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Room temperature ionic liquids as useful overlayers for estimating food quality from their odor analysis by quartz crystal microbalance measurements

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Abstract : An array of quartz crystals coated with different room-temperature ionic liquids (RTILs) is proposed for the analysis of flavors by quartz crystal microbalance (QCM) measurements. Seven RTILs were adopted as sensing layers, all containing imidazolium or phosphonium cations, differing from one another in the length and branching of alkyl groups, and neutralized by different anions. The array was at first applied to the analysis of 31 volatile organic compounds (VOCs) such as alcohols, phenols, aldehydes, esters, ketones, acids, amines, hydrocarbons and terpenes, chosen as representative components of a wide variety of food flavors. Multivariate data analysis by the principal component analysis (PCA) approach of the set of the corresponding responses led to separated clusters for these different chemical categories. To prove further the good performance of the RTIL coated quartz crystal array as “electronic nose”, it was applied to the analysis of headspaces from cinnamon samples belonging to different botanical varieties (*cinnamon zeylanicum* and *cinnamon cassia*). PCA applied to responses recorded on different stocks of samples of both varieties showed that they could be fully discriminated.

■ Introduction

Odor analysis has received a growing interest in recent years owing to its large concern in environmental protection, public health, food process monitoring and food quality control.¹⁻³ In particular, odor analysis can provide valuable information on food quality and safety, which is especially welcome when achieved by simple, rapid, on-line and real-time detection methods. Thus, volatile organic compounds (VOCs) involved in food metabolic pathways (carboxylic acids, alcohols, carbonyl compounds, lactones) or food ripening (terpenes, esters, ethers) contribute significantly to agreeable flavors.⁴ These compounds are not only typical for any raw food product, but also they make possible to detect alterations, to classify food products by their botanical or geographical origin and even to distinguish their different stocks, thus allowing food traceability to be accomplished.⁵⁻¹¹

Several amperometric sensors were proposed for VOC monitoring, in that they make possible to perform multicomponent analyses with wide linearity ranges and good selectivity, which can be suitably tuned resorting to convenient modifications of electrode surfaces. Thus, sensors designed to generate current responses and exploiting both gas permeable membranes^{12,13} and membrane-free devices were developed, these last based on either solid polymer electrolytes (SPEs)¹⁴⁻¹⁶ or room temperature ionic liquids (RTILs).¹⁷⁻²³ Unfortunately, these sensors provides responses for specific classes of VOCs alone, while flavors come out almost always from the contribution of different volatile species.

Although the ability of the human nose to detect even the most subtle of scents is at present difficult to replicate, most electronic noses were proposed. They provide responses combining outputs from arrays of non-specific chemical sensors to produce fingerprints which are often statistically analyzed using multivariate analysis or neural network techniques.^{24,25} They are frequently assembled by sets of metal oxide (MOSFET), surface acoustic wave (SAW)^{26,27} or quartz crystal microbalance (QCM)^{28,29} gas sensors.

Odor detection by QCM measurements requires that immobilization of vapor molecules onto overlayers of quartz crystal resonators leads to : (i) sensitive and repeatable mass changes; (ii) easy analyte removal, concomitantly with a fast restoration of the coating layer; (iii) signals stable with time under detection conditions, thus enabling prolonged sensor durability. To achieve retention of volatile compounds, overlayers consisting of GC stationary phases displaying adsorption properties,³⁰ supramolecular compounds,³¹ organic polymers,³² biomolecules³³ or room temperature ionic liquids (RTILs)^{17-23,28,29} have been employed.

Among these, RTILs appear to be particularly attractive for their good thermal and electrical conductivity, negligible vapor pressure and ability to dissolve several compounds, thanks to their amphiphilic character which can be tuned by tailoring suitably their cations and anions. Just these profitable properties have promoted their increasing use for several applications, such as organic synthesis,³⁴ chemical analysis,³⁵ GC separations³⁶ microextractions³⁷ and electrochemical gas sensing.^{17-23,38-40} Moreover, they have been adopted as soft-coatings for QCM gas sensors planned for the detection of some organic volatile species at either room or high temperature.^{29,41}

In this paper we propose an array of QCM sensors filmed with different RTIL overlayers for the analysis of flavors with complex composition. Seven RTILs, chosen at random among those commercially available, all containing imidazolium or phosphonium cations differing from one another in the length and branching of alkyl groups and in the anion, were adopted for the detection of 31 different VOCs, chosen as representative components of a wide variety of food components. Responses provided by this array produced proper fingerprints which were statistically processed by the principal component approach (PCA), which allowed different chemical classes of VOCs to be discriminated. To confirm further the ability of this prototype sensor to discriminate odors from even similar enough flavor sources, it was subsequently applied to the analysis of headspaces from real cinnamon samples belonging to different botanical varieties (*cinnamon zeylanicum* e *cinnamon cassia*).

■ EXPERIMENTAL SECTION

Chemicals and Real Samples. All RTILs used in this investigation are listed in Table 1, where their structural formulae, acronyms, densities (ρ) and viscosities (η) are also reported.

[THTDP][AQS]²¹ and [BMPyr][NTF₂]⁴² were synthesized as reported previously. [BMIM][PF₆] was purchased from Aldrich (Milan, Italy), while the remaining RTILs were obtained from Merck (Munich, Germany). Before use, these RTILs were kept at 100 °C under vacuum for at least 48 h in the presence of phosphorous pentoxide.

- Table 1 near here -

Stock standard solutions (0.1-2.0% w/v) of each RTIL were prepared by dissolving weighed amounts in dichloromethane, ethanol or acetonitrile which were all Aldrich solvents of analytical grade quality, used without further purification. 31 different volatile organic compounds, belonging to 9 different chemical categories, were adopted as representative odor components. These compounds, listed in Table 2, were all analytical grade products from Aldrich (Milan, Italy) and were used as received.

- Table 2 near here -

Three different batches of cinnamon sticks belonging to both *cinnamom zeylanicum* (CZ1-3) and *cinnamom cassia* (CC1-3) species were used as prototypes of real smelling samples. All batches, purchased from different local markets, were grinded just before their use. Two different portions ((a) and (b)) of each batch were analyzed

A solution, prepared by mixing H_2O_2 30% w/v and H_2SO_4 98% v/v in a volume ratio of 1:3 was employed for cleaning quartz crystal resonators before each set of measurements. Ultrapure nitrogen, previously passed through concentrated H_2SO_4 to remove traces of water, was used as the carrier gas in flow measurements. In all instances, deionized water, purified with an Elgastat UHQ-PS system (Elga Lab Water, Siershahn, Germany), was used.

Instrumentation and General Procedures. Microgravimetric measurements were performed by a quartz crystal microbalance CHI 400 (CH Instruments, Austin, TX, USA) driven by a CHI software 2.07 installed on a Pentium IV computer. It comprised a transistor oscillator, a frequency counter and 8-MHz AT-cut quartz crystals coated on both side by gold disc-shaped films (100 nm thick, 0.196 cm^2 surface) deposited on chromium underlayers (10 nm thick) by metal vapor deposition. The sensitivity of the 8 MHz QCM was $0.739 (\pm 0.020)\text{ Hz ng}^{-1}$, according to the Sauerbrey equation $\Delta f = -K\Delta m$.

Prior to subject gold films to the coating procedure described below, they were soaked in the cleaning $H_2O_2 + H_2SO_4$ solution for 1 min at room temperature and subsequently washed first with deionized water and then with ethanol or dichloromethane. Gold surfaces were finally allowed to dry in air.

Headspace gas chromatographic (HSGC) analyses were conducted under temperature programmed conditions by a GC-2010 gas chromatograph Shimadzu (Kyoto, Japan) equipped with a SE52 capillary column Supelco (Bellefonte, PA, USA) and coupled to a Shimadzu MS-DP2010 Plus mass spectrometric detector. Nitrogen was used as the mobile phase in chromatographic runs with a flow rate of 90 mL min^{-1} . The temperature program implied first 5 min equilibration at $80\text{ }^\circ\text{C}$ and then a linear temperature increase to $250\text{ }^\circ\text{C}$ in 17 min ($10\text{ }^\circ\text{C min}^{-1}$ gradient), followed by a final 5 min step at this last temperature. Finally, a 10 min gradient was imposed to restore linearly the temperature to $80\text{ }^\circ\text{C}$. Headspace vapors were drawn by gas-tight microsyringes (5-250 μL) from vials (24 mL) thermostated at $20\text{ }^\circ\text{C}$, whose 5% volume alone was filled with either volatile compounds adopted as representative odor components (see Table 2) or real samples of cinnamon powder.

Morphological characterization of RTIL covered quartz crystal surfaces was performed by a field emission scanning electron microscope Carl Zeiss Sigma FE.SEM (Oberkochen, Germany) at an acceleration voltage of 10 kV, after their coating with a thin platinum film (1-2 nm) by an Emitech sputter coater K575X (Ashford, UK). It was equipped with a Sigma electron optic column to reduce the effect of interfering fields.

A version 7.0 OPUS statistical software was used to perform principal component analyses (PCA) of the results found. Frequency changes were inserted as raw data without pretreatment; sensing layers were considered as objects, while samples were treated as variables.

Quartz Crystal Coating and Vapor Sensing by QCM Arrays. One gold surface of each quartz crystal was coated by droplet evaporation of a controlled volume (1-4 μL) of dichloromethane solution of one of the RTILs listed in Table 1. Steadily adherent RTIL films were thus prepared, located prevalently at the center of gold discs. The excellent adhesion of RTILs onto metal surfaces was previously highlighted in some articles concerning the tribological properties displayed by these low-melting salts, where it was ascribed to van der Waals interactions and the unique dipolar nature of RTILs, favoring their strong adsorption.^{43,44} Quartz crystals thus covered were then kept at 40 °C for 48 h in a vacuum oven. Film thickness was estimated by assuming that for all RTILs an uniform distribution of their mass loaded on gold surfaces was achieved, so that it could be calculated as the ratio between the RTIL volume applied (inferred from density values in Tab. 1) and the gold surface area.

To perform flow injection analysis (FIA) of headspace vapors by RTIL coated quartz crystals, they were lodged into a 150 mL glass cell, whose bottom was provided with a central hole sealed by a drilled stopper through which the glass tube (internal diameter 1 mm) conveying the flowing gas (ca. 9 cm below quartz crystals) was pierced. Its upper stopper was provided with 8 holes, 7 of which were used to introduce coated quartz crystals. They hanged by their electrical connections to the QCM instrumentation, piercing through suitable gas-tight stoppers. The additional hole in the upper stopper served as the gas outlet. The cell was provided with a thermostatic jacket connected to a Neslab Endocal RTE-210 (Thermo Scientific, Palm Beach, FL, USA) thermostatic bath. The schematic view of this flow apparatus is shown in Figure 1.

- Figure 1 near here -

FIA analyses were performed by injecting controlled volumes (0.1-5.0 mL) of headspace in equilibrium with thermostated samples. Since QCM measurements were performed by a single channel instrumentation, each injection was repeated 7 times and in each run a single RTIL coated crystal was connected to the channel input. A constant flow rate of 20 mL min⁻¹ was adopted for the N₂ carrier gas, because it turned out to assure good repeatability of recorded signals.

■ RESULTS AND DISCUSSION

Optimisation of the Coating Procedure and Morphological Inspection of RTIL Films. First of all, RTIL solutions in different organic solvents were assayed to perform the droplet deposition process. For all RTILs considered the best results were attained when dichloromethane solutions were used, in view not only of the quicker evaporation of this solvent, but also because they led to smooth RTIL films homogeneously distributed on gold overlayers, without apparent networks of piled islands.

To evaluate the film thickness effect, ethyl acetate was used as the prototype flavor. With this purpose, quartz crystals coated with RTIL films prepared by laying different volumes (1-4 μL) of their dichloromethane solutions with different concentrations (0.1-2.0 % w/v) were installed in the thermostated detection cell of the FIA apparatus in Fig. 1 and 0.5-4.0 mL of headspace, in equilibrium at 20 °C with a pure sample of ethyl acetate, were injected. Sensitivity increased with film thickness, but the corresponding linear dynamic range became concomitantly narrower since resonator overloading conditions for the resonator were attained for progressively lower ethyl acetate amounts injected. On the basis of these preliminary tests, all subsequent investigations were conducted with quartz crystals covered with about 10 μg of RTIL, so as to achieve a film thickness ranging from about 0.3 to 0.5 μm , depending on the RTIL applied.

Self-assembled overlayers were investigated by SEM analysis which pointed out that the different RTIL coatings displayed three different structures which were conceivably conditioned by their different steric arrangement and chemical and/or secondary interactions, such as van der Waals, hydrogen bonding, ionic and/or amphiphilic associations.^{44,45} (SEM images, Figure S1, Supporting Information). [DMIM][BF₄] films displayed a rather flat and packed enough structure, due probably to both interdigitation of hydrophobic tails in the cation and electrostatic self-assembly of the relevant ionic heads. [BMIM][PF₆], [THTDP][AQS], [OMIM][NTF₂], [BMIM][NTF₂], and [THTDP][NTF₂] films instead consisted of aggregates with extended structures, displaying hemispheric prominences which could be accounted for by admitting that they are quite less prone to wet gold surfaces. Finally, films prepared by [BMPyr][NTF₂] displayed a more fragmented structure characterized by sets of crystallites, suggesting that nucleation phenomena, unusual enough in supramolecular processes,³⁶ took place in this case, conceivably owing to the presence of residual saline impurities.

Main Features of QCM Measurements at RTIL Coated Quartz Crystals. The performance provided by QCM measurements at RTIL coated quartz crystals was first estimated for ethyl acetate, adopted as the model gaseous analyte. With this aim, quartz crystals coated with the different RTILs were installed in the detection cell of the FIA apparatus in Fig. 1 and 0.1-4.0 mL (corresponding to 0.42-17.00 μmol) of headspace in equilibrium at 20 °C with a pure sample of ethyl acetate were injected. Frequency changes recorded with time for each covered crystal resulted in sharp peak readouts (peak-base widths ranged from 30 to 100 s, depending upon the sample volume injected) superimposed on a rather flat baseline. These rapid wash-out characteristics came conceivably from the easier and faster diffusion of analyte vapors in a liquid matrix such as RTIL films, in comparison with that encountered when solid overlayers (polymeric or adsorbent materials) are used as for monitoring flowing analytes.

Ethyl acetate injected caused positive frequency changes (i.e. mass decreases) for all RTILs, with the sole exception of [THTDP][AQS]. This finding is not surprising in view of viscoelastic properties of RTIL⁴⁶⁻⁴⁹ coatings, whose rheology causes energy dissipation with concomitant attenuation of QCM oscillations. Consequently, the mass increase (frequency decrease) expected for the transient trapping of analytes in the RTIL film is accompanied by a change of viscoelastic effects (frequency increase) which frequently prevails when liquid or liquid-like films are involved.⁴⁹

Oscillation frequency for all RTIL coated quartz crystals changed linearly with the ethyl acetate amount injected, but only until it did not exceed 10 μmol , since higher amounts led always to a downward tendency (see Figure S2, Supporting Information).

The different coated crystals were characterized by comparable enough sensitivities, except for that coated with [THTDP][NTF₂] which displayed quite smaller frequency changes.

Peak heights recorded for seven replicate injections of similar samples, irrespective of their analyte amount, was characterized by a satisfactory repeatability (ranging from about 2.5 to 4.0 % for the different RTILs). Moreover, inter-sensor reproducibility, estimated by renewing different RTIL films onto quartz crystals, turned out to be restricted in the range $\pm 8\%$, thus indicating that quite reproducible coatings could be achieved by the procedure here suggested. Finally, in order to roughly estimate the long-term stability of these QCM sensors, frequency changes were recorded in replicate injections (n=7) of head space samples equilibrated with pure ethyl acetate, which were repeated every day for three weeks. On average, the signal decreased only by about 5 % on passing from the first to the last day.

QCM-FIA Measurements of Volatile Organic Compounds. With the aim of verifying whether QCM arrays here proposed really enable discrimination of different classes of VOCs, they were tested on a wide variety of flavor components. Thus, seven quartz crystals, each coated with one of the mentioned RTILs, were once again installed in the thermostated detection cell of the FIA apparatus in Fig. 1 and 0.1-4.0 mL of headspace in equilibrium at 20 °C with pure samples of each volatile organic compound listed in Table 2 were injected.

Sharp enough peaks were recorded at each QCM sensor for all compounds assayed. A representative example of frequency change vs. time responses typically recorded at the [BMIM][PF₆] filmed QCM sensor for some VOCs considered is reported in Figure 2 and quite similar peak readouts were found at quartz crystals coated with other RTILs.

- Figure 2 near here -

In all cases, frequency changes turned out to increase linearly with the analyte amount injected, like for ethyl acetate. However, sensitivities depended markedly on the RTIL coating. Thus, high sensitivities were displayed by almost all VOCs at quartz crystals coated with [DMIM][BF₄], while poor enough signals were in general provided by QCM sensors covered with [THTDP][NTF₂].

In order to give a more effective illustration of the different sensitivities found at crystals coated with different RTILs for the classes of VOCs here considered, Figure 3 collects the signals recorded at each RTIL coating for some representative components of each VOC class considered.

- Figure 3 near here -

At each QCM sensor and for any VOC analyzed, frequency changes depended linearly on the analyte amount injected. The relevant regression equations were characterized in all cases by correlation coefficients equal to or higher than 0.997. From their slope (Table S1, Supporting Information), the corresponding detection limits were inferred for a signal-to-noise ratio of 3 (Table S2, Supporting Information).

Responses recorded at each RTIL coated QCM sensor resulted from overlapping contributions when headspaces with a complex composition were tested, so that they were unable to provide selective indications of VOCs present. This notwithstanding, the different and specific contributions given by each flavor component to each signal recorded at the different RTIL coated QCM sensors is expected to allow a discriminating information to be achieved by subjecting the whole set of responses to multivariate data analysis. Therefore, the principal component analysis (PCA) approach, i.e. the simplest of the true eigenvector-based multivariate analysis, was applied to the whole data collected at the QCM array for all VOCs assayed. Thus, the multivariate set of data could be visualized in a two-dimensional data space, as shown in the loading plot reported in Figure 4 where groups of VOCs belonging to different chemical categories can be recognized. It shows that alcohols and hydrocarbons are the sole classes of VOCs located in upper quadrants, so as to be satisfactorily discriminated from other types of possible flavor components. Even though other seven classes of compounds are all located in lower quadrants, they are grouped in fairly enough distinct clusters. In fact, separated enough clusters for acids, aldehydes and esters are apparent, while less resolved but however localized clusters can be observed near the left-hand edge of the lower left quadrant for phenols and terpenes, as well as at the right-hand side of the lower right quadrant for amines and ketones.

- Figure 4 near here -

Probably, a better discrimination could be achieved by resorting to more sophisticated chemometric approaches, using for instance more than two principal components to arrange data in multidimensional data spaces or even exploiting neural network techniques. However, no attempt was made for gaining further insight into this matter, in view of the fact that our attention was mainly focused on the technical aspects of the sensor array.

Application to Real Cinnamon Samples. To confirm that the good results gained by the significant application of RTIL-QCM arrays to the discrimination of a wide variety of odorous VOCs reported above were not obtained by chance, a further more difficult problem was tackled, concerning the differentiation of odors released from quite similar flavor sources. Thus, cinnamon sticks purchased from different local markets were tested to verify whether their botanical species (*cinnamon zeylanicum* or *cinnamon cassia*) could be distinguished. With this purpose, three batches of cinnamon sticks (2 portions of each batch, suitably grinded before use) belonging to each botanical species were analyzed.

Preliminarily headspace GC-MS analyses of these samples pointed out that flavors from the two varieties differ essentially for a different terpenes/cinnamic aldehyde molar ratio, which is higher for *C. zeylanicum* samples, as well as for the presence of small amounts of eugenol in samples of this botanical species, which is instead absent in *C. cassia* samples (see Figure S3, Supporting Information). In spite of these small differences, the array of modified QCM sensors proved to be able of discriminating these two botanical varieties. In fact, application of PCA to frequency changes recorded at all RTIL coated quartz crystals when 2 mL of headspace in equilibrium at room temperature with each cinnamon sample were injected in the flow apparatus led to their visualization in a two-dimensional data space which is shown in Figure 5 (the variance explained by the first two PCs was 85.09%). This loading plot points out that cinnamon samples of the two botanical varieties assayed are grouped in well distinct clusters, thus confirming that this QCM array display a profitable performance for the monitoring of aroma patterns, even enabling botanical classification.

- Figure 5 near here -

■ CONCLUSIONS

To our best knowledge, this is the first investigation showing the characterization of odors assessed by RTIL coated QCM arrays able to provide a qualitative and quantitative information on aroma patterns. The specific prototype applications to both the monitoring of several VOCs and classification of cinnamon samples belonging to different botanical varieties herein reported provide evidence for the good results which can be achieved by this type of “electronic nose”. Furthermore, a better performance has to be expected if recorded sets of data are treated by chemometric approaches more sophisticated than the principal component analysis herein adopted.

Improvement of the performance of this electronic nose could be conceivably gained by using RTIL coatings suitably chosen for the specific nature of VOCs which are intended to be identified and determined in headspaces. In fact, VOC sensitivities are expected to increase with their increasing solubility in RTIL coatings, which depends in its turn on the “affinity” of VOC molecular structures for those of RTIL cations (including polarity, van der Waals interactions and mixing entropy). In this connection, the attractive RTIL features as solvents come out just from the fact that they can be tailor made by varying suitably length and branching of alkyl groups present in cations and/or charge density of anions, so as to achieve a fine tuning of their compatibility with polar or non polar analytes. This notwithstanding, it has to be underlined that scarce enough attention is usually paid to selectivity of any single probe in all instrumentations providing data by combining outputs from sensor arrays, in that a specific information is almost always gained by multivariate data analysis.

Further investigations are now in progress just aimed at going deeper into the criteria to be followed whenever the most appropriate RTILs must be selected for analyzing specific types of flavors.

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Table 1. RTILs adopted and their density (ρ) and viscosity (η) values at 293 K.

Name	Cation	Anion	ρ (g/cm ³)	η (cP)
trihexyl(tetradecyl)phosphonium anthraquinonesulfonate [THTDP] [AQS]			1.010	450
1-octyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide [OMIM][NTF2]			1.326	115
1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide [BMIM][NTF2]			1.429	63
1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide [BMPyr][NTF2]			1.401	96
1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF6]			1.371	294
trihexyl(tetradecyl)phosphonium bis(trifluoromethanesulfonyl)imide [THTDP][NTF2]			1.070	350
1-decyl-3-methylimidazolium		-	1.072 (298 K)	316

Name	Cation	Anion	ρ (g/cm ³)	η (cP)
trihexyl(tetradecyl)phosphonium anthraquinonesulfonate [THTDP] [AQS]			1.010	450
1-octyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide [OMIM][NTF2]			1.326	115
1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide [BMIM][NTF2]			1.429	63
1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide [BMPyr][NTF2]			1.401	96
1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF6]		PF_6^-	1.371	294
trihexyl(tetradecyl)phosphonium bis(trifluoromethanesulfonyl)imide			1.070	350

Table 2. Volatile compounds used as representative odour components.

Figure captions

Fig. 1.
Layout of
the flow
system
adopted for
FIA
analysis.

Fig. 2. Frequency changes vs. time responses recorded under flow conditions (20 mL min^{-1}) at a quartz crystal coated with [BMIM][PF₆] for the injection of 2 mL of headspace in equilibrium at 20 °C with pure samples of : a) propanal; b) hexane; c) phenol; d) i-octane; e) 2-propanol; f) ethylacetate; g) ethylbutanoate; h) butylformate; i) methylacetate; l) acetic acid; m) p-cresol; n) methanol.

Fig. 3. Frequency responses recorded under flow conditions at each RTIL coated quartz crystal in the QCM array for the injection of 8.31×10^{-6} mol of each of the indicated VOC belonging to the different classes considered. Numbers in abscissa identify the different RTIL coatings as follows : (1) [THTDP][AQS]; (2) [OMIM][NTF₂]; (3) [BMIM][NTF₂]; (4) [BMPyr][NTF₂]; (5) [BMIM][PF₆]; (6) THTDP][NTF₂]; (7) [DMIM][BF₄].

Fig. 4. Loading plot obtained for all VOCs listed in Table 2. Sensing layers were considered as objects, while samples were treated as variables.

Fig. 5. Loading plot obtained by PCA for grinded samples of *Cinnamon zeylanicum* (CZ) and *Cinnamon cassia* (CC). Numbers refer to different cinnamon batches and letters (a) and (b) refer to replicate measurements on different portions of the same cinnamon batch. Sensing layers were considered as objects, while samples were treated as variables.

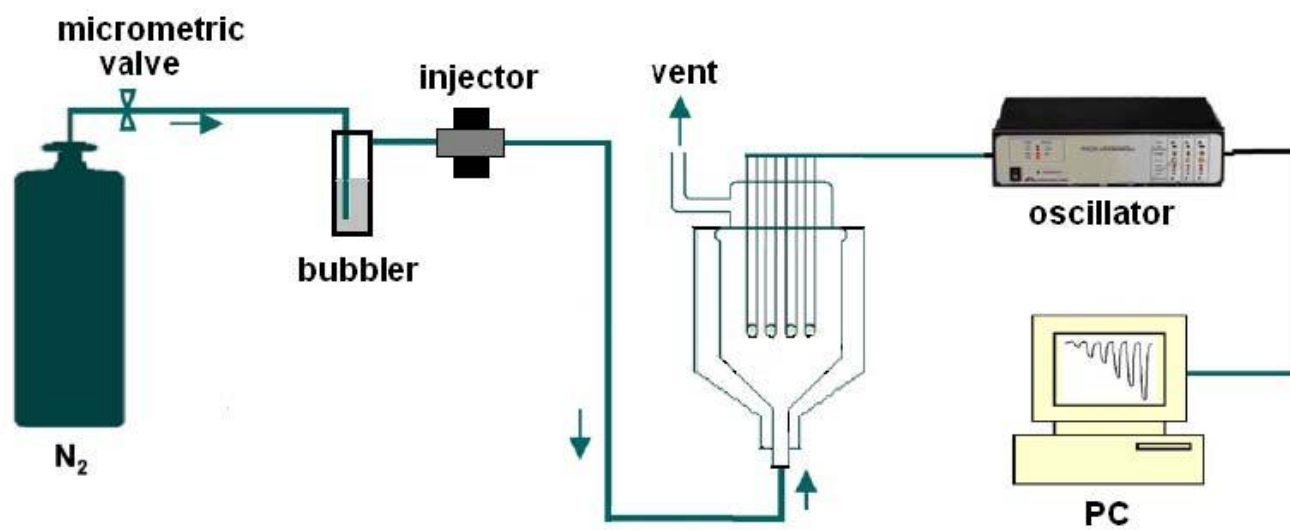


Fig. 1. Layout of the flow system adopted for FIA analysis.

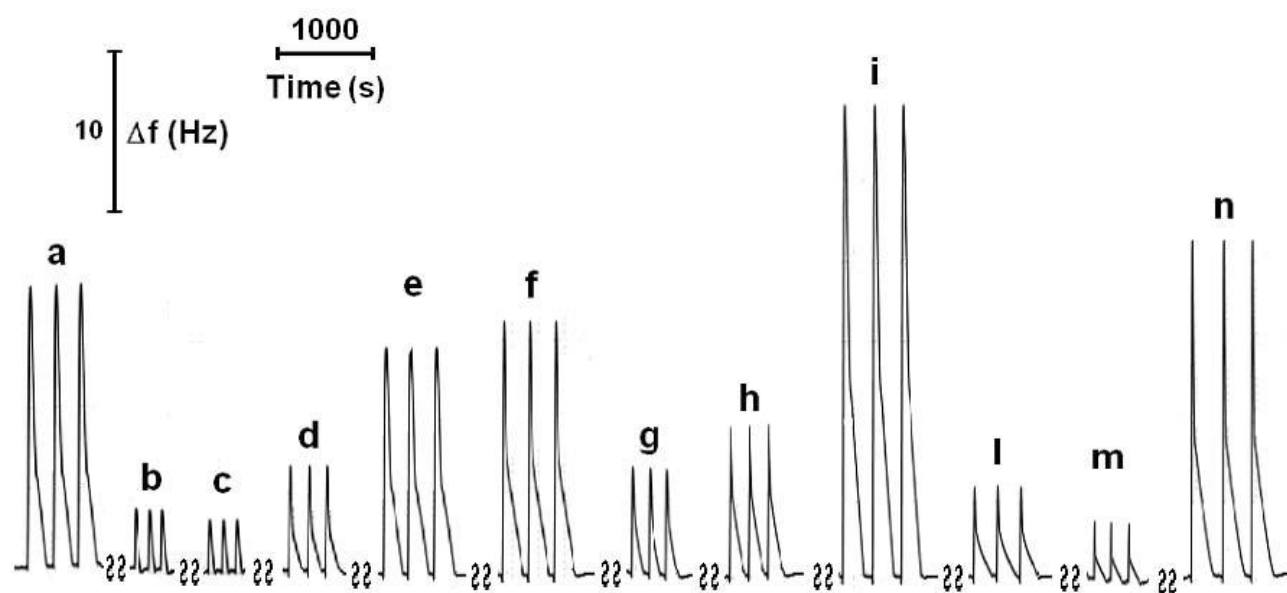


Fig. 2. Frequency changes vs. time responses recorded under flow conditions (20 mL min^{-1}) at a quartz crystal coated with $[\text{BMIM}][\text{PF}_6]$ for the injection of 2 mL of headspace in equilibrium at $20 \text{ }^\circ\text{C}$ with pure samples of :
a) propanal; b) hexane; c) phenol; d) i-octane; e) 2-propanol; f) ethylacetate; g) ethylbutanoate; h) butylformate; i) methylacetate; l) acetic acid; m) p-cresol; n) methanol.

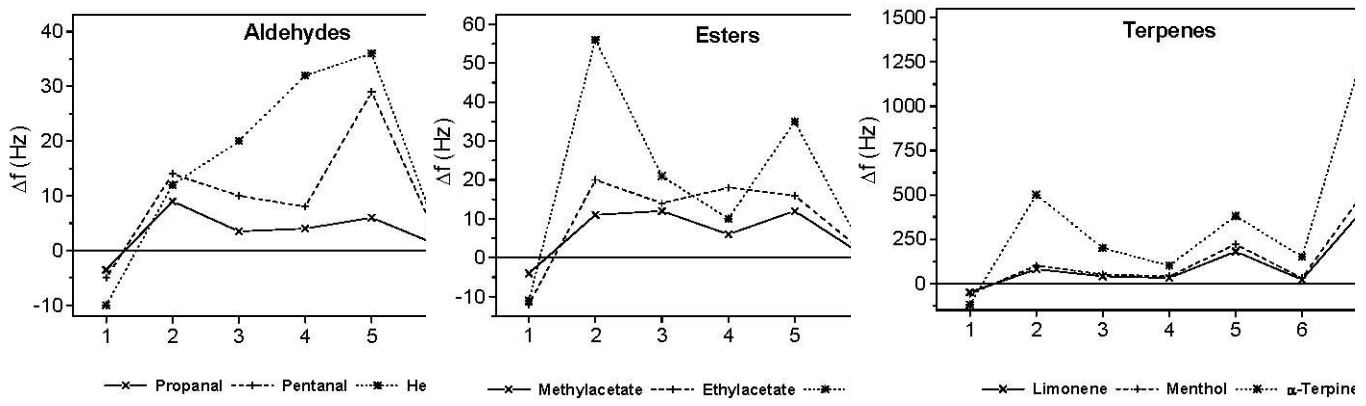
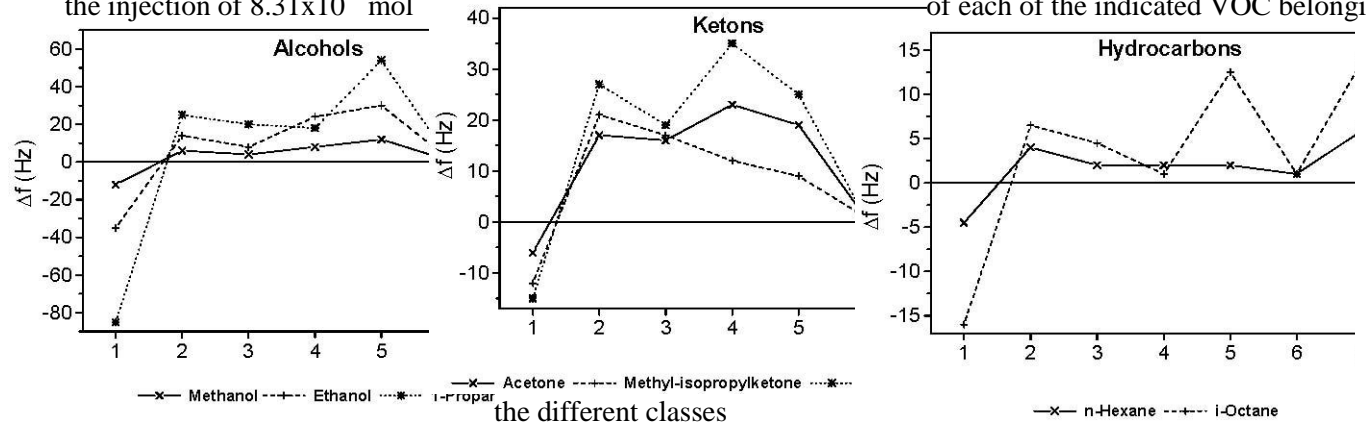
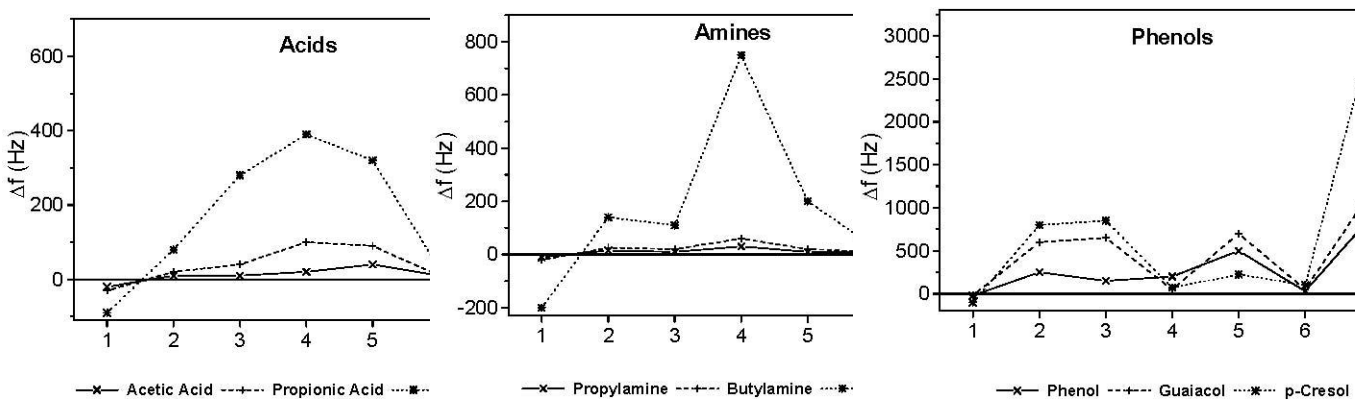


Fig. 3. Frequency responses recorded under flow conditions at each RTIL coated quartz crystal in the QCM array for the injection of 8.31×10^{-6} mol of each of the indicated VOC belonging to



the different classes considered. Numbers in abscissa identify the different RTIL coatings as follows : (1) [THTDP][AQS]; (2) [OMIM][NTF₂]; (3) [BMIM][NTF₂]; (4) [BMPyr][NTF₂]; (5) [BMIM][PF₆]; (6) THTDP][NTF₂]; (7) [DMIM][BF₄].



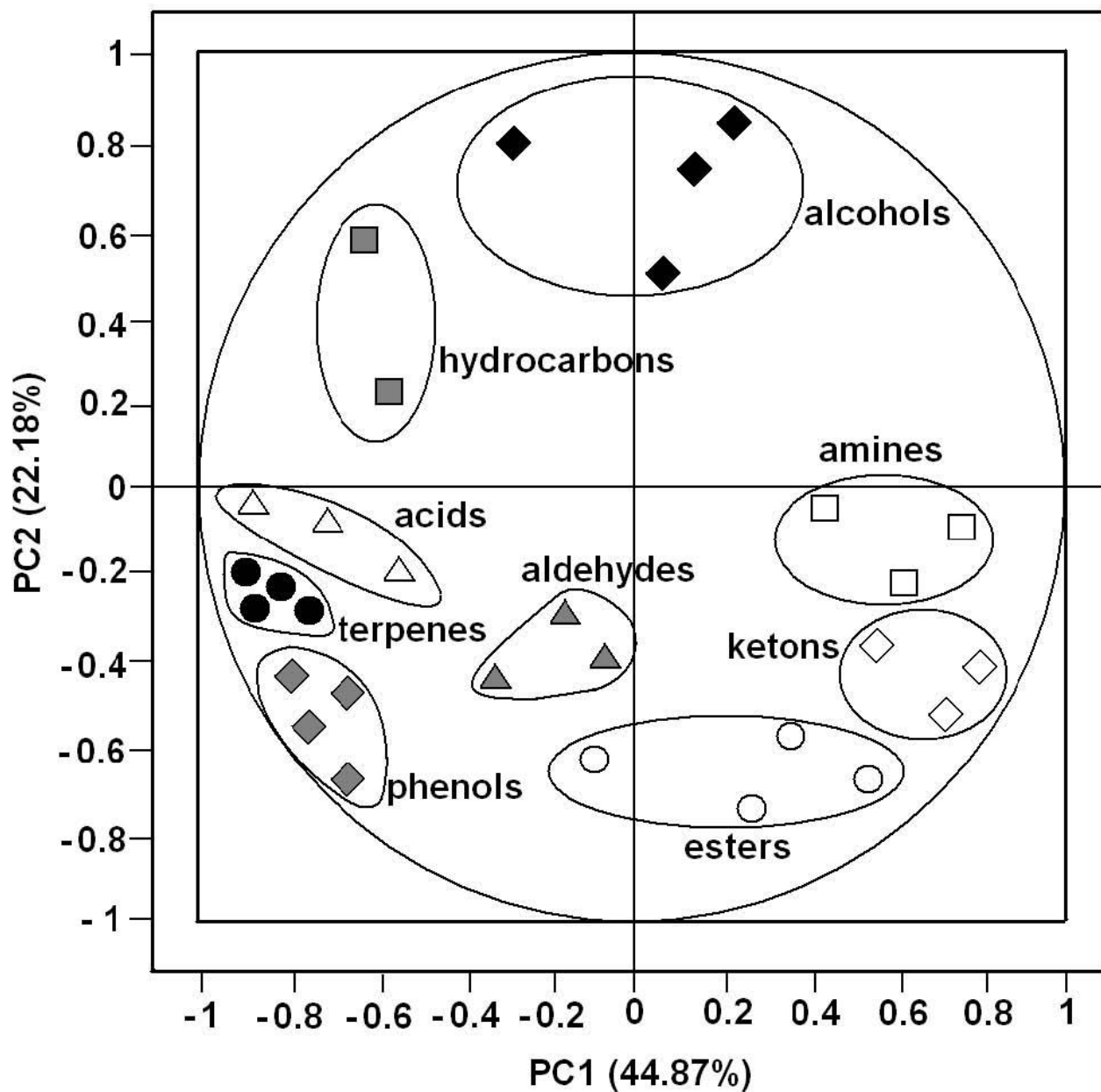


Fig. 4. Loading plot obtained for all VOCs listed in Table 2. Sensing layers were considered as objects, while samples were treated as variables.

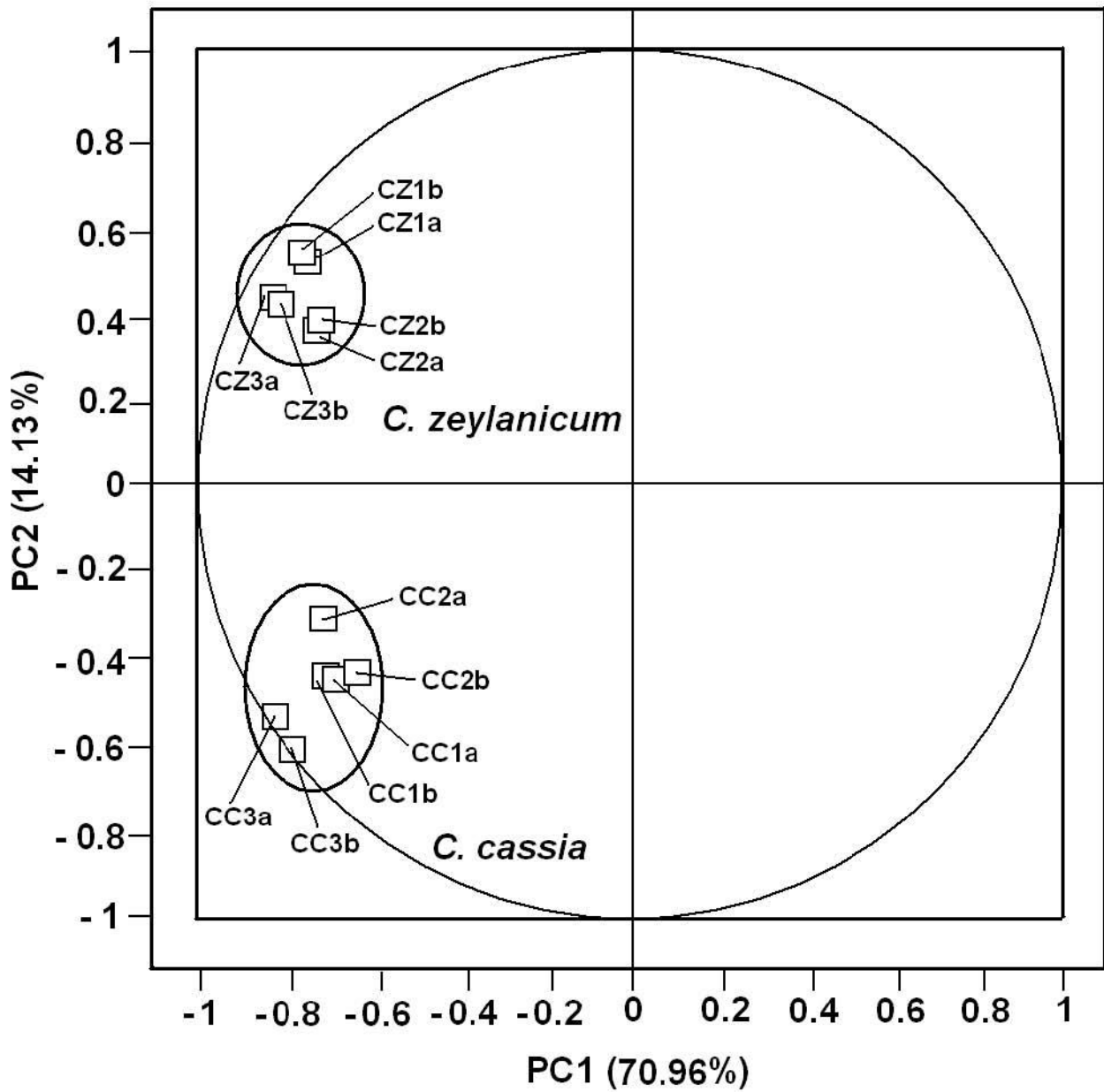


Fig. 5. Loading plot obtained by PCA for grinded samples of *Cinnamomum zeylanicum* (CZ) and *Cinnamomum cassia* (CC). Numbers refer to different cinnamon batches and letters (a) and (b) refer to replicate measurements on different portions of the same cinnamon batch. Sensing layers were considered as objects, while samples were treated as variables.

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