Tracing coffee origin by direct injection headspace analysis with PTR/SRI-MS

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ARTICLE INFO

ABSTRACT

The headspace of six roasted *Coffea arabica* coffees, both brew and powder, of different geographical origins (Brazil, Ethiopia, Guatemala, Costa Rica, Colombia, and India) was analysed by Proton Transfer Reaction-Time of Flight-Mass Spectrometry. For the first time, in the case of coffee, a Switching Reagent Ion System has been used to produce different ionisation agents: H_3O^+, NO^+ and O_2^+. Significant differences were found among volatile concentrations for the different origins both for powders and brews, in particular high concentrations of terpenes for Ethiopia, sulphur compounds for Colombia and thiazoles for Brazil and India. Effective classification models have been set for the different ionisation modes and data fusion of the data obtained by different reagent ions further reduced the classification errors.

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1. Introduction

Globalization brings a great variety of food products to the market and increases consumers' awareness on food authenticity and product specification. Therefore more information about food products and their geographical and/or botanical origin is required and could support marketing in the positioning of their products. The increasing consumption trend towards single origin food products induces the necessity to verify and certify origin during quality assurance (Carcea et al., 2009). Coffee, one of the most important agricultural products traded worldwide, is consumed mostly for its pleasing aroma. Besides its stimulatory effects, the aroma of coffee is one of the most contributory factors for its high acceptability (Illy & Viani, 2005; Tomas & Jana, 2011). It is composed of a mixture of more than 800 different volatile compounds (VOCs) (Belitz, Grosch, & Schieberle, 2004) which can play a role even if present at trace levels. Therefore coffee flavour research and quality control can take advantage from fast and high sensitivity analytical techniques. Coffee origin is usually determined by elemental composition analysis (Pohl, Stelmach, Welna, & Szymczycha-Madeja, 2013) and stable isotope techniques (Kelly, Heaton, & Hoogewerff, 2005; Rodrigues et al., 2009). These methods are highly developed and used by legal authorities. However, they do not measure properties related to the perceived quality of coffee. A coffee origin signature in its volatile profile would have a direct link to the sensory attributes related to aroma which is significant for the acceptance of coffee.

Proton transfer reaction-mass spectrometry (PTR-MS) enables the analysis of VOCs at very low concentrations by direct injection. A soft chemical ionisation is applied in this system by using H_3O^+ ions as proton donors which can react with a wide variety of volatile compounds (Lindinger, Hansel, & Jordan, 1998a). The coupling of PTR-MS to Time-of-Flight (TOF) mass analysers increases the sensitivity of the VOC analysis by detecting the concentrations at parts per billion per volume level (ppbv) (Blake, Whyte, Hughes, Ellis, & Monks, 2004) with high mass resolution (Jordan et al., 2009). H_3O^+ is the mostly used ionisation agent in PTR-MS studies, however, recently a Switchable Reagent Ion system (SRI) was developed which allows the usage of NO^+, O_2^+, Kr^+ and Xe^+ as precursor ions. The PTR-ToF-MS with SRI system allows the analysis of volatiles which are not detectable with H_3O^+ as alkanes (due to lower proton affinities than H_2O) and moreover the separation of isobaric compounds is possible as in the case of aldehydes and ketones (with NO^+) (Jordan et al., 2009). PTR-MS has been widely used in food science and technology especially for fingerprinting and profiling of food products (Biasioli, Yeretzian, Gasperi, & Märk, 2011; Biasioli, Yeretzian, Märk, Dewulf, & Van Langenhove, 2011). Besides, PTR/SRI-MS system has been recently applied for detection of isoprene (Karl et al., 2012) and ethylene (Cappellin et al., 2014) emissions, in drug research (Acton et al., 2014; Lanza et al., 2013) and homeland

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security (Sulzer et al., 2013) and lastly in food science for product discrimination (Sánchez del Pulgar et al., 2013). To the best of the authors' knowledge no studies have been published so far on the application of SRI system for geographical origin discrimination of food products and in particular: coffee.

In a recent paper we demonstrated the possibility of using PTR-ToF-MS for rapid discrimination of coffee origin in the case of coffee powder (Yener et al., 2014). In this follow up study we extend the number of coffee origins considered (from 3 to 6), measure both powder and brewed coffee being the latter the product actually consumed and extend the analytical capability of our method by using different precursor ions. Therefore in this study, we aimed to (1) analyse the volatile profiles of six roasted and ground coffees (*Coffea arabica*) from different geographical origins (Brazil, Colombia, Costa Rica, Ethiopia, Guatemala and India) in powder and brew headspace (2) investigate the applicability of SRI system coupled with PTR-ToF-MS on coffee by using H_3O^+, NO^+ and O_2^+ as precursor ions and compare their classification efficiencies both separately and combined by data fusion methods.

2. Experimental

2.1. Sample preparation

2.1.1. Coffee powder

Six coffees from different geographic origins, Brazil (BRA), Colombia (COL), Costa Rica (CRC), Ethiopia (ETH), Guatemala (GUA) and India (IND) were supplied by Illycaffè S.p.A (Trieste, Italy) in commercially available forms (Monoarabica™). The coffee beans, *C. arabica*, were medium roasted (total weight loss: 15–18% w/w) at temperatures up to 220 °C, coarsely ground to powder for stove-top coffee maker (moka) and packed in inert atmosphere under pressure in 125 g stainless steel cans in the production plant by the producer.

For coffee powder headspace measurements two different jars were taken from one batch. After opening the jars, 100 mg of powder coffee was weighed into 22-ml glass vials (Supelco, Bellefonte, PA) and 3 analytical replicates were prepared for each jar. Four empty vials were analysed and considered as blanks.

2.2. Coffee brew

Coffee brewing was performed by steam pressure coffee extraction in a stove-top coffee maker known as "moka" in Italy (two-cup version, Bialetti, Omegna, Italy). For each preparation 100 ml mineral water (bicarbonate 313 mg/l, calcium 50.3 mg/l, magnesium 30.8 mg/l, sodium 6.0 mg/l, potassium 0.9 mg/l, chlorides 2.2 mg/l, as specified by the producer (San Benedetto S.p.A., Venice, Italy)) and 10 g of coffee powder were used. The coffee maker was heated on an electrical plate at 150 °C for about 14 min. When almost all coffees were brewed and air started to come out of the nozzle (i.e. at the onset of the so-called "Strombolian" phase (Navarini, Nobile, Pinto, Scheri, & Suggi-Liverani, 2009)) the moka was immediately removed from the heating plate. Brewed coffee was poured into a glass vessel, stirred well and 1 ml aliquots were transferred into 22-ml glass vials. Coffee brewing was performed once for each coffee origin and 6 vials were prepared for headspace analysis as analytical replicates. The coffee brews were analysed immediately after the preparation. Four blank vials were also analysed with coffee brews.

3. PTR/SRI-MS analysis

The headspace measurements were performed by using a commercial PTR-ToF-MS 8000 instrument (Ionicon Analytik GmbH, Innsbruck, Austria). The instrument was equipped with a switchable reagent ion system that allowed the operation of PTR-ToF-MS in H_3O^+, NO^+ or O_2^+ modes as described elsewhere (Cappellin et al., 2014; Sánchez del Pulgar et al., 2013). The instrumental conditions in the drift tube were

kept the same for the three ionisation modes as following: drift voltage 550 V, drift temperature 110 °C, drift pressure 2.33 mbar affording an E/N value of 140 Td (1 Td = 10^{-17} cm^2/V·s). Sampling was performed with a flow rate of 40 sscm. The mass resolution (m/Δm) was at least 3900. Measurements were performed in an automated way by using a multipurpose GC automatic sampler (Gerstel GmbH, Mülheim an der Ruhr, Germany) as previously described (Yener et al., 2014). The measurement order was randomized to avoid possible systematic memory effects. All the vials were incubated at 40 °C for 30 min before PTR-MS analysis. Each sample was measured for 30 s, at an acquisition rate of one spectrum per second. One sample was analysed at every 5 min.

4. Data processing and analysis

Data processing of ToF spectra included dead time correction, internal calibration and peak extraction steps performed according to a procedure described elsewhere (Cappellin et al., 2010) to reach a mass accuracy (≥ 0.001 Th) which is sufficient for sum formula determination. The baseline of the mass spectra was removed after averaging the whole measurement and peak detection and peak area extraction was performed by using a modified Gaussian to fit the data (Cappellin et al., 2011). Whenever a peak was detected, the volatile concentrations were calculated directly via the amount of detected ions in ppbv (part per billion by volume) levels according to the formulas described by Lindinger, Hansel, and Jordan (1998b) by assuming a constant reaction rate coefficient ($k_R = 2 \times 10^{-9}$ cm^3/s) for H_3O^+ as a primary ion. Concentration data in ppbv are called "raw data" and used directly for most data analysis. Each spectrum was also normalized to unit area, in order to remove sources of systematic variation and produce the "normalized data", which was used for discriminant analysis. Further tentative peak identification was performed by using an in-house library developed by the authors where the peak annotations were done automatically with the scripts developed under R programming language (Vienna, Austria).

The mass spectrometric data obtained by using H_3O^+ as the primary ion were subjected to three different analyses. First, principal component analysis (PCA) was applied on the dataset containing all the mass peaks extracted for the three ionisation modes to explore clustering of coffee samples in terms of their volatile compound composition.

Second, supervised classification methods were employed on the data obtained by three precursor ions to assess the separation of the classes. Random Forest (RF), Penalized Discriminant Analysis (PDA), Discriminant Partial Least Squares (dPLS) and Support Vector Machines (SVM) methods were applied following to Granitto et al. (2007). A six-fold cross-validation procedure was used by dividing the full dataset in six folds, each containing six samples, one from each origin. Then we repeated six times the following procedure: At each time, one of the folds was removed and used as a test set; the rest of the data was used to adjust the discriminant methods, and all methods were used to predict the origins of the samples in the corresponding test set. Results were evaluated using mean classification errors and confusion matrices. In addition to the individual analysis of the three precursor ions, the same data was merged into a multi-precursor dataset, following a data fusion strategy (Hall & Llinas, 1997). The same discriminant procedure was applied to the merged dataset. Third, a one-way ANOVA followed by Tukey's *post hoc* comparison test (where appropriate) was applied to the three datasets, in order to find the mass peaks that are significantly different between the 6 coffees, both in powder and brew.

5. Results and discussion

5.1. Classification of coffees according to geographical origin in switching reagent ion system

5.1.1. Data exploration by multivariate analysis (PCA)

Analysis of mass spectral data resulted in the extraction of 563, 524 and 563 mass peaks for H_3O^+, NO^+ and O_2^+, respectively. The whole

data matrix was mean centred and scaled after eliminating the interfering ions and the mass peaks with a concentration lower than 1 ppbv. The resulting data matrices with 263 (for H_3O^+), 260 (for NO^+) and 233 (for O_2^+) mass peaks were separately subjected to Principal

Component Analysis (PCA) for visualisation of the data. In a first analysis, the powder and brew headspace data were treated together. Two big groups were observed in the score plots located far from each other showing a clear separation of powder and brewed coffee (data
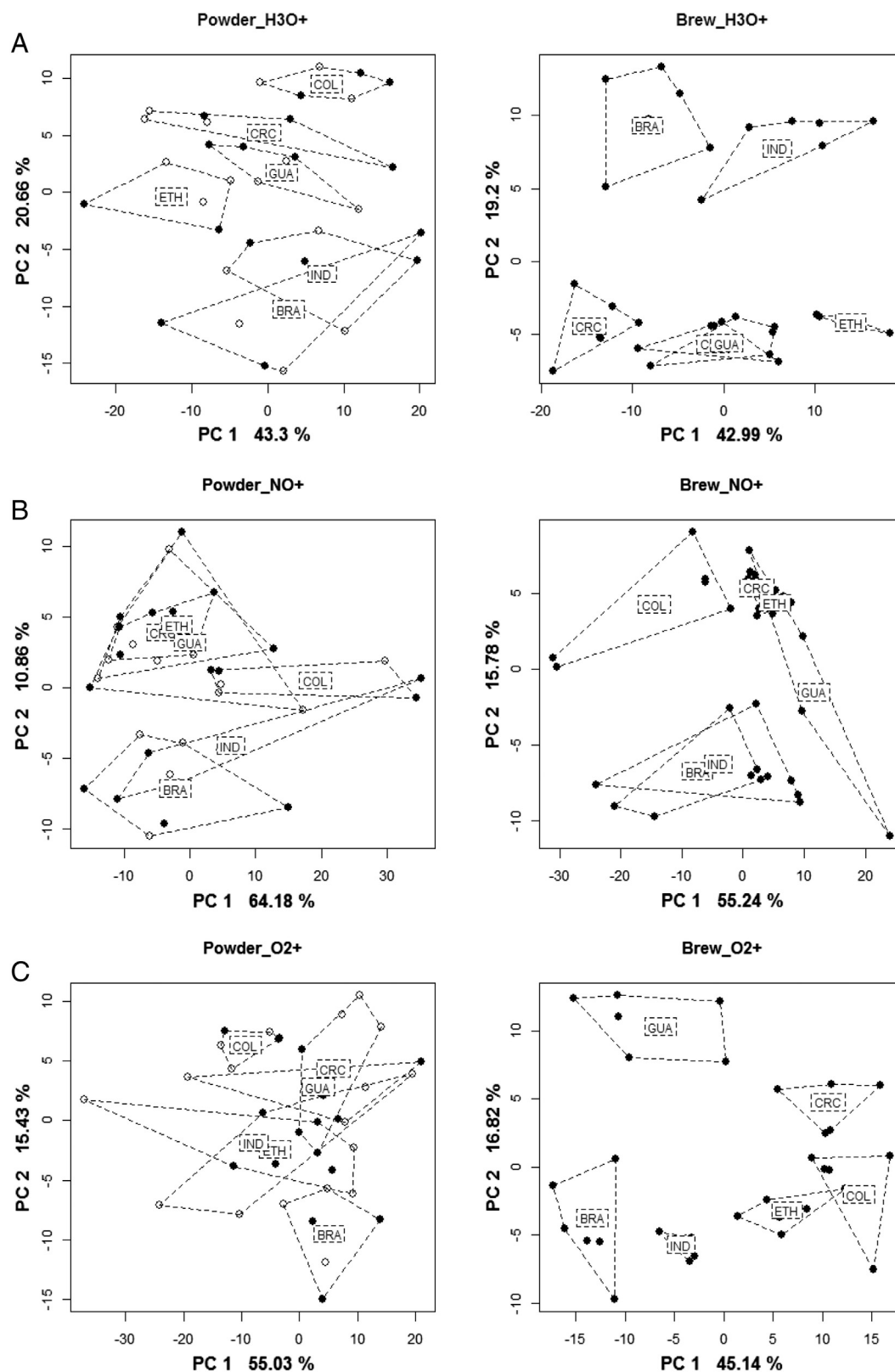
Fig. 1. Score plots of principal components analysis (PCA) for 3 ionisation modes. Panel A: H_3O^+, Panel B: NO^+ and Panel C: O_2^+. The first two principal components are shown. Open and solid circles indicate different jars of the same batch.

Table 1

Classification errors (%) obtained by random forest (RF), penalized discriminant analysis (PDA), discriminant partial least square analysis (dPLS) and support vector machine (SVM) classification models for 3 ionisation modes showing before and after data normalization.

			Primary ion			
		Classification method	H_3O^+	NO^+	O_2^+	Aggregate matrix
Powder	Raw data	RF	16.7	19.4	19.4	0.0
		PDA	2.8	8.3	5.6	0.0
		SVM	8.3	16.7	8.3	0.0
		dPLS	5.6	8.3	11.1	0.0
	Normalized data	RF	2.8	8.3	5.6	0.0
		PDA	0.0	0.0	2.8	0.0
		SVM	0.0	2.8	8.3	0.0
		dPLS	5.6	2.8	8.3	0.0
Brew	Raw data	RF	5.6	8.3	11.1	0.0
		PDA	0.0	2.8	5.6	0.0
		SVM	11.1	2.8	5.6	0.0
		dPLS	0.0	5.6	8.3	0.0
	Normalized data	RF	5.6	2.8	8.3	0.0
		PDA	0.0	0.0	0.0	0.0
		SVM	5.6	0.0	2.8	0.0
		dPLS	2.8	0.0	2.8	0.0

not shown). Then data referring to brew and powder coffees were analysed separately.

Fig. 1-Panel A shows the score plots of the first two principal components (PCs) explaining more than 62% of the total variance in H_3O^+ data. A good discrimination of coffees in the powder and brew headspace was observed. Separation of coffees according to origin was clear except for BRA and IND in the powder headspace. However these coffees were well separated when they were brewed. On the contrary COL and GUA were well separated in the powder form but not in the brew headspace. These two plots also point out grouping of "BRA–IND" and "ETH–GUA–COL–CRC" both in powder and brew headspace indicating potential similarities within each

group. However this grouping was not related to the geographical location of the coffees.

When PCA was performed on the NO^+ and O_2^+ data separately, the separation of coffees was not clear for the powder headspace. Fig. 1-Panel B and -Panel C show the score plots of the first two components explaining more than 75% variance in NO^+ data and more than 60% variance in O_2^+ data, respectively. Similarly to the score plots obtained by H_3O^+ data, "BRA–IND" was located close to each other as one group and "ETH–GUA–COL–CRC" as another group in the powder and brew headspace for NO^+ and O_2^+. Interestingly, data obtained by using O_2^+ as a precursor ion suggested a good discrimination of coffees in the brew headspace better than the other two ionisation agents.

5.1.2. Classification models by RF, PDA, SVM and dPLS models

Table 1 shows the mean classification errors obtained by RF, PDA, SVM and dPLS models using the 3 different ionisation agents. The cross-validation experiments resulted in good classification performance with the lowest errors for PDA for all coffees, both conditions (powder and brew) and ionisation modes. The classification errors were lower for brewed coffees than powder for each classification method in all cases. Furthermore, normalized data seems to be more appropriate for discriminant analysis than the raw data.

The classification methods produced "confusion matrices" for the three ionisation agents, an example has been shown in Table 2, for H_3O^+ which allows us to visualize the prediction of the origins as sample-wise. In Table 2, the rows correspond to the actual coffee origins and the columns to the coffee origins assigned by the specific discrimination method. The numbers correspond to the number of coffee samples per coffee origin. CRC coffee was mostly confused with COL and GUA (and oppositely); IND was mostly confused with BRA and lastly ETH was confused with GUA only once. Results with the other reagent ions (not shown) are similar, with sparse errors distributed uniformly among the different origins. Overall the discriminant methods confirm the indications of PCA score plots shown in Fig. 1 (Panels A, B, C).

Table 2

Confusion matrices obtained by random forest (RF), penalized discriminant analysis (PDA), discriminant partial least square analysis (dPLS) and support vector machine (SVM) classification models by using raw and normalized H_3O^+ data.

Classification method	Coffees	Raw data												Normalized data											
		Powder						Brew						Powder						Brew					
		BRA	COL	CRC	ETH	GUA	IND	BRA	COL	CRC	ETH	GUA	IND	BRA	COL	CRC	ETH	GUA	IND	BRA	COL	CRC	ETH	GUA	IND
RF	BRA	5	0	0	0	0	1	6	0	0	0	0	0	6	0	0	0	0	0	6	0	0	0	0	0
	COL	0	5	1	0	0	0	0	5	1	0	0	0	0	6	0	0	0	0	0	5	1	0	0	0
	CRC	0	1	4	0	1	0	0	0	6	0	0	0	0	0	5	0	1	0	0	0	6	0	0	0
	ETH	0	0	0	5	1	0	0	0	0	6	0	0	0	0	0	6	0	0	0	0	0	6	0	0
	GUA	0	0	0	0	6	0	0	0	0	0	6	0	0	0	0	0	6	0	0	0	0	0	6	0
	IND	1	0	0	0	0	5	1	0	0	0	0	5	0	0	0	0	0	6	1	0	0	0	0	5
PDA	BRA	6	0	0	0	0	0	6	0	0	0	0	0	6	0	0	0	0	0	6	0	0	0	0	0
	COL	0	6	0	0	0	0	0	6	0	0	0	0	0	6	0	0	0	0	0	6	0	0	0	0
	CRC	0	1	5	0	0	0	0	0	6	0	0	0	0	0	6	0	0	0	0	0	6	0	0	0
	ETH	0	0	0	6	0	0	0	0	0	6	0	0	0	0	0	6	0	0	0	0	0	6	0	0
	GUA	0	0	0	0	6	0	0	0	0	0	6	0	0	0	0	0	6	0	0	0	0	0	6	0
	IND	0	0	0	0	0	6	0	0	0	0	0	6	0	0	0	0	0	6	0	0	0	0	0	6
SVM	BRA	5	0	0	0	0	1	5	0	0	0	0	1	6	0	0	0	0	0	6	0	0	0	0	0
	COL	0	6	0	0	0	0	0	4	1	0	1	0	0	6	0	0	0	0	1	5	0	0	0	0
	CRC	0	0	4	0	2	0	0	0	6	0	0	0	0	0	6	0	0	0	0	0	6	0	0	0
	ETH	0	0	0	6	0	0	0	0	0	6	0	0	0	0	0	6	0	0	0	0	0	6	0	0
	GUA	0	0	0	0	6	0	0	0	0	0	6	0	0	0	0	0	6	0	0	0	0	0	6	0
	IND	0	0	0	0	0	6	1	0	0	0	0	5	0	0	0	0	0	6	1	0	0	0	0	5
dPLS	BRA	6	0	0	0	0	0	6	0	0	0	0	0	6	0	0	0	0	0	6	0	0	0	0	0
	COL	0	6	0	0	0	0	0	6	0	0	0	0	0	6	0	0	0	0	0	5	1	0	0	0
	CRC	0	0	4	0	1	1	0	0	6	0	0	0	0	0	5	0	1	0	0	0	6	0	0	0
	ETH	0	0	0	6	0	0	0	0	0	6	0	0	0	0	0	6	0	0	0	0	0	6	0	0
	GUA	0	0	0	0	6	0	0	0	0	0	6	0	0	0	0	1	5	0	0	0	0	0	6	0
	IND	0	0	0	0	0	6	0	0	0	0	0	6	0	0	0	0	0	6	0	0	0	0	0	6

5.1.3. Data fusion: classification methods using more than one parent ion

Last column of Table 1 shows the results corresponding to the merged dataset, which contains 1650 masses from the 3 reagent ions. For all classification methods and all experimental conditions (brewed/powder, raw/normalized) there is perfect discrimination: all samples are correctly classified. Adding the information gained by 3 ionisation agents significantly increased the performance of classification and provided an optimum discrimination of coffees. As an additional experiment, we developed discriminant methods over all three possible combinations of two diverse reagent ions. Results (not shown) indicate that any combination of reagent ions improves the results of single ions, but cannot reach the complete discrimination of the merged dataset. These results suggest that each ion provides some new information about the volatile profile of each coffee improving the fingerprinting of the different products.

5.2. Monovariate analysis

5.2.1. Coffee powder and brew with H_3O^+ as precursor ion

The mass peaks extracted from H_3O^+ data was subjected to one-way ANOVA ($p < 0.01$) separately on powder and brewed coffee. In the powder headspace 151 mass peaks where found to be significant between the different coffee origins whereas 210 mass peaks were at significantly different concentrations in the brew headspace. Among the mass peaks have been extracted sum formulas could be assigned to 102 which leads a possible tentative identification (Table 3).

To better visualize the differences between aroma profiles of coffees, the tentatively identified mass peaks were grouped according to their chemical classes (alcohols, carbonyl compounds, esters/acids, pyrans/furans, oxazoles, phenols, pyrazines, pyridines, pyrroles, sulphur compounds, terpenes and thiazoles). The concentrations of compounds belonging to the same group were summed for each coffee type and condition and an average value of each group was calculated including all coffees as the basis of comparison. The percentage difference (%) between a chemical group belonging to one coffee and the averaged value was calculated and presented by column charts for brew and powder, separately (Figs. 2A-B).

In Fig. 2A and B the most noticeable difference was found in terpene levels. The coffee from Ethiopia had the highest amount of terpenes (more than 3 times) in both powder and brew. High levels of terpenes in Ethiopian coffee powder has been reported by the authors in a recent paper (Yener et al., 2014) which has been supported by these recent findings once more and also for brewed coffee. Moreover in the coffee powder, ETH was also higher in esters/acids, pyrans/furans and alcohols. Coffees from COL, CRC and GUA were rich in sulphur compounds in the powder and brew headspace being COL the richest. BRA and IND had similar volatile profiles in the powder headspace having high levels in pyridines, pyrroles and thiazoles than the average.

Coffee brews showed similar distribution of volatiles to coffee powder for some chemical groups. The alcohols, carbonyl, acids/esters and terpenes for ETH can be given as an example. When the similar powder headspace compositions were compared for IND and BRA, however in the brewed form, the difference in the concentration levels were higher for IND than BRA for the mentioned chemical groups and others like esters/acids, oxazoles and phenols. Overall, the change in the percentage distribution of a chemical group was dependent on coffee origin which will be explained in the following section (5.2.2).

Lastly, the results of the current study were compared with our previous study on coffee powder (Yener et al., 2014). All the previously identified mass peaks in the headspace of coffees from Brazil, Ethiopia and Guatemala were found in the same origin samples. The differences among volatile concentrations of the new and former studies were found to be very small for most of them and the trend of the volatiles was found to be same for the majority.

5.2.2. The effect of brewing on volatile release

Brewing of coffees affected the release of diverse chemical compounds in the headspace by a shift in the concentration those led significant changes in the volatile profiles (Fig. 2A, B and Table 3). The headspace concentrations of brewed coffee were in general lower than that of powder. The total concentrations of some chemical groups tend to increase or decrease: alcohols, esters/acids, furans and pyrans, phenols, pyrazines, pyridines, pyrroles, oxazoles, terpenes and thiazoles were always higher in the powder for all coffee types. However the level of total carbonyls and sulphur compounds was higher in the brew. The biggest losses were recorded for pyrazines, followed by alcohols and pyridines whereas the minimum reduction was observed in pyrrole levels. As previously showed (Blank, Sen, & Grosch, 1992) significant increase in methional, 5-Ethyl-3-hydroxy-4-methyl-2(5H)-furanone (sotolon) and vanillin levels and significant decrease in some thiols and pyrazines was observed when an arabica coffee was brewed. Our results are in accordance with these findings except the changes for methional and sotolon together with some thiols which might be due to the coffee bean structure and the method used for aroma analysis (Akiyama et al., 2002; Mayer, Czerny, & Grosch, 1999). The formation of volatile organic compounds depends on several physical and chemical reactions that occur during roasting of coffee and highly affected by the non-volatile composition of coffee as being precursors of volatile production (Illy & Viani, 2005). The release of volatiles from coffee is highly dependent on preparation technique that may significantly affect the amount of different chemical groups (Caporaso, Genovese, Canela, Civitella, & Sacchi, 2014; Illy & Viani, 2005; Navarini et al., 2009). Moreover, these changes can be due to the lower solubility of aroma compounds in the brew or their degradation by hot water (Blank et al., 1992). Since the chemical composition of coffee beans is important for their evolution during roasting and the final structure of beans (Gloess et al., 2014) it is expected that the degree of chemical reactions responsible for flavour formation and their texture-dependent release behaviour (Guichard, 2002) would be different for coffees from different geographical origins.

To assess whether the release of a mass peak during brewing is dependent on coffee origin a two way-ANOVA was performed. The models with and without interactions were compared by means of an F-test which allowed selection of the interacting variables (Table 3). In most cases, significant interactions were found between coffee origins and brewing. More than 60% of the mass peaks pointed out significant interactions ($p < 0.01$) due to the brewing of coffees from different origins.

6. Conclusions

The rapid analysis of volatile compounds in the headspace of six arabica coffees, brew and powder, was performed with PTR-ToF-MS allowing successful separation according to their geographical origins. The high sensitivity and high resolution of PTR-MS technique enabled quantification of mass peaks at ppb levels and further tentative identification of volatile compounds. The results showed significant differences in the concentrations of volatile compounds in the powder headspace. When the coffees were brewed the release of these volatiles was less in general and significant interactions were recorded between volatile release and coffee origin.

The switching reagent ion system in PTR-MS instrumentation was applied for the first time to coffee by using not only H_3O^+ but also NO^+ and O_2^+ as precursor ions. All methods and precursor ions provided low classification errors. PDA showed the best classification performance in all ionisation modes. The data obtained by all ionisation modes provided valuable information on highlighting the applicability of SRI system on real complex food matrix like coffee. Although data obtained using O_2^+ allow the classification of the samples, the spectra interpretation in this case is more difficult. In general, the data produced showed the possibility and advantages of switching reagent ion system in coffee for successful discrimination of geographic origin by extending

Table 3

Average concentrations (ppbv) of tentatively identified mass peaks in the headspace of coffees detected by PTR-ToF-MS. Mean concentrations are reported for each sample with Tukey letters ($p < 0.01$) showing the significant differences between coffee origins in the powder and brew forms separately. p-Values for powder and brew coffees were obtained on the basis of one-way ANOVA; p-values for interaction were obtained by two-way ANOVA.

Measured mass (m/z)[**]	Sum formula	Tentative identification[***]	Powder headspace[*]							Brew headspace[*]							p-Value interaction
			BRA	COL	CRC	ETH	GUA	IND	p-Value powder	BRA	COL	CRC	ETH	GUA	IND	p-Value brew	
49.010	CH_5S^+	Methanethiol[10]	11[a]	16[bc]	14[ac]	13[ab]	11[a]	16[c]	$<10^{-3}$	58[a]	114[ab]	171[b]	93[a]	112[a]	74[a]	$<10^{-3}$	$<10^{-3}$
59.048	$C_3H_7O^+$	Propanal/acetone[2]	5045[ab]	4834[ab]	5021[ab]	6064[b]	4745[a]	5854[ab]	0.036	9149[b]	8526[b]	6743[a]	9237[b]	9004[b]	10277[c]	$<10^{-3}$	$<10^{-3}$
61.028	$C_2H_5O_2^+$	Acetic acid/methyl-formate[3]	3945[a]	7426[c]	6392[c]	6182[bc]	5645[ac]	4388[ab]	$<10^{-3}$	2001[a]	3257[c]	2146[a]	3358[c]	2693[b]	2793[b]	$<10^{-3}$	0.001
63.027	$C_2H_7S^+$	Ethanethiol/dimethylsulfide[10]	19[a]	86[d]	68[c]	66[c]	71[cd]	46[b]	$<10^{-3}$	43[a]	212[c]	144[b]	128[b]	211[c]	114[b]	$<10^{-3}$	$<10^{-3}$
68.049	$C_4H_6N^+$	Pyrrole[9]	298[e]	140[a]	199[c]	185[bc]	160[ab]	265[d]	$<10^{-3}$	346[e]	146[a]	166[b]	205[d]	183[c]	331[e]	$<10^{-3}$	$<10^{-3}$
69.033	$C_4H_5O^+$	Furan[4]	572[a]	637[a]	652[a]	809[b]	630[a]	582[a]	0.003	933[b]	897[a]	1124[ac]	1321[d]	1131[ac]	1157[bc]	0.001	0.037
73.064	$C_4H_9O^+$	Isobutanal/butanone[2]	3066[ab]	2452[a]	3612[ab]	4248[c]	3183[ab]	2837[ab]	0.001	5265[ab]	5687[abc]	5143[a]	6628[d]	6299[cd]	6017[bd]	$<10^{-3}$	0.002
75.043	$C_3H_7O_2^+$	Methyl-acetate/acetol[3]	1856[a]	2490[bc]	2537[bc]	2807[c]	2180[ab]	1985[a]	$<10^{-3}$	2031[b]	1860[b]	1157[a]	2723[c]	1913[b]	2642[c]	$<10^{-3}$	$<10^{-3}$
78.967	$CH_3S_2^+$	Dimethyl-disulfidefragment[10]	21[a]	23[ab]	24[ab]	27[b]	23[ab]	25[ab]	0.031	47[a]	56[ab]	53[a]	52[a]	46[a]	70[b]	0.001	0.002
80.049	$C_5H_6N^+$	pyridine[8]	5348[d]	1649[a]	2535[b]	3474[c]	2340[ab]	3733[c]	$<10^{-3}$	1219[c]	448[a]	358[a]	664[b]	490[a]	1138[c]	$<10^{-3}$	$<10^{-3}$
81.035	$C_5H_5O^+$	Furan fragment[4]	2929[a]	2626[a]	2843[a]	2809[a]	2719[a]	2750[a]	0.846	1104[ab]	1201[b]	841[a]	1169[b]	1143[b]	1312[b]	0.003	0.191
82.065	$C_5H_8N^+$	Methyl-pyrrole[9]	887[d]	303[a]	492[b]	657[c]	498[b]	611[bc]	$<10^{-3}$	881[d]	380[a]	405[a]	723[c]	558[b]	803[cd]	$<10^{-3}$	0.001
83.049	$C_5H_7O^+$	Methyl-furan[4]	2522[ab]	1811[a]	2199[ab]	3685[c]	2638[b]	2388[ab]	$<10^{-3}$	2428[a]	2410[a]	2319[a]	3603[b]	2977[ab]	3247[b]	$<10^{-3}$	0.095
85.065	$C_5H_9O^+$	Methyl-butenal[2]	548[bc]	370[a]	517[bc]	590[c]	528[bc]	468[b]	$<10^{-3}$	247[b]	195[a]	173[a]	282[c]	258[b]	262[bc]	$<10^{-3}$	$<10^{-3}$
86.007	$C_3H_4NS^+$	Thiazol[12]	26[c]	16[a]	22[b]	22[b]	19[ab]	23[bc]	$<10^{-3}$	20[c]	14[a]	14[a]	18[b]	16[b]	22[d]	$<10^{-3}$	$<10^{-3}$
87.045	$C_4H_7O_2^+$	Butanedione/butyrolactone[2]	952[a]	1039[a]	1306[bc]	1449[c]	1172[ab]	1000[a]	$<10^{-3}$	799[a]	903[b]	974[b]	944[b]	936[b]	808[a]	$<10^{-3}$	0.002
87.079	$C_5H_{11}O^+$	Methyl-butanal[2]	1671[bc]	1127[a]	2038[cd]	2279[d]	1858[bd]	1438[ab]	$<10^{-3}$	2051[a]	2126[ab]	2368[ab]	3104[d]	2801[cd]	2481[bc]	$<10^{-3}$	0.003
89.059	$C_4H_9O_2^+$	Methyl-propanoate/hydroxy-butanone[3]	406[a]	433[a]	540[c]	580[c]	497[bc]	372[a]	$<10^{-3}$	86[b]	100[c]	61[a]	128[c]	95[b]	105[c]	$<10^{-3}$	$<10^{-3}$
91.054	$C_4H_{11}S^+$	Diethylsulphide[10]	7[cd]	5[a]	6[ac]	8[d]	7[bc]	6[ab]	$<10^{-3}$	3[a]	3[a]	4[a]	3[a]	3[a]	3[a]	0.405	$<10^{-3}$
91.073	$C_4H_{11}O_2^+$	Butandiol[1]	2[a]	2[ab]	2[b]	2[b]	2[ab]	2[a]	0.003	4[a]	5[ac]	4[ab]	6[d]	5[cd]	5[bcd]	$<10^{-3}$	0.001
95.059	$C_5H_7N_2^+$	Methyl-pyrazine[7]	4464[c]	2253[a]	3293[b]	3209[b]	2996[b]	3307[b]	$<10^{-3}$	387[a]	337[a]	548[a]	366[a]	341[a]	390[a]	0.337	$<10^{-3}$
96.083	$C_6H_{10}N^+$	Dimethyl-pyrrole/ethyl-pyrrole[9]	129[bc]	70[a]	102[ab]	118[b]	97[ab]	160[c]	$<10^{-3}$	77[c]	33[a]	39[a]	62[b]	54[b]	83[c]	$<10^{-3}$	0.162
97.028	$C_5H_5O_2^+$	Furfural[4]	890[a]	2098[bc]	2471[d]	2263[cd]	1947[b]	909[a]	$<10^{-3}$	649[a]	1553[e]	1315[c]	1578[e]	1419[d]	754[b]	$<10^{-3}$	$<10^{-3}$
97.064	$C_6H_9O^+$	Dimethyl-furan[4]	644[b]	444[a]	575[b]	818[c]	689[b]	583[b]	$<10^{-3}$	200[a]	198[a]	215[ab]	312[d]	272[cd]	255[bc]	$<10^{-3}$	0.001
98.063	$C_5H_8ON^+$	Dimethyl-oxazole[5]	129[d]	69[a]	98[b]	124[cd]	108[bc]	109[bd]	$<10^{-3}$	49[b]	36[a]	34[a]	54[c]	48[b]	55[c]	$<10^{-3}$	$<10^{-3}$
99.041	$C_5H_7O_2^+$	Furfuryl alcohol/a-angelica lactone[4]	262[a]	328[b]	408[c]	341[b]	312[ab]	262[a]	$<10^{-3}$	91[a]	114[b]	95[ab]	105[ab]	101[ab]	104[ab]	0.105	$<10^{-3}$
99.080	$C_6H_{11}O^+$	Hexenal/methyl-pentenone[2]	97[bc]	66[a]	85[b]	101[c]	94[bc]	93[bc]	$<10^{-3}$	49[b]	42[a]	39[a]	59[c]	55[c]	58[c]	$<10^{-3}$	0.001
100.022	$C_4H_6NS^+$	Methyl-thiazole[12]	72[d]	34[a]	49[bc]	44[b]	42[b]	56[c]	$<10^{-3}$	33[c]	19[a]	19[a]	23[b]	22[b]	32[c]	$<10^{-3}$	$<10^{-3}$
101.059	$C_5H_9O_2^+$	Pentanedione/methyl-tetrahydrofuranone[2]	2828[a]	3106[b]	4207[d]	4398[d]	3908[b]	2621[a]	$<10^{-3}$	541[a]	825[d]	683[c]	1009[f]	915[e]	612[b]	$<10^{-3}$	$<10^{-3}$
103.075	$C_5H_{11}O_2^+$	Hydroxy-pentanone/methyl-butanoic acid[3]	213[ab]	217[ac]	257[cd]	264[d]	239[bcd]	191[a]	$<10^{-3}$	27[ab]	37[ab]	22[a]	39[b]	29[ab]	28[ab]	0.037	$<10^{-3}$
105.039	$C_4H_9OS^+$	Methional[10]	10[bc]	7[a]	10[bc]	11[c]	10[bc]	9[b]	$<10^{-3}$	5[b]	4[a]	5[b]	5[b]	4[b]	5[b]	$<10^{-3}$	$<10^{-3}$
105.069	$C_8H_9^+$	Styrene/phenylethanol fragment[13]	15[c]	11[a]	12[b]	14[c]	12[b]	13[b]	$<10^{-3}$	6[a]	6[a]	7[ab]	7[ab]	6[ab]	7[b]	0.026	$<10^{-3}$
105.093	$C_5H_{13}O_2^+$	Methyl-butanol[1]	1[abc]	1[a]	1[d]	1[cd]	1[bd]	1[ab]	$<10^{-3}$	3[a]	3[a]	4[ab]	5[c]	4[b]	4[ab]	$<10^{-3}$	$<10^{-3}$
107.053	$C_7H_7O^+$	Benzaldehyde[2]	44[c]	28[a]	35[b]	35[b]	33[ab]	36[b]	$<10^{-3}$	23[c]	18[a]	18[a]	21[b]	19[ab]	23[c]	$<10^{-3}$	$<10^{-3}$
109.074	$C_6H_9N_2^+$	Dimethylpyrazine/ethylpyrazine[7]	2998[c]	1691[a]	2174[b]	2205[b]	2070[b]	2317[b]	$<10^{-3}$	197[a]	205[a]	177[a]	221[a]	207[a]	220[a]	0.264	$<10^{-3}$
111.044	$C_6H_7O_2^+$	Acetylfuran/methylfurfural[4]	788[a]	1081[b]	1247[b]	1191[b]	1107[b]	762[a]	$<10^{-3}$	187[a]	308[b]	216[ab]	280[ab]	244[ab]	210[ab]	0.020	$<10^{-3}$
111.079	$C_7H_{11}O^+$	2/3-Dimethyl-2-cyclopenten-1-one[2]	221[bc]	176[a]	204[ab]	243[c]	227[bc]	212[b]	$<10^{-3}$	54[a]	54[a]	52[a]	70[b]	64[b]	67[b]	$<10^{-3}$	$<10^{-3}$
112.078	$C_6H_{10}ON^+$	Trimethyl-oxazole[5]	75[d]	41[a]	52[b]	61[bc]	55[bc]	64[c]	$<10^{-3}$	22[c]	15[a]	14[a]	21[c]	19[b]	24[d]	$<10^{-3}$	$<10^{-3}$
113.019	$C_5H_5O_3^+$	Furancarboxylic acid[4]	7[b]	6[a]	7[ab]	7[b]	7[ab]	7[b]	0.008	9[c]	5[ab]	9[c]	5[a]	5[ab]	6[b]	$<10^{-3}$	$<10^{-3}$
113.059	$C_6H_9O_2^+$	Methyl-furfuryl-alcohol/dimethyl-furanone/ methyl-cyclopentanedione/cyclotene[4]	222[a]	236[ab]	271[b]	259[ab]	238[ab]	216[a]	0.032	34[a]	41[a]	31[a]	40[a]	35[a]	40[a]	0.115	0.014
113.095	$C_7H_{13}O^+$	Heptenone[2]	40[c]	26[a]	34[b]	34[b]	33[b]	36[bc]	$<10^{-3}$	21[bc]	18[a]	19[ab]	22[c]	22[c]	25[d]	$<10^{-3}$	$<10^{-3}$
114.039	$C_5H_8NS^+$	Ethyl-thiazole/dimethyl-thiazole[12]	24[d]	12[a]	15[ab]	14[ab]	14[ab]	20[c]	$<10^{-3}$	9[b]	5[a]	5[a]	6[a]	6[a]	9[b]	$<10^{-3}$	$<10^{-3}$
115.039	$C_5H_7O_3^+$	Dihydroxy-cyclopentenone[2]	6[b]	5[ab]	6[ab]	6[ab]	5[a]	6[b]	0.008	24[b]	8[a]	30[b]	4[a]	11[a]	10[a]	$<10^{-3}$	$<10^{-3}$
115.076	$C_6H_{11}O_2^+$	4-Methyltetrahydro-2H-pyran-2-one[4]	377[abc]	327[a]	396[bd]	431[d]	411[cd]	355[ab]	$<10^{-3}$	86[a]	101[b]	86[a]	135[d]	122[c]	97[b]	$<10^{-3}$	$<10^{-3}$
115.108	$C_7H_{15}O^+$	Heptanal/heptanone[2]	19[b]	14[a]	18[b]	20[b]	19[b]	18[b]	$<10^{-3}$	9[ab]	9[ab]	8[a]	12[c]	10[b]	12[c]	$<10^{-3}$	$<10^{-3}$
117.053	$C_5H_9O_3^+$	2-Oxopropyl-acetate[3]	278[abc]	243[a]	308[cd]	333[d]	308[bd]	256[ab]	$<10^{-3}$	22[a]	34[a]	20[a]	22[a]	21[a]	22[a]	0.570	$<10^{-3}$
117.091	$C_6H_{13}O_2^+$	Hexanoic acid/C6 ester[3]	39[c]	25[a]	31[ab]	72[d]	35[bc]	40[c]	$<10^{-3}$	19[b]	16[a]	15[a]	50[d]	21[b]	29[c]	$<10^{-3}$	$<10^{-3}$
119.052	$C_8H_7O^+$	Benzofuran[4]	8[a]	8[a]	9[ab]	10[b]	9[ab]	9[ab]	0.018	4[a]	6[d]	4[ab]	6[cd]	5[bc]	6[d]	$<10^{-3}$	$<10^{-3}$
121.073	$C_7H_9N_2^+$	2-Ethenyl-6-methyl-pyrazine 6/7-dihydro-5H-cyclopentapyrazine[7]	22[a]	20[a]	21[a]	22[a]	20[a]	19[a]	0.692	9[ab]	12[bc]	8[a]	11[bc]	10[ab]	12[c]	$<10^{-3}$	0.034
122.061	$C_7H_8NO^+$	2-Acetylpyridine[8]	8[a]	7[a]	7[a]	8[a]	7[a]	7[a]	0.594	5[bcd]	4[ab]	3[a]	5[d]	4[ac]	5[cd]	$<10^{-3}$	0.389

m/z	Formula	Identification															
122.095	$C_8H_{12}N^+$	Propyl-pyridine[8]	5c	1a	3b	4bc	3b	4bc	$<10^{-3}$	3c	2a	2a	4c	3b	4c	$<10^{-3}$	0.002
123.089	$C_7H_{11}N_2^+$	Ethyl-methyl-pyrazine/trimethylpyrazine[7]	348b	229a	248a	278a	258a	281a	$<10^{-3}$	50ab	56ac	47a	65d	58bcd	65cd	$<10^{-3}$	$<10^{-3}$
124.079	$C_7H_{10}ON^+$	2-Acetyl-1-methylpyrrole[9]	33a	32a	32a	35a	32a	29a	0.624	21b	22b	15a	23b	20ab	25b	0.001	0.032
124.109	$C_8H_{14}N^+$	Butylpyrrole/methyl-propylpyrrole[9]	34d	15a	20b	21b	20b	28c	$<10^{-3}$	9c	6a	7b	7b	7b	11d	$<10^{-3}$	$<10^{-3}$
125.060	$C_7H_9O_2^+$	Guaiacol/methyl-benzenediol/furyl acetone[6]	69ab	79ab	81ab	82b	79ab	67a	0.023	38a	45b	34a	48b	41ab	46b	$<10^{-3}$	0.003
125.096	$C_8H_{13}O^+$	Butylfuran/methyl-propylfuran[4]	49b	42a	48ab	50b	49b	48ab	0.021	17a	17a	19ab	20bc	18ab	22c	$<10^{-3}$	0.044
126.094	$C_7H_{12}NO^+$	Acetyl-dimethylpyrrole/alkyloxazole[9]	21c	13a	15b	16b	14ab	19c	$<10^{-3}$	7b	5a	5a	6b	5a	8c	$<10^{-3}$	0.000
127.038	$C_6H_7O_3^+$	Maltol/methyl-furoate[4]	26a	29a	30a	28a	27a	26a	0.778	11a	11a	12a	12a	11a	12a	0.519	0.670
127.076	$C_7H_{11}O_2^+$	3-Ethyl-1-2-cyclopentanedione[2]	58a	65a	65a	64a	59a	55a	0.598	17a	24a	17a	24a	20ab	23b	$<10^{-3}$	0.431
129.091	$C_7H_{13}O_2^+$	Pentenyl-acetate heptanedione[2]	67b	58a	62ab	69b	67b	68b	0.006	19a	22ab	20a	26c	24bc	25c	$<10^{-3}$	0.028
131.070	$C_6H_{11}O_3^+$	Acetyloxy-butanone/ethanediol diacetate/oxopropoxy-propanone/ethyl-oxobutanoate[3]	34ab	34ab	38ab	41b	38ab	32a	0.038	3a	5a	4a	4a	4a	3a	0.587	0.041
131.107	$C_7H_{15}O_2^+$	Heptanoic acid/C7 ester[3]	4b	3a	4b	5c	4b	4b	$<10^{-3}$	3a	3a	3a	4c	4bc	4b	$<10^{-3}$	1.041
134.061	$C_8H_8ON^+$	Methyl-benzoxazole[5]	2a	2a	2a	2a	2a	2a	0.312	2ab	2ac	2a	2bc	2ac	3c	0.005	0.002
135.044	$C_8H_7O_2^+$	Bifuran[4]	3a	4c	4c	4c	4bc	3ab	$<10^{-3}$	4a	5c	5c	5b	4ab	5bc	$<10^{-3}$	0.009
135.091	$C_8H_{11}N_2^+$	2-Ethyl-6-vinyl-cyclopentapyrazine 6/7-dihydro-methyl-cyclopentapyrazine[7]	15a	13a	16a	16a	14a	12a	0.164	5ab	6ab	5a	7ab	6ab	7b	0.025	0.030
135.121	$C_{10}H_{15}^+$	Terpene fragment[13]	2a	2ab	2a	6d	3bc	3c	$<10^{-3}$	1a	1ab	1ab	4d	1bc	2c	$<10^{-3}$	$<10^{-3}$
136.077	$C_8H_{10}NO^+$	Acetyl-methylpyridine[8]	8a	7a	8a	8a	7a	7a	0.518	2b	4ac	3a	5bc	4ab	5c	0.001	0.054
136.112	$C_8H_{14}N^+$	Butyl-pyridine/ethyl-propylpyridine[8]	3bc	2a	2ab	4c	2ab	3ab	$<10^{-3}$	2b	1a	1a	2c	1ab	2c	$<10^{-3}$	0.005
137.108	$C_8H_{13}N_2^+$	Ethyl-dimethyl-pyrazine[7]	23a	23a	25a	27a	24a	21a	0.542	13ab	12ab	10a	14ab	12ab	15b	0.082	0.308
137.135	$C_{10}H_{17}^+$	Various monoterpenes[11]	13a	17a	17a	60b	16a	18a	$<10^{-3}$	5a	5a	7b	27c	6ab	6ab	$<10^{-3}$	$<10^{-3}$
138.059	$C_7H_8O_2N^+$	Pyridinecarboxylic acid methyl ester[8]	5a	5a	5a	5a	5a	4a	0.506	5ac	5ac	4a	5bc	4ab	5c	0.004	0.022
138.093	$C_8H_{12}NO^+$	Dimethylpyrrolyl ethanone/ethylpyrrolyl ethanone/2-acetyl-1-ethylpyrrole/1-acetyl-2,5-dimethylpyrrole[9]	9a	11a	11a	10a	10a	9a	0.695	4ab	5b	3a	5b	5ab	6b	0.001	0.160
138.131	$C_9H_{16}N^+$	Butyl-pyridine[8]	7b	5a	6a	13c	6a	8b	$<10^{-3}$	3b	2a	3b	5d	3ab	4c	$<10^{-3}$	$<10^{-3}$
139.076	$C_8H_{11}O_2^+$	4-Ethyl-1/2-benzenediol[6]	16a	19a	20a	18a	17a	15a	0.224	13ab	17bc	12a	18c	15ac	18c	$<10^{-3}$	0.007
139.113	$C_9H_{15}O^+$	E/E-2/4-nonadienal[2]	12a	12a	12a	14b	13ab	13a	$<10^{-3}$	5a	5a	6bc	6c	5ab	6bc	$<10^{-3}$	0.260
141.053	$C_7H_9O_3^+$	Furfuryl-acetate[4]	35a	35a	35a	34a	35a	35a	1.000	18ab	18ab	15a	20bc	18ab	22c	$<10^{-3}$	0.335
141.127	$C_9H_{17}O^+$	Nonenal[2]	1a	1a	1a	2a	1a	1a	0.232	1a	1ab	1a	1b	1ab	1b	0.001	0.302
143.107	$C_8H_{15}O_2^+$	Methyl-heptanedione/octenoic acid[2]	7a	7a	10b	8a	8a	8a	$<10^{-3}$	3a	4b	4bc	4bc	4b	4c	$<10^{-3}$	$<10^{-3}$
145.123	$C_8H_{17}O_2^+$	Ethyl-hexanoic acid/C8 ester[3]	1ab	1a	1bc	2c	1ab	1ab	$<10^{-3}$	3a	3a	2a	4c	4bc	4b	$<10^{-3}$	$<10^{-3}$
148.076	$C_9H_{10}ON^+$	1-Furfurylpyrrole[9]	5ab	7ab	8b	7ab	6ab	5a	0.085	8ab	11bc	5a	14c	10ac	13bc	0.001	$<10^{-3}$
149.060	$C_9H_9O_2^+$ $C_6H_{13}O_2S^+$	Furfuryl-furan[4] mercapto-3-methylbutylformate[10]	4a	4a	5a	4a	4a	4a	0.131	5ab	6cd	4a	6bd	5abc	7d	$<10^{-3}$	$<10^{-3}$
149.106	$C_9H_{13}N_2^+$	Ethenyl-ethyl-methylpyrazine dihydrocyclopentapyrazines/quinoxalines[7]	7b	5a	7b	7b	6ab	6ab	0.002	2a	2ac	2a	3c	2ab	3bc	$<10^{-3}$	$<10^{-3}$
151.078	$C_9H_{11}O_2^+$	Vinylguaiacol[6]	11ab	11ab	13b	12ab	11ab	10a	0.117	9bc	10c	4a	12c	8b	11c	$<10^{-3}$	$<10^{-3}$
151.121	$C_9H_{15}N_2^+$	Diethyl-methyl-pyrazine[7]	5a	6a	6a	7a	6a	5a	0.217	3ab	3ab	3a	4ab	3ab	4b	0.027	0.046
153.056	$C_8H_9O_3^+$	Vanillin[6]	7ab	8ab	9b	7ab	7ab	6a	0.119	5a	7b	5a	6ab	5a	7b	$<10^{-3}$	0.001
153.093	$C_9H_{13}O_2^+$	4-Ethyl-guaiacol[6]	6ab	7ab	8b	7ab	7ab	6a	0.081	5a	7ab	5a	8bc	6ab	8c	$<10^{-3}$	0.000
153.128	$C_{10}H_{17}O^+$	E/E-2/4-decadienal[2]	5a	5a	5a	10b	5a	6a	$<10^{-3}$	2a	3bc	2ab	6d	3ab	4c	$<10^{-3}$	0.001
157.085	$C_8H_{13}O_3^+$	4-Ethoxy-2/5-dimethyl-3-2H-furanone/ethylfuraneol[4]	3ab	3ab	4b	4ab	3ab	3a	0.046	1a	1c	1ab	1bc	1ac	1ac	0.008	0.033
159.140	$C_9H_{19}O_2^+$	Nonanoic acid/C9 ester[3]	1ab	1a	1ab	1b	1ab	1ab	0.061	2a	2a	2a	3b	3b	2a	$<10^{-3}$	$<10^{-3}$
161.072	$C_9H_9ON_2^+$	Furyl-methylpyrazines[7]	2a	2a	2a	2a	2a	2a	0.553	1c	1cd	0a	1c	1b	1d	$<10^{-3}$	$<10^{-3}$
163.077	$C_{10}H_{11}O_2^+$	Methyl-furfurylfuran[4]	2a	2a	2ab	2ab	2a	2a	0.015	1b	3a	3bc	1a	2ac	3c	$<10^{-3}$	$<10^{-3}$
165.095	$C_{10}H_{13}O_2^+$	Methyl-cinnamate[6]	2a	2a	2b	2ab	2a	2a	0.002	1b	2c	1a	2c	1b	2c	$<10^{-3}$	$<10^{-3}$
166.088	$C_9H_{12}O_2N^+$	Methyl-pyrrolyl-butanedione[9]	1ab	1ab	2b	1ab	1ab	1a	0.034	1a	1bcd	1ab	1cd	1ac	2d	$<10^{-3}$	$<10^{-3}$
167.069	$C_9H_{11}O_3^+$	Methylvanillin[6]	3ab	3bc	4c	3bc	3ab	2a	$<10^{-3}$	3ab	3bc	2a	3c	3bc	3c	$<10^{-3}$	$<10^{-3}$
167.112	$C_{10}H_{15}O_2^+$	Ethyl-dimethoxy-benzene[6]	1a	1ab	2b	1ab	1ab	1a	0.029	1a	1bc	1ab	1ac	1ac	1c	0.004	0.001
175.087	$C_{10}H_{11}ON_2^+$	Dimethyl-furanyl-pyrazine[7]	1b	1a	1ab	1ab	1ab	1ab	0.082	<1cd	<1cd	<1a	<1c	<1c	<1d	$<10^{-3}$	$<10^{-3}$
176.070	$C_{10}H_{10}O_2N^+$	Furylmethyl-pyrrole-carboxaldehyde[9]	1ab	1a	1b	1ab	1ab	1a	0.036	1c	1c	<1a	1c	1b	1c	$<10^{-3}$	$<10^{-3}$
179.073	$C_{10}H_{11}O_3^+$	-syringol[6]	1a	1a	1a	1a	1a	<1a	0.142	1c	1d	<1a	1cd	<1b	1e	$<10^{-3}$	$<10^{-3}$
183.103	$C_{10}H_{15}O_3^+$	Ethyl-syringol[6]	<1a	1ab	1b	1ab	1ab	<1a	0.008	<1a	<1bc	<1ab	1d	1ac	<1c	$<10^{-3}$	$<10^{-3}$
191.148	$C_{13}H_{19}O^+$	Beta-damascenone[2]	<1a	<1a	<1a	<1a	<1a	<1a	0.176	<1a	<1b	<1a	<1c	<1bc	<1bc	$<10^{-3}$	$<10^{-3}$

* Coffee samples in powder and brew forms: BRA: Brazil, COL: Colombia, CRC: Costa Rica, ETH: Ethiopia, GUA: Guatemala, IND: India.

** m/z = mass to charge ratio.

*** The chemical classes annotated to mass peaks after tentative identification: 1. alcohols, 2. carbonyls, 3. esters/acids, 4. pyrans/furans, 5. oxazoles, 6. phenols, 7. pyrazines, 8. pyridines, 9. pyrroles, 10. sulphur compounds, 11. terpenes, 12. thiazoles, and 13. various fragments.

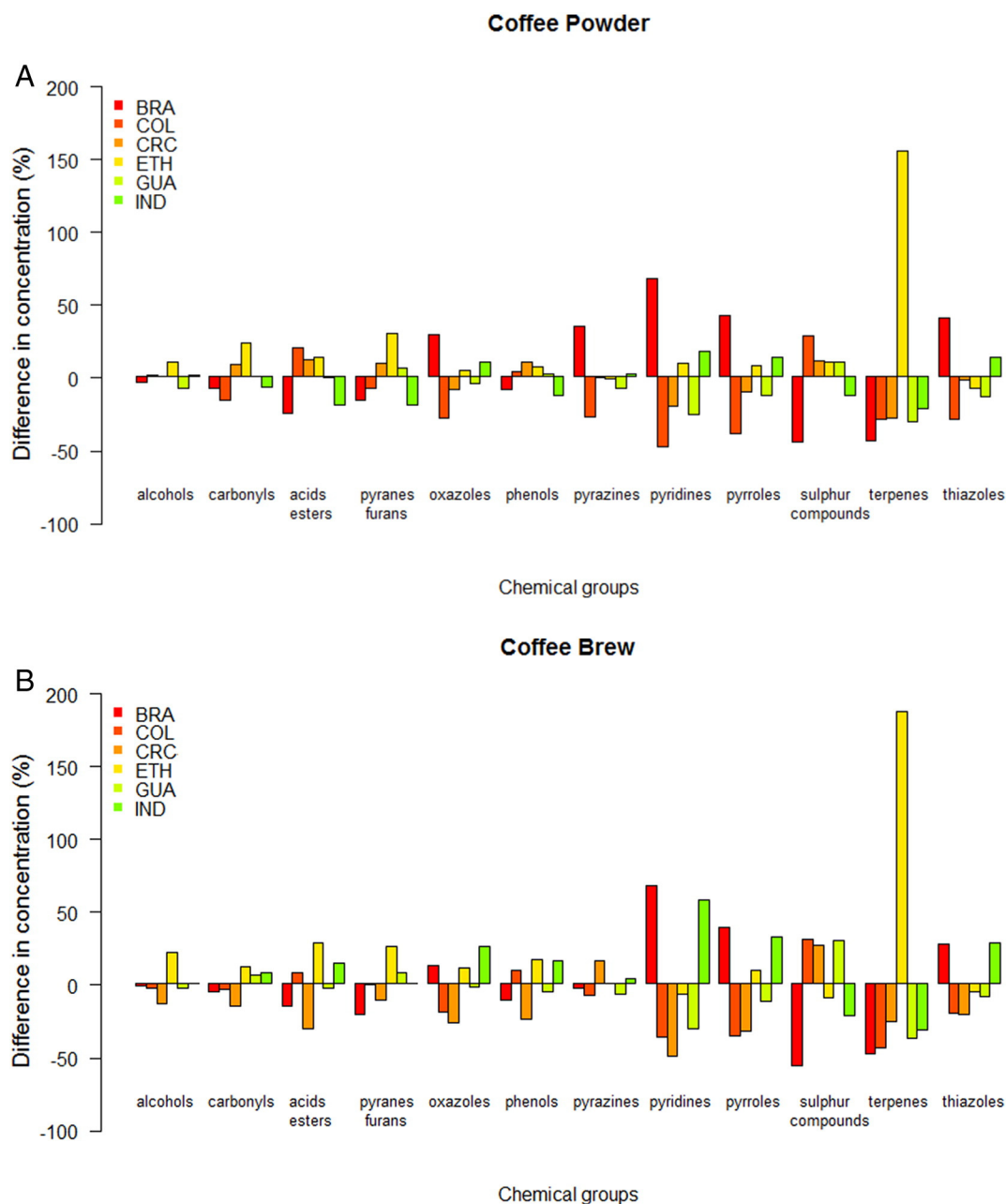## Coffee Powder

Coffee Brew

Fig. 2. Column charts showing the differences (%) between chemical groups of the volatile compounds identified for coffee powder (a) and coffee brew (b).

the fingerprinting capabilities of PTR-ToF-MS. Merging all the information of the different reagent ions by means of data fusion increased the efficiency of classification.

In conclusion PTR-MS and the SRI system provide a rapid non-invasive method that allows the classification of coffee with different origins. This approach is based on the measuring of volatile compound concentration and is thus expected that the differences observed should be reflected on the sensory characteristics of the investigated samples.

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