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Fingerprinting mass spectrometry by PTR-MS: heat treatment vs. pressure treatment of red orange juice—a case study

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Abstract

Proton transfer reaction mass spectrometry (PTR-MS) is more and more applied to rather different fields of research and applications showing interesting performances where high sensitivity and fast monitoring of volatile organic compounds (VOCs) are required. Based on this technique and aiming at the realisation of an automatic system for routine applications in food science and technology, we tested here a novel approach for fingerprinting mass spectrometric detection and analysis of complex mixtures of VOCs. In particular, we describe and discuss corresponding head space (HS) sampling methods and possible data analysis techniques. As a first test case we studied here the properties of four red orange juices processed by different stabilisation methods starting from the same industrial batch: untreated juice, thermal pasteurised (flash and standard) juice and high pressure stabilised juice. We demonstrate the possibility of a fast automatic discrimination/classification of the samples with the further advantage, compared to the use of electronic noses, of useful information on the mass of the discriminating compounds. Moreover, first comparisons with discriminative analysis by a sensory panel shows evidence that there is a correlation between the ability of the PTR-MS to distinguish different juice samples and that of a panel of trained judges with the obvious advantages of an instrumental approach. (Int J Mass Spectrom 223–224 (2003) 343–353)

Keywords: Proton transfer reaction mass spectrometry; Volatile organic compounds; Red orange juice; Pasteurisation

1. Introduction

Sometimes exciting ideas in science evolve far away from the field and time where they were originally developed and open, besides the applause of academia, the possibility to realise useful applications. Among these is certainly the proton transfer reaction mass spectrometry (PTR-MS) introduced by Lindinger and co-workers in the early nineties [1]. Even though this technique arises from a very "defined" field, i.e., ion molecules reactions, and from a very defined experimental approach, i.e., swarm methods (see [2]), it was clear from the first applications proposed by Lindinger that the properties of PTR-MS can be useful in many fields, both fundamental and applied, where the detection and quantification of volatile organic compounds (VOCs) is important, i.e., ranging from medical applications [3] to food science and technology [4], from plant physiology [5] to atmospheric chemistry and environmental monitoring [6].

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In particular in the agroindustrial sector VOCs are of utmost importance because they are often directly connected to (i) the real and/or perceived quality of food, to (ii) their sensorial characteristics, and to (iii) the effects of transformation and preservation processes. Moreover, odour and flavour are among the most important hedonistic aspects leading the consumer choice [7]. The fact that in 1995 the market for the flavour sector amounted to about 9.5 billion US dollars should rationalise the growing interest for new developments such as the use of PTR-MS in this field [8].

Because of the role they play in so many different fields, VOCs are widely investigated and many techniques have been proposed to analyse and monitor them (for agroindustrial applications, see [9]). The sensitivity of some of these methods available today is very high, but normally the price to be paid is high in terms of a number of draw backs in the measurements, e.g., in the sample preparation, time needed, calibration with internal standards, data interpretation and necessity of highly trained people. Only large companies or institutions can afford the cost of these analytical tools and often it is simple impossible both economically and technically, to implement them into the production processes, usually deferring the quality control to the end of the production line involving only small statistically selected samples.

Therefore, it is quite urgent to develop techniques that can circumvent these problems and, in the last decade, the so-called “electronic noses” resulted in a very promising approach towards fast and cost-effective VOCs detection [10]. Besides being an interesting and useful approach in itself, “electronic noses” take the credit of demonstrating a general approach to VOCs detection that can be extended to other techniques and moreover, together with sensorial application, to get people acquainted with multivariate statistical analysis. The three steps involved in this technique are, in general: (i) a sampling system for the air containing the VOCs of interest, (ii) an array of sensors reacting in a different way to different compounds or classes of compounds (usually some kind of solid state devices), and (iii) an automatic system for data analysis allowing to display in a concise way the information obtained. If the numbers produced by the array of sensors are substituted by a mass spectrum measured with a mass spectrometer, we have a kind of (mass resolved) fingerprinting system where the mass spectrum is simply used as an image, a fingerprint, of the total volatile profile ([11] and reference therein) of a sample under study.

There exist some commercial applications of this philosophy based on quadrupole or time-of-flight mass spectrometers [12] and recently the use of a PTR-MS in this mode was proposed by Lindinger and co-workers in [13]. Here we want to demonstrate that indeed the realisation of a complete fingerprinting mass spectrometric system based on PTR-MS is useful and possible and we will also discuss an example of application involving a practical problem. The important characteristics needed for the detection system in such a fingerprinting technique are, in our opinion, some of the outstanding properties that make PTR-MS so interesting, i.e., (i) no pretreatment of the sample is needed, (ii) the measurements can be carried out very fast and the PTR-MS is extremely sensitive. In the fingerprinting techniques based, for instance, on electron impact ionisation mass spectrometry, there is a pay off between gaining speed but loosing analytical information (e.g., no previous GC separation). We expected that due to the reduced fragmentation in the case of PTR-MS it is possible to have a fast analysis method without loosing valuable information for compound identification.

One of the main topics in food science is the development of the so-called “mild technologies” that is production processes that can achieve certain effects on food (typically microbiological safety or shelf-life increase) with minor changes on the sensorial and nutritional properties [14]. Many techniques have been proposed to substitute the traditional heat treatment, i.e., electron beam irradiation, ultrasonic treatment, pulsed electrical field application, etc. [15]. Stabilisation of food by very high pressures is one of the most interesting possibilities because it appears to preserve the sensorial characteristics of the treated products [16]. Moreover, the consumers are open to pressure

treatment because it does not involve any additive and/or the use of radioactive substances. In this paper we address the problem to determine fast and effectively if there are differences in the volatile fraction of red orange juices treated by different means by measuring with a PTR-MS the head space (HS) of untreated, thermally stabilised and pressure stabilised juices. We will present here first results concerning the general method and more details on the investigated products and processes will be published at a later stage. The analysed juices are quite similar and this is a good test bench for our approach.

2. Experimental method

2.1. General

In Fig. 1, we show a schematic view of a VOC detection system based on the usual approach for electronic noses (dotted rectangle on the top of Fig. 1). First, the gas mixture to be analysed is collected by a suitable sampling system. The principal requirements are that (i) this system should be fast, (ii) to use as small a gas sample as possible to avoid dilution and artefacts in case the available sample is limited, (iii) the gas should not get in contact with reactive surfaces, (iv) the surfaces exposed to the gas sampled should also have a homogeneous and constant temperature, and (v) the system should allow the automatic measurement of several samples. The second panel represents the array of solid state sensors that should provide different signals in presence of different volatile compounds. Typically this array encompasses from 5 to 32 sensors and these sensors should be somehow selective for classes of compounds. The sensors have to be reliable in time and should not show memory effects (i.e., previous measurements should not affect subsequent measurements). Several sensors have been proposed and tested and we refer to the numerous literature on

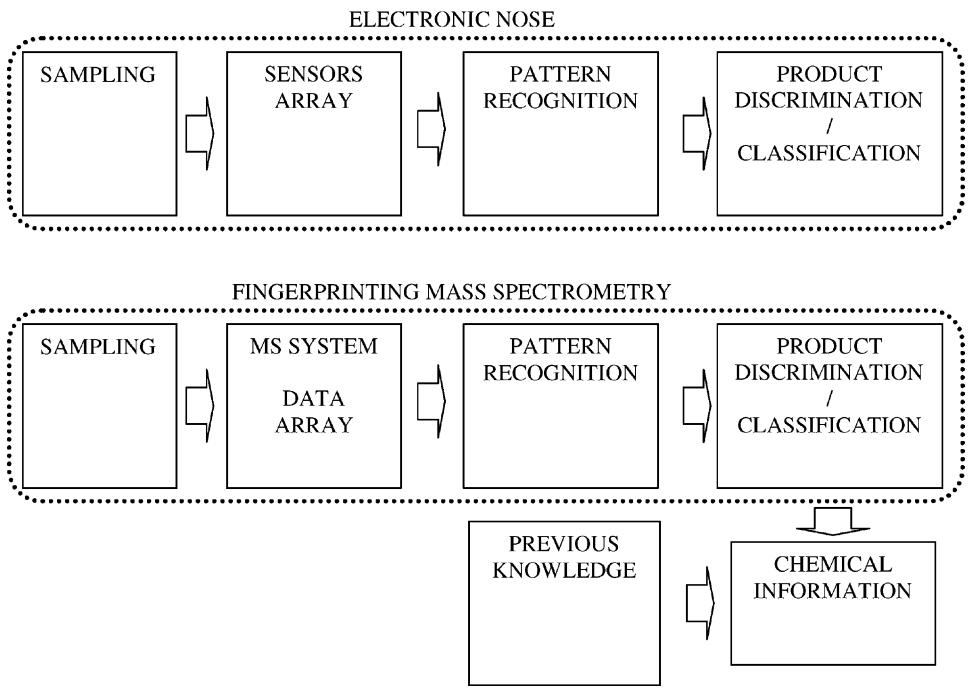

Fig. 1. Block diagrams of the working principle of an electronic nose (above) and of a fingerprinting mass spectrometric system (below). The main difference, beside the intrinsic sensibility of the sensor, is the possibility of use previous knowledge to get analytical information from the pattern recognition data. See text for details.

this topic [10]. Here we only consider that this second stage produces a series of numbers related to the actual composition of the measured gas mixture. The last step is the application of one of the available pattern recognition techniques to this series of numbers produced by each sample to generate some sort of (visual) description of the data to discriminate the samples. There are many techniques (a description can be found in [17]) ranging from simple data display (e.g., spider plot) to the more fashionable artificial neural networks [18]. We want to remark that, in any case, the low discriminative power of electronic noses does not, in general, allow a correlation of the final result with defined chemical species present in the sample. This method allows a useful discrimination between different samples, the final result being at best "the products are different but don't ask in what respect and why."

PTR-MS, even if relatively new, is already recognised as an important tool where fast and sensitive measurement of VOCs need to be carried out. Details on the PTR-MS can be found in [19] and references therein. Here we only reiterate the most important features: an intense beam of H_3O^+ ions is produced in a hollow cathode discharge source burning in water vapour and this virtually pure H_3O^+ ion beam enters after some treatment a drift tube where these ions are guided by an homogeneous electrical field and are allowed to interact with VOCs present in the gas flow in this flowing drift tube. In the drift region every molecule R with a proton affinity greater than that of water will eventually interact with H_3O^+ exchanging the proton:

$$R + H_3O^+ \rightarrow RH^+ + H_2O \quad (1)$$

The produced ion RH^+ is then detected by a commercial quadrupole mass spectrometer. Some of the characteristics of this PTR-MS of importance for the present study are listed below:

(1) the normal air constituents are not detected due to their higher proton affinity and thus normal air can be used as carrier gas avoiding the necessity of sample pretreatment;
(2) this technique is very fast (typically about 1 min for a complete mass spectrum) thus allowing on-line application and measurements;
(3) the fragmentation induced by proton transfer is usually either negligible or quite simple, e.g., leading to 1–3 fragment ions. This reduces the compounds responsible for a certain mass in the spectrum to few possibilities and facilitates identification and quantitative analysis;
(4) there exist simple methods to distinguish isomers by PTR-MS [13];
(5) the sensitivity to be achieved can be very high, thus allowing to analyse also very diluted gases.

It is interesting to note that the sensitivity is often in the range of the sensitivity of the human receptors allowing an easy comparison between the machine response and the human response.

These properties are exactly the prerequisites needed for a "sensor" in a fingerprinting mass spectrometer system and this convinced us to carry out here an exploratory study on the possibility to use PTR-MS in this kind of application (see also Fig. 1 lower dotted panel).

2.2. Sampling

Two different sampling systems (see Fig. 2) with quite different characteristics have been tested here. In the first one (Fig. 2A), called here "syringe pump method" (SPM) and based on the Precidor 5003 (INFORS) model, the juice sample (approximately 1 mL) is filled into a glass syringe (volume 100 mL) and after 15–30 min the HS that forms is injected under controlled flux (4 mL/min) into a sampling flow tube where it is diluted with air or another carrier gas (25 sccm of nitrogen for the present measurements). From this diluted mixture the gas flow needed for the measurement (11 sccm) is introduced into the PTR-MS. The liquid sample and the syringe are at room temperature, whereas the gas lines are heated to 40 °C. This SPM set-up constitutes a good approach if one wants to understand the evolution of concentration in the HS of the sample and if an equilibrium value is needed to compare, for instance, with other

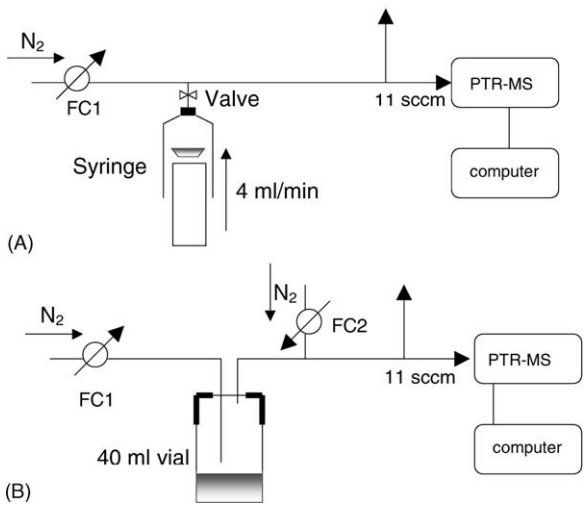

Fig. 2. A schematic representation of the two sampling methods presented. (A) Syringe pump method, (B) vials method. FC1 and FC2 are the flow controllers, N_2 is the carrier gas used in this experiment. See text for details.

static techniques such as solid phase micro-extraction [20]. A possible disadvantage of this SPM set-up is the difficulty to operate and thermalise the syringe and the necessity of a very stable motor to move the syringe piston to inject the HS into the sampling tube. Some attention must also be paid to the possible increase of the pressure in the syringe due to the possible pressure drop in the gas line with intense fluxes. An appropriate choice concerning the sampling tube diameter, length and flow can reduce this problem.

The second method tested here (see Fig. 2B), called "vial method (VM)," is to sample (through a Teflon-coated silicone septum) the HS formed in a 40 mL glass vial containing the juice sample (10 mL) to be measured. In this case the nitrogen carrier gas flows through a stainless steel needle into the vial and the ensuing mixture leaves the vial by another similar needle. The gas mixture, diluted if necessary, is measured by the PTR-MS. The vial is placed into an oven at 30 °C for a fixed time (1 h) before and during (20 min) the measurement. Again the gas lines are heated to 40 °C. This is probably the method we will follow in the future because it can be very simply implemented in an automatic sampling system, it allows the preparation of several samples at a time and the measurements can be carried out very fast. A point deserving some attention is that in the VM technique the measured concentration is not constant because of the dilution induced by the carrier gas. But the time evolution of the concentration can be easily evaluated and a zero time value can be extrapolated from the data. Moreover reducing the carrier gas inlet flow reduces this effect giving an almost constant concentration during the few minutes of measurement.

Both methods have been tested for stability and reproducibility with red orange juice samples, cheese samples and pure standards yielding satisfactory results. All gas lines were either 1/8 in. Teflon tubes or untreated fused silica tubes (0.25 mm internal diameter) connected by stainless steel fittings. The carrier gas used was pure nitrogen (purity: 99.999%). Between successive measurements a high flow (500 sccm) of pure nitrogen was used to clean the gas lines.

2.3. PTR-MS measurements

In several previous studies with the PTR-MS the samples were deposited into a cuvette, the cuvette was closed and then the increase in the VOCs concentration of a carrier gas flowing through the cuvette was measured (dynamic HS measurement [21]). In this case one has to wait until equilibrium is reached between the emitted VOCs and the flowing air through the cuvette. This gives the possibility to follow processes that vary with time but the method is slow (long time to evacuate the cuvette) and gives only indirect information on the static equilibrium values. With the presently employed methods, to the contrary, equilibrium is reached before the starting of the measurement and we need only to measure a few spectra to get the information on the HS concentration. With the "SPM" the signal is constant and in principle only a couple of measuring cycles (in each cycle a complete mass spectrum up to mass 240 amu is monitored within a time span of approximately 50 s) are necessary, while in the case of the VM the dilution effect discussed above has to be taken into account. Nevertheless, this

VM could be developed to eventually separate isomers based on their different decay time in the HS [13].

After starting the measurements we usually skip 4 cycles and than average the data of the next 5 cycles (SPM) or we skip 2 cycles and than extrapolate to zero time concentration based on the next 10 cycles (VM). The data collected are converted in ppb by the following relation [19]:

$$C = \frac{1}{kt}\frac{[RH^+]}{[H_3O^+]}\frac{V}{N} \times 10^9 \quad (2)$$

where C is the concentration in ppb, k the reaction rate constant for a given molecule in s cm^3, t the ion travel time in the drift tube (about 100 μs) $[RH^+]$ indicates the measured counts per second for the protonated species and $[H_3O^+]$ is the measured intensity of the primary beam (counts per second). N/V is the gas density in the drift tube (molecules/cm^3). We assume the reaction rate constant to be 2×10^9 s cm^3 for all compounds thus introducing a systematic error which is in most cases however negligible [22]. Some of the mass peaks measured are not considered in the present analysis, i.e., masses smaller than 33 amu because they are often related to spurious products from the ion source (e.g., O_2^+), and masses at 37 and 55 amu that are related to protonated water dimer and trimer ions.

2.4. Data analysis

Among the many possible pattern recognition techniques, i.e., simple plotting, principal component analysis (PCA), neural network, multidimensional scaling, cluster analysis, etc., we choose here PCA because it does not need stringent assumption concerning the data and because the interpretation of PCA plots is becoming quite natural for people involved in food science. Moreover it gives, through "loadings," valuable information if one is interested in understanding the reason of the observed differences [23]. We tested also cluster analysis and multidimensional scaling but there appeared for the present study no advantage of these methods in comparison to PCA.

A simple way to identify those masses which are responsible for the observed differences between different samples is to use the ANOVA method on the repeated sets of mass spectrometric data. This is useful because often a simple look at the PTR-MS spectra for complicated mixtures, as often occurs in food, does not allow a simple identification of the significant differences due to sample variability and various sources of noise. For this purpose the present data were analysed by two computer programs, i.e., Senstools [24] and Statistica [25].

2.5. Samples studied

For the present measurements we used the juice of red oranges produced in Sicily and, after a soft thermal treatment, frozen to −20 °C and sent under those conditions in 200 L vessel to Verona, Italy (Zuegg). Small batches of the juice were defrosted and treated in four different ways and labelled in the following with FF, FP, LP, HP:

(i) FF, untreated juice, this is the reference product being, according to industrial standards, the closest product to the real fresh juice;
(ii) FP, flash-pasteurised juice, it corresponds to a premium commercial product that should be stored at 4 °C to reach a minimum shelf-life of about 1 month;
(iii) LP, juice pasteurised with higher temperature for a longer time with respect to FP, it has a longer shelf-life of several months even at room temperature;
(iv) HP, juice stabilised by high pressure, i.e., applying 6000 bar for 30 s.

The corresponding samples from these treatments for the present measurements were three PET bottles of each type frozen after these treatments and preserved at −20 °C. About 12 h before the PTR-MS analysis the samples (bottles) were immersed into a water-bath (10 °C) to defrost the frozen juices. After that the liquid samples, e.g., in the case of the SPM method 1 mL of the defrosted juice was put in the syringe and measured.

3. Results and discussion

We measured the juices from the 12 bottles prepared here as follows: on the first day we started with a sample from one of the FF bottles repeating the measurement after a few hours, the second day we measured samples from all of the remaining bottles (2 FF, 3 HP, 3 LP, 3 FP) repeating again the measurements after a few hours, the third day we measured samples from all the bottles again which were kept in the meantime after the defrosting at 5 °C. It is important to note that, because of the time elapsed between the first measurement of a bottle (effective data) and the repeat measurements we expect some time evolution and some possible difference in the data. The samples were measured in random order to avoid systematic memory effects and spurious trends.

It is interesting to note that already by simply looking at the four different kind of juices it is apparent that the HP samples are quite different from the rest, i.e., the three HP samples were not homogeneous but they have a different content of dry matter and particulate. Thus, in an additional experiment we separated, by simple deposition, dry matter and liquid phase of the HP orange juice and then we reconstructed the HP juice preparing various samples containing different percentages of dry matter and measured the HS of these different samples using in this case the "VM" (all the other measurements discussed below and displayed in Figs. 4 and 5 have been carried out with the SPM method). The result for some selected mass peaks is shown in Fig. 3. The data displayed are normalised, for better comparison, to data of the sample containing 0% of dry matter (note that the three repeat runs carried out for the sample containing 0% of dry matter were quite reproducible). It is clear that the HS equilibrium is strongly affected by the dry matter content and the effect is different for different masses. We do not elaborate here any further on this effect, but it is clear that it has important consequences on the properties of juices having different particulate content.

In Fig. 4, we have plotted the first two dimensions of the PCA applied to all the data points available. Here

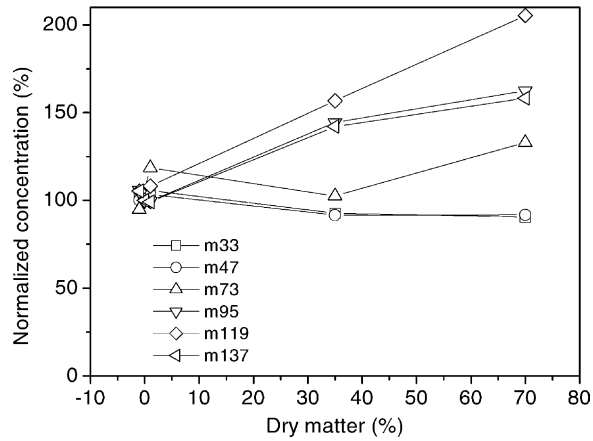

Fig. 3. Dependence on dry matter content of the HS concentration of reconstructed orange juice for some selected masses. The data are normalised to the pure liquid phase (0%) were three replicates have been measured.

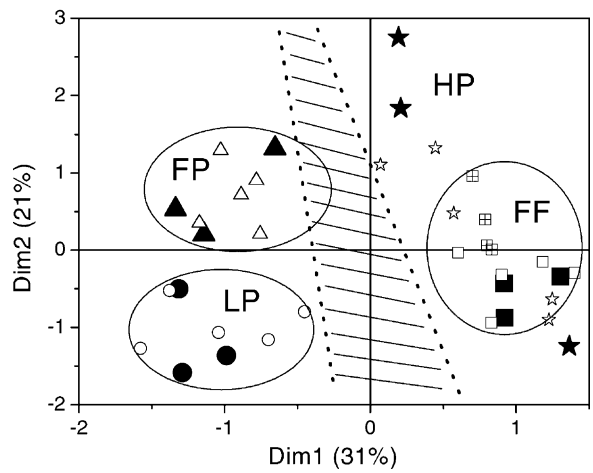

Fig. 4. First and second dimensions of PCA (replicates as different measurements) on the spectral data of HS measurements for different orange juices: FF, untreated reference product (□); HP, pressure stabilised juice (☆); FP, flash-pasteurised juice (△); LP, pasteurised juice (○). Solid points refer to measurements immediately after the opening of the samples, open points refer to replicates within the next 2 days. Crossed squares indicate the replicates for FF on the last day. Ellipsis indicates the clear discrimination for FF, FP and LP. Hatched region separates thermal treated juices from others. Percentages indicate the explained variance associated with each dimension.

solid points refer to the data of the first measurement for each sample while the smaller open points refer to the repeat measurements. It is immediately apparent from these results that this analysis leads to a clear distinction in this plot between the untreated juice FF (designated by squares) and the thermally stabilised juices FP (designated by triangles) and LP (designated by circles), i.e., in each case all PCA data of a specific juice variant fall within a clearly defined area (ellipse), this ellipse encompassing the data of the three bottles and of the samples measured at different times after the initial defrosting. It is interesting to note that in case of the untreated juice FF the solid points are relatively close to each other (indicating possibly a better homogeneity of the samples in the three bottles than in the case of the thermally treated samples). Moreover, in this case (where we have measurements for 3 days) we see also evidence for some evolution in time, i.e., all the data points of the third day, designated by the crossed squares, lie above the other data points, thus clearly indicating the possibility to distinguish samples with different history.

On the other side, the HP juice data are surely affected by a non-homogeneity of the three bottles (see above), the points being much more scattered as we can expect based on the data of the other juices. The data of Fig. 3 allow us to attribute, at least partly, this difference to the different dry matter content of the pressure stabilised juices probably due to some difference in the preparation process. Additional experiments to be carried out in the near future will hopefully shed more light on these effects. We are aware of the difficulties connected with static HS techniques [26], leading to today's situation where other dynamic methods based on distillation, adsorption, extraction, etc. are still often preferred.

In Fig. 5, we show the first two dimensions of the PCA obtained by considering only the data from the first measurement of each bottle (that is without any repeat measurements) and in addition also the "loading" [23] connected with a few selected masses. An interesting advantage of the PCA data display is that it gives immediately an idea about the similarity of the samples. From Fig. 5 we can argue that all the

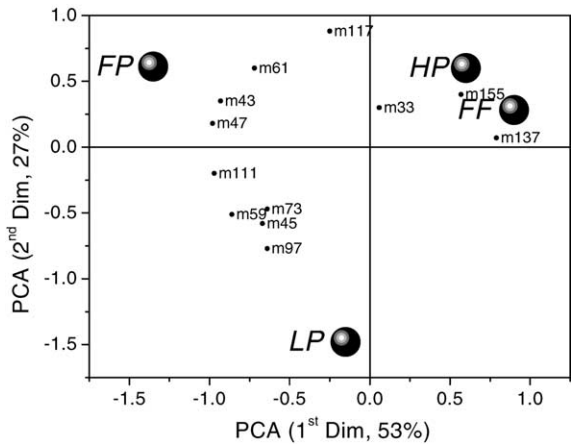

Fig. 5. First and second dimensions of PCA (average on replicates) on the spectral data of HS measurements for different orange juices. FF, untreated reference product; HP, pressure stabilised juice; FP, flash-pasteurised juice; LP, pasteurised juice. Small symbols indicate the loadings connected with some selected masses. Percentages indicates the explained variance associated with each dimension.

samples are well separated but the untreated juice FF and the pressure stabilised juice HP are quite close. Assuming that we can average the three different HP samples, we can immediately conclude that the effect of pressure stabilisation on the aromatic profile of red orange juice is much less severe than that of thermal treatments. It is apparent that assuming that such a measurement would be carried out automatically (all the way from the sampling to the PCA analysis) one can easily distinguish if the samples are similar or different thus demonstrating the working principle of the PTR-MS as an easy to apply fingerprinting technique with the further advantage that one can also obtain some information on the mass peaks which are characteristic for the different samples and lead to differences between samples apparent in the PCA analysis.

Referring to Fig. 1 the results discussed so far demonstrate the capability of the PTR-MS as a fingerprinting mass spectrometer (as outlined within the dotted line in the lower part). It could thus be employed in a similar manner as an electronic nose, but with a much greater sensitivity and with some very

useful information on the masses of VOCs present in the samples. Nevertheless, with PTR-MS and the information at hand one can go one step further and obtain information about the chemical identity of the VOCs present. For this purpose we have first carried out a literature search thus obtaining a list of the possible compounds of some importance for the juices studied. We did this by referring to specific publications, e.g., [27,28], and using a commercial database on volatile compounds in food [29].

In order to relate mass peaks to chemical compounds we need also the fragmentation patterns (due to the proton transfer reaction [1]) for the identified compounds. To date, we did not measure all the fragmentation pattern of interest for orange juice (a systematic study on the compounds interesting for citrus juices and cheese is in progress in our labs). Nevertheless, based on the present (limited) information and on a selection of the most abundant compounds discussed in literature we can already tentatively identify some of the discriminating masses. For instance mass 33 discriminating HP (having there a concentration of 290 ppb) from other juices (FP with a concentration of 250 ppb; FF a concentration $<$240 ppb) is protonated methanol, the measured differences are probably related to a different activity of pectinase. Mass 43, mostly being due to propanol, because from the intensity of other peaks the contribution from larger molecules on this mass must be below a few percent, discriminates thermal treatment (FP: 5.5 ppb) from HP and FF ($<$4.7 ppb). Mass 45, identified as acetaldehyde, is present in higher concentration in the treated juices (FP: 126 ppb; HP: 118 ppb) than in FF (106 ppb). Mass 47, identified as ethanol, discriminates thermal treatment (FP: 92 ppb) from pressure treatment and untreated juice (HP: 75 ppb; FF: 70 ppb); the same holds for mass 59, acetone (FP: 6 ppb, FF and HP: 4 ppb). Mass 61 mostly related to acetic acid and a fragment of ethyl acetate, discriminates FP (9 ppb) and HP (8.3 ppb) from FF (7.3 ppb). Mass 73 discriminates strongly HP from other juices (HP: 1 ppb; FF: 10 ppb; FP: 20 ppb) and is probably due to a carbonilic compound with four C atoms (with our limited data we can relate it only to methyl ethyl ketone and butanal). Masses 69 and 111, mostly related to octanal, discriminate HP and FF again from thermal treatments. Another interesting peak is mass 97, probably related to furfural, that discriminates HP and FF (2 ppb) from thermal treatments (0.3 ppb) possibly indicating, in this latter case, a stronger degradation of ascorbic acid. Mass 117 (ethyl butyrate and ethyl isobutyrate) separates untreated juice (FF: 6.5 ppb) from the others ($<$5.5 ppb). Mass 137 is a measure, with its fragment at mass 81, of a mixture of terpenes typical for citrus juices and discriminates again FF ($>$200 ppb) from the others (HP: 185 ppb; FP: 177 ppb), the related oxidation products at mass 155 do not show any consistent difference (about 1 ppb). Finally, the highest characteristic mass 157 discriminates again thermal treatments from the other juices and is probably mostly related to decanal. Even if far from being definitive, these mentioned identifications show that a comparison between the (automatic) generated data, a fragmentation data base, and literature data can give valuable information to explain the differences observed among the different products and eventually correlate them to the investigated processes.

Finally, in a previous study on the VOCs from mozzarella cheese [30] we have demonstrated an interesting correlation between the ability of the PTR-MS to distinguish different cheese samples and that of a panel of trained judges indicating that the sensitivity and completeness of PTR-MS data can mimic the complexity of human perception. For the present juices we do not have the results of a quantitative descriptive analysis [31] from a panel of trained judges but only that of a discriminative triangular tests [31]. Nevertheless from these exploratory investigations we can conclude that a panel of trained judges cannot distinguish, based only on aroma and taste, between HP (pressure stabilised juice) and FF (untreated juice), but can easily distinguish these two from the thermal pasteurised juices FP and LP. So there is again, even if much less detailed, evidence that there is a correlation between the ability of the PTR-MS to distinguish different juice samples and that of a panel of trained judges.

4. Conclusions

In this paper we demonstrate that there exists a fingerprinting mass spectrometric procedure based on PTR-MS, that can be in principle easily automated and that allows to distinguish the effect of different stabilisation treatments applied to red orange juice. Similar to standard electronic nose applications the present method exhibits a fast response, does not need a sample preparation and has a very high sensitivity. In particular it provides (i) a measure of the differences and similarities among the samples even if as in the present case they are very similar and (ii) an indication of the masses responsible for the observed differences and an estimate of their concentrations in ppb. Moreover, if literature information and measurements (break-up patterns upon proton transfer) on pure standards are available quantitative assignment of masses to one or a few compounds is possible giving valuable information on the investigated processes and/or products. The proposed approach takes advantage of all the important characteristics of PTR-MS and we believe that the present development it is an important step in making the PTR-MS useful not only to research labs but also to food companies in more practical situations like quality and process control, in particular in relation to sensory characterisation.

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