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Analysing the headspace of coffee by proton-transfer-reaction mass-spectrometry

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Abstract

An extensive analysis of the headspace (HS) of coffee brew using proton-transfer-reaction mass-spectrometry (PTR-MS) is presented. In particular, we present a set of methods that link mass spectral peaks, as observed in PTR-MS, to chemical compounds in the HS of coffee. Combining all this information, a tentative assignment and rough quantification of liquid coffee HS is presented. Coffee was chosen because it contains a large number of chemically diverse volatile organic compounds (VOCs), representing a challenging system for on-line analysis by PTR-MS. (Int J Mass Spectrom 223–224 (2003) 115–139)

Keywords: On-line analysis; Proton-transfer-reaction mass-spectrometry (PTR-MS); Coffee brew; Coffee aroma; Headspace; Partition coefficients; Fragmentation

1. Introduction

Scientific efforts to elucidate the origin of the rich and distinctive flavour of coffee, and ultimately to understand "*What Makes that Coffee Smell so Good*" [1,2], can be traced back to the 19th century (1880) when Bernheimer identified the first few volatile organic compounds (VOCs) of coffee [3]. In 1926, Reichenstein and Staudinger identified and patented several important flavour active compounds of coffee [4,5]. Mainly fuelled by progress in analytical techniques, and due to increasing economic interest in mastering coffee flavour, the number of publications on coffee aroma and concomitantly the number of identified coffee VOCs has rapidly increased since then. Today close to 900 VOCs have been reported in coffee [6]. These comprise compounds found in green and roasted coffee (all roasting levels) from different botanical origins and post-harvest treatments, as well as off-flavours and process-flavours. Furthermore, depending on the technique used to extract VOCs, and the specificity and sensitivity of the detector, only part of the genuine headspace (HS) will be observed in one particular experiment. Therefore, for any specific sample, analysed by a given technique, the total number of detected VOCs will be less than 900.

For many years, scientists have concentrated on identifying an ever-increasing number of VOCs of coffee. But already in the 1970s it became clear that only a small fraction of these volatiles—perhaps 5%—are odoriferous, and the focus started to shift towards these

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few sensory relevant VOCs. Several methods were developed which should achieve the following objective: identify and quantify the odour-relevant VOCs, assess their odour impact and recombine a coffee aroma with the minimum number of impact compounds. Currently, less than 30 VOCs are believed to be important flavour compounds of roasted coffee [7–11]. Omission experiments from Grosch and co-workers suggest that the actual number of key coffee aroma compounds could be as small as 9 [12–14]. For a review on the development of food flavour analysis, and on our current understanding of coffee flavour, see [15].

Besides identification, quantification and recombination of coffee aroma, several groups have developed on-line methods for VOC analysis that are capable of monitoring in real-time the fast dynamic processes of flavour formation and release. When it comes to applications in an industrial setting, sensitive and fast methods for on-the-spot decisions and simple modes of probing without tedious sample preparation are essential. Furthermore, short analysis times allow acting upon the process being measured. In that respect, shortening the analysis time is not simply a quantitative gain of time, but allows new and qualitatively different experiments to be performed.

A promising approach is direct injection mass spectrometry in combination with soft ionisation. The critical element is the ionisation mode. It determines the sensitivity and chemical selectivity of the methods, and may lead to fragmentation. In this respect, the two soft ionisation modes that have been applied to coffee flavour analysis are laser ionisation and chemical ionisation. In a series of recent papers, advantages and limitations of the various direct inlet MS methods were reviewed [16–19].

Here, we will discuss proton-transfer-reaction mass-spectrometry (PTR-MS), as applied to coffee. After a brief introduction to PTR-MS, a typical HS spectrum of coffee brew is presented in Section 2. We then examine in Section 3 a range of approaches and strategies aimed at identifying chemical compounds in a PTR-MS HS spectrum of coffee. The objective of the paper is to demonstrate how to *link mass spectral peaks, as observed in PTR-MS, to chemical compounds in the HS*. We chose coffee because it contains a large number of chemically diverse VOCs, and hence represents a challenging system for on-line analysis by PTR-MS.

2. Experimental and results

2.1. Proton-transfer-reaction mass-spectrometer

PTR-MS [20–22] is based on a novel design for the chemical ionisation cell [23], which was developed out of the swarm technique [24]. The sample gas is continuously introduced through a ventury type inlet system into the chemical ionisation (Cl) cell. Volatiles that have proton affinities higher than water (proton affinity of H_2O: 166.5 kcal/mol) are ionised by proton transfer from H_3O^+ and mass analysed in a quadrupole MS.

The CI-source was designed to achieve high sensitivity, low fragmentation, and allows for a rough quantification of VOCs. To achieve these targeted specifications, generation of the primary H_3O^+-ions and the CI process are spatially and temporally separated and individually controlled. This allows (i) maximising signal intensity by increasing the generation of primary reactant ions, H_3O^+, (ii) reducing fragmentation and clustering by optimising the conditions for proton transfer in the CI cell, and (iii) quantifying VOCs. Consequently, the key features of PTR-MS can be summarised as follows. *First*, it is fast. Time-dependent variations of the HS can be monitored with a sub-seconds time-resolution. *Second*, VOCs are not subjected to work-up with solvents, trapping and desorption or thermal stress and little fragmentation is induced in the ionisation step. Hence, mass spectral profiles closely reflect genuine HS distributions. *Third*, mass spectral intensities can be transformed into absolute HS concentrations. Finally, it is not invasive.

Since its introduction in 1993, PTR-MS has been applied to a variety of fields. Medical and nutritional applications include breath analysis to monitor metabolic processes in the human body [25,26]. Environmental applications include investigations of volatile emissions from decaying bio-matter, or

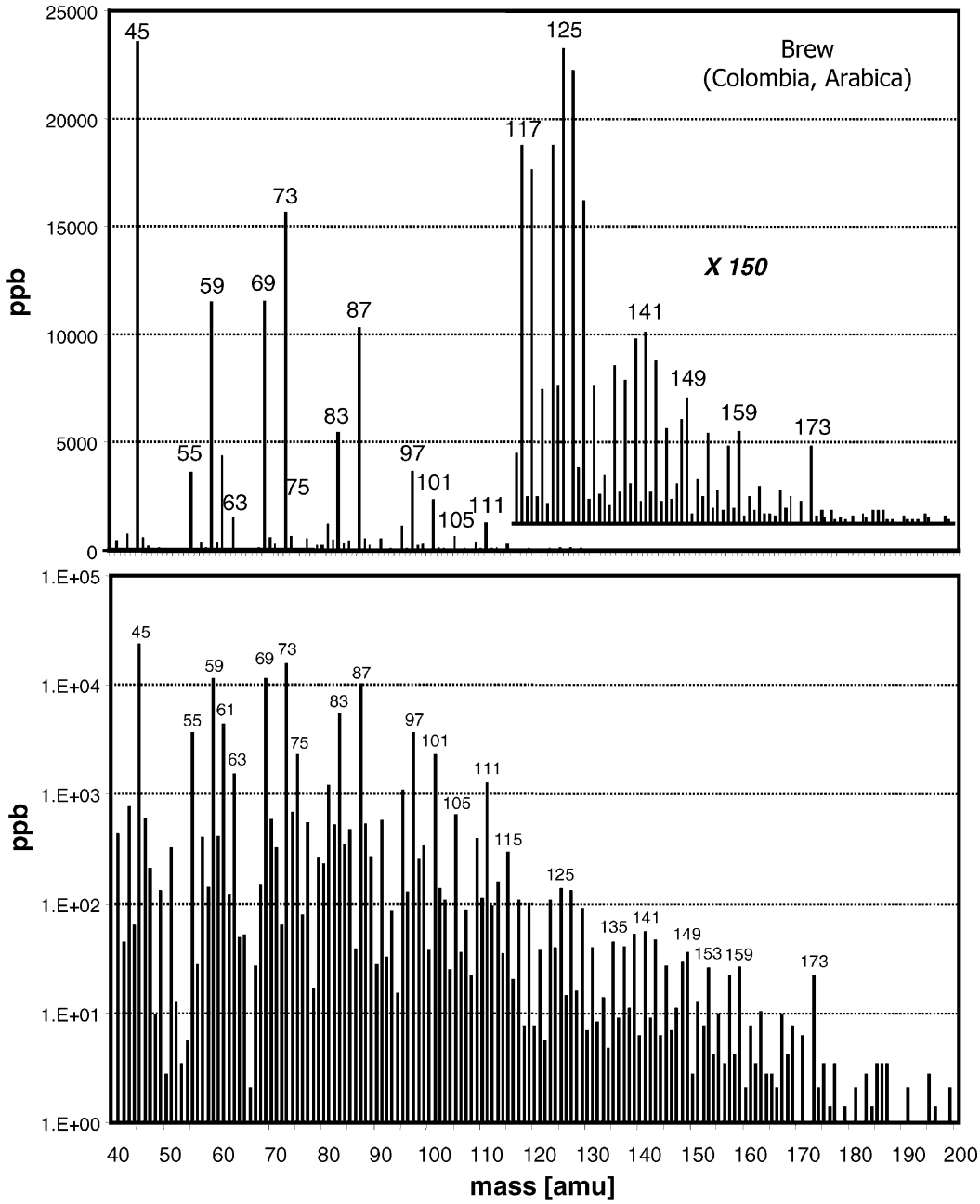

Fig. 1. PTR-MS equilibrium HS of coffee brew. The brew was equilibrated in a closed vessel at 40 °C for 100 min. The equilibrium HS composition was measured over a mass range from 40 to 200. In the upper frame, the spectrum is shown on a linear scale, whereas a logarithmic scale was chosen on the lower frame. The ppb concentrations refers to concentrations in the HS.

diurnal variations of organic compounds in the troposphere [27,28]. Coffee roasting, as an example for food processing, was investigated via on-line monitoring of the roaster exhaust-gas [29,30]. Finally, PTR-MS was shown to be an ideal tool for nose-space analysis while consuming food [31], and to measure Henry's law constants [32,33].

2.2. PTR-MS headspace profile of coffee brew

A filter brew, prepared from Colombian coffee (Arabica, medium roasted), was analysed by PTR-MS (Fig. 1). Sixty-five grams of freshly ground coffee was extracted in a coffee filter machine (Double Technovorm coffee marckers) with 400 mL water at about 95 °C, through a filter paper (Melita). The 500 mL glass vial used to recover the filter coffee was closed immediately after extraction with a cover that had an inlet and an outlet on the top. Under this experimental conditions, it took 118 ± 1.23 s for the 400 mL water to pass, while 389 ± 1.05 mL were recovered in the vial. This left a HS gas volume of 111 mL above the liquid. The closed vial was put into an oven at 40 °C for 100 min (without stearing). Then HS-gas was sampled through the outlet at a rate of 17 cm^3/min by purging the HS with synthetic air. The first 10 min purge were discarded, to allow the HS profile to reach a dynamic equilibrium. Then the HS was measured as an averaged over the next 10 min. This experimental approach mimics the situation of an open coffee cup that was served from a thermos. In a separate experiment the HS of the empty vial was measured (background) and subtracted from the brew spectrum. The background intensity was found to be negligible at most masses.

3. Discussion: relating mass peaks to chemical compounds

In order to assign chemical compounds to mass spectral intensities in PTR-MS, two important issues have first to be addressed.

First: PTR-MS is a one-dimensional method that characterises compounds by their mass. There are, however, a large number of potential VOCs in coffee having the same nominal mass (isobaric). Hence, mass-information alone is often insufficient for unambiguous identification. An analogous problem is encountered in gas chromatography (GC). Retention-indices alone are generally not sufficient for identification. That is why two or multiple detectors are often used simultaneously in GC. In analogy, PTR-MS data have to be complemented with additional information in order to achieve an unambiguous identification. High resolution MS can resolve some of the problems related to overlapping isobaric compounds, yet this requires sophisticated and expensive equipment. One other option is to combine CI with ion-trap mass spectrometry [34–36]. This allows running multi-dimensional mass analyses with consecutive mass selection and collision-induced dissociation (CID). Yet, by doing this, we sacrifice the simplicity and robustness of the current method.

Second: PTR-MS suffers from some ionisation-induced fragmentation, which can complicate the interpretation of mass spectra. While more than 80% of the mass spectral intensity appear at the parent masses, it is nonetheless important to consider fragmentation for a proper assignment of PTR-MS spectra.

Both the one-dimensionality of the method and ionisation-induced fragmentation make a direct identification of HS compounds, based solely on PTR-MS spectrum, questionable. This is particularly true for coffee. In order to circumvent these limitations, a series of specific PTR-MS experiments have been developed [21]. Each one of these experiments adds some useful information in order to get one step closer to an unambiguous assignment of PTR-MS and consequently link mass peaks in PTR-MS to chemical compounds. Making this link between PTR-MS spectra and the underlying compounds is the subject of this paper.

3.1. Literature on coffee VOCs

Today an extensive literature on the HS of coffee is available, and around 900 different VOCs have been reported. Most of this work is consolidated into a database on "Volatile Compounds in Food" from the

TNO [6]. We believe that this list is almost complete and hence forms an exhaustive list of compounds that can potentially contribute to mass spectral intensities in PTR-MS.

As outlined in the introduction, any "real-life" sample will contain only a fraction of the VOCs listed in the TNO. Therefore, for any specific sample analysed by PTR-MS the actual number of detected HS compounds is less than 900.

3.2. Quantification of coffee VOCs in the literature

The first criterion for a VOC to be considered for the assignment of PTR-MS spectra is its HS concentration. In order for a compound to contribute significantly to a PTR-MS spectrum, its HS concentration ought to be 1 ppb or more.

We have extensively searched the literature on quantification of VOCs in coffee. It was found that quantification of VOCs in the HS is not available (to our knowledge). Most quantifications were performed on roast and ground powder (R&G). Some data exist on soluble powder, brew or reconstituted powder. To make use of these reported quantifications some approximations were adopted.

- *Air–waterpartition coefficient*: Air–water partition coefficients are assumed here to be 10^{-2} for all VOCs. Alternatively, one could distinguished between polar (10^{-3} to 10^{-4}) and non-polar (10^{-1} to 10^{-2}) compounds, in order to get more acurate approximations. Eventually, one could use actually measured partition coefficients. While partition coefficients for flavour compounds in coffee can be found in the literature, the list is very incomplete and reported values from various authors scatter over a large range [32]. We are currently in the process of measuring systematically partition coefficients in water and coffee. Here, we prefer to stay with an average value of 10^{-2}, until we have a more complete set of accurate partition coefficients in liquid coffee.

  It should also be beared in mind that what we term here air–liquid partition coefficient is effectively the outcome of partitionings of flavour compounds between multiple components. Liquid coffee is composed of non-volatile coffee solids which interact with the volatiles. Furthermore, filter-coffee can have as much as 1% lipid content, which may strongly interact with volatiles. Hence, the term partition coefficients, as used here, reflect the partitioning of volatiles in this multiple component systems.
- *Extractability*: Compounds quantified in R&G are assumed to be 100% extractable. Here again, many compounds are known to be not completely extractable [10].
- *2% solids content*: For the preparation of liquid coffee from R&G or soluble coffee, a solids content (T_c) of 2% is assumed. This corresponds to average consumption habits.
- *Highest reported concentration*: If several quantifications were published on the same compound, the largest reported value is used to estimate the HS concentration.

Using these above approximations we calculate that a 1 ppb threshold HS concentration translates into 100 ppb and 1 ppm threshold concentrations in liquid and powder coffee, respectively (see Table 1).

Several comments have to be made at this stage.

On the one hand, the approximations used here tend to overestimate the concentration of compounds in the HS:

- Various VOCs in coffee have smaller air–water partition coefficients than 10^{-2} (higher solubility) [37–44]. This is the case for polar compounds or compounds that form ions in solution (e.g., organic acids).
- Reported quantification can be spread over more than one order of magnitude (e.g., 2,3-butandione, guaiacol, pyrazines). This reflects experimental difficulties involved in quantification as well natural variability. Since we always refer to the largest reported value, we are prone to include quantifications that are too high.
- Some compounds, e.g., glyoxal or methylglyoxal, are very unstable. Although they are quite abundant in the roasted beans, they are not found in the HS.

Table 1
Approximations adopted to convert quantification in liquid or powder coffee into HS concentrations

threshold HS concentration	**1 ppb**
assumption: air/water partition coefficient is smaller than 10^{-2}	⇓
threshold concentration in liquid preparation (brew or reconstituted coffee)	**100 ppb**
assumption: 100% extractability and 2% T_c	⇓
threshold concentration in coffee powder (R&G or soluble powder)	**5 ppm**

Consequently, several compounds in this list are present in the HS of liquid coffee only at sub-ppb concentrations.

On the other hand, some compounds, which are obviously present at concentrations higher than 1 ppb are not in the list. This is because they have not been quantified in coffee due to their low odour impact (methanol and acetone), or because they are difficult to quantify (e.g., eluting with the solvent peak in GC).

Applying the above approximations to published quantitative data, together with the ensuing threshold concentrations in liquid and powder coffee, we end up with a list of 92 compounds, as shown in Table 2. The list of VOCs compiled in Table 2 provides helpful information for assigning PTR-MS mass peaks.

3.3. Fragmentation patterns of pure compounds

Any mass spectral analysis requires that the molecules to be analysed be ionised. Unfortunately, ionisation can lead to fragmentation. When complex mixtures are analysed, fragmentation may obscure the link between measured mass spectra and the actual HS composition. MS profiles of different samples tend to look increasingly similar with increasing amount of fragmentation, since different parent compounds may fragment into the same set of characteristic fragments. One of the particularities of PTR-MS is the use of a soft chemical ionisation mode, which strongly reduces ionisation-induced fragmentation. Yet, since some fragmentation is still occurring, it is important to have data on ionisation-induced fragmentation prior to assigning chemical compounds to mass spectral ion intensities. We have analysed around 150 pure VOCs by PTR-MS, under conditions typical for HS analysis. An extract of this list is given in Table 3. The majority of these compounds ionise without fragmentation. When compounds do fragment, most often a very simple fragmentation pattern is observed.

An overview of Table 3 reveals some systematic patterns for certain chemical functionalities. Molecules with alcohol (–OH) and thiol (–SH) groups often selectively fragment by loss of H_2O (−18 amu) or H_2S (−34 amu). For these compounds the characteristic fragment can take the role of the parent ions in order to identify the VOC. In contrast guaiacol, pyrazine, hydrocarbons, pyrrols, furans and other compound families can be ionised with negligible fragmentation. Such systematic patterns can help to develop rough guidelines for fragmentation patterns in PTR-MS. We believe that the type of information collected in Table 3 is crucial when it comes to identifying compounds contributing to ion peak intensities in PTR-MS.

3.4. Energy-dependent break-up patterns of pure compounds

In a typical PTR-MS experiment, VOCs are introduced into the chemical ionisation cell containing the H_3O^+ chemical reagent, and are ionised in center-of-mass collisions of about 0.25 eV. Once ionised they are accelerated in a series of homogeneous

Table 2
VOCs present in the HS of a liquid coffee at a concentration of at least 1 ppb

Number	MW	Formula	Compound name	Solid: R&G/ sol.[a] ppm (mg/kg)	Liquid: brew/ recon.[b] ppb (μ/L)	Reference	$c_{estimate}$ HS: ppb
1	17.02655	H_3N	Ammonia	560–820		[45]	164
2	31.04220	CH_5N	Methylamine	16–80		[45]	16
3	45.05785	C_2H_7N	Dimethylamine	2 3–6		[46] [45]	1.2
4	46.00548	CH_2O_2	Formic acid	644–1472		[47]	294.4
5	48.00337	CH_4S	Methanethiol		210–600	[10]	6
6	58.00548	$C_2H_2O_2$	Ethanedial Glyoxal	20–127 1–25		[48] [49]	25.4
7	58.04187	C_3H_6O	Propanal		435	[10]	4.35
8	60.02113	$C_2H_4O_2$	Acetic acid	2520–3360		[47]	672
9	71.07350	C_4H_9N	Pyrrolidine	6 7–11 5.3–10		[46] [45] [60]	2.2
10	72.02113	$C_3H_4O_2$	2-Oxopropanal Pyruvaldehyde Methylglyoxal	60–150 23–47 273–994 70–217		[50] [51] [48] [49]	198.8
11	72.05752	C_4H_8O	Methylpropanal Isobutanal		800–1380	[10]	13.8
12	74.03678	$C_3H_6O_2$	Propanoic acid Propionic acid	49.6–125.8		[47]	25.2
13	79.04220	C_5H_5N	Pyridine	49 37 27 20–50 26–190		[56] [54] [67] [55] [60]	38
14	80.03745	$C_4H_4N_2$	Pyrazine	6.4 3.5–6		[54] [55]	1.3
15	86.03678	$C_4H_6O_2$	2,3-Butanedione diacetyl	2.7 0.05–0.15 14–85 13–42 47.8–50.8	 1300–1700 2400–2750	[56] [55] [48] [49] [52] [53] [10]	27.5
16	86.07317	$C_5H_{10}O$	3-Methyl-2-buten-1-ol Prenol	54 0.2–0.3		[54] [55]	1.1
17	86.07317	$C_5H_{10}O$	2-Methylbutanal	26–190			
18	86.07317	$C_5H_{10}O$	3-Methylbutanal Isopentanal Isovaleraldehyde	6.7	 550–925	[56] [10]	1.3
19	87.10480	$C_5H_{13}N$	Pentylamine	2–15		[45]	3

Table 2 (*Continued*)

Number	MW	Formula	Compound name	Solid: R&G/ sol.[a] ppm (mg/kg)	Liquid: brew/ recon.[b] ppb (μ/L)	Reference	$c_{estimate}$ HS: ppb
20	88.05243	$C_4H_8O_2$	Butanoic acid Butyric acid	50.2–75.7		[47]	15.1
21	94.04187	C_6H_6O	Phenol	9.5–63 1.55 8.8 53.7–141 1.2–2.2		[57] [58] [54] [63] [55]	28.2
22	94.05310	$C_5H_6N_2$	Methylpyrazine	104 25 60–80 26.2 30–130		[54] [56] [55] [67] [60]	26
23	95.03711	C_5H_5NO	2-Pyrrolecarbaldehyde 2-Formylpryrrole	12.7 1.3–1.5		[54] [55]	2.5 60
24	96.02113	$C_5H_4O_2$	Furfural 2-Formylfuran 2-Furan-carbaldehyde 2-Furaldehyde	225 60 55–80 56 12–58 10–300 100–250		[54] [56] [55] [67] [60] [59] [48]	
25	98.03678	$C_5H_6O_2$	Furfuryl alcohol (2-Furyl)methanol 2-Furanmethanol	150–520 678 226 560 338–881 90–135 1682 140 250–710		[65] [54] [56] [69] [70] [55] [65] [67] [60]	336.4
26	100.05243	$C_5H_8O_2$	2-Methyldihydro-3 (2*H*)-furanone	10–16 13.3 8–42		[55] [67] [60]	8.4
27	100.05243	$C_5H_8O_2$	2,3-Pentanedione	4 1–3 5–13 19.8–39.6	700–1300 750–1570		15.7
28	100.08882	$C_6H_{12}O$	4-Methyl-2-pentanone	6.5		[54]	1.3
29	102.06808	$C_5H_{10}O_2$	2-Hydroxy-3-pentanone	5.2 0.05–0.15		[54] [55]	1
30	102.06808	$C_5H_{10}O_2$	2-Methylbutanoic acid	25–40		[55]	8

Table 2 (*Continued*)

Number	MW	Formula	Compound name	Solid: R&G/ sol.[a] ppm (mg/kg)	Liquid: brew/ recon.[b] ppb (μ/L)	Reference	$c_{estimate}$ HS: ppb
31	108.05752	C_7H_8O	2-Methylphenol	0.7–12.4		[57]	2.5
			o-Cresol	1.8–2.8		[63]	8
				0.7–1.1		[55]	
				0.45		[58]	
32	108.05752	C_7H_8O	3-Methyphenol	0.7–7.4		[57]	1.5
			m-Cresol	2.3		[54]	
				3.6–5.5		[63]	
				0.2		[58]	
				0.15–0.5		[55]	
33	108.05752	C_7H_8O	4-Methylphenol	0.3–13.2		[57]	2.6
			p-Cresol	0.5–2.1		[63]	
				0.3–0.6		[55]	
				1.5		[67]	
34	108.06875	$C_6H_8N_2$	Ethylpyrazine	18		[54]	3.6
				13.5–16.5		[55]	
				10.1		[67]	
				7–15		[60]	
35	108.06875	$C_6H_8N_2$	2,3-Dimethylpyrazine	8.5		[54]	3.2
				4		[56]	
				4.5–5.3		[55]	
				3.45		[67]	
				4–16		[60]	
36	108.06875	$C_6H_8N_2$	2,5-Dimethylpyrazine	40		[54]	9
				17		[56]	
				25–35		[55]	
				12.2		[67]	
				15–45		[60]	
37	108.06875	$C_6H_8N_2$	2,6-Dimethylpyrazine	56		[55]	11.2
				19		[56]	
				30–35		[55]	
				12.8		[67]	
				18–45		[60]	
38	109.05276	C_6H_7NO	1-Methyl-2-pyrrolecarbaldehyde	8.5		[66]	3.4
			2-Formyl-1-methylpyrrole	17		[54]	
				1.15–1.3		[55]	
				3.8–6		[60]	
39	109.05276	C_6H_7NO	2-Acetylpyrrole	10.9		[54]	2.2
			Methyl-2-pyrrolyl ketone	1.5–1.8		[55]	
				3–10		[60]	
40	110.03678	$C_6H_6O_2$	1,2-Benzenediol	80–120		[64]	139.2
			Pyrocatechol	60		[69,70]	
			Catechol	207–667		[63]	
			Catecin	696		[65]	
				225		[67]	

Table 2 (*Continued*)

Number	MW	Formula	Compound name	Solid: R&G/sol.[a] ppm (mg/kg)	Liquid: brew/recon.[b] ppb (μ/L)	Reference	$c_{estimate}$ HS: ppb
41	110.03678	$C_6H_6O_2$	1,4-Benzenediol Hydroquinone	25–40 5.6 1.25 385 342		[64] [63] [58] [67] [65]	77
42	110.03678	$C_6H_6O_2$	5-Methylfurfural	216 39 50–70 74.2 10–35 25–180		[54] [56] [55] [67] [60] [48]	36
43	110.03678	$C_6H_6O_2$	2-Acetylfuran (2-Furyl)methyl ketone 1-(2-Furyl)ethanone	24.1–31.4 10 6–12 11.5 7–10		[54] [56] [55] [67] [60]	6.3
44	112.01605	$C_5H_4O_3$	2-Furancarboxylic acid 2-Furoic acid	50–80 40–95		[64] [60]	19
45	112.05243	$C_6H_8O_2$	2,4-Dimethyl-3(2*H*)-furanone	0.5–0.6 2–6		[55] [60]	1.2
46	112.05243	$C_6H_8O_2$	5-Methylfurfuryl alcohol	24.9 1.2–1.8		[54] [55]	5
47	112.05243	$C_6H_8O_2$	2,5-Dimethyl-3(2*H*)-furanone	10.7		[54]	2.1
48	112.05243	$C_6H_8O_2$	3-Methyl-1,2-cyclopentanedione Cyclotene 2-Hydroxy-3-methyl-2-cyclopentene-1-one	17–40 9.78 9–20		[64] [61] [60]	8
49	116.04735	$C_5H_8O_3$	2-Oxopropyl acetate Acetol acetate 1-Acetoxyacetone Acetonyl acetate	2–5 2.5–4.4		[55] [60]	1
50	116.08373	$C_6H_{12}O_2$	Hexanoic acid Caproic acid	7.2–29		[47]	5.8
51	120.06875	$C_7H_8N_2$	6,7-Dihydro-5*H*-cyclopentapyrazine	8.2 0.25–0.3		[54] [55]	1.6
52	122.08440	$C_7H_{10}N_2$	2-Ethyl-3-methylpyrazine	14 0.15–0.2 2.4		[54] [55] [67]	2.8
53	122.08440	$C_7H_{10}N_2$	2-Ethyl-5-methylpyrazine	2.2–3.5 7.5–8.6 6.7 6–17		[54] [55] [67] [60]	3.4

Table 2 (*Continued*)

Number	MW	Formula	Compound name	Solid: R&G/ sol.[a] ppm (mg/kg)	Liquid: brew/ recon.[b] ppb (μ/L)	Reference	$c_{estimate}$ HS: ppb
54	122.08440	$C_7H_{10}N_2$	2-Ethyl-6-methylpyrazine	3.1–9.6 8.5–10.5 5.2 6–15		[54] [55] [67] [60]	3
55	122.08440	$C_7H_{10}N_2$	Trimethylpyrazine	20.3 4 8–10 6–14		[54] [56] [55] [60]	4.1
56	123.06841	C_7H_9NO	2-Acetyl-1-methylpyrrole	2.6 7.5 1.8–2.1		[66] [54] [55]	1.5
57	124.05243	$C_7H_8O_2$	3-Methyl-1,2-benzenediol	9 15.3 32.5 142		[69,70] [63] [58] [65]	28.4
58	124.05243	$C_7H_8O_2$	4-Methyl-1,2-benzenediol	10–16 16.7–24.6 8.5 64 130		[64] [63] [58] [65] [67]	26
59	124.05243	$C_7H_8O_2$	2-Methoxyphenol Guaiacol	2.7–10.6 6.1 35.8–95.5 2–3 1.6 7.2 4.2–28.2	 170–1230	[57] [54] [63] [55] [58] [67] [68] [10]	19.1
60	126.03170	$C_6H_6O_3$	1,2,4-Benzenetriol Hydroxyhydroquinone	6–20 60 0.15 138		[64] [69,70] [58] [67]	27.6
61	126.03170	$C_6H_6O_3$	1,2,3-Benzenetriol Pyrogallol	25–55 35 <0.1 2 280		[64] [69,70] [63] [58] [65]	56
62	126.03170	$C_6H_6O_3$	5-(Hydroxymethyl)furfural	10–35 15–45 60–600 730		[64] [60] [59] [62]	146
63	126.03170	$C_6H_6O_3$	2-Acetyl-3-hydroxyfuran, isomaltol	1.5–8		[64]	1.6
64	126.03170	$C_6H_6O_3$	3-Hydroxy-2-methyl-4-pyrone Maltol	20–45 30–75		[64] [60]	15

Table 2 (*Continued*)

Number	MW	Formula	Compound name	Solid: R&G/ sol.[a] ppm (mg/kg)	Liquid: brew/ recon.[b] ppb (μ/L)	Reference	$c_{estimate}$ HS: ppb
65	126.06808	$C_7H_{10}O_2$	3-Ethyl-1,2-cyclopentanedione (enol)	5.72		[61]	1.1
66	128.04735	$C_6H_8O_3$	4-Hydroxy-2,5-dimethyl-3 (2*H*)-furanone	25–50		[64]	66
				13–32		[60]	
			Furaneol		1500–6600	[52]	
				57–109		[68]	
					2480–4510	[10]	
67	130.09938	$C_7H_14O_2$	Heptanoic acid, enanthic acid	29.9–107.9		[47]	21.6
68	134.08440	$C_8H_{10}N_2$	6,7-Dihydro-5-methyl-5*H*-cyclopentapyrazine	8.8		[54]	1.8
				0.45–0.55		[55]	
				0.4–0.6		[60]	
69	136.05243	$C_8H_8O_2$	4-Vinyl-1,2-benzenediol	15–25		[64]	32
				16		[69,70]	
				4.4–6		[63]	
				160		[65]	
				68		[67]	
70	136.10005	$C_8H_{12}N_2$	5-Ethyl-2,3-dimethylpyrazine	10		[54]	2
71	136.10005	$C_8H_{12}N_2$	2-Ethyl-3,5-dimethylpyrazine	8		[54]	1.6
				2–2.2		[55]	
				0.49–0.82	16.8–26.6	[62]	
				1.8–2.4		[60]	
				0.33–0.94		[68]	
					13.1–35.2	[10]	
72	138.03170	$C_7H_6O_3$	2,3-Dihydroxybenzaldehyde	2.9–5.6		[63]	1.1
73	138.03170	$C_7H_6O_3$	3,4-Dihydroxybenzaldehyde	8–20		[64]	4
				<0.1		[65]	
				252			
74	138.03170	$C_7H_6O_3$	1-(2-Furyl)-1,2-propanedione	3.9		[54]	3
				0.1–15		[55]	
75	138.06808	$C_8H_{10}O_2$	4-Ethyl-1,2-benzenediol	20–80		[64]	35.8
				9		[69]	
				106–179		[63]	
				130		[65]	
				65		[67]	
76	140.04735	$C_7H_8O_3$	Furfuryl acetate	16.3		[54]	3.3
			2-Furanmethanol acetate	5.4		[56]	
				3.5–5.5		[55]	
77	142.02661	$C_6H_6O_4$	3,5-Dihydroxy-2-methyl-4-pyrone	6–15		[64]	3
				4–10		[60]	
			5-Hydroxymaltol				

Table 2 (*Continued*)

Number	MW	Formula	Compound name	Solid: R&G/ sol.[a] ppm (mg/kg)	Liquid: brew/ recon.[b] ppb (μ/L)	Reference	$c_{estimate}$ HS: ppb
78	142.06300	$C_7H_{10}O_3$	2-Ethyl-4-hydroxy-5-methyl-3(2*H*)furanone + 5-ethyl-4-hydroxy-2-methyl-3(2*H*) furanone homofuraneol	14.3–17.3		[68]	3.46
					670–840	[10]	
79	144.04226	$C_6H_8O_4$	5,6-Dihydro-3,5-dihydroxy-2-methyl-4-pyrone	10–13		[64]	3
			5,6-Dihydro-5-hydroxymaltol	4–15		[60]	
80	144.11503	$C_8H_{16}O_2$	Octanoic acid Caprylic acid	2.3–6.2		[47]	1.2
81	146.04801	$C_8H_6N_2O$	(2-Furyl)pyrazine	1.8–7.6		[54]	1.5
				0.6–0.7		[55]	
				0.5–0.7		[60]	
82	147.06841	C_9H_9NO	1-Furfurylpyrrole	2.2		[66]	1.6
				7.8		[54]	
				2		[56]	
				2.6		[67]	
				2–4.4		[60]	
83	148.10005	$C_9H_{12}N_2$	6,7-Dihydro-2,5-dimethyl-5*H*-cyclopentapyrazine	5.1		[54]	1.0
				0.75–0.8		[55]	
84	150.06808	$C_9H_{10}O_2$	2-Methoxy-4-vinylphenol 4-Vinylguaiacol	7.9–19.5		[57]	
				46.6		[54]	
				115–117		[63]	
				8–20		[55]	
				8.7		[58]	
				19.2		[67]	
					1000	[52]	
				64.8–177.7		[68]	
					1640–5380	[10]	
85	152.04735	$C_8H_8O_3$	Vanillin 4-Hydroxy-3-methoxy-benzaldehyde	2–3		[64]	7.4
				4.4–5.9		[63]	
				17		[68]	
				4.8–16.1		[68]	
					220–740	[10]	
86	152.08373	$C_9H_{12}O_2$	4-Ethyl-2-methoxyphenol 4-Ethylguaiacol	0.3–2.2		[57]	7.2
				2.4		[54]	
				13.9–36.1		[63]	
				0.8–1.5		[55]	
				0.85		[58]	
				4.1		[67]	
					60–400	[52]	
				1.63–18.1		[68]	
					51–635	[10]	
87	154.02661	$C_7H_6O_4$	2,5-Dihydroxybenzoic acid	15		[69,70]	3

Table 2 (*Continued*)

Number	MW	Formula	Compound name	Solid: R&G/ sol.[a] ppm (mg/kg)	Liquid: brew/ recon.[b] ppb (μ/L)	Reference	$c_{estimate}$ HS: ppb
88	156.07865	$C_8H_{12}O_3$	4-Ethoxy-2,5-dimethyl-3(2*H*)-furanone ethylfuraneol	2–8		[64]	1.6
89	158.13068	$C_9H_{18}O_2$	Nonanoic acid Pelargonic acid	2.5–20.5		[47]	4.1
90	164.04735	$C_9H_8O_3$	3,4-Dihydroxycinnamaldehyde	5–12 76		[64] [67]	15.2
91	172.14633	$C_{10}H_{20}O_2$	Decanoic acid Capric acid	5–29.2		[47]	5.8
92	175.06333	$C_{10}H_9NO_2$	1-Furfuryl-2-pyrrolecarbaldehyde	3.4		[66]	1.6
			2-Formyl-1-furfurylpyrrole	6.5 2.5–3 2.5 3–8		[54] [55] [67] [60]	

They are ordered by increasing molecular weight (MW). The last column gives the estimated concentration of the compounds in the HS, based on the approximations in Table 1 and the concentration for liquid of solid coffees reported in the literature.

[a] Quantification measured in R&G powder or in soluble coffee powder.

[b] Quantification measured in liquid coffee (brew or reconstituted soluble coffee).

field regions, with 7 V potential differential through each region. These settings are a good compromise between avoiding on the one hand formation of too much $H_3O(H_2O)^+$ and higher clusters $H_3O(H_2O)^{n+}$, and on the other hand, breaking up of product ions due to collisions with neutrals in the drift region. Yet, in some cases, such as in the presence of isobaric ion interferences, some fragmentation can be beneficial to distinguish between alternative compounds. Investigations by Glosik et al. on CID of ions have shown that ions of the same mass can have distinctive break-up patterns [71–73]. By scanning the potential in the final field region from 7–50 V, energy-dependent break-up patterns can be monitored. We have investigated break-up patterns for more than 40 pure compounds, including a broad range of chemical functionalities relevant to coffee. Some examples are shown in Fig. 2.

Fig. 2a and b show energy-dependent break-up patterns of formic acid (HCOOH; 46.0055 amu) and ethanol (C_2H_5OH; 46.0417 amu). Only 0.0362 mass units separate the parent masses. For separation of these two compounds by MS, a resolution of about 1300 is required. Yet, even good quadrupole MS do not exceed a resolution of 1000. In typical PTR-MS experiments, a mass resolution of approximately 1 mass unit is used in order to collect the largest possible ion counts per mass channel. Formic acid and ethanol can, therefore, not be separated by PTR-MS. Comparing Fig. 2a with b, we see that both molecules have different energy dependent break-up patterns. Formic acid will fragment only above 30 V. In contrast, ethanol fragments already at 20 V by loss of H_2O.

Propanal and acetone in Fig. 2c and d are examples of VOCs that have exactly the same sum-formula, C_3H_6O, and the same monoisotopic mass, 58.0419 amu. Yet, the relative intensities in the break-up channels are dependent on the applied voltage. While for protonated propanal the break-up has nearly gone to completion at 35 V, at this voltage hardly any break-up occurs for acetone. Furthermore, the appearance of a fragment at mass 31 is indicative of propanal.

In Fig. 2e–g, break-up patterns of three volatile compounds of intermediate molecular mass (60–80 amu) are shown. They illustrate typical break-up patterns for different molecular families.

Table 3
Product ion distributions from reactions of H_3O^+ ions with various VOCs

name	formaldehyde	methanol	ethanal	dimethylamine	formic acid	propanal	acetone	acetic acid	n-propanol	dimethyl sulfide	pyrrol	furan	isobutanal	propandiol	pyridine	pyrazine	methylfuran	3-pentanone	3-Methyl-butanal	2-Methyl-butanal	2,3-butane-dione	2-methyl-3-buten-2-ol	3-methyl-2-buten-1-ol	3-methyl-3-buten-1-ol	3-methyl-1-butanol	butyric acid	vinylfurane	dimethyldisulfide	furfural	furfuryl-alcohol	2,3-pentane-dione	benzaldehyde	2-ethylpyrazine	5-methyl-furfural	2-furfuryl-thiol	2-phenylacetaldehyd	guaiacol	dimethyltrisulfide	furaneol	3-octanone	octanal	1-octen-3-ol	2-E-nonenal	4-vinyl-guaiacol	2,3-diethyl-5-methylpyrazine	ethyl-guaiacol	vanilin	2-isopropyl-3-methoxypyrazine	2-isobutyl-3-methoxypyrazine	E(ß)-damascenone	name
no.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	
Mass	30	32	44	45	46	58	58	60	60	62	67	68	72	76	79	80	82	86	86	86	86	86	86	86	88	88	94	94	96	98	100	106	108	110	114	120	124	126	128	128	128	128	140	150	150	152	152	166	180	190	Mass
31	100													3																																						31
33		100																																																		33
41														3					11	2		10	17	12	15																	8	11								41
43								11	97												0.5				46						20																		43
45			100															3	5.5	32																											1					45
46				100																																															46
47					100																																														47
55													1																															3								55
59						100	100							93																																						59
61								89	2																						5																				61
63										100																																									63
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191																																																		100	191
no.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	

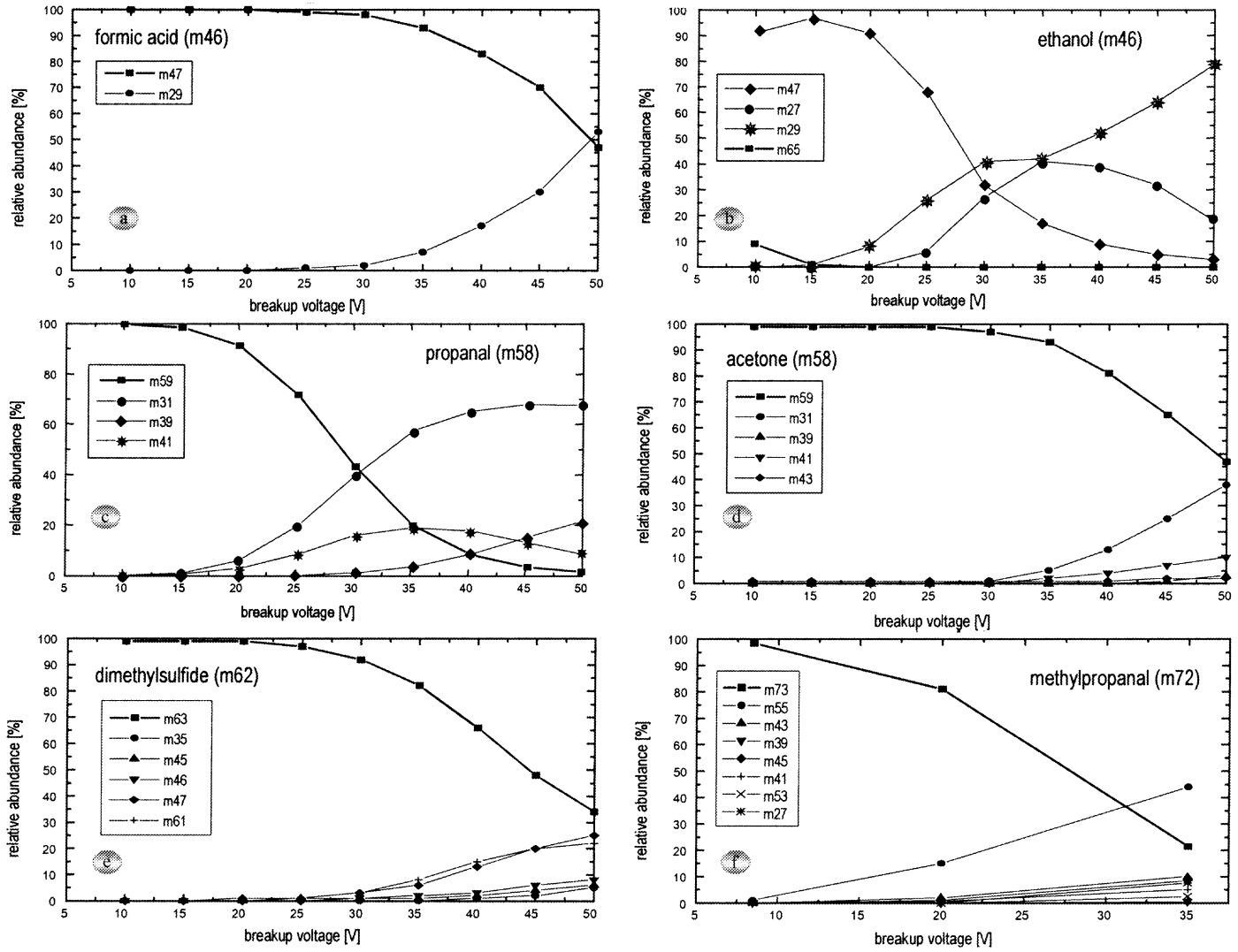

Fig. 2. Energy-dependent break-up patterns of VOCs. Neglecting the drift velocity caused by the flow velocity of the air through the drift tube (pumping), the break-up voltages applied in the final field region of the drift tube become proportional to collision energy.

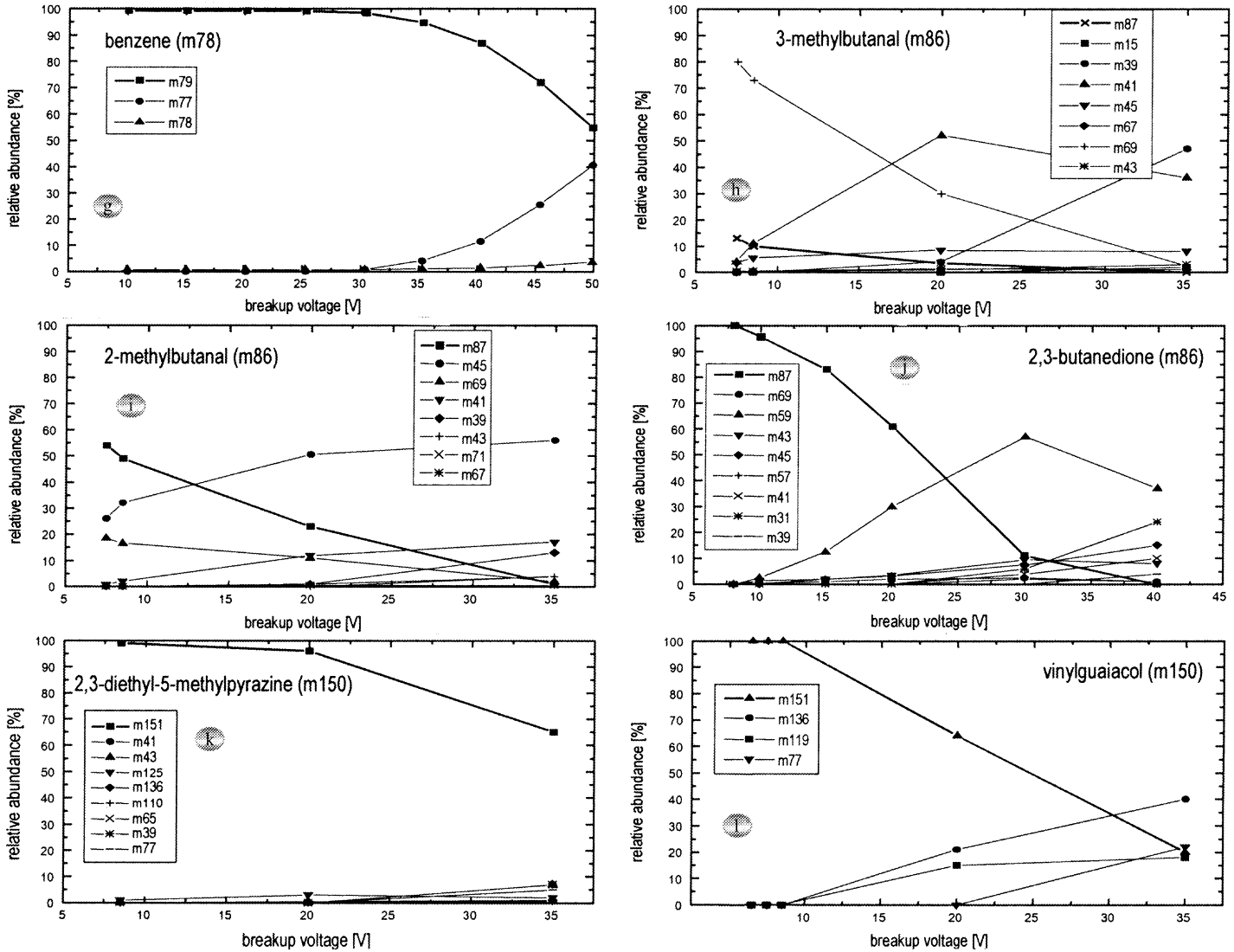

Fig. 2. (*Continued*).

2-Methylbutanal (Fig. 2h), 3-methylbutanal (Fig. 2i) and 2,3-butanedione (Fig. 2j) are isobaric within the resolution of the quadrupole MS. While 2-, and 3-methylbutanal have exactly the same monoisotopic mass (86,0731 amu), the mass of 2,3-butanedione is lower by 0.0364 mass units (86.0368 amu). All three compounds are of importance to coffee aroma. Energy-dependent break-up patterns help to distinguish the three pure compounds.

Finally the two VOCs 2,3-diethyl-5-methylpyrazine and vinylguaiacol in Fig. 2k and l are examples of VOC of higher masses. They differ in their monoisotopic mass by only 0.0476 mass units. Yet, energy-dependent break-up patterns allow distinguishing between the two compounds.

These examples illustrate that energy dependent break-up patterns can help distinguishing among isobaric compounds. For simple HS spectra with only a few compounds or spectra where a few compounds are dominating the HS, break-up experiments can provide conclusive evidence for an assignment. In the case of coffee, CID experiments are useful to assign the most intense peaks as well as to check for consistency of an assignment.

3.5. Bracketing proton affinities: proton transfer from H_3O^+ vs. NH_4^+

When H_2O is used as discharge gas in a hollow cathode ion source, due to fortuitous ion–molecule reaction sequences only H_3O^+ ions (with less than 5% of other traces) are extracted [74]. Similarly, when NH_3 is used, only NH_4^+ ions emerge from the source and can thus be used as primary reactant ions. While H_3O^+ ions transfer protons to all VOCs having a proton affinity higher than 166.5 kcal/mol, NH_4^+ transfer only protons to compounds with proton affinities in excess of 204.0 kcal/mol.

The non-selectivity of the ionisation process with H_3O^+ has various beneficial aspects to flavour science applications. In particular, it provides protonated mass spectral profiles that closely match actual HS distributions. Yet, for the purpose of chemical assignment, it can be interesting to have in addition a more selective ionisation. Changing the ionising agent from H_3O^+ to NH_4^+, we can eliminate from a PTR-MS profile compounds with proton affinities lower than 204.0 kcal/mol (an extensive list of proton affinities can be found in [75]).

Bracketing of proton affinities provides supporting evidence for chemical assignment. In combination with other pieces of evidence, it can help to identify compounds in the HS of coffee. In Fig. 3, the HS of coffee brew is shown, ionised with H_3O^+ and NH_4^+, respectively. Some mass peaks disappear or strongly decrease when NH_4^+ is used as primary reactant ion, indicating that the compound(s) contributing to the respective ion-masses have proton affinities lower than 204.0 kcal/mol. At other masses the intensities are hardly affected, indicating that these compounds have proton affinities higher than 204.0 kcal/mol.

3.6. Energy-dependent break-up patterns of coffee headspace

Just as energy-dependent beak-up patterns can be examined for pure compounds, one can increase the break-up voltage when a full coffee HS is being analysed. This results in a series of energy dependent HS profiles of coffee (Fig. 4). In analogy, the primary reactant ions can be switched from H_3O^+ to NH_4^+, to bracket proton affinities, and fragmentation can be induced by step-wise increasing the break-up voltage (Fig. 4).

For coffee, the complexity of the HS spectra makes this type of data rather difficult to exploit. Yet, one can imagine that once (i) a complete list of VOCs contributing to a PTR-MS HS, (ii) exhaustive databases of energy-dependent break-up patterns of pure compounds, and (iii) proton affinities are available, one could determine the HS composition (and concentrations) by fitting a series of break-up spectra of coffee HS collected at various energies with H_3O^+ and NH_4^+, as a superposition of a set of VOCs.

3.7. Liquid–gas partitioning

Recently, we have introduced a novel, dynamic technique to measure Henry's law constants (H)

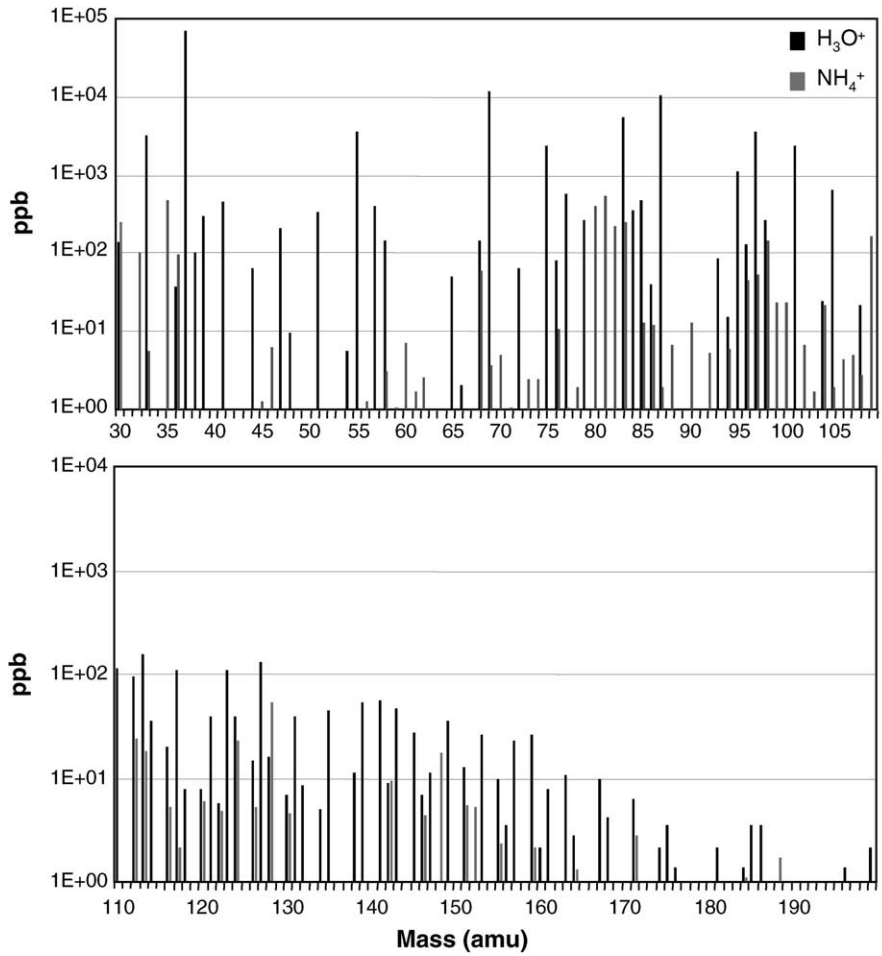

Fig. 3. HS profiles of coffee analysed by PTR-MS with different primary reactant ions. The black spectrum was ionised with H_3O^+ (proton affinity: 166.5 kcal/mol). In contrast, the grey spectrum was ionised with NH_4^+ ions (proton affinity: 204.0 kcal/mol).

[32,33]. Combining the concept of dynamic stripping of a solution by a flow of gas [76] with on-line measurement of VOCs by PTR-MS, a simple relation was derived which links the ratio, $\ln(\mathrm{cps}(t)/\mathrm{cps}_0)$, to the Henry's law constant, H:

$$\ln\left(\frac{\mathrm{cps}(t)}{\mathrm{cps}_0}\right) = -\frac{F}{HVRT}t,$$

H can be calculated from the slope, with $\mathrm{cps}(t)$ being the count rate of $[\mathrm{VOC}{\cdot}\mathrm{H}^+]$ at time t, and cps_0 being the count rate of $[\mathrm{VOC}{\cdot}\mathrm{H}^+]$ at time 0. Except H, all values in the slope are known (V: volume of liquid; F: gas flow through vessel; T: temperature; R: molar gas constant).

While the main objective of the method is to determine H, a particular variant of the method allows examining whether multiple compounds contribute to a given ion mass in PTR-MS.

Bubbling N_2 through liquid coffee, the concentration of the VOCs in the liquid will be reduced with time. The depletion is monitored by on-line analysis of the N_2 stripping-gas. Besides determining H from the slope we also obtain the count-rate (or concentration) at time '0' for each of the compounds (for details

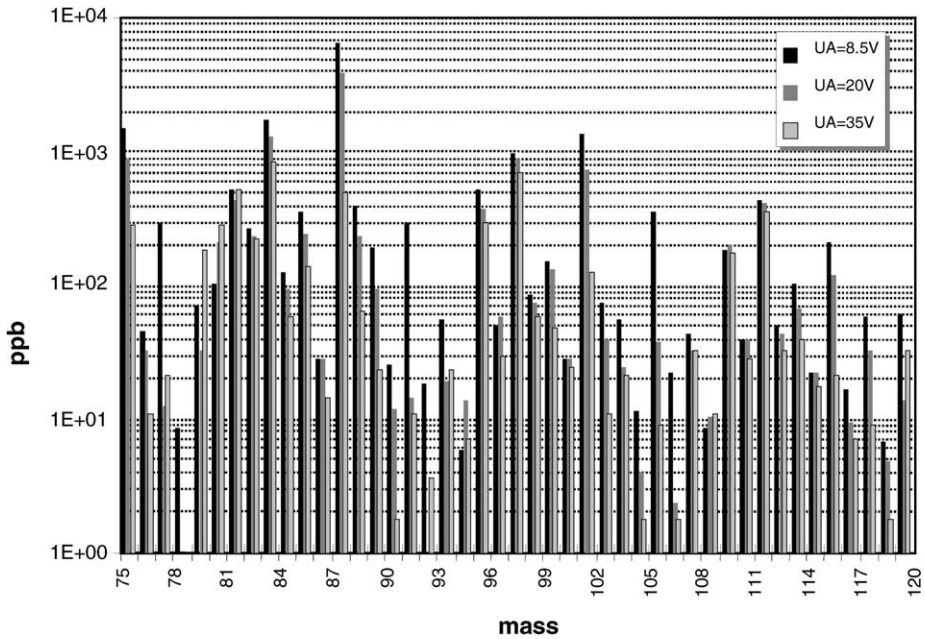

Fig. 4. Mass spectra obtained from HS air of coffee brew (Colombia, Arabica) using H_3O^+ primary ions. The different colours represent different break-up voltages as indicated. UA is the potential applied between the final two lenses in the drift tube in order to accelerate the protonated VOCs prior to leaving the drift tube and entering the mass filter.

see [32,33]). For this we extrapolate each linear section of the traces in Fig. 5 to time 0, and determine the respective count-rates at the intercept. In this way we obtain the percentage of each individual isobaric compound at time 0.

Four selected masses, 80, 81, 87 and 97 amu, are shown in Fig. 5. Here we will briefly discuss how to exploit these data. A more detailed analysis will soon be published [77].

3.7.1. Mass 80

At mass 80 (Fig. 5a), we find a linear relationship between time and $\ln(\mathrm{cps}(t)/\mathrm{cps}_0)$, over the entire time window of the experiments. This is indicative that only one compound is contributing to the ion intensity at 80 amu. From the coffee aroma literature (Table 2), we know that pyridine is the most abundant compound at mass 80 (protonated). Furthermore, Table 3 shows that pyridine does not fragment. Hence, we can establish with confidence that the only compound significantly contributing to the ion signal at 80 amu is pyridine.

3.7.2. Mass 97

As for mass 80, mass 97 shows a linear depletion with time over a very large HS concentration range. This is again indicative that one compound is dominating the PTR-MS HS intensity at this ion mass. Referring to Table 2, we can assign this mass peak to furfural. As for pyridine, furfural essentially does not fragment upon protonation (see Table 3). Hence, the ion signal observed at the ion-mass 97, is due to furfural.

3.7.3. Mass 81

After about 220 min of stripping we observe an abrupt change in the slope of the trace. This break is related to a change in volatility and hence to two compounds contributing to the mass spectral intensity at 81 amu. Stripping the coffee solution will predominantly deplete the most volatile compound. The compound of highest volatility initially dominates the slope. After 220 min, the most volatile compound is totally depleted and we observe a change (decrease)

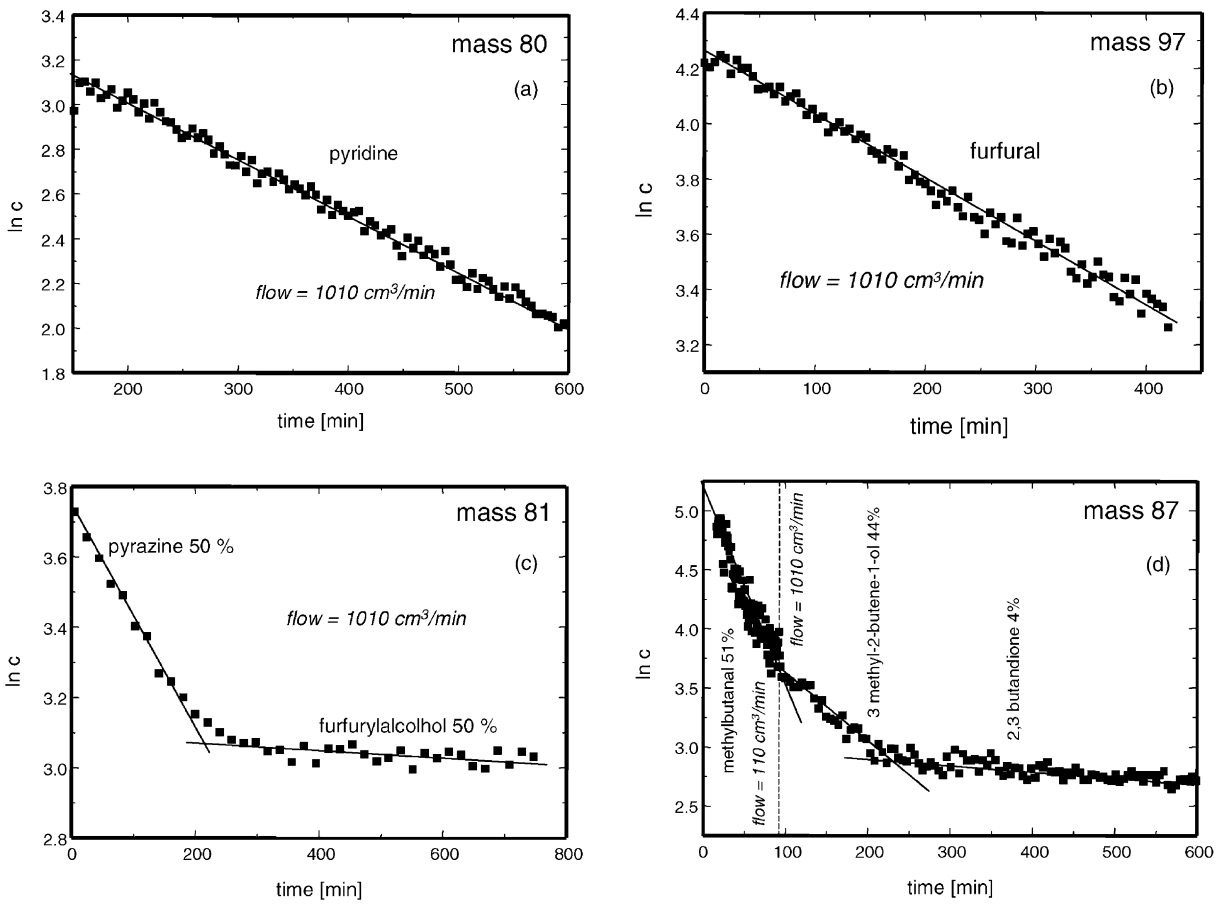

Fig. 5. Measuring on-line changes in the HS concentration of VOCs, while stripping a liquid coffee with a flow of N_2, one can asses whether one or multiple compounds contribute to a given mass, determine H and quantify the compounds in coffee. ln(c) is the ratio between the concentration at time t and the initial concentration and can be expressed as the natural logarithm of the ratio between count-rates at time 't' and count-rates at time '0'; ln(cps(t)/cps$_0$).

of the slope. From that time on, the most volatile compound among those remaining mainly determines the slope.

In order to identify the VOCs, we refer to Tables 2 and 3 and to reported Henry's lay constants for the potential candidates. Among the potential candidates, the one with the highest volatility will be first depleted. Without going into details (unpublished results), we can conclude that the compound being first depleted is pyrazine, while the second compound with lower volatility is furfurylalcohol (main fragment of furfurylalcohol at 81 amu; loss of H_2O).

3.7.4. Mass 87

At mass 87, breaks in the slope occur twice. Via an analysis similar to mass 81, we conclude that methylbutanal (2- and 3-), 3-methyl-2-butene-1-ol and 2,3-butanedione are the three major candidates. All three compounds are quite abundant in coffee (see Table 2). The most volatile of these compounds is methylbutanal [77]. The volatilities of the other compounds have not yet been determined. Based on arguments of polarity and dipole moment, we believe that 3-methyl-2-butene-1-ol is more volatile than 2,3-butanedione. Extrapolating the three linear

domains to time '0', we find that the mass spectral intensity at 87 amu is composed of 51% methylbutanal, 44% 3-methyl-2-buten-ol and 4% 2,3-butanedione.

4. Headspace composition of coffee based on PTR-MS data

In the preceding section, we have discussed a series of experiments and literature data that each provides relevant pieces of information towards linking measured mass spectral intensities to chemical compounds contributing to the respective peaks. Integrating and exploiting this information, Table 4 gives our current best estimate for the assignment of the PTR-MS brew HS in Fig. 1.

At this point, it must be clearly stated that PTR-MS can only give rough quantification, and should not be compared to more accurate and systematic approaches such as developed by Grosch [15]. Nevertheless, one should bear in mind that PTR-MS directly measures HS concentrations, and does not required calibration or addition of external standards.

Furthermore, the assignment shown in Table 4 has to be considered tentative. Yet, as PTR-MS is expected to become widespread within the flavour-science community, it is important to explore and develop means that assist in assigning ion-mass peaks of complex PTR-MS spectra, coffee being just one example. Here we propose a strategy for the chemical assignment of ion-peaks in PTR-MS. It consists in combining and cross-correlating various types of experimental data

Table 4
Assignment and rough concentrations of VOCs in the HS of coffee brew at 40° C

Mass	Compound	Proton affinity	Formula	Coffee (Colombia) (ppb)
42	Acetonitrile	188.2	C_2H_3N	35
45	Acetaldehyde	186.6	C_2H_4O	21500
47	Ethanol	188.3	C_2H_6O	20–30
47	Formic acid	178.8	CH_2O_2	160
59	Acetone	196.7	C_3H_6O	9200
59	Propanal	189.6	C_3H_6O	2300
61	Acetic acid	190.2	$C_2H_4O_2$	2000
63	Dimethyl sulfide	197.0	C_2H_6S	250
68	Pyrrole	207.6	C_4H_5N	90
69	Furan	192.2	C_4H_4O	5000
73	2-Butanone	199.8	C_4H_8O	7000
73	Isobutanal	∼192	C_4H_8O	8300
73	Butanal	192.6	C_4H_8O	<200
75	Methyl acetate	193.1	$C_3H_6O_2$	2300
80	Pyridine	220.8	C_5H_5N	320
81	Pyrazine	209.0	$C_4H_4N_2$	500
82	Methyl pyrrole		C_5H_7N	530
83	Methyl furan	204.0	C_5H_6O	5500
84	Methyl oxazole	>208	C_4H_5NO	20
85	Dihydro pyran	206.9	C_5H_8O	450
87	2,3-Butanedione	194.8	$C_4H_6O_2$	7000
87	2-Methyl butanal	∼195	$C_5H_{10}O$	5000
87	3-Methyl butanal	∼195	$C_5H_{10}O$	4500
89	Ethyl acetate	∼200	$C_4H_8O_2$	270
94	Methyl pyridine		C_6H_7N	6
95	Vinyl furan		C_6H_6O	870
95	Methyl pyrazine		$C_5H_6N_2$	230
96	Ethyl pyrrole		C_6H_9N	50
97	Furfural		$C_5H_4O_2$	3700
97	Dimethyl furan	213	C_6H_8O	95

Table 4 (*Continued*)

Mass	Compound	Proton affinity	Formula	Coffee (Colombia) (ppb)
98	Dimethyl oxazole	>208	C_5H_7NO	120
99	Furfuryl alcohol		$C_5H_6O_2$	900
100	Methyl thiazole		C_4H_5SN	14
101	2,3-Pentanedione	~207	$C_5H_8O_2$	3000
103	2-Hydroxy-3-pentanone		$C_5H_4O_3$	22
105	Methional		C_4H_8OS	30
109	Methyl vinyl furan		C_7H_8O	<150
109	2,3(-5,-6)-Dimethyl pyrazine		$C_6H_8N_2$	<250
110	2-Formyl-1-methylpyrrole		C_6H_7NO	60
	Acetyl pyrrole		C_6H_7NO	
111	5-Methyl furfural		$C_6H_6O_2$	1200
112	Trimethyl oxazole	>208	C_6H_9NO	28
113	Furfuryl methyl ether		$C_6H_6O_2$	160
115	Furfurylthiol		C_5H_6OS	600
115	Hexanedione		$C_6H_{10}O_2$	300
117	2-Oxopropyl acetate		$C_5H_8O_3$	60
123	2,3(-5,-6)-Ethyl methyl pyrazine		$C_7H_{10}N_2$	110
124	2-Acetyl-1-methylpyrrole		C_7H_9NO	21
125	Guaiacol		$C_7H_8O_2$	140
127	1,2,3(4)-Benzenetriol		$C_6H_6O_3$	130
135	6,7-Dihydro-5-methyl-5*H*-cyclopentapyrazine		$C_8H_{10}N_2$	3
137	Ethyl dimethyl pyrazine (isomers)		$C_8H_{12}N_2$	60
139	Dimethoxy benzene		$C_8H_{10}O_2$	80
141	Furfuryl acetate, Kahweofuran		$C_7H_{10}O_3$	80
143	Homofuraneol		$C_7H_{10}O_3$	40
148	Furfuryl pyrrole		C_9H_9NO	20
149	6,7-Dihydro-2,5-dimethyl-5*H*-cyclopentapyrazine		$C_9H_{12}N_2$	10
151	Diethyl methyl pyrazine (isomers)		$C_9H_{14}N_2$	10
151	4-Vinyl guaiacol		$C_9H_{10}O_2$	15
153	4-Ethyl guaiacol		$C_9H_{12}O_2$	20
153	Vanillin		$C_8H_8O_3$	10
157	Ethyl furaneol		$C_8H_{10}O_3$	22
181	3-Isobutyl 2-methoxy pyrazine		$C_{10}H_{16}N_2O$	8–9
191	(*E*)β-Damascenone		$C_{13}H_{18}O$	1–2

compiled in databases (HS concentrations, break-up patterns, proton affinities) for a given food product, in order to reach the most consistent chemical assignment. We have shown how to build and exploit such collateral information, and concluded with a tentative assignment of a coffee HS profile.

Finally, we would like to remind that the strength and prime reason for the remarkable rise of PTR-MS is its capacity to monitor on-line VOCs with a high time resolution (1 s) and sensitivity (sub-ppb HS concentrations). This has opened the possibility to investigate directly and in real time fast processes such as coffee roasting or flavour release. Hence, PTR-MS is best used in situations where the time–intensity behaviour of known VOCs is at stake. In order to identify unknown VOCs, various GC-based methods are more appropriate. PTR-MS is after all a one-dimensional method, and any confident assignment requires collateral information, such as discussed here.

5. Conclusions

Throughout this paper we presented means to link mass peaks in PTR-MS to chemical compounds. We have chosen to address this question on one of the

most challenging systems, namely coffee. A series of specific experiments were discussed, each one contributing to the chemical assignment of PTR-MS mass peaks. This includes information on fragmentation and energy-dependent break-up patterns, bracketing of proton affinities and liquid–gas partition coefficients. Integrating all this information, we have come up with a tentative chemical assignment for the HS composition of a coffee brew.

We would like to conclude by reminding the reader that often progress in science is closely linked to advances in analytical capabilities, opening up windows towards new and unexpected phenomena, and triggering novel applications. PTR-MS is definitely a method of this calibre.

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