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# Piezoelectric peptide-hpDNA based electronic nose for the detection of terpenes; Evaluation of the aroma profile in different *Cannabis sativa L.* (hemp) samples

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ABSTRACT

A piezoelectric peptide-hpDNA based gas sensor array has been used for the detection of terpenes coming from *Cannabis sativa* samples. The array consisted in 11 sensors, 6 having pentapeptides and 5 having hairpin DNA as binding elements. The volatile composition of 28 *Cannabis sativa* samples, assessed by GC–MS analysis, allowed their classification into 2 groups having as monoterpenes and sesquiterpenes in different amounts. The response of the gas sensor array to the same samples demonstrated that both type of sensors are sensitive to the terpenes and contribute to classification. A satisfactory classification (79 % of correctly identified samples) was found using a PLS-DA approach. Using the same dataset and a simple ANN approach the headspace analytical profile of the two different groups was predicted with an average prediction error ≤1 %.

## 1. Introduction

Olfactory indicators in plants include volatile organic compounds (VOCs) that are mainly represented by the terpenoid fraction. Terpenes are an important class of plant constituents deriving from different combinations of C5 isoprene subunits. They are known to possess various medicinal and pharmacological properties [1]. The volatile and semi-volatile fractions of terpenoids can be divided into two different classes based on the number of carbon atoms in their structure, specifically monoterpenes (C10) and sesquiterpenes (C15). Larger terpenes exist as waxes and resins, as well as oxygenated terpenoids. Terpenoids are quite potent and affect animal and even human behavior when inhaled from ambient air [2].

*Cannabis sativa* L. (family Cannabaceae) has been widely used in the past for different purposes, such as the production of tissues or in the medical/pharmacological field since it is considered a valuable medicinal plant with a variety of therapeutic benefits [3–8]. A recent cannabis use survey revealed that 60 % of cannabis users rely on smelling the flower to select their cannabis [9]. Among the chemical constituents of *C. sativa* terpenes play a major role. The most prevalent monoterpenes found were: a) α-pinene and β-pinene which are characterized by pine fragrance and antiseptic effect; they are acetylcholinesterase inhibitor aiding memory and may counteract THC intoxication side effects; b) myrcene with a musky fragrance and anti-oxidant and anti-carcinogenic properties; c) limonene having a citrus fragrance and antifungal and anti-carcinogenic activity; d) linalool potentially effective for anxiety and convulsions with a floral fragrance [2,10,11]. The sesquiterpene β-caryophyllene, the most predominant sesquiterpene found in cannabis, has been reported to interact with cannabinoid receptors type 2, and be responsible for the anti-inflammatory effects of some cannabis preparations. Interestingly, caryophyllene oxide has been reported as the main component for cannabis identification by drug-sniffing dogs [12,13]. Casano and colleagues in 2010 [14] found that in *Cannabis* the relationship between monoterpenes and sesquiterpenes in leaves and inflorescences is different. The monoterpenes have higher volatility and dominate in the inflorescences to repel insects, the more bitter sesquiterpenes dominate in the leaves acting as anti-herbivores for grazing animals. Moreover, different content in terpenes pattern can be associated to different cultivars of Cannabis such as Futura 75, Antal, Carmagnola, and Kompolti [15–18].

Gas chromatography coupled with flame ionization (GC/FID) or mass spectrometric detector (GC/MS) are most frequently used approaches for the analysis of volatile terpenes are [14,19,20]. However, other techniques such as headspace-GC/FID, headspace-GC/MS, two-

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dimensional (GC × GC/qMS), solid phase headspace micro-extraction (HS-SPME) GC–MS and GC × GC/MS have been also used for analysis of the volatile fraction of cannabis and hashish samples [21,22]. Very few gas sensors have been reported in the literature for the detection of terpenes. Attempts to measure pure compounds were made using C-MOS [23] based sensors while QCMs coupled with molecularly imprinted polymers [24] were used to differentiate fresh and dried herbs.

In this work the terpenes fraction of different hemp samples purchased from 3 Italian regions were detected. A QCMs based electronic nose (e-nose) equipped with two different types of sensors was used for the purpose. A set of penta-peptides and hairpin DNA (hpDNA) with different loops were used to modify QCMs and used as binding elements. The peptides and hpDNA were selected via molecular modelling in previous works [25,26]; and were tested giving satisfactory results in the assay different food commodities from olive oil [27], chocolate [28], candies [29], fruit juices [30], carrots [31,32], and pasta [33].

The use of the mixed peptide-hpDNA array resulted in the discrimination of different cultivars of Cannabis sativa. The results, obtained on 28 cannabis samples showed that both peptides and hp-DNA possess, to different extent, the ability to interact with different terpenes, allowing the discrimination of the cultivars because of the different aromatic profiles.

## 2. Materials and methods

### 2.1. Standards reagents and samples preparation

The 28 hemp samples used in this study were bought in different shops from Italian regions (Emilia Romagna, Lazio, Lombardia) as whole flowers in small zip-lock bags and were stored at room temperature until use. Samples were ground using a Kenwood mixer chopper (De Longhi Appliances s.r.l., Treviso, Italy) and sifted with a 1 μm sieve. After grinding, they were stored in hermetically sealed plastic bags (see Fig. S1.).

### 2.2. SPME-GC–MS analysis

A Clarus 580 Gas Chromatography (GC) coupled to a Clarus SQ 8 Mass Spectrometer (MS) (PerkinElmer - Waltham, Massachusetts, USA) was used. 1 g of sample was inserted in a 20 ml-vial closed with crimp top caps and rubber septa. The samples were kept 20 min at 50 °C and then exposed to the fiber (Divinylbenzene/Carboxen/Polydimethylsiloxane, DVB/CAR/PDMS, 50/30 μm, Supelco, Bellefonte, PA) for 10 min at a fixed temperature (40 °C). The fiber was then inserted in the desorption chamber and GC analysis was carried out using the following temperature gradient: start at 50 °C (1 min), ramp 7 °C/min to 145 °C (hold 5 min), ramp 4 °C/min to 175 °C and ramp 7 °C/min to 250 °C (hold 5 min). Helium at flow rate of 1 mL/min was used as carrier; Split of the injector was set to 1:50 and injector transfer line temperature were at 250 °C. A fused silica Zebron- ZB-Semi-Volatile column (30 m × 250 μm × 0.25 μm – Phenomenex, Torrance, California, USA) was used according to [34]. The compounds were identified by matching the obtained spectra with the NIST Mass Spectral Library 2.0 (NIST - Gaithersburg, Maryland, USA) and confirmed by retention index ($R_{Index}$) as proposed in a previous works [17].

### 2.3. Gas sensors array procedure

A UTV E-nose developed by Sensors group, University of Rome Tor Vergata (Italy) equipped with 11 QCM (20 MHz) sensor array was used. QCMs were from KVG GmbH (Germany). Six QCMs were functionalized with different pentapeptides (IHRIC, KSDSC, LAWHC, LGFDC, TGKFC and WHVSC) that were purchased from Espikem (Italy, purity > 85 %). 5 QCMs were functionalized with different sequences of hpDNA (see Fig. S2.). The tetrameric loop hpDNA (CGGG) were from Thermo Fischer Scientifics (Italy), pentameric loops (TAAGT and CCCGA) and hexameric loops (CATCTG and ATAATC) from Integrated DNA Technologies (USA). The loops were extended with the same double helix stem of four base pair DNA (GAAG to 5′ end and CTTC to 3′ end). The peptides and hpDNA were functionalized respectively with zinc oxide nanoparticles (ZnONPs) and gold nanoparticles (AuNPs); the structures of the biomolecules and preparation of the sensors were reported in previous works [25,26]. Nitrogen ($N_2$) was used as gas carrier. The analysis of the samples was carried out using 1 g of dry hemp in glass lab bottles (100 mL) heated at 40 °C for 10 min. This time was selected as optimal to sample the VOCs of hemp samples headspace. The gas carrier enriched with all VOCs was directed to the E-nose chamber and measured for 5 min. The signal obtained was expressed in terms of Frequency shift (ΔF in Hz) that represented the maximum of interaction between sensors and VOCs.

### 2.4. Statistical analysis

Univariate analysis was performed using XLSTAT software (Addinsoft, USA). Experimental results were expressed as means ± standard deviations. Statistical significance was assessed using analysis of variance (ANOVA) with the Tukey HSD (honestly significant difference) multiple comparison analysis and Persons correlation test. The criterion for statistical significance of differences was p-value < 0.05 for all comparisons.

Multivariate statistical analysis was performed using three different approaches, principal component analysis (PCA), hierarchical cluster analysis (HCA) and partial least square discriminant analysis (PLS-DA) using MatLab R2011b (MathWorks, Natick, MA, USA) integrated with two toolboxes for MatLab obtained from Milano Chemometrics and Quantitative structure activity relationship (QSAR) Research Group [35,36]. PLS-DA was run on the dataset with a cross validation of the model using a 'venetian blinds' approach with number of cv groups equal to 3. The dataset of gas sensors array, or GC−MS were auto scaled (zero mean and unitary variance) before statistical procedures. Artificial Neural Network (ANN) was run using JustNN software (www.justnn.com).

## 3. Results and discussion

### 3.1. Hemp samples classification using SPME /GC–MS

28 different VOCs were identified in the headspace of the hemp samples. The relative amount of these compounds expressed as peak area vs. total area of the chromatogram is reported in Table S1 (supplementary material). High relative amount of the sesquiterpene β-caryophyllene and the monoterpene β-myrcene were found having respectively an average concentration of 25.7 % and 19.8 %. Only other three VOCs (D-limonene, α-pinene and humulene) were found above 5 %; the average amount of the other 23 VOCs was below 5 % with 9 VOCs below of 1 %.

The majority of the 28 VOCs detected were monoterpenes (19 in total); among these 5 had hydroxylic group, one had epoxide group, one with thiol-ketone group and three aromatics. The 9 sesquiterpenes included one alcohol, one epoxide and three aromatics. The structural and physicochemical properties of the 28 VOCs found are reported in Table S2.

The relative amount of the 28 VOCs found in the 28 hemp samples were analyzed with the unsupervised multivariate agglomerative hierarchical clustering (AHC) algorithm; Ward's method using as dissimilarity parameter the Euclidean distance was applied. As shown in Fig.1, the AHC algorithm classified the 28 hemp samples in two groups containing 12 (group A) and 16 (group B) samples. According to the ANOVA test (Tukey HSD multiple comparison analysis; P < 0.05) reported in Table 1, 13 VOCs were significant in classifying the 28 hemp samples in two groups.

High relative amounts of the sesquiterpenes β-caryophyllene,

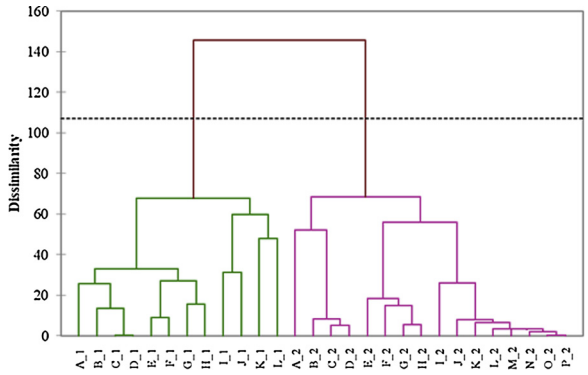


**Fig. 1.** AHC dendrogram of the 28 VOCs detected by SPME/GC–MS in the 28 hemp samples. The data were auto scaled (zero mean and unitary variance) before AHC in order to remove differences in the concentration range.

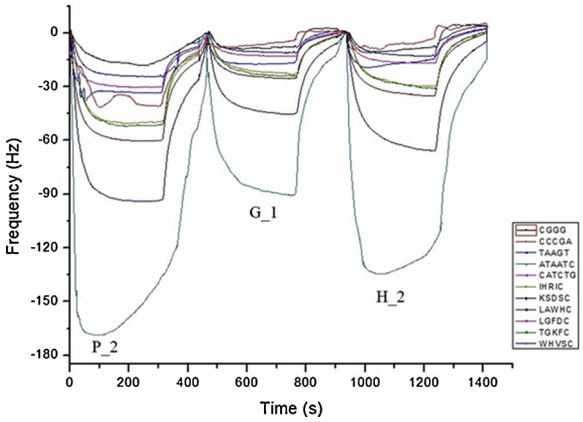


**Fig. 2.** Frequency shift recorded with hpDNA and peptides using 3 different hemp samples (P_2, G_1 and H_2).

humulene, α-selinene, caryophyllene oxide, α-bergamotene and β-selinene was crucial to classify group A samples; according to literature data these aromatic profiles are peculiar of some cultivars (Carmagnola CS, Antal, Finola, Futura 75, KC Zuzana). Group B had a higher concentration of the monoterpenes β-myrcene and D-limonene; the samples volatile profile can be associated to different cultivars (Fibrant, Tiborszallasi, Carmagnola, Ferimon, and Kompolti) [34,37,38].

### 3.1.1. HpDNA and peptides gas sensors array response vs hemp samples

Previous works have demonstrated that these set of sensors based on peptides functionalized with ZnONPs or hpDNA functionalized with AuNPs can be used for the analysis of VOCs (other than terpenes) present in food matrices [30–33]. In order to carry out analysis on different hemp samples it was necessary to find the optimal conditions for the gas sensor array analysis. Three different temperatures (25 °C; 40 °C and 50 °C) and four different amounts (0.10 g; 0.50 g; 1 g and 3 g) of samples were tested. From the data reported in Fig.S3 it is possible to observe that the optimal temperature was 40 °C. Increasing the temperature to 50 °C there was a significant drift of the signal, and in particular, the AuNP-hpDNA sensor with CATCTG as loop gave a very low response. The response at 25 °C was much lower indicating that the headspace was not yet saturated. The amount selected for the analysis was 1 g of sample, no significant increase of the frequency shift was observed using 3 g.

Fig. 2. reports a typical measurement of 3 hemp samples from both groups. Both hpDNA and peptides sensors gave similar kinetic behavior. The sensor having higher response was hpDNA with ATAATC loop followed by the peptide KSDSC, while the smallest signal was given by hpDNA with CGGG loop. A similar trend was observed also using pure terpenes (data not shown). The inter-day RSDs were in all case lower than 15 %. It is important to notice that the sensors were used for hundreds of measurements for 3 consecutive months and no significant drift of the signal was observed proving the robustness of the gas sensor

**Table 1**
Statistical significance of single VOCs detected in the 28 hemp samples to classify the hemp samples by using analysis of variance (ANOVA) with the Tukey HSD (honestly significant difference) multiple comparison analysis. The criterion for statistical significance of differences was $P < 0.05$ for all comparisons. The parameter F was used to sort in descending order the VOCs.

| compound | $R^2$ | F | Pr > F | Group A Mean | Group B Mean | Significant |
|---|---|---|---|---|---|---|
| β-caryophyllene | 0.859 | 158.316 | 0.000 | 1.051 a | −0.788 b | Yes |
| humulene | 0.564 | 33.671 | 0.000 | 0.852 a | −0.639 b | Yes |
| β-myrcene | 0.536 | 30.085 | 0.000 | −0.830 b | 0.623 a | Yes |
| D-limonene | 0.451 | 21.369 | 0.000 | −0.762 b | 0.571 a | Yes |
| α-selinene | 0.440 | 20.445 | 0.000 | 0.752 a | −0.564 b | Yes |
| caryophyllene oxide | 0.414 | 18.397 | 0.000 | 0.730 a | −0.547 b | Yes |
| α-bergamotene | 0.321 | 12.292 | 0.002 | 0.642 a | −0.482 b | Yes |
| eucalyptol | 0.309 | 11.652 | 0.002 | 0.631 a | −0.473 b | Yes |
| β-selinene | 0.306 | 11.460 | 0.002 | 0.627 a | −0.470 b | Yes |
| p-Mentha-8-thiol-3-one | 0.193 | 6.202 | 0.019 | 0.498 a | −0.373 b | Yes |
| L-borneol | 0.189 | 6.057 | 0.021 | 0.493 a | −0.370 b | Yes |
| p-cymene-8-ol | 0.184 | 5.867 | 0.023 | 0.487 a | −0.365 b | Yes |
| α-terpineol | 0.184 | 5.858 | 0.023 | 0.486 a | −0.365 b | Yes |
| β-pinene | 0.084 | 2.370 | 0.136 | −0.328 a | 0.246 a | No |
| α-pinene | 0.069 | 1.923 | 0.177 | −0.298 a | 0.223 a | No |
| β-phellandrene | 0.068 | 1.895 | 0.180 | −0.296 a | 0.222 a | No |
| γ-terpinene | 0.048 | 1.320 | 0.261 | −0.249 a | 0.187 a | No |
| α-phellandrene | 0.047 | 1.287 | 0.267 | 0.246 a | −0.185 a | No |
| β-bisabolol | 0.042 | 1.140 | 0.296 | 0.232 a | −0.174 a | No |
| 3-carene | 0.029 | 0.768 | 0.389 | −0.192 a | 0.144 a | No |
| linalool | 0.024 | 0.640 | 0.431 | −0.176 a | 0.132 a | No |
| β-Farnesene | 0.019 | 0.512 | 0.481 | 0.158 a | −0.118 a | No |
| o-cymene | 0.005 | 0.143 | 0.708 | 0.084 a | −0.063 a | No |
| camphene | 0.005 | 0.124 | 0.727 | −0.078 a | 0.059 a | No |
| p-Cymene | 0.001 | 0.017 | 0.897 | −0.029 a | 0.022 a | No |
| β-guaiene | 0.000 | 0.008 | 0.931 | −0.020 a | 0.015 a | No |
| fenchol | 0.000 | 0.008 | 0.931 | 0.019 a | −0.015 a | No |
| terpinolene | 0.000 | 0.001 | 0.980 | 0.006 a | −0.004 a | No |

array. The whole lot of samples were then analyzed to test the discrimination ability of the sensor arrays. The ΔF (Hz) response of hpDNA and peptide modified sensors array for the 28 hemp samples are reported in Table S3. This dataset was used to analyze the correlation among gas sensors array and GC−MS response by computing the Pearson coefficients. The correlation matrix between the 28 VOCs and the 11 sensors is reported in Table S4. The correlation coefficients, calculated using the response to the 28 hemp samples of both sensors array and GC−MS, evaluate the degree of linear correlation among variables. The hpDNA had higher correlation than peptides toward the VOCs significant to classify the hemp samples. The hpDNA loops CCCGA and TAAGT were significantly anticorrelated with β-caryophyllene, L-borneol and α-terpineol. A positive correlation was observed for hpDNA loop ATAATC and p-Mentha-8-thiol-3-one and for the loop CATCTG with both L-borneol and α-terpineol. These two alcohols correlated also with the peptide KSDSC that was the only peptide showing a significant correlation with the VOCs significant to classify the hemp samples. All sensors correlated with β-pinene, α-pinene and camphene. It should be highlighted that peptides binds the VOCs particularly via electrostatic interactions (hydrogen bond, van der Waals forces) and the 28 terpenes found in the hemp headspace differs each other in structural conformation but not in electrostatic molecular surface. On the other hand, hpDNA showed more variability in terms of correlation towards the VOCs tested, unlike the results obtained in previous work [39] where this correlation was greater in peptides than in hpDNAs. These results indicate that hpDNA and peptides have different interaction with volatiles confirming that a mixed set of hpDNA and peptides can provide a synergistic response in the detection of VOCs in real samples. The sensors dataset was, then, processed by PCA to find every possible combination between the aromatic compounds present in the samples analyzed and the 11 sensors used. PCA algorithm was carried out after rows normalization of ΔF signals and then autoscaling (zero mean and unitary variance) in order to remove differences in concentration range. Fig.3 reports the score (A) and loading (B) plots. The loadings represents the contribution of each sensor to the principal components. As shown in Fig.3B, the PC 1 axis highlighted the differences between hpDNA and peptides. Peptides had very similar pattern recognition performance contributing only in separating hemp samples on PC 1. All hpDNA loops played an important role in separation of the hemp samples. The sequence CGGG didn't give a significant contribution to separate the groups, while TAAGT and CCCGA along the PC2 contributes to the discrimination for the A group. Finally, the ATAATC along the PC3 seems to strongly contribute to the separation of group A as well as the CATCTG along PC1 to group B The score plot in Fig. 3A exhibited, as expected using an explorative analysis as PCA only a partial discrimination of the 2 groups.

A supervised multivariate discriminant analysis was then applied.

**Table 2**
PLS-DA confusion matrices using all the 5 hp DNA and 6 peptides sensors. True groups are read along the columns and estimated groups along the % correct. The total accuracy was also reported.

| 6 pentapeptides | | | | |
|---|---|---|---|---|
| real/pred | group 1 | group 2 | Total | % correct |
| **group 1** | 8 | 4 | 12 | 67% |
| **group 2** | 3 | 13 | 16 | 81 % |
| **Total** | | | 28 | 74 % |
| | | | | |
| **5 hpDNA** | | | | |
| **real/pred** | **group 1** | **group 2** | **Total** | **% correct** |
| **group 1** | 9 | 3 | 12 | 75 % |
| **group 2** | 3 | 13 | 16 | 81 % |
| **Total** | | | 28 | 78 % |
| | | | | |
| | **5 hpDNA and the 6 pentapeptides** | | | |
| **real/pred** | **group 1** | **group 2** | **Total** | **% correct** |
| **group 1** | 10 | 2 | 12 | 83% |
| **group 2** | 4 | 12 | 16 | 75 % |
| **Total** | | | 28 | 79 % |

Data are reported in Table S3. A numerical evaluation of the classification properties was obtained using the specificity, sensitivity and precision of the two groups along with the real-predicted samples reported using the confusion matrix format. The statistical summary results of the PLS-DA algorithm is reported in Table 2. The results showed partial discrimination between the two groups with a sensitivity that contributed to significant classification error. The percentage of correctness using all sensors or only hpDNA and peptides was satisfactory but not enough to correctly classify the whole set of samples. Considering all the sensors together the correct classification was achieved in 79 % of the samples; this was higher than using only peptides (74 %) or hpDNA (78 %).

A more complex statistical approach to implement class recognition was then attempted. To this aim, an artificial neural network (ANN) was developed (Fig. 4). The ANN was carried out using as inputs the frequency shift of the 11 sensors and as outputs, the two hemp groups. The network structure was composed of one hidden layer, where the information is automatically processed in a blind manner, connecting nodes as in Fig. 4A. The network had a growth rate of 10 cycles or 5 s, 1 hidden layer, and a learning rate of 0.7. The target error was fixed at < 0.01, one hundred cycles before the validating cycle and 100 cycles per validating cycle were used, and the learning process was stopped when all the validating examples were within the 10 % as validating error. The system has been trained, through the back-propagation error algorithm [40]. The dataset obtained from 28 hemp samples was used as training examples, and the output value was generated after only 506 learning cycles, with a progressive end of the

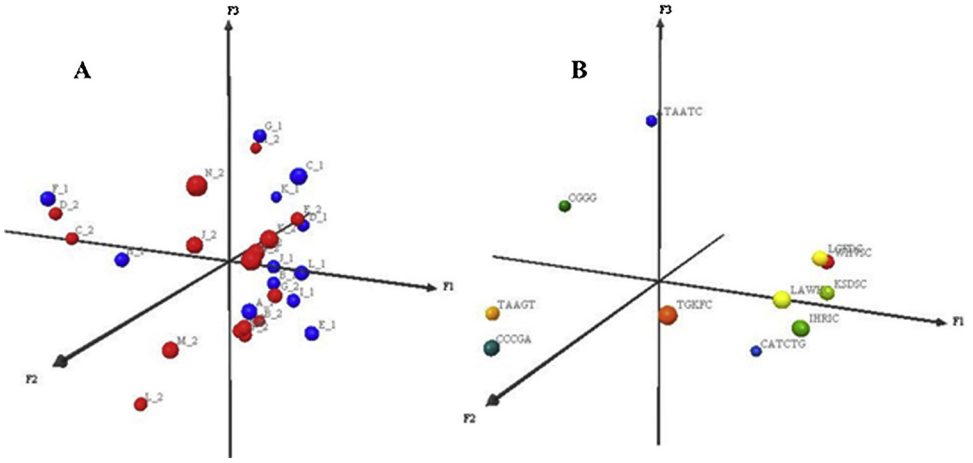


**Fig. 3.** Scores plot (A) and loadings plot (B) obtained from the PCA on the 28 hemp samples and the 5 hpDNA and the 6 pentapeptides sensors after rows normalization of ΔF signals. Plots of the first three components (explained variance: PC1 = 56.0 %; PC2 = 25.4 %; PC3 = 9.7 %; total = 91.1 %). Data have been auto scaled (zero mean and unitary variance) before PCA. In score plot (A) the two groups of hemp found using the relative concentration in VOCs detected by SPME/GC−MS analysis was highlighted with different colors (blue for group 1 and red for group 2).

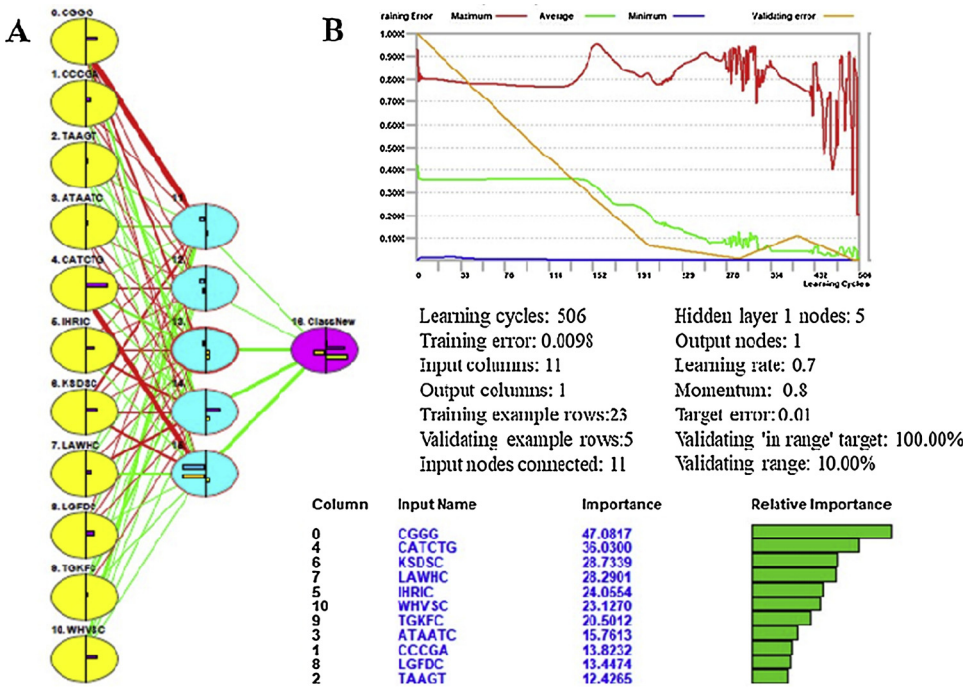


**Fig. 4.** Artificial Neural Network (ANN). (A) Diagram showing the structure of the ANN made using the sensors array response. Connections with a positive weight in the network are showed by the green lines, the red lines are of negative weights, and the dashed lines indicate insignificant one. The thickness of the lines is directly proportional to the weights of the edges in the network architecture. (B) ANN learning process after the introduction of response of the sensors (inputs) and the head space analytical profile groups (outputs). Learning cycles parameters were reported along with the relative importance for each sensor.

learning process, 0.0000, 0.2047, and 0.0098 (Fig. 4B). As a quality control, validating cycles were performed, in which five randomly selected datasets of the ANN were used as examples to test, at the end of the validating procedure, the error value. The network successfully completed the validating step, as indicated by the decline of the validating error which drops down below 10 % (Orange line in Fig. 4B). The relative importance of each input could be estimated by considering the weights automatically attributed to each of them by the system. Noteworthy, the ANN designed in this study successfully provided a tool capable of predicting the headspace analytical profile of the two different groups of hemp with a very high predictivity (average prediction error $\leq 1$ %).

## 4. Conclusions

This study demonstrate, for the first time, that an electronic nose consisting of pentapeptides and hpDNA can be used for the detection of aroma patterns rich in terpenes. These molecules are present in plants, are of utmost importance in different fields and have been rarely detected using gas sensors. The gas sensor array reported in here can represent a valid tool for the traceability, rapid quality and process control for plants or plant derived extracts or products containing high amount of terpenes.

## Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.snb.2020.127697.

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# Supplementary data

**Table S1**. Relative concentrations of the 28 volatile organic compounds (VOCs) detected by means of SPME/GC-MS analysis in the 28 hemp samples. Data were expressed as percentage of the total GC area. The VOCs were sorted in descending order of the average concentration. The IDs of the VOCs were reported in Table S2.

| ID | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **A_1** | 44.0 | 11.3 | 1.8 | 3.8 | 6.6 | 3.8 | 1.7 | 1.2 | 2.8 | 2.0 | 1.9 | 1.8 | 1.8 | 1.5 | 1.8 | 1.6 | 1.3 | 3.8 | 1.0 | 0.4 | 0.7 | 2.0 | 0.2 | 0.4 | 0.2 | 0.2 | 0.1 | 0.2 |
| **B_1** | 45.1 | 9.9 | 1.8 | 2.2 | 11.4 | 7.3 | 1.2 | 1.0 | 2.4 | 2.2 | 1.6 | 1.9 | 1.8 | 1.1 | 1.9 | 1.3 | 1.1 | 1.4 | 1.0 | 0.5 | 0.4 | 0.0 | 0.1 | 0.6 | 0.1 | 0.1 | 0.1 | 0.3 |
| **C_1** | 41.0 | 4.8 | 4.1 | 5.9 | 12.4 | 2.8 | 1.2 | 1.2 | 4.1 | 1.8 | 4.2 | 3.0 | 1.7 | 1.4 | 1.6 | 1.4 | 1.0 | 1.0 | 1.2 | 0.6 | 0.7 | 0.9 | 0.2 | 0.5 | 0.3 | 0.2 | 0.2 | 0.6 |
| **D_1** | 40.2 | 5.7 | 3.1 | 5.9 | 13.5 | 2.8 | 1.2 | 1.2 | 4.1 | 1.8 | 4.2 | 3.0 | 1.7 | 1.4 | 1.6 | 1.4 | 1.0 | 1.0 | 1.2 | 0.6 | 0.7 | 0.9 | 0.2 | 0.5 | 0.3 | 0.2 | 0.2 | 0.5 |
| **E_1** | 31.7 | 14.7 | 7.0 | 9.0 | 6.8 | 1.6 | 5.3 | 1.1 | 1.8 | 2.2 | 2.4 | 1.7 | 3.7 | 1.2 | 1.1 | 1.5 | 1.5 | 1.2 | 1.3 | 0.6 | 0.3 | 0.1 | 0.2 | 0.4 | 0.4 | 0.0 | 0.3 | 1.0 |
| **F_1** | 34.0 | 21.4 | 1.5 | 12.2 | 3.8 | 1.7 | 5.1 | 1.4 | 1.1 | 1.4 | 1.9 | 1.2 | 1.6 | 1.3 | 1.4 | 1.4 | 1.2 | 1.6 | 1.8 | 1.0 | 0.2 | 0.2 | 0.5 | 0.2 | 0.2 | 0.1 | 0.2 | 0.8 |
| **G_1** | 42.7 | 1.2 | 5.1 | 7.0 | 9.9 | 2.0 | 2.7 | 1.3 | 1.5 | 2.8 | 5.1 | 1.6 | 2.6 | 1.3 | 3.7 | 1.5 | 1.1 | 1.7 | 1.2 | 0.5 | 0.6 | 0.2 | 0.7 | 0.2 | 0.3 | 1.1 | 0.2 | 0.1 |
| **H_1** | 37.5 | 1.2 | 1.1 | 15.2 | 12.0 | 3.2 | 6.6 | 1.3 | 1.6 | 1.1 | 2.4 | 1.2 | 4.4 | 1.3 | 2.2 | 1.3 | 1.1 | 1.0 | 1.0 | 0.4 | 0.5 | 0.2 | 0.7 | 0.2 | 0.6 | 0.2 | 0.1 | 0.5 |
| **I_1** | 51.0 | 9.1 | 0.4 | 2.3 | 11.3 | 4.2 | 0.7 | 0.2 | 2.1 | 2.2 | 2.0 | 1.8 | 2.1 | 0.1 | 0.9 | 0.6 | 1.4 | 0.2 | 0.2 | 1.9 | 1.6 | 0.2 | 1.0 | 1.6 | 0.4 | 0.1 | 0.2 | 0.2 |
| **J_1** | 46.7 | 7.6 | 2.9 | 1.4 | 11.2 | 4.2 | 1.2 | 1.2 | 2.2 | 1.8 | 3.0 | 1.6 | 1.1 | 0.1 | 1.2 | 1.3 | 1.2 | 0.2 | 1.2 | 1.3 | 1.3 | 1.8 | 1.5 | 0.1 | 0.5 | 1.2 | 1.1 | 0.2 |
| **K_1** | 39.5 | 9.7 | 1.3 | 1.5 | 7.4 | 6.4 | 1.3 | 1.2 | 2.8 | 3.2 | 1.5 | 4.2 | 1.5 | 1.5 | 2.5 | 2.0 | 1.6 | 1.2 | 1.7 | 0.9 | 0.6 | 0.2 | 3.3 | 2.2 | 0.0 | 0.0 | 0.3 | 0.3 |
| **L_1** | 46.1 | 1.2 | 3.6 | 1.6 | 1.0 | 7.6 | 1.4 | 1.8 | 2.4 | 3.3 | 1.6 | 3.2 | 1.9 | 11.2 | 2.6 | 1.1 | 1.5 | 1.7 | 1.2 | 2.1 | 0.4 | 0.2 | 0.1 | 0.3 | 0.3 | 0.1 | 0.6 | 0.0 |
| **A_2** | 12.0 | 1.0 | 1.2 | 3.2 | 1.1 | 2.9 | 19.1 | 41.9 | 2.7 | 1.5 | 1.6 | 1.6 | 1.0 | 2.2 | 1.0 | 1.4 | 1.2 | 1.0 | 1.1 | 0.1 | 0.3 | 0.2 | 0.1 | 0.0 | 0.2 | 0.3 | 0.2 | 0.0 |
| **B_2** | 11.2 | 21.2 | 3.9 | 31.2 | 2.8 | 1.8 | 4.2 | 1.4 | 1.9 | 3.4 | 1.2 | 1.9 | 1.6 | 1.4 | 1.4 | 1.3 | 1.4 | 2.6 | 1.1 | 0.5 | 0.3 | 0.2 | 0.2 | 0.2 | 0.6 | 0.2 | 0.5 | 0.2 |
| **C_2** | 13.0 | 23.0 | 3.6 | 24.5 | 3.2 | 1.7 | 8.8 | 1.2 | 1.7 | 4.7 | 1.2 | 1.2 | 1.2 | 1.1 | 1.3 | 1.5 | 1.4 | 1.4 | 1.2 | 0.2 | 0.1 | 0.0 | 0.3 | 0.7 | 0.8 | 0.2 | 0.5 | 0.2 |
| **D_2** | 14.2 | 21.2 | 7.1 | 22.3 | 2.9 | 1.4 | 8.5 | 1.5 | 1.6 | 4.4 | 1.3 | 1.2 | 1.4 | 1.2 | 1.4 | 1.2 | 1.5 | 1.3 | 1.9 | 0.2 | 0.1 | 0.1 | 0.5 | 0.2 | 0.8 | 0.1 | 0.2 | 0.0 |
| **E_2** | 11.1 | 32.0 | 14.4 | 2.8 | 2.1 | 9.4 | 1.7 | 1.3 | 4.3 | 5.1 | 1.0 | 1.9 | 1.5 | 1.3 | 1.2 | 2.0 | 1.6 | 1.4 | 1.7 | 0.1 | 0.9 | 0.4 | 0.3 | 0.0 | 0.2 | 0.1 | 0.2 | 0.1 |
| **F_2** | 27.9 | 13.8 | 14.5 | 1.3 | 6.2 | 10.0 | 1.2 | 1.2 | 5.7 | 1.0 | 2.6 | 2.2 | 2.1 | 1.2 | 1.0 | 1.7 | 1.8 | 1.0 | 1.0 | 0.1 | 0.9 | 1.0 | 0.1 | 0.1 | 0.1 | 0.1 | 0.2 | 0.1 |
| **G_2** | 23.0 | 20.0 | 11.1 | 6.2 | 6.5 | 13.5 | 1.2 | 1.1 | 1.8 | 1.4 | 1.7 | 1.7 | 1.0 | 1.1 | 1.4 | 1.4 | 1.2 | 1.1 | 1.0 | 0.4 | 0.4 | 0.9 | 0.2 | 0.3 | 0.1 | 0.0 | 0.1 | 0.1 |
| **H_2** | 19.6 | 25.0 | 12.6 | 1.2 | 1.0 | 18.2 | 1.5 | 1.2 | 3.9 | 1.7 | 1.5 | 1.5 | 1.7 | 1.7 | 1.0 | 1.5 | 1.3 | 1.1 | 1.0 | 0.1 | 0.7 | 0.5 | 0.1 | 0.1 | 0.1 | 0.0 | 0.2 | 0.1 |
| **I_2** | 20.0 | 32.5 | 12.2 | 5.8 | 4.3 | 2.0 | 2.1 | 1.1 | 1.3 | 1.2 | 1.7 | 1.5 | 1.2 | 1.4 | 1.6 | 1.3 | 1.1 | 1.0 | 1.4 | 0.6 | 0.2 | 0.7 | 0.1 | 0.0 | 0.1 | 3.4 | 0.2 | 0.0 |
| **J_2** | 11.1 | 26.4 | 32.3 | 3.2 | 2.1 | 3.7 | 2.0 | 1.1 | 2.9 | 1.5 | 1.6 | 1.8 | 1.2 | 1.4 | 1.1 | 1.4 | 1.2 | 1.2 | 1.3 | 0.2 | 0.4 | 0.2 | 0.1 | 0.1 | 0.3 | 0.0 | 0.1 | 0.0 |
| **K_2** | 5.1 | 42.0 | 11.6 | 10.9 | 1.0 | 3.5 | 5.9 | 1.4 | 2.4 | 1.3 | 1.3 | 1.6 | 1.2 | 1.8 | 1.2 | 1.5 | 1.6 | 1.0 | 1.4 | 0.2 | 0.4 | 0.4 | 0.2 | 0.4 | 0.4 | 0.1 | 0.2 | 0.0 |

| | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **L_2** | 6.4 | 39.0 | 16.0 | 11.7 | 1.2 | 2.0 | 5.6 | 1.2 | 1.9 | 1.3 | 1.7 | 1.3 | 1.0 | 1.7 | 1.1 | 1.3 | 1.2 | 1.0 | 1.5 | 0.3 | 0.2 | 0.1 | 0.1 | 0.2 | 0.6 | 0.4 | 0.1 | 0.0 |
| **M_2** | 11.0 | 43.6 | 19.4 | 2.3 | 1.9 | 3.6 | 1.9 | 1.2 | 1.3 | 1.1 | 1.6 | 1.4 | 1.0 | 1.5 | 1.2 | 1.3 | 1.2 | 1.1 | 1.0 | 0.2 | 0.2 | 0.2 | 0.1 | 0.2 | 0.3 | 0.0 | 0.2 | 0.0 |
| **N_2** | 9.3 | 38.1 | 14.2 | 9.3 | 1.7 | 5.9 | 3.8 | 1.2 | 1.1 | 1.7 | 1.4 | 1.6 | 1.3 | 1.3 | 1.1 | 1.3 | 1.2 | 1.2 | 1.5 | 0.2 | 0.2 | 0.6 | 0.2 | 0.2 | 0.2 | 0.1 | 0.1 | 0.1 |
| **O_2** | 11.7 | 37.3 | 16.4 | 9.2 | 3.0 | 1.8 | 3.2 | 1.2 | 1.9 | 1.8 | 1.5 | 1.3 | 1.2 | 1.3 | 1.3 | 1.2 | 1.2 | 1.2 | 1.5 | 0.2 | 0.1 | 0.1 | 0.1 | 0.1 | 0.2 | 0.0 | 0.1 | 0.0 |
| **P_2** | 11.5 | 41.5 | 14.4 | 8.3 | 2.6 | 1.7 | 3.4 | 1.0 | 1.7 | 1.3 | 1.4 | 1.2 | 1.1 | 1.3 | 1.2 | 1.2 | 1.2 | 1.1 | 1.6 | 0.2 | 0.1 | 0.2 | 0.0 | 0.1 | 0.2 | 0.1 | 0.2 | 0.0 |
| **Max** | 51.0 | 43.6 | 32.3 | 31.2 | 13.5 | 18.2 | 19.1 | 41.9 | 5.7 | 5.1 | 5.1 | 4.2 | 4.4 | 11.2 | 3.7 | 2.0 | 1.8 | 3.8 | 1.9 | 2.1 | 1.6 | 2.0 | 3.3 | 2.2 | 0.8 | 3.4 | 1.1 | 1.0 |
| **Min** | 5.1 | 1.0 | 0.4 | 1.2 | 1.0 | 1.4 | 0.7 | 0.2 | 1.1 | 1.0 | 1.0 | 1.2 | 1.0 | 0.1 | 0.9 | 0.6 | 1.0 | 0.2 | 0.2 | 0.1 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.1 | 0.0 |
| **Median** | 21.5 | 20.6 | 6.0 | 5.9 | 3.5 | 3.3 | 2.1 | 1.2 | 2.0 | 1.8 | 1.6 | 1.6 | 1.5 | 1.3 | 1.3 | 1.4 | 1.2 | 1.2 | 1.2 | 0.4 | 0.4 | 0.2 | 0.2 | 0.2 | 0.3 | 0.1 | 0.2 | 0.1 |
| **Average** | 25.6 | 19.8 | 8.5 | 7.9 | 5.4 | 4.7 | 3.7 | 2.7 | 2.4 | 2.2 | 2.0 | 1.8 | 1.7 | 1.7 | 1.5 | 1.4 | 1.3 | 1.3 | 1.3 | 0.5 | 0.5 | 0.4 | 0.4 | 0.4 | 0.3 | 0.3 | 0.2 | 0.2 |
| **SD** | 15.2 | 14.1 | 7.5 | 7.6 | 4.2 | 4.0 | 3.8 | 7.7 | 1.1 | 1.1 | 1.0 | 0.7 | 0.8 | 1.9 | 0.6 | 0.3 | 0.2 | 0.7 | 0.3 | 0.5 | 0.3 | 0.5 | 0.7 | 0.5 | 0.2 | 0.7 | 0.2 | 0.2 |
| **RSD %** | 59 | 71 | 88 | 96 | 77 | 86 | 102 | 289 | 47 | 52 | 50 | 39 | 47 | 115 | 40 | 18 | 15 | 52 | 27 | 100 | 73 | 113 | 164 | 134 | 67 | 215 | 86 | 129 |

*SD= standard deviation; **RSD= coefficient of variation.

Table S2. Structural and physicochemical properties of the 28 VOCs found in the headspace of the 28 hemp samples used in this work. The average concentration was used to sort in descending order the VOCs. The 11 VOCs used as standard for testing the gas sensors array response were reported in-italic format. Terpene type: M= Monoterpene; S= Sesquiterpene. PSA=polar surface area. MW=molecular weight. HA= hetero atoms RB=rotatable bond.

| **0VOC** | **ID** | **Structure** | **DB** | **Functional group** | **Terpene Type** | **LogP** | **PSA** | **MW** | **HA** | **RB** |
|---|---|---|---|---|---|---|---|---|---|---|
| *β-caryophyllene* | 1 | Bicyclic | 2 | | S | 4.61 | 0 | 204.4 | 0 | 0 |
| *β-myrcene* | 2 | Linear | 3 | | M | 3.46 | 0 | 136.2 | 0 | 4 |
| *D-limonene* | 3 | Cyclic | 2 | | M | 2.78 | 0 | 136.2 | 0 | 1 |
| *α-pinene* | 4 | Bicyclic | 1 | | M | 3.02 | 0 | 136.2 | 0 | 0 |
| *humulene* | 5 | Cyclic | 3 | | S | 4.39 | 0 | 204.4 | 0 | 0 |
| *linalool* | 6 | Linear | 2 | Alcohol | M | 2.19 | 20 | 154.2 | 1 | 4 |
| *β-pinene* | 7 | Bicyclic | 1 | | M | 3.36 | 0 | 136.2 | 0 | 0 |
| 3-carene | 8 | Bicyclic | 1 | | M | 2.85 | 0 | 136.2 | 0 | 0 |
| fenchol | 9 | Bicyclic | 0 | Alcohol | M | 2.5 | 20 | 154.2 | 1 | 0 |
| *terpinolene* | 10 | Cyclic | 2 | | M | 2.34 | 0 | 136.2 | 0 | 0 |
| α-bergamotene | 11 | Bicyclic | 2 | | S | 4.4 | 0 | 204.4 | 0 | 3 |
| *α-terpineol* | 12 | Cyclic | 1 | Alcohol | M | 1.61 | 20 | 154.2 | 1 | 1 |
| eucalyptol | 13 | Bicyclic | 0 | Epoxide | M | 2.82 | 9 | 154.2 | 1 | 0 |
| β-farnesene | 14 | Linear | 4 | | S | 4.48 | 0 | 206.4 | 0 | 7 |
| β-selinene | 15 | | Aromatic | | S | 5.26 | 0 | 204.4 | 0 | 1 |
| p-Cymene | 16 | | Aromatic | | M | 3.89 | 0 | 134.2 | 0 | 1 |
| γ-terpinene | 17 | Cyclic | 2 | | M | 2.98 | 0 | 136.2 | 0 | 1 |
| *o-cymene* | 18 | | Aromatic | | M | 3.89 | 0 | 134.2 | 0 | 1 |
| β-phellandrene | 19 | Cyclic | 2 | | M | 3.66 | 0 | 136.2 | 0 | 1 |
| α-selinene | 20 | | Aromatic | | S | 4.92 | 0 | 204.4 | 0 | 1 |
| L-borneol | 21 | Bicyclic | 0 | Alcohol | M | 2.5 | 20 | 154.2 | 1 | 0 |
| β-bisabolol | 22 | Cyclic | 2 | Alcohol | S | 2.72 | 20 | 222.4 | 1 | 4 |
| p-mentha-8-thiol-3-one | 23 | Cyclic | 0 | Thiol-ketone | M | 2.48 | 17 | 186.3 | 2 | 1 |
| p-cymene-8-ol | 24 | | Aromatic | Alcohol | M | 2.35 | 20 | 150.2 | 1 | 1 |
| camphene | 25 | Bicyclic | 1 | | M | 3.46 | 0 | 136.2 | 0 | 0 |
| β-guaiene | 26 | | Aromatic | | S | 3.87 | 0 | 204.4 | 0 | 0 |
| α-phellandrene | 27 | Cyclic | 2 | | M | 3.32 | 0 | 136.2 | 0 | 1 |
| *caryophyllene oxide* | 28 | Tricyclic | 1 | Epoxide | S | 3.62 | 12 | 220.4 | 1 | 0 |

**Table S3.** Frequency shift (ΔF in Hz) response of the 5 hpDNA and the 6 peptides modified sensors array for the 28 hemp samples. The coefficient of variation calculated using three measurements taken in three different days was in all cases below 15%.

| Hemp Sample | CGGG | CCCGA | TAAGT | ATAATC | CATCTG | IHRIC | KSDSC | LAWHC | LGFDC | TGKFC | WHVSC |
|---|---|---|---|---|---|---|---|---|---|---|---|
| A_1 | 13 | 49 | 45 | 172 | 87 | 56 | 109 | 68 | 32 | 65 | 26 |
| B_1 | 8 | 28 | 31 | 161 | 93 | 45 | 90 | 53 | 27 | 50 | 21 |
| C_1 | 8 | 22 | 24 | 150 | 49 | 43 | 87 | 49 | 24 | 54 | 20 |
| D_1 | 10 | 13 | 22 | 149 | 79 | 39 | 81 | 45 | 24 | 40 | 19 |
| E_1 | 15 | 20 | 28 | 119 | 92 | 46 | 89 | 50 | 26 | 50 | 22 |
| F_1 | 48 | 115 | 157 | 348 | 30 | 82 | 147 | 95 | 42 | 107 | 33 |
| G_1 | 12 | 9 | 15 | 83 | 31 | 20 | 39 | 24 | 13 | 23 | 11 |
| H_1 | 25 | 78 | 104 | 249 | 68 | 64 | 115 | 80 | 36 | 78 | 28 |
| I_1 | 8 | 26 | 23 | 144 | 91 | 44 | 91 | 50 | 25 | 49 | 21 |
| J_1 | 8 | 25 | 31 | 162 | 87 | 45 | 90 | 52 | 26 | 51 | 21 |
| K_1 | 8 | 7 | 18 | 146 | 72 | 32 | 65 | 37 | 19 | 33 | 15 |
| L_1 | 7 | 27 | 31 | 152 | 78 | 47 | 94 | 55 | 27 | 50 | 23 |
| A_2 | 7 | 49 | 48 | 170 | 51 | 57 | 106 | 66 | 33 | 71 | 24 |
| B_2 | 17 | 17 | 26 | 116 | 97 | 36 | 71 | 42 | 21 | 38 | 17 |
| C_2 | 54 | 122 | 164 | 381 | 87 | 82 | 148 | 100 | 44 | 106 | 35 |
| D_2 | 66 | 122 | 171 | 396 | 74 | 83 | 146 | 103 | 44 | 109 | 34 |
| E_2 | 7 | 17 | 21 | 152 | 73 | 40 | 80 | 47 | 24 | 46 | 20 |
| F_2 | 10 | 41 | 36 | 165 | 106 | 51 | 100 | 58 | 28 | 62 | 23 |
| G_2 | 7 | 28 | 40 | 158 | 86 | 47 | 97 | 58 | 27 | 57 | 24 |
| H_2 | 11 | 7 | 19 | 134 | 51 | 26 | 55 | 31 | 17 | 28 | 14 |
| I_2 | 7 | 43 | 43 | 163 | 90 | 51 | 97 | 60 | 29 | 61 | 24 |
| J_2 | 18 | 59 | 71 | 205 | 60 | 61 | 112 | 74 | 35 | 72 | 28 |
| K_2 | 5 | 45 | 46 | 171 | 56 | 52 | 98 | 63 | 33 | 65 | 25 |
| L_2 | 13 | 64 | 125 | 191 | 114 | 61 | 109 | 70 | 33 | 70 | 26 |
| M_2 | 14 | 69 | 70 | 182 | 81 | 59 | 112 | 69 | 34 | 78 | 26 |
| N_2 | 17 | 49 | 65 | 170 | 24 | 55 | 103 | 65 | 31 | 67 | 25 |
| O_2 | 11 | 44 | 40 | 165 | 62 | 52 | 97 | 62 | 30 | 59 | 24 |
| P_2 | 7 | 43 | 42 | 161 | 92 | 50 | 95 | 58 | 28 | 58 | 23 |

Table S3. Correlation matrix (Pearson coefficients) between the 28 VOCs and the 5 hpDNA and 6 peptides modified sensors. The correlation coefficients were calculated using the dataset of the 28 hemp samples. The 28 VOCs were sorted considering the statistical significance reported in Table 2, reporting in italic format the significant ones. The Person coefficients computed between the 11 modified sensors were reported at the end of the correlation matrix. Values in bold are different from 0 with a significance level alpha=0.05.

| Variables | **CG GG** | **CCC GA** | **TAA GT** | **ATAA TC** | **CATC TG** | **IHR IC** | **KSD SC** | **LAW HC** | **LGF DC** | **TGK FC** | **WHV SC** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| ***β-caryophyllene*** | -0.04 | **-0.42** | **-0.42** | 0.22 | 0.30 | 0.06 | 0.31 | -0.01 | 0.12 | -0.24 | 0.21 |
| ***humulene*** | -0.03 | -0.37 | -0.36 | 0.16 | 0.29 | 0.05 | 0.24 | -0.01 | 0.11 | -0.18 | 0.18 |
| ***β-myrcene*** | -0.11 | 0.37 | 0.33 | -0.26 | -0.18 | -0.03 | -0.21 | 0.01 | -0.11 | 0.20 | -0.12 |
| ***D-limonene*** | -0.16 | 0.23 | 0.17 | -0.24 | -0.13 | 0.12 | -0.04 | 0.19 | 0.08 | 0.25 | 0.12 |
| ***α-selinene*** | -0.13 | -0.28 | -0.28 | 0.02 | 0.28 | 0.09 | 0.28 | 0.01 | 0.06 | -0.20 | 0.15 |
| ***caryophyllene oxide*** | 0.25 | -0.17 | -0.05 | 0.03 | 0.05 | 0.04 | 0.08 | -0.13 | -0.05 | -0.08 | -0.01 |
| ***α-bergamotene*** | 0.12 | -0.34 | -0.29 | 0.17 | 0.10 | 0.14 | 0.22 | 0.04 | 0.29 | 0.00 | 0.29 |
| ***eucalyptol*** | 0.26 | -0.16 | -0.10 | 0.00 | 0.13 | -0.03 | 0.01 | -0.05 | 0.03 | -0.19 | 0.07 |
| ***β-selinene*** | 0.25 | -0.28 | -0.16 | 0.32 | 0.06 | -0.12 | -0.06 | -0.06 | 0.11 | -0.29 | 0.12 |
| ***p-Mentha-8-thiol-3-one*** | 0.06 | -0.33 | -0.18 | **0.46** | 0.17 | -0.25 | -0.06 | -0.27 | -0.14 | **-0.38** | -0.10 |
| ***L-borneol*** | -0.29 | **-0.51** | **-0.55** | 0.21 | **0.43** | 0.12 | **0.42** | 0.05 | 0.24 | -0.15 | 0.33 |
| ***p-cymene-8-ol*** | -0.08 | -0.34 | -0.26 | 0.28 | 0.27 | -0.11 | 0.12 | -0.18 | -0.04 | -0.31 | 0.00 |
| ***α-terpineol*** | -0.30 | **-0.60** | **-0.55** | 0.29 | **0.39** | 0.21 | **0.45** | 0.11 | 0.27 | -0.20 | 0.36 |
| **β-pinene** | 0.22 | **0.46** | **0.46** | -0.10 | **-0.46** | -0.05 | -0.33 | -0.02 | -0.14 | 0.27 | **-0.38** |
| **α-pinene** | **0.64** | 0.36 | **0.52** | -0.08 | -0.21 | **-0.46** | **-0.61** | **-0.41** | **-0.53** | -0.24 | **-0.55** |
| **β-phellandrene** | 0.25 | 0.22 | 0.37 | 0.20 | **-0.38** | -0.16 | **-0.38** | -0.14 | -0.26 | -0.01 | -0.27 |
| **γ-terpinene** | 0.03 | -0.09 | -0.12 | 0.02 | 0.23 | -0.14 | -0.07 | -0.18 | -0.12 | -0.14 | -0.07 |
| **α-phellandrene** | 0.02 | -0.23 | -0.18 | 0.07 | 0.27 | -0.08 | 0.07 | -0.14 | -0.08 | -0.24 | -0.01 |
| **β-bisabolol** | -0.30 | -0.17 | -0.31 | -0.03 | 0.16 | 0.23 | 0.35 | 0.26 | 0.19 | 0.15 | 0.28 |
| **3-carene** | -0.17 | 0.13 | 0.01 | -0.09 | -0.20 | 0.29 | 0.15 | 0.28 | 0.26 | **0.40** | 0.03 |
| **linalool** | -0.25 | **-0.45** | -0.35 | 0.37 | 0.25 | -0.08 | 0.25 | -0.03 | 0.11 | -0.19 | 0.26 |
| **β-Farnesene** | -0.16 | -0.07 | -0.08 | -0.04 | 0.03 | 0.17 | 0.18 | 0.20 | 0.15 | -0.01 | 0.18 |
| **o-cymene** | 0.26 | 0.03 | 0.00 | -0.11 | 0.04 | -0.03 | -0.08 | 0.02 | -0.03 | -0.10 | -0.02 |
| **camphene** | **0.51** | **0.38** | **0.53** | -0.11 | -0.21 | **-0.43** | **-0.57** | **-0.37** | **-0.48** | -0.21 | **-0.53** |
| **p-Cymene** | 0.05 | -0.30 | -0.19 | **0.38** | 0.08 | -0.10 | -0.04 | -0.11 | 0.04 | -0.14 | 0.07 |
| **β-guaiene** | -0.11 | -0.02 | -0.08 | -0.09 | 0.13 | 0.05 | -0.01 | 0.02 | 0.09 | 0.04 | 0.07 |
| **fenchol** | -0.32 | **-0.45** | **-0.49** | 0.25 | 0.34 | 0.14 | 0.36 | 0.05 | 0.22 | -0.07 | 0.28 |
| **terpinolene** | **0.44** | -0.18 | -0.03 | 0.37 | 0.06 | -0.36 | -0.26 | -0.35 | -0.29 | **-0.41** | -0.22 |
| **CGGG** | **1.00** | 0.24 | **0.48** | 0.35 | **-0.41** | **-0.64** | **-0.70** | **-0.61** | **-0.58** | -0.37 | **-0.58** |
| **CCCGA** | 0.24 | **1.00** | **0.83** | -0.33 | **-0.73** | -0.20 | **-0.58** | -0.05 | **-0.49** | **0.42** | **-0.62** |
| **TAAGT** | **0.48** | **0.83** | **1.00** | -0.11 | **-0.70** | **-0.51** | **-0.82** | **-0.40** | **-0.71** | 0.04 | **-0.79** |
| **ATAATC** | 0.35 | -0.33 | -0.11 | **1.00** | -0.19 | **-0.50** | -0.24 | **-0.42** | -0.20 | **-0.45** | -0.17 |
| **CATCTG** | **-0.41** | **-0.73** | **-0.70** | -0.19 | **1.00** | 0.14 | **0.46** | -0.04 | 0.29 | **-0.44** | **0.42** |
| **IHRIC** | **-0.64** | -0.20 | **-0.51** | **-0.50** | 0.14 | **1.00** | **0.86** | **0.93** | **0.85** | **0.69** | **0.82** |
| **KSDSC** | **-0.70** | **-0.58** | **-0.82** | -0.24 | **0.46** | **0.86** | **1.00** | **0.76** | **0.86** | **0.39** | **0.91** |
| **LAWHC** | **-0.61** | -0.05 | **-0.40** | **-0.42** | -0.04 | **0.93** | **0.76** | **1.00** | **0.81** | **0.72** | **0.77** |
| **LGFDC** | **-0.58** | **-0.49** | **-0.71** | -0.20 | 0.29 | **0.85** | **0.86** | **0.81** | **1.00** | **0.43** | **0.94** |
| **TGKFC** | -0.37 | **0.42** | 0.04 | **-0.45** | **-0.44** | **0.69** | **0.39** | **0.72** | **0.43** | **1.00** | 0.32 |
| **WHVSC** | **-0.58** | **-0.62** | **-0.79** | -0.17 | **0.42** | **0.82** | **0.91** | **0.77** | **0.94** | 0.32 | **1.00** |


**Figure S1**. Photo of some samples studied in this work (sample: A_1, B_2, F_1, M_2, K_1, P_2, L_1, and O_2), bought in different Italian hemp-shops

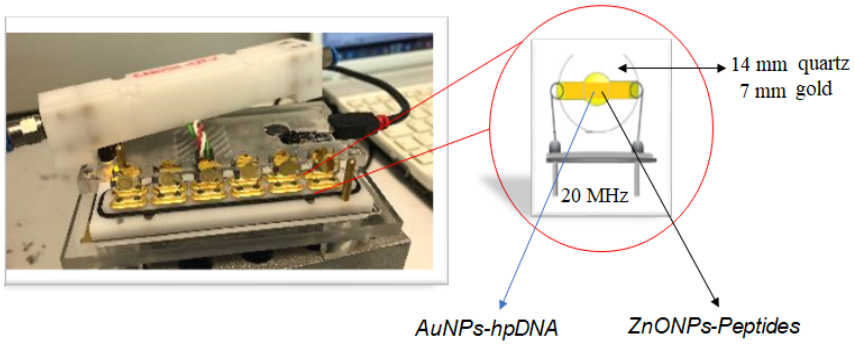


**Figure S2**. Photo of the electronic nose sensors-chamber equipped with the eleven QCMs. Scheme of the QCMs modification with AuNPs-hpDNA and ZnONPs-peptide.

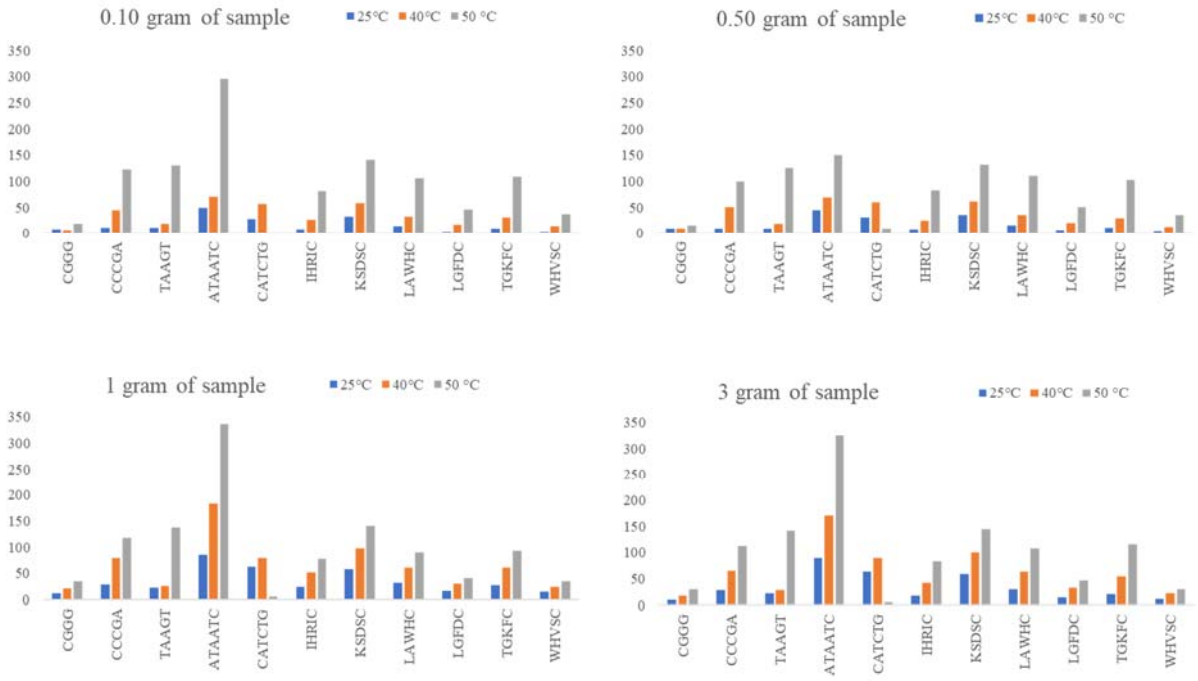


**Figure S3.** Optimization of temperature and quantity of samples (grams). Y axis= Frequency shift (□□F in Hz); X axis= the 5 hpDNA and the 6 peptides immobilized on the QCM sensors.