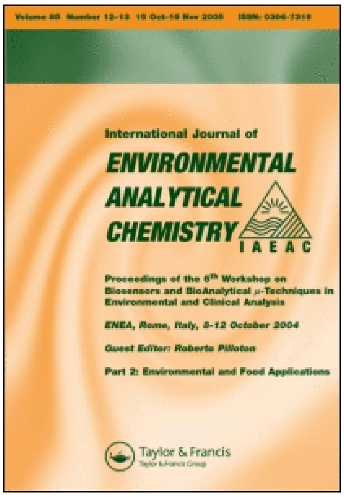

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Comparison of gas chromatography–mass spectrometry and electronic tongue analysis for the classification of onions and shallots

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Onions and Jersey shallots belong to the same species (*Allium cepa* L.), but are from two different groups: *cepa* and *aggregatum*. The grey shallot belongs to *Allium oschaninii* O. Fedtsch. Onions and shallots differ in taste but however both contain same sulfur volatile compounds making sensory evaluation difficult. There is a practical need to reliably discriminate onion from shallot. The aim of this study was to evaluate and compare the classification of several cultivars of onions and shallots by the 'electronic tongue' and by the chemical analysis of their fresh aroma. The 'e-tongue' is an analytical instrument comprising an array of cross-sensitive chemical sensors. The fresh aroma of onion and shallot due to sulfur compounds (thiosulfinates and zwiebelanes) was analysed by GC-MS. Data processing was performed by PCA. The 'e-tongue' and GC-MS chemical analysis were able to separate onions from shallots. The grey shallot and the white onion were separated from all samples by the two techniques, a result which fits well with its botanical nature. The differentiation between seed-propagated cultivars (all onions and a few shallots) from the vegetative produced ones (all the classic shallots) was also done. The two methods appeared compatible and sometimes complementary.

Keywords: Onion; Shallot; Sensor array; Electronic tongue; Sulfur compounds; PCA; GC-MS

1. Introduction

Allium, which belongs to the Liliaceae family, is a very large genus in which six subgenera and 43 sections have been recognized [1, 2]. Included within the genus *Allium* are around 700 different species and some, such as garlic, onion, shallot, leek and chive are edible and used as vegetables or condiments throughout the world.

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As shown by morphology, floral biology, isozymes and molecular markers [3–7], onion and Jersey (or pink) shallot belong to the same species (*Allium cepa* L.), but are from different groups, *A. cepa* group cepa and *A. cepa* group aggregatum, whereas grey shallot belongs to another species, *Allium oschaninii* O. Fedtsch. It is a specific type of shallot grown in Southern and Eastern France and differs from the Jersey shallot especially in its coriaceous external 'shell' and its typical taste.

Onions are seed-propagated and sown, whereas shallots are vegetative multiplied and bulbs are planted and give rise to a cluster of bulbs. Therefore shallots are more expensive than onions. This has given rise to cases where onions, or mixtures of onion type bulbs and shallot type bulbs, have been marketed and sold as shallots. Seed-propagated hybrid cultivars have been recently released with the name of seed-propagated shallots.

The fresh aroma of *Allium* species is mainly composed of sulfur compounds: the thiosulfinates, Ti. In this genus, the aroma of the species *A. cepa* including shallot and onion is more complex than other *Allium* species on account of the abundance of lachrymatory factor and other characteristic sulfur compounds of onion and shallot: the zwiebelanes, Zw [8, 9]. So Ti and Zw are the constituents of the fresh aroma of onion and shallot. The simultaneous analysis of these labile compounds is not easy but a recently developed GC-MS method using a short and thick capillary column allows it [10].

Furthermore, onions and shallots also differ in taste. Therefore, a rapid analytical technique for the discrimination of onions and shallots would be of practical interest and importance to growers and those involved in post-harvest applications.

For this purpose, two analytical methods can be used. One is based on the headspace chemical analysis using a method allowing the quantification of the labile sulfur volatiles [11]. The other one, the electronic tongue ('e-tongue') is an analytical instrument which has an array of semi-selective chemical sensors with partial sensitivity to different solution components (inorganic ions, organic ions, polar soluble organic substances, etc.) along with an appropriate pattern recognition instrument, capable of recognizing the quantitative and qualitative composition of simple and complex solutions [12]. In an earlier work, the 'e-tongue' was successfully applied in the recognition and classification of different foodstuffs, including non-liquid food, such as meat and fruits [13, 14].

The aim of this study was on one hand to demonstrate the applicability of the 'e-tongue' and the chemical analysis of fresh aroma in the discrimination of onion and shallot cultivars and on the other hand to compare these two methods.

2. Material and methods

2.1 *Plant material*

One cultivar of grey shallot, nine cultivars of Jersey shallot, five cultivars of onion and two seed-propagated hybrid cultivars were included in the experiment. These two seed-propagated hybrid cultivars are heterogeneous for bulb shape, flesh colour and flesh structure, that is, some bulbs look like shallots, some resemble onions and some are intermediate between onions and shallots. All samples were supplied under a code number (table 1) and their names and dry matter content were not disclosed before

Table 1. List of grey shallot (■), onions (●), Jersey shallots (▲) and seed propagated hybrid cultivars (✦) samples used in the experiments.

Codes	Cultivar	Plant and bulb shape	Dry matter contents
▲ A	Jermor	Long shallot	20.2%, 17.0%
● B	Rosé de Roscoff	Onion	11.0%
▲ C	Mikor	Half-long shallot	17.1%, 16.0%
▲ F	Bretor	Long shallot	19.6%
● G	Jaune des Cévennes	Onion	10.5%
✦ H	Ambition	Hybrid (shallot type)	–
▲ I	Longor	Long shallot	19.3%, 17.0%
▲ J	Pikant	Half-long shallot	22.1%
▲ K	Golden Gourmet	Half-long shallot	16.7%
■ L	Griselle	Grey shallot	27.9%
▲ M	Arvro	Half-long shallot	16.7%
▲ O	Santé	Half-long shallot	15.1%
✦ Q	Matador	Hybrid (shallot type)	–
✦ R	Matador	Hybrid (onion type)	–
✦ S	Ambition	Hybrid (onion type)	–
● T	Echalion	Onion-échalion	12.0%
▲ U	Vigarmor	Long shallot	20.0%
● V	White onion	Onion	21.0%
● W	Yellow onion	Onion	9.0%

experiments. Plant material used in the first series of experiments was a wide panel of cultivars: grey shallot (Griselle, sample L), onions (Rosé de Roscoff sample B, Jaune des Cévennes, sample G and Echalion, sample T), Jersey shallots (Jermor, sample A, Mikor, sample C, Bretor, sample F, Longor, sample I, Pikant, sample J, Golden Gourmet sample K, Arvro, sample M and Santé, sample O) and two seed-propagated hybrid cultivars (Ambition, samples H and Q and Matador, samples R and S). In the second series, the grey shallot was removed in order to keep only *A. cepa* material, i.e onions, shallots and hybrids including typical white and yellow onions (V, W) and shallot Vigarmor (U). In the third series, onions and shallots were considered especially regarding their dry matter content. Therefore, an onion cultivar with high dry matter (V) was included such as in the second series and seed-propagated shallots were removed.

2.2 *'e-Tongue' analysis*

As no data on the use of the 'e-tongue' on *Allium* sp. were available, a very preliminary series of experiments had been carried out in order to determine the best methods of sample preparation, homogenate concentration, as well as optimizing the potentiometric chemical sensors in the 'e-tongue'.

2.3 *Sampling for 'e-tongue' analysis*

The method established during the very preliminary series was used here. The bulbs were stored at 4°C throughout the experiment. Since the 'e-tongue' works in liquid media some sample preparation before measurements was necessary. A pulp (from 5 to 15 g of bulb) was prepared by vigorously grinding each sample (a piece of a bulb) with a plastic, metal-free grinder. The pulp was immediately placed into 50 mL of distilled water and stirred intensively for a few minutes. Measurements with the 'e-tongue' were then performed. The sensor array was immediately dipped into the homogenate and, after 3 min stirring, sensor readings were recorded. At least three replicates of each sample were run. All samples were measured in random order.

In the course of the experiments, it was found that a quantity of 15 g of onion in 50 mL of water was often necessary to obtain a satisfactory level of reproducibility. Therefore, the concentration of homogenate was increased up to 15 g in 50 mL of water, which was favourable for stability of sensor readings and final classification. The whole procedure was aimed at performing sample preparation and analysis as quickly as possible, so as to avoid sample oxidation and any other deleterious chemical changes.

The sensor array was comprised of 21 potentiometric chemical sensors. Sensors used were constructed with either a chalcogenide glass and crystalline membranes, or polymer (PVC) plasticized membranes containing different active substances. A pH glass electrode was also included in the sensor array. Details of sensors composition and preparation can be found elsewhere [12]. Potentiometric measurements with the sensor array were made using a high-input impedance multichannel voltmeter *versus* conventional Ag/AgCl reference electrode.

2.4 *GC-MS analysis of the fresh aroma*

Analytical method was according to Mondy *et al.* [11]. GC-MS analysis was carried on a Perkin Elmer Turbomass system (Boston, MA, USA) with a fused silica capillary column: $10\,\text{m} \times 0.32\,\text{mm} \times 4\,\mu\text{m}$ (Supelco Sigma-Aldrich, St Louis, MO, USA). Total ion chromatograms and mass spectra were recorded in electronic impact ionization mode at 70 eV. Data were treated both in full-scan and SIM mode.

2.5 *Sampling for GC-MS analysis*

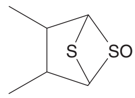
Onion bulbs were crushed according to Arnault *et al.* [10] and after an optimal time of Ti formation, 80 min, the juice was filtered and saturated with sodium chloride. Volatiles present in the headspace were extracted using 10% of the juice volume of diethyl ether (Sigma-Aldrich, St Louis, MO, USA). This step was conducted at 4°C to avoid loss of the volatiles present in the headspace. Then organic phase was dried and directly injected into GC-MS system. At least three replicates were analysed for each cultivar.

2.6 *Principal component analysis of GC-MS and 'e-tongue' data*

During data processing both the whole array and various optimized sub-arrays were considered. Data processing was aimed at sample recognition and classification. Recognition was done using PCA. Commercial software Xlstat version 5.0 (b8) (Addinsoft, Brooklyn, NY, USA) and Unscrambler (CAMO AS, Norway) was used.

Seven Ti and three Zw were identified (table 2) in chromatogram profiles (figure 1) of each *Allium* spp. sample. The PCA done with relative proportion of these compounds allowed exploiting data and marked differences between and within *cepa* and *aggregatum* groups and between cultivars.

Table 2. Ti and Zw found in onion and shallot.

Compound	Name	Structure
1	Dimethyl thiosulfinate	CH_3–SO–S–CH_3
2	Methyl propyl thiosulfinate	CH_3–SO–S–CH_2–CH_2–CH_3
3	Methyl 1-propenyl thiosulfinate	CH_3–SO–S–CH=CH–CH_3
4	Propyl methyl thiosulfinate	CH_3–CH_2–CH_2–SO–S–CH_3
5	1-Propenyl methyl thiosulfinate	CH_3–CH=CH–SO–S–CH_3
6	*cis*-Zwiebelane	
8	*trans*-Zwiebelane	
9	Zwiebelane isomer	
7	Propyl 1-propenyl thiosulfinate	CH_3–CH_2–CH_2–SO–S–CH=CH–CH_3
10	1-Propenyl propyl thiosulfinate	CH_3–CH=CH–SO–S–CH_2–CH_2–CH_3

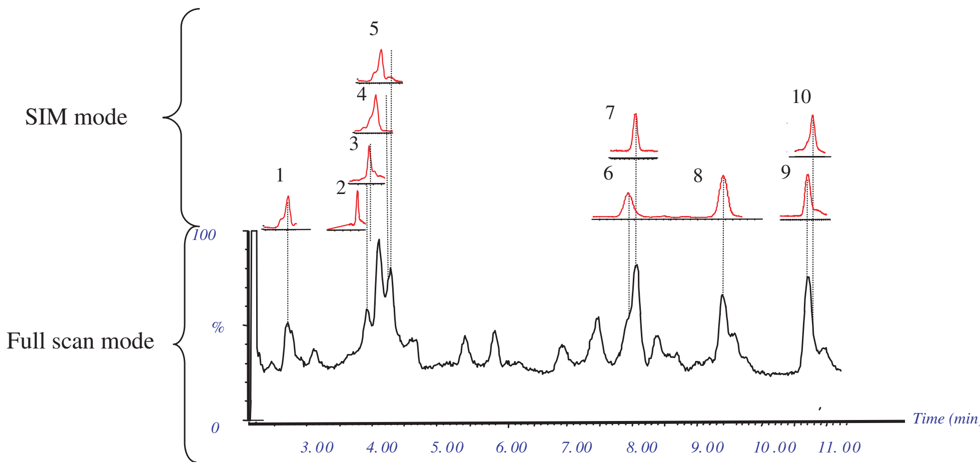


Figure 1. Total ion current chromatogram of *Allium cepa* extract in full scan and in SIM mode.

3. Results and discussion

3.1 *'e-Tongue' analysis*

The results of recognition of the samples using the 'e-tongue' are shown in the form of PCA score plot.

The 'e-tongue' classification by PCA in figure 2(a) shows the separation of the grey shallot (L) from all other onions and shallots. Grey shallot individuality was clearly demonstrated, which is in full accordance with its botanical nature. However, some shallot samples could not be distinguished. This was probably due to an insufficient sensitivity of the sensor system. Thus, the concentration of homogenate was increased from 5 to 15 g per 50 mL of water to improve reproducibility and subsequently the ability of the 'e-tongue' to discriminate onions and shallots.

Figure 3(a) shows classification of all onions (B, W and G), shallots (A, C, U and I) and seed-propagated hybrid cultivars Ambition and Matador (H, Q, R and S). Sample V, the white onion with high dry matter content, was distinguished from the

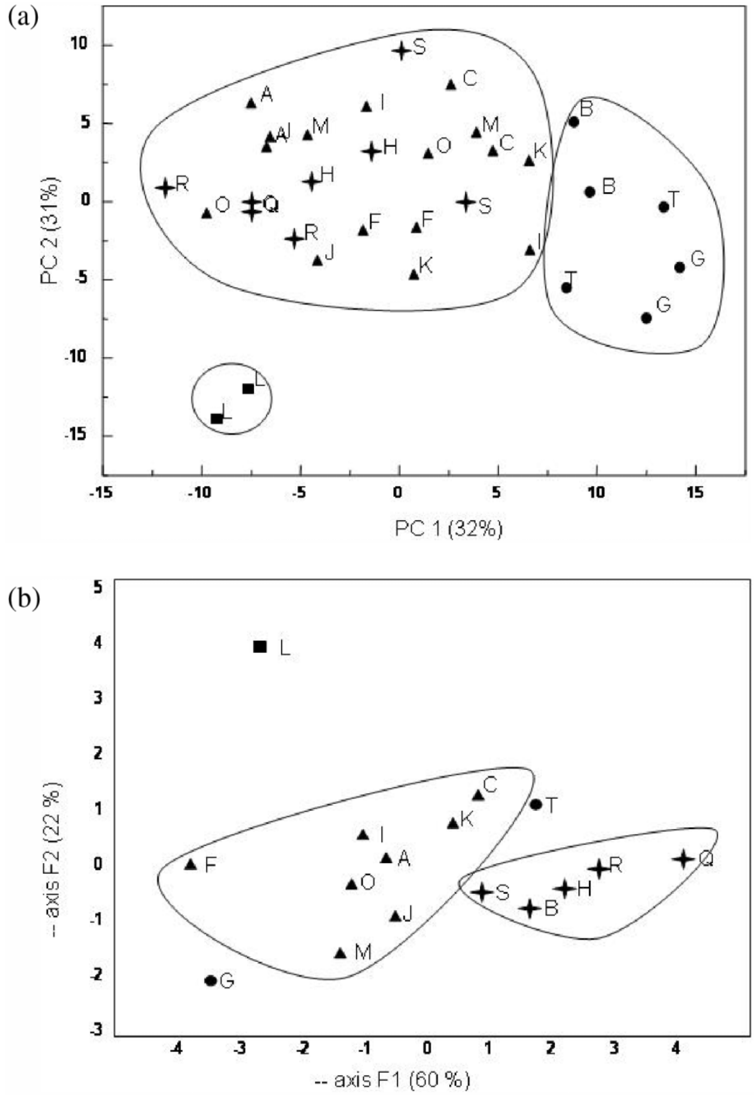


Figure 2. (a) PCA score plot classification obtained with 'e-tongue' analysis of *Allium oschaninii* (grey shallot, L) and *Allium cepa* cultivars (onions B, T, G; Jersey shallots A, C, F, I, J, K, M, O; seed-propagated hybrids cultivars H, Q, R, S). (b) PCA score plot classification obtained with GC-MS analysis of *Allium oschaninii* (grey shallot, L) and *Allium cepa* cultivars (onions B, T, G; Jersey shallots A, C, F, I, J, K, M, O; seed-propagated hybrids cultivars H, Q, R, S).

three other onions and shallots forming a distinct cloud. The seed propagated cultivars were well separated from onions and shallots.

Only onions (V, W, B, and G) and shallots (A, I, U and C) were shown in figure 4(a). All onions were easily distinguished from all shallots.

It must be pointed out that the first two principal axes of the PCA map of figure 1(a), figure 2(a) and figure 3(a) stood for 50, 64 and 77% of the total variance, respectively.

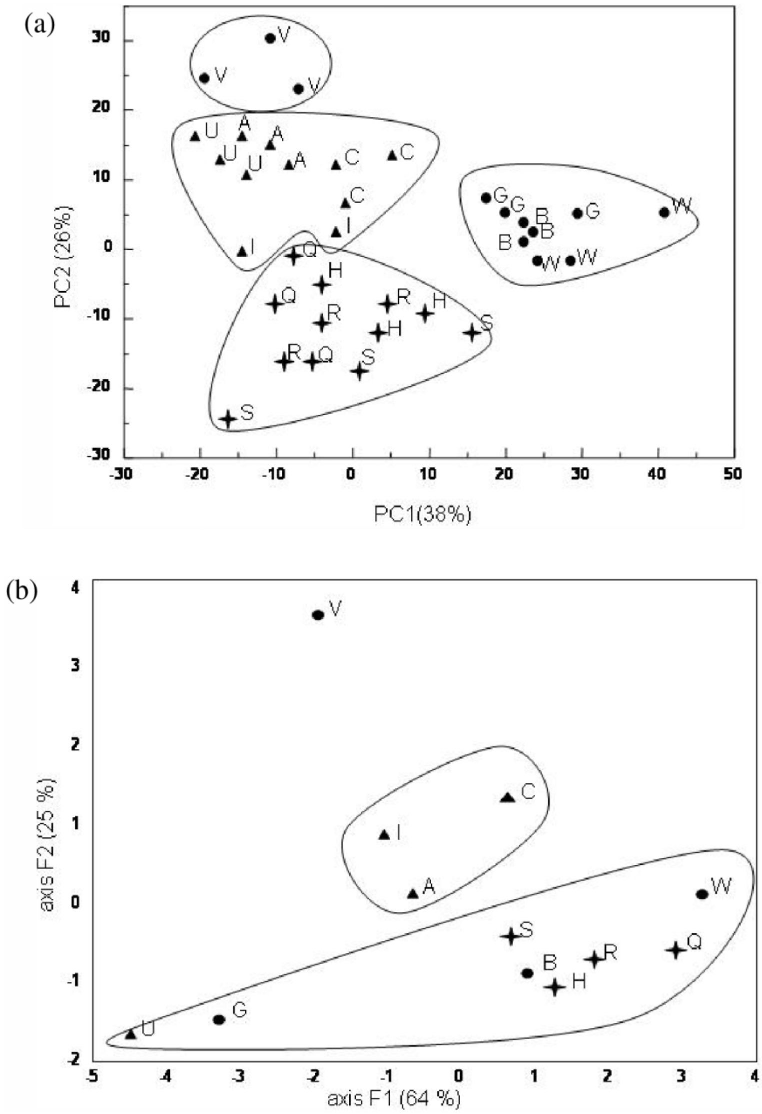


Figure 3. (a) PCA score plot classification obtained with 'e-tongue' analysis of onions (B, G, V, W), Jersey shallots (A, C, I, U), seed seed-propagated hybrid cultivars (H, Q, R, S). (b) PCA score plot classification obtained with GC-MS analysis of onions (B, G, V, W), Jersey shallots (A, C, I, U), seed seed-propagated hybrid cultivars (H, Q, R, S).

3.2 *GC-MS chemical analysis*

The classification by PCA of all samples (figure 2b) showed a clear distinction of Griselle (L). The sweet onion (G) was also isolated. Jersey shallots formed a distinct cloud whereas no clear distinction was observed between onions and seed-propagated hybrid cultivars.

Figure 3(b) presents the PCA classification of the same samples used for figure 3(a). First, the white onion (V) is clearly distinguished from all other cultivars.

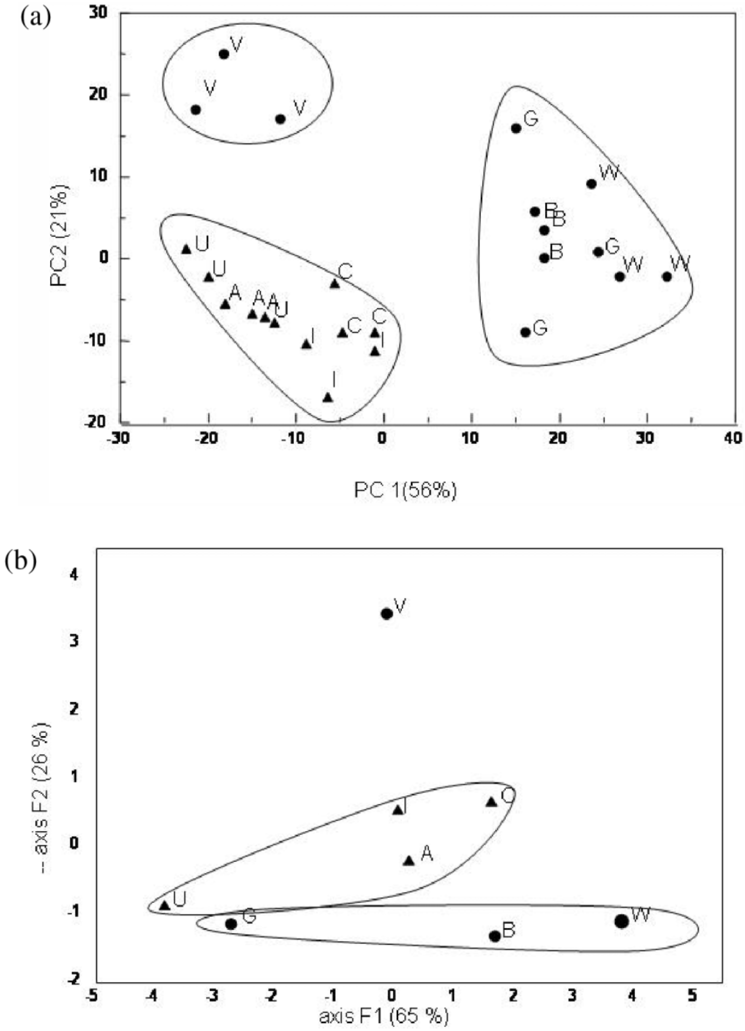


Figure 4. (a) PCA score plot classification obtained with 'e-tongue' analysis of Jersey shallots (A, C, I, U) and onion*s* (B, G, V, W). (b) PCA score plot classification obtained with GC-MS analysis of Jersey shallots (A, C, I, U) and onions (B, G, V, W).

Second, seed-propagated hybrid cultivars (H, Q, R and S) and onions (B, G and W) were easily distinguished from vegetative multiplicated shallot cultivars (A, C and I). Contrary to 'e-tongue' analysis, seed propagated cultivars Matador and Ambition were not separated from onion cultivars. This could be explained by the fact that different lots could mean different materials because of heterogeneity.

The distinction between shallots and onions is demonstrated by the PCA map on figure 4(b). White onion was always separated from the other onions.

The first two principal axes stood for 82, 89 and 91% of the total variance for figure 2(b), figure 3(b) and figure 4(b), respectively. Therefore GC-MS chemical analysis of the fresh aroma of shallots and onions distinguished the very characteristic samples like grey shallot and the onion with a high dry matter. Furthermore, a clear separation has been established between seed-propagated hybrid cultivars Matador and Ambition and Jersey shallots.

The results obtained with both methods are similar and complementary. The grey shallot separation from all others samples was proved by both methods (figure 2a and figure 2b).

The white onion with a high dry matter is also distinguished (figure 3a and figure 3b) and the distinction between onions and shallots was done with both methods (figure 4a and figure 4b).

It is known that 'e-tongue' recognition ability is based on direct sensitivity of the sensor array to various substances, mainly of ionogenic or polar nature. Probably, the 'e-tongue' is also sensitive to the same specific sulfur compounds as the GC-MS chemical analysis, because some of the sensors in the 'e-tongue' array are sensitive to sulfur containing substances. However, this supposition demands direct experimental proof. It is very interesting and rather rare to obtain such a close correlation between methods based on different principles. In fact, both methods are dealing even with liquid phase, directly for the 'e-tongue' and indirectly for GC-MS chemical analysis after an organic extraction of sample juice with diethyl ether.

We obtained the same kind of correlation with GC-MS analysis and sensorial analysis [15] on cheese odours, which are partly constituted of sulfur compounds.

In this study we proved that the two methods, GC-MS and 'e-tongue', were able of classifying onions and shallots in a very similar way. A strong advantage of GC-MS is explicit information about analysed substances, while 'e-tongue' analysis procedure is rapid and simple. Both methods appear to be very effective tools for plant material analysis, easily compatible and complementary in certain cases. Results obtained concur with biological data. Both methods can reliably distinguish shallots from onions and from heterogeneous hybrid cultivars. Data obtained with both methods bring a new proof of the heterogeneous status of these hybrid cultivars. Thus, both GS-MS and 'e-tongue' can be applied for product quality assessment.

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Abbreviations

GC-MS, gas chromatography-mass spectrometry; PCA, principal component analysis; PVC, polyvinylchloride; SIM, selected ion monitoring.

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