to different doping of the semiconductors and/or working temperature. Each sensor was labelled by the producer together with the classes of volatiles to which it presented most of its selectivity (see table 1).

5 g of sample (dried at 40°C , dried at 60°C and freeze-dried), were placed into a glass chamber ($V = 681 \pm 1 \text{ mL}$) hermetically sealed with a cap having a Teflon septum and placed in a thermostatic bath at 40°C for 120 s to establish equilibrium between headspace and sample and prevent thermal degradation of the samples (Majchrzak, Wojnowski, Dymerski, Gębicki, & Namieśnik, 2018). Operative conditions of the electronic nose were: sampling flux = 400 mL/min ; sampling time = 60

s, sampling value = Integral of G/G_0 , washing flux = 600 mL/min, washing time = 80 s. The reported working conditions, as well as sampling time, were selected to give sufficient time to the array in reaching a steady state signal of the sensors. Washing time interval was selected to allow the restoring of the baseline of the sensors and the system was purged with charcoal filtered air prior to the collection of the next sample to allow the restoring of the instrument baseline. Electronic nose sampling was made with five replicates for each of the dried @ 40°C, @ 60°C and freeze-dried samples, in a randomized way, composing a dataset matrix of 15 samples.

2.5 Statistical analysis

Statistical analysis was performed following the guidelines for the statistical analysis in food science (Granato, de Araújo Calado, & Jarvis, 2014). The datasets obtained by chemical analysis and electronic nose sampling have been explored by unsupervised (PCA on normalized and centered data) and supervised (LDA, QDA, Bayes and KNN) methods of classification, with both Matlab R2016a (The Mathworks Inc. Apple Hill Drive Natick, MA, USA) and R software package (version 3.1.2 – 2014, The R Foundation for Statistical Computing©) equipped with devtools, ggbiplot, klaR and Mass libraries. PCA analysis is used to analyze and reduce the dimensionality of the numerical datasets of a multivariate problem in an unsupervised manner. The coordinates of the data in the new base are represented by the scores plot whereas the contributions to each component of the VOCs the loading plot. The score plot is usually used for studying the classification of the data clusters whereas the loading plot can be used for giving information on the relative importance of each principal component and their mutual correlation. In the case of the electronic nose the score plot is used for studying the classification and grouping of the data clusters whereas the loading plot is used to understand the contribution of the sensors to each principal component and collinearity and redundancy issues (also known as cross-sensitivity issues) (Penza et al., 2015). Data were confirmed with Parvus software (Forina, Lanteri, Casale, & Cerrato Oliveros, 2007; Pizarro,

Esteban-Díez, González-Sáiz, & Forina, 2007). Stepwise variable selection for classification has been used in forward direction using the supervised LDA, QDA, Bayes and KNN classification methods (indicated with S-LDA, S-QDA, S-Bayes and S-KNN) using leave-one-out cross-validation (Giungato et al., 2017). The QDA (quadratic discriminant analysis) assumes normality but allows unequal covariance matrices (Venables & Ripley, 2002). Naïve-Bayes classifier assumes both independence of the predictor variables and, in this case, Gaussian distribution (given the target class) of metric predictors. It computes the conditional a-posterior probabilities of a categorical class variable using the Bayes rule (Richard O. Duda, Peter E. Hart, 2000). In KNN an object is classified by a majority vote of its neighbors, with the object being assigned to the class most common among its k-nearest neighbors (Altman, 1992). As a rule, a variable was selected and added provided it improved the model more than 5% of the performance of the preceding one evaluated by cross-validation. Accuracy of the supervised method was tested with a cross-validation after selection of predictors as every model corresponding to each sea fennel sample, has been reduced using stepwise forward selection of predictors so the reduced model has not enough data available to partition it into separate training and test sets without losing significant modelling or testing capability (Houwelingen & Sauerbrei, 2013).

3. Results and discussion

Color measurements revealed darkening of samples with increasing drying temperature from 40 to 60°C as also visible in figure 1. In fact, shifting of L^* from a mean of 45.6 to a mean of 41.7 means browning of samples confirmed also by the a^* component which shifted from a mean of -9.7 to a mean of -1.75 (table 2). Freeze drying preserved initial appearance of the fresh sample as mean L^* of freeze-dried sea fennel (53.6) is the highest between all samples examined. Weight loss of samples remained almost constant with mean values of 85.0%, 85.8% and 85.1 % for dried samples at 40°C, at 60°C and freeze-dried samples, respectively. Mean water activity was higher in the case

of air-dried sample at 40°C (0.31) followed by the freeze-dried sample (0.28) and the dried at 60°C sample (0.19). The outcomes highlighted that, among the preservation processes, the freeze-drying one was the most preservative in terms of limiting darkening without compromising weight loss and water activity to prevent mold growth.

HS-SPME-GC/MS analysis of samples revealed the presence of 35 VOCs (table 3) grouped as follows: terpene hydrocarbons (limonene, 2,6-dimethyl-1,3,5,7-octatetraene, E,E- or cosmene, cis-beta-terpinene, 4-carene, gamma-terpinene, cis-beta-ocimene, alpha-terpinolene, beta-mircene, alpha-pinene, alpha-thujene, p-cimene, sabinene); oxygenated terpenes (p-thymol, (+)-carvone, sabina ketone, alpha-terpineol, 4-terpineol, 4-thujanol, trans-p-mentha-2,8-dienol, beta-linalool); sesquiterpen hydrocarbons (beta-sesquiphellandrene, beta-bisabolene, alpha-zingiberene, alpha-bergamotene, gamma-elemene, beta-caryophyllene, (+)-cuparene, alpha-curcumene); phenyl propanoids (apiol); not-terpenic aldehydes (esanal, eptanal, octanal, decenal) and not-terpenic ketones (2-nonanone, 3,5-octadien-2-one).

Hexanal, heptanal, octanal, 3,5-Octadien-2-one, 4-thujanol, 2-nonanone, 2,6-Dimethyl-1,3,5,7-octatetraene, E,E-, trans-p-mentha-2,8-dienol, Bicyclo[3.1.0]hexan-2-one, 5-(1-methylethyl)- (Sabina ketone), 4-terpineol, (+)-carvone, Decenal, beta-cariophyllene, gamma-elemene, alfa-curcumene, (+)-cuparene have been identified for the first time in the headspace of samples of fresh or processed sea fennels. By summing the peak areas of the volatiles per samples, terpene hydrocarbons (TH) represented 90% of the peak areas in all samples followed by oxygenated terpenes (OT, 2%) and sesquiterpene hydrocarbons (SH, 2%). Terpene hydrocarbons were the most represented volatiles in the headspace of sea fennel samples in this case study and among them, limonene had the highest chromatographic peak area percent (71.96% for freeze-dried, 79.55% for

dried@60°C and 69.24% for dried@40°C) of all identified species, representing the most important terpene in the headspace of sea fennel samples.

Loadings and scores biplot of the first and second principal component of peak areas of the sea fennel samples grouped per classes of volatiles revealed that the first two principal components accounted for the 100% of the total variance (73.9% and 29.7% for PC1 and PC2, respectively, figure 2). The score relative to the sample of sea fennel dried at 40°C is positioned in the lower-left quadrant of the biplot in which the loadings of TH and SH were located. The score relative to the freeze-dried sample of sea fennel is positioned in the upper-right quadrant in which the loading of phenyl propanoids (but the only one component is apiol) were located. Apiol was the only one volatile largely presents in the headspace of the freeze-dried sample and with lower peak areas in the dried samples (@40°C and @60°C). The score relative to the sample of sea fennel dried at 60°C is positioned in the lower-right quadrant in which the loadings of not-terpenic aldehydes and ketones (NTA and NTK, respectively) are located. The lower temperature drying process preserves terpenic hydrocarbons and characterizes the headspace of dried@40°C samples. A higher drying temperature reduces the amounts of volatile terpenes and enhances the presence of aldehydes and ketones of non-terpenic structure. The freeze-drying process led to a higher content of apiol, a phenyl propanoid. Loadings and scores biplot of first and second principal component of the electronic nose sensor responses for the sea fennel samples revealed that the first two principal components accounted for the 89.2% of the total variance (68.7% and 20.5% for first and second principal component, respectively, figure 3).

Four of five scores of the freeze-dried samples fall in the lower-left quadrant of the biplot, all the scores of the dried@40°C samples fall in the upper-left quadrant of the biplot and all the

dried@60°C scores fall in the half-right part of the biplot. There could be individuated cross-sensitive issues or collinearities between sensors of the array in the electronic nose used, as among loadings of the PCA biplot there were the same direction and almost the same contribution on the first and second principal component. A first group of collinearities among sensors is visible considering sulphur-organic, sulph-chlor, broad-range and in minor part broad-methane and hydrogen sensors. A second one comprises aromatic1, aromatic2 and arom-aliph sensors. These sensors had redundant signals and one or more of them could be omitted in the sample classification without significant loss of information providing money savings in manufacturing a new tailored sensor array tailored for the specific purpose. The first group comprised the sensors with declared selectivity towards terpene molecules, as stated by the producer (as sulphur-organic sensor was declared in the datasheet as “otherwise sensitive to many terpenes and sulphur organic compounds, which are important for smell, limonene, pyrazine”), whereas the second group collected the sensors with declared higher selectivity towards aromatics. The hydrogen sensor has the major contributions on the first and second principal components. The scores relative to sensors signals of samples of sea fennel dried at 40°C were in the upper-left quadrant of the biplot where loadings of methane-aliph and broad-alcohol sensors are pointing to. Four of the five scores representing the dried samples dried at 60°C were in the lower right quadrant where loadings of hydrogen, sulphur-organic, sulph-chlor and broad-range sensors are pointing to. Four of five scores of the freeze-dried sample fall in the lower left quadrant where are pointing loadings of aromatic1, aromatic2 and arom-aliph sensors. The major contribution to the first principal component was due to sulphur-organic, sulph-chlor, broad-range sensors which are discriminant with respect to the different processed samples of sea fennel characterized by terpene volatiles present in the headspace. This result is in agreement with that reported by Longobardi (Longobardi et al., 2015), who also noted how the sulphur-organic sensor in the same electronic nose used, was crucial in discrimination of the geographical origin of sweet cherries, as it was particularly selective to terpene molecules, whatever was the information extracted from the signal of the sensor (a single point at the end of the

sampling time, one point every 10 s, every point of the curve during sampling time). Moreover, this result confirms also the selectivity towards terpene molecules declared by the producer about sulphur-organic sensor to which we can add in this particular case, that of the sulph-chlor and broad-range sensors. An interesting correlation was among Arom-aliph, aromatic1 and aromatic2 sensors and phenyl propanoids (apiol). This result is in agreement with the consideration that apiol contains an aromatic ring and all the three sensors are sensitive to aromatics as declared by the producer. To apply discriminant analysis, it is necessary that the number of variables does not exceed the number of objects, to prevent overloading of the computations required to calculate the Mahalanobis distances and some strategies of variable reduction have been implemented in literature (Armanino, Casolino, Casale, & Forina, 2008; Forina et al., 2007). The variables in this case are the sensors in the array, the observations are the samples, and such a very high ratio between the number of descriptors and number of samples may increase also the risk of chance correlations and overfitting (Roberts & Cozzolino, 2016). Collinearity or redundancy between variables (also known as cross-sensitivity or a sensor's reaction to an interfering gas, causing an undesirable response, either positive or negative) in the electronic nose sampling, may be due to the sensor manufacturing technique especially in the case of arrays made with sensing elements of the same technology (MOS in this case) leading to a model with poor predictive ability. By using two electronic noses with arrays made of different technologies and considering a virtual array of sensors made by a combination of the two, better discriminations have been achieved in recognizing malodors from wastes (Giungato et al., 2016). For these reasons the contemporary trend of firms consists on releasing arrays with sensors made with different technologies (MOS, Photoionization detectors PID and conducting polymer) to enhance discrimination capabilities of the proposed commercial devices. The use of a stepwise method for variable selection can reduce the ratio between the number of variables and the number of samples (i.e. variables/objects ratio) and it would give a more robust predictive model for classification among processed samples of sea fennel

also in the presence of collinearity. In table 4 the results of the stepwise forward classification methods adopted in comparison with the LDA used without variable reduction are reported.

LDA which is a supervised classification model, showed 78.4% and 21.6% of proportion of trace for the first and second canonical component with prediction ability of the model of 15/15 correctly classified (100%) and cross-validation (with leave-one-out) prediction ability of the model of 14/15 (93.3%) (table 4). The LDA model made using all the sensors correctly classified 100% of the samples but when the model was built with $n-1$ samples, in the leave-one-out cross validation, the correct classification rate slightly decreased, and this may be due to the aforementioned variables/objects over-ratio. The forward variable selection has been used in stepwise direction for classification using LDA, QDA, Bayes and KNN methods (indicated with S-LDA, S-QDA, S-Bayes and S-KNN in table 4). The correct classification varied among the classification methods ranging from 100% of S-LDA and S-KNN to 93.3% of S-QDA and S-Bayes, in leave-one-out cross validation. It is interesting to note that two of the classification methods individuated the hydrogen sensor as the most representative to discriminate among categories of the sea fennel although with 93.3% right classification rate whereas the broad-range sensor was recognized by S-KNN with 100% of correct classification rate. Those results confirmed the PCA analysis of sensor signals as the hydrogen sensor showed the major contributions to both the principal components with respect to the other sensors. With the comparative analysis between PCA biplot of peak areas of VOCs emitted by the samples and signals of the sensors in the array of the electronic nose, and the selection of sensors in classification algorithms, we had all the tools we needed to select the sensors of the array more useful for the identification purposes. With the synergistic combination of all the methods we highlighted the most important sensitivity and selectivity characteristics of sensors useful to manufacture a specific tailored array for a customized electronic nose. The slight differences among performances of classification models need to be further deepened and the

combination of different technologies in the manufacture of a tailored array of sensors in an electronic nose, in the aim to reduce redundancy and foster the discrimination capabilities, should be the argument of next research challenges, in which more than one electronic nose should be used possibly equipped with different technologies.

4. Conclusions

The sea fennel, *Crithmum maritimum* L., could be a new interesting spice to be launched in the food market. Three possible processes have been tested for flavor preservation and shelf-life increase: drying @ 40°C, drying @ 60°C and freeze-drying. Color measurements revealed darkening of samples with increasing drying temperature from 40 to 60°C whereas freeze drying preserved initial appearance of the fresh sample. Weight loss of all samples remained almost constant (about 85% of the initial weight) but mean water activity was higher in the case of air-dried sample at 40°C, but in all cases low enough to prevent mold growth. The development of VOCs during HS-SPME-GC/MS revealed 35 volatiles grouped in: terpene hydrocarbons (limonene, E,E-2,6-dimethyl-1,3,5,7-octatetraene or cosmene, cis-beta-terpinene, 4-carene, gamma-terpinene, cis-beta-ocimene, alpha-terpinolene, beta-mircene, alpha-pinene, alpha-thujene, p-cimene), oxygenated terpenes (p-thymol, carvone, sabina ketone, alpha-terpineol, 4-terpineol, 4-thujanol, trans-p-mentha-2,8-dienol, beta-linalool), sesquiterpen hydrocarbons (beta-sesquiphellandrene, beta-bisabolene, alpha-zingiberene, alpha-bergamotene, gamma-elemene, beta-caryophyllene, cuparene, alpha-curcumene), one phenyl propanoid (apiol), not-terpenic aldehydes (esanal, eptanal, octanal, decenal) and not-terpenic ketones (2-nonanone, 3,5-octadien-2-one). A comparative analysis between PCA of VOCs and that of electronic nose sensor signals revealed the strong contribution of sulphur-organic, sulph-chlor, broad-range sensors which are discriminant with respect to the different processed samples of sea fennel characterized by an important presence of terpene volatiles in the headspace of processed samples. The result confirms the selectivity declared by the producer towards terpene molecules for

the sulphur-organic sensor to which we can add in this particular case, that of the sulph-chlor and broad-range sensors. An interesting correlation has been found among Arom-aliph, aromatic1 and aromatic2 sensors and phenyl propanoids (apiol). This result is in agreement with the consideration that apiol contains an aromatic ring and all the three sensors are sensitive to aromatics as declared by the producer. Stepwise LDA and simple K-nearest neighbors obtained a 100% overall correct classification rate in leave-one-out cross-validation of the electronic nose, stepwise K-means and Naive-Bayes gave 93.3%. Among sensors selected by the statistical stepwise method, hydrogen and broad-range were the preferred predictors selected by the classification algorithms used in this work. The stepwise selection algorithm selected two sensors useful for classification purposes the hydrogen and broad-range. Signals from both sensors were sufficient to realize a useful discrimination, signals from others were noising or redundant, hence negligible for classification purposes. This means that those two sensors of the array may be used to arrange a tailored array of an electronic nose targeted for the market of sea fennel processing control. This work confirms that the electronic nose used is an effective tool both for assessing the quality of a spice in food processing and to monitor product quality in-situ and real-time. Interesting synergies could be achieved by comparing chemical headspace analysis with sensors responses of the electronic nose, in terms of selectivity toward volatiles, enhancing the most useful for the classification purpose we had in mind. Stepwise techniques are useful in selecting sensors of the array for better classification of samples in groups, or in other words, individuating the reaching of targeted quality parameters during drying or freeze-drying, and to stop the process at the right end-time. The work has achieved the goal to provide to producers and researchers useful tools to prototype new arrays made with fewer, cheaper and efficient sensors, tailored for specific purposes of customers.

Authors' contributions

Pasquale Giungato and Massimiliano Renna both participated in study conception and design of experiments, Massimiliano Renna provided the samples, made color, water activity and weight analysis, Pasquale Giungato acquired e-nose data, drafted and supervised the manuscript, performed statistical analysis. Roberto Rana supervised the manuscript contributing to data collection and interpretation. Sabina Licen and Pierluigi Barbieri performed set-up of the method, chemical analysis and supervised the manuscript. All authors carefully read and approved the final manuscript.

Conflict of interest statement

All authors declare no actual or potential conflict of interest including any financial, personal or other relationships with other people or organizations within three years of beginning the submitted work that could inappropriately influence, or be perceived to influence, their work.

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Abbreviations

HS-SPME-GC/MS	Head-Space Solid Phase Micro-Extraction Gas-Chromatography/Mass Spectrometry
KNN	Simple k-Nearest Neighbors
LDA	Linear Discriminant Analysis
LOO	Leave-one-out;
MOS	Metal Oxide Semiconductor
PCA	Principal Component Analysis
PLS-DA	Partial Least Squares Discriminant Analysis
QDA	Quadratic Discriminant Analysis
S-Bayes	Stepwise forward Naive Bayes Classifier
S-KNN	Stepwise forward Simple k-Nearest Neighbors classifier
S-LDA	Stepwise forward Linear Discriminant Analysis
S-QDA	Stepwise forward Quadratic Discriminant Analysis

Figure captions

Figure 1. Samples of fresh sea fennel, dried @ 40 °C, dried @ 60 °C and freeze-dried.

Figure 2. Loadings and scores biplot of the first and second principal component for GC/MS mean peak areas of classes of VOCs in the headspace of the sea fennel samples (dried @ 40°C, dried @ 60°C and freeze-dried). Legend: NTA = not-terpenic aldehydes; NTK = not-terpenic ketones; TH = terpene hydrocarbons; OT = oxygenated terpenes; PP = phenyl propanoids; SH = sesquiterpen hydrocarbons. To avoid misunderstandings I attached the pdf (FOODRES-D-18-01598R2).

Figure 3. Loadings and scores biplot of first and second principal component of the electronic nose sensor responses for the sea fennel samples (dried @ 40 °C, dried @ 60 °C and freeze-dried, five replicates per type).

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Table 1. Sensors sensitivity features of the PEN3 electronic nose labelled by the producer together with the classes of volatiles to which it presented most of its selectivity and reference gas.

Sensor name	Classes of volatile	Reference
Aromatic 1	Aromatic compounds	Toluene 10 mg/kg
Broad-range	very sensitive, broad range selectivity, react on nitrogen oxides, very sensitive with negative signals	NO ₂ , 1 mg/kg
Aromatic 2	used as sensor for ammonia and aromatic compounds	benzene, 10 mg/kg
Hydrogen	mainly hydrogen, selectively, breath gases	H ₂ , 0.1 mg/kg
Arom-aliph	alkanes, aromatic compounds, less polar compounds	propane, 1 mg/kg
Broad-methane	sensitive to methane (environment) c.a. 10 mg/kg, with broad-range similar to the following sensor broad-alcohol	CH ₄ , 100 mg/kg
Sulphur-organic	react with sulphur compounds, H ₂ S 0.1 mg/kg, otherwise sensitive to many terpenes and sulphur organic compounds, which are important for smell, limonene, pyrazine	H ₂ S, 1 mg/kg
Broad-alcohol	detects alcohols, partially aromatic compounds, broad range response	CO, 100 mg/kg
Sulph-chlor	aromatic compounds, sulphur organic compounds	H ₂ S, 1 mg/kg
Methane-aliph	reacts on high concentrations > 100 mg/kg, sometimes very selective to methane	CH ₄ , 100 mg/kg

Table 2. Color, weight loss and water activity of sea fennel samples (dried @ 40 °C, dried @ 60 °C and freeze-dried).

	L*	a*	b*	Weight loss (%)	Water activity
Calibrating White	98.01	0.09	1.67		
air-dried@40 °C	45.6±1	-9.7±0.6	26.2±0.7	85.0±0.1	0.31±0.02
air-dried@60 °C	41.7±1	-1.75±0.05	26.7±1.7	85.8±0.2	0.19±0.01
freeze-dried	53.6±1	-16.22±0.05	33.8±1.4	85.1±0.1	0.28±0.01

Table 3. Main constituents identified in the HS-SPME-GC/MS of sea fennel samples.

Peak #	Retention time (min)	CAS	Name	Molecular weight (g/mol)	Family
1	8.0	000066-25-1	hexanal	100.16	NTA
2	12.1	000111-71-7	heptanal	114.18	NTA
3	12.9	002867-05-2	alfa-thujene	136.23	TH
4	13.2	000080-56-8	alfa-pinene	136.23	TH
5	14.8	003387-41-5	sabinene	136.23	TH
6	15.3	000123-35-3	beta-myrcene	136.23	TH
7	15.9	000124-13-0	octanal	128.21	NTA
8	16.3	029050-33-7	alfa-terpinolene	136.23	TH
9	16.6	000099-87-6	p-cimene	134.21	TH
10	17.1	138-86-3	limonene	136.24	TH
11	17.4	003338-55-4	beta-cis-ocimene	136.24	TH
12	17.8	000099-85-4	gamma-terpinene	136.23	TH
13	18.1	038284-27-4	3,5-Octadien-2-one	124.18	NTK
14	18.1	546-79-2	4-thujanol	154.25	OT
15	18.6	029050-33-7	4-carene	136.23	TH
16	18.8	000821-55-6	2-nonanone	142.24	NTK
17	19.1	000078-70-6	beta-linalool	154.25	OT
18	19.1	007299-41-4	cis-beta-terpinene	136.23	TH
19	19.7	460-01-5	2,6-Dimethyl-1,3,5,7-octatetraene, E,E-	134.21	TH
20	19.8	NIST 139653	trans-p-mentha-2,8-dienol	152.23	OT
21	20.9	000513-20-2	Bicyclo[3.1.0]hexan-2-one, 5-(1-methylethyl)- (Sabina ketone)	138.20	OT
22	21.6	020126-76-5	4-terpineol	154.24	OT
23	22.1	022771-44-4	alfa-terpineol	154.25	OT
24	23.5	002244-16-8	(+)-carvone	150.22	OT
25	24.0	003913-81-3	decenal	154.25	NTA
26	25.0	003228-02-2	p-thymol	150.22	OT
27	28.3	000087-44-5	beta-cariophyllene	204.36	SH
28	28.5	339154-91-5	gamma-elemene	204.35	SH

29	28.6	017699-05-7	alfa-bergamotene	204.35	SH
30	30.1	000644-30-4	alfa-curcumene	202.34	SH
31	30.5	000495-60-3	alfa-zingiberene	204.35	SH
32	31.0	000495-61-4	beta-bisabolene	204.35	SH
33	31.1	016982-00-6	(+)-cuparene	202.34	SH
34	31.6	020307-83-9	beta-sesquiphellandrene	204.35	SH
35	34.8	000523-80-8	apiol	222.23	PP

Legend: The components are listed in order of their elution on the column. **NTA** = not-terpenic aldehydes; **NTK** = not-terpenic ketones; **TH** = terpene hydrocarbons; **OT** = oxygenated terpenes; **PP** = phenyl propanoids; **SH** = sesquiterpen hydrocarbons.

Table 4. Results of discriminant analysis and stepwise forward discriminant analysis with cross-validation per method applied on the sea fennel samples.

	Cross validation	Correctness rate (%)	Selected Predictors	
LDA	none	100	all	
LDA	LOO	93.3	all	
S-LDA	LOO	100	all	
S-QDA	LOO	93.3	Hydrogen	
S-Bayes	LOO	93.3	Hydrogen	
S-KNN	LOO	100	Broad-range	

Legend: LOO = Leave-One-Out; LDA=Linear Discriminant Analysis, S-LDA= Stepwise forward Linear Discriminant Analysis, S-QDA=Stepwise forward Quadratic Discriminant Analysis, S-Bayes= Stepwise forward Naive Bayes Classifier, S-KNN= Stepwise forward Simple k-Nearest Neighbors classifier.

Highlights

- Air-dried and freeze-dried sea fennel (*Crithmum maritimum* L.) samples were prepared
- VOCs emitted by samples were chemically characterized
- Classification capability of an electronic nose among samples was tested
- Correlations emerged between sensor responses and detected VOCs
- Supervised methods of classification with reduction techniques were used



Freeze-dried

Dried at 40 °C

Dried at 60 °C

Figure 1

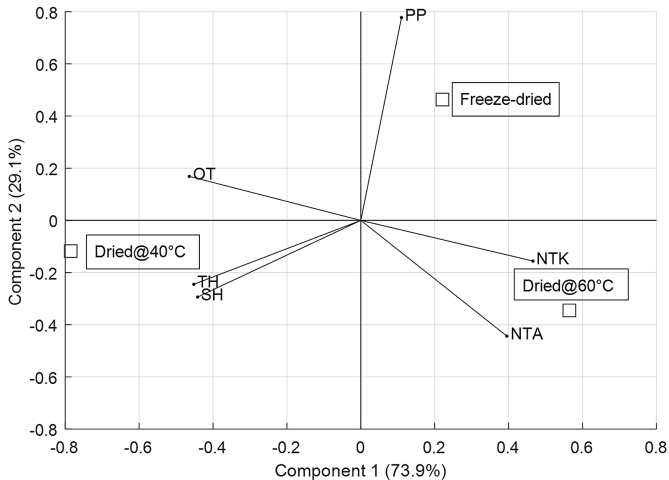


Figure 2

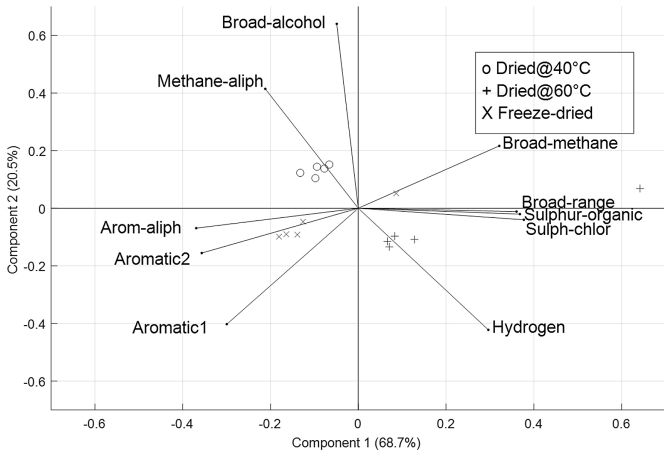


Figure 3