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Characterization of wine with PTR-MS

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Abstract

A new method for measuring volatile profiles of alcoholic beverages (or other ethanol-containing analytes such as perfumes or herbs) has been developed. The method is based on proton transfer reaction mass spectrometry (PTR-MS). However, instead of hydronium ions (H_3O^+) protonated ethanol clusters ($C_2H_5OH_2^+(C_2H_5OH)_{n=1,2}$) are used as chemical ionization reagent ions. A stable reagent ion distribution is obtained by a 10-fold dilution of analyte headspace into ethanol-saturated nitrogen. Samples with different ethanol content can thus be directly compared. Characteristic mass spectral fingerprints have been obtained for four wine varieties. Principal component analysis discriminates between different wine varieties and shows specific correlations between wine variety and selected ions.

Keywords: Wine; Volatile profile; PTR-MS; PCA

1. Introduction

Rapid and low-cost methods enabling quality, origin and history assessment of food and raw products, including measurements on-site, are of urgent interest for industry. Traditionally used analytical techniques of food and flavor analysis and wine in particular include high pressure liquid chromatography (HPLC), gas chromatography (GC) [1–3], site-specific natural isotope fractionation–nuclear magnetic resonance (SNIF–NMR), isotopic ratio mass spectrometry (IRMS) [4], sensory analysis [5], and others. Use of these techniques can be highly selective and reliable, but they require expensive instrumentation, sample preparation, experienced operators and can hardly be fully automated. An increasing effort has been made to develop more rapid and informative analytical methods to explore the possibility of direct analysis of foods avoiding the need for specific fractionation procedures, which may alter the nature of the sample and may be accompanied by loss of certain compounds. Non-invasive and direct techniques include NMR spectroscopy [6], electronic tongues or noses [1] and direct mass spectrometric techniques such as atmospheric pressure chemical ionization (APCI) [7] and proton transfer reaction mass spectrometry (PTR-MS) [8–10].

PTR-MS has been used in recent years to classify different kinds of food products such as Mozzarella or Grana cheeses, juices and strawberries. Analysis of the volatile profile allowed to distinguish between:

- different types of Mozzarella depending on raw material and production process [11]
- different types of Grana cheeses depending on the place of origin [12]
- different types of juices based on pasteurization treatment [13]
- different types of strawberries based on cultivars [14]

Volatile organic compounds (VOCs) in the headspace of wine are responsible for its organoleptic characteristic and hence for its quality. Volatile compounds may also be correlated with the place of origin, treatment, adulteration and manufacturing process of the wine. As in the case of cheeses, juices or berries a fast non-invasive analysis of the VOCs may give a first indication of the quality or origin of wine. The aim of this work is to characterize wine by direct analysis of headspace

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VOCs. Compared to the other food so far analyzed with PTR-MS wine contains a large amount of ethanol. This interferes with the measurement principle of PTR-MS. PTR-MS is a chemical ionization mass spectrometry technique based on proton transfer reactions from H_3O^+ ions to VOCs with a linear range from 10 ppt_v to ~10 ppm_v. At ethanol volume mixing ratios (VMRs) > 100 ppm_v, however, H_3O^+ primary ions are depleted and protonated ethanol and protonated ethanol clusters are the dominating chemical ionization reagent ions. The basic principles for product identification and quantification which are at the base of standard PTR-MS operation [8,9] can no longer be applied. In this work, an experimental procedure is proposed by which mass spectral fingerprints of ethanol-containing analytes (e.g., the headspace of alcoholic beverages, herbs or perfumes) can be generated. It will be shown that PTR-MS can be used to determine VOC profiles of wine. Multivariate statistics will be applied to discriminate between different wine varieties.

2. Experimental

2.1. Set-up

A PTR-MS instrument operated at standard conditions (drift tube voltage: 600 V, drift tube pressure: 2.0 mbar) was used. A detailed description of the instrument is reported in literature [8,9]. A scheme of the inlet used for the measurement of ethanol-containing analytes is shown in Fig. 1. 18 ml/min of nitrogen are bubbled through a temperature stabilized (T = 28 °C) stripping cell containing 120 ml of absolute ethanol (99.8%, Sigma-Aldrich) or an ethanol/distilled water solution (5% or 10%, v/v). Under these conditions an ethanol saturated nitrogen flow is generated. A 20 ml wine aliquot is contained in a temperature stabilized (T = 28 °C) 40 ml vial (Supelco) capped with a Teflon septum. The wine headspace is flushed with 2 ml/min of nitrogen. This flow is 10-fold diluted into the ethanol/nitrogen flow downstream of the stripping cell. The ethanol concentration in the analyte headspace thus only marginally affects the ethanol concentration in the total flow. About 13 ml/min of the total flow are fed to the PTR-MS, with the overflow being discarded. The inlet lines are made of Silcosteel (Restek Corp., Bellefonte, PA, USA) and PFA Teflon. All inlet lines are heated to 60 °C. The PTR-MS drift tube is also kept at 60 °C.

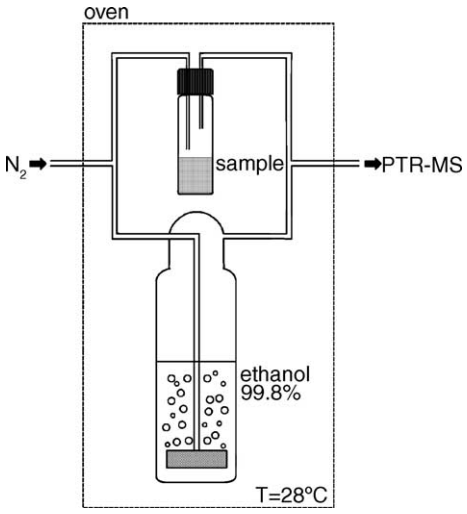

Fig. 1. Scheme of the experimental set-up.

2.2. Wine

Two varieties of red wine, Montepulciano d'Abruzzo (2002, 12% vol., Ora, Italy) and Chateau Fonfroide-Bordeaux (2001, 12% vol., Coubeyrac, France), and two varieties of white wine, Grüner Veltliner (2002, 12% vol., Keptal, Austria) and Chardonnay Veneto (2002, 11% vol., Chiari, Italy) were purchased in a local store. These will be referred in this study as MA, CF, GV and CV, respectively. Three bottles of each variety and four replicas of each bottle were analyzed. Samples were kept at 28 °C in closed vials 1 h prior to analysis.

2.3. Data acquisition and analysis

Mass spectrometric data were collected over a mass range of m/z 20–250 using a dwell time of 0.2 s per mass (46 s per cycle). Count rates were normalized to the total ion current (TIC). The average of the 3rd to 5th cycle for each sample was used for data analysis. Background values of an empty vial were subtracted. The Statistica program (StatSoft Inc., Tulsa, OK, USA) was used for principal component analysis (PCA). Only ions with significant differences between the four wine varieties were included in the PCA analysis.

3. Results and discussion

3.1. Ion chemistry

Identification and quantification of VOCs by PTR-MS is based on two major premises. First, the chemical ionization process is dominated by exothermic proton transfer reactions from H_3O^+ primary ions to organic molecules M to produce quasimolecular MH^+ ions which do not undergo secondary ion–molecule reactions. Second, pseudo-first-order kinetics applies, meaning that the H_3O^+ primary ion signal is not depleted by reactions with organic analyte molecules. Both premises are fulfilled for VOC VMRs < 10 ppm_v. These prerequisites are however not fulfilled for samples with high ethanol content, e.g., the headspace of alcoholic beverages or perfumes. In order to circumvent this problem analyte ethanol VMRs can be reduced by dilution. At high dilution rates, however, VMRs of other trace VOCs fall below the detection limit of the instrument. Since it is not possible to eliminate ethanol from analyte headspace without introducing artefacts, a different analytical approach has to be used.

By feeding ethanol saturated nitrogen to the PTR-MS H_3O^+ primary ions are converted to protonated ethanol ions and protonated ethanol cluster ions:

$$H_3O^+ + C_2H_5OH \rightarrow C_2H_5OHH^+ [m/z\,47] + H_2O \quad (1a)$$

$$C_2H_5OHH^+ + C_2H_5OH \xrightarrow{M} C_2H_5OHH^+(C_2H_5OH) [m/z\,93] \quad (1b)$$

$$C_2H_5OHH^+(C_2H_5OH) + C_2H_5OH \xrightarrow{M} C_2H_5OHH^+(C_2H_5OH)_2 [m/z\,139] \quad (1c)$$

M is a third body collision partner. Dehydration of product ions produces $C_2H_5^+$ [*m*/*z* 29], $C_2H_5^+(C_2H_5OH)$ [*m*/*z* 75] and $C_2H_5^+(C_2H_5OH)_2$ [*m*/*z* 121] ions, respectively. Different amounts of ethanol vapor were fed to the PTR-MS to investigate the influence on product ion distribution. Fig. 2 shows mass spectra obtained when (a) a 5% ethanol/water solution, (b) a 10% ethanol/water solution, and (c) absolute ethanol (99.8%) were placed in the stripping cell. As expected, the amount of cluster ions $C_2H_5OHH^+(C_2H_5OH)_{n=1,2}$ increases with the concentration of ethanol. As shown in Table 1 the most intense ions are $C_2H_5OHH^+$ [*m*/*z* 47] and $C_2H_5OHH^+(C_2H_5OH)$ [*m*/*z* 93] for 5% and 10% ethanol solutions. In these cases, however, H_3O^+ ions are still present, meaning that they act as competing chemical ionization reagent ions. In addition, the product ion distribution is sensitive to the ethanol concentration in the PTR-MS feed. For absolute ethanol, $C_2H_5OHH^+(C_2H_5OH)_{n=1,2}$ ions account for more than 90% of the total ion signal. The chemical ionization detection scheme for the detection of trace VOCs is thus simplified to two reaction channels: proton transfer reactions and ligand switching reactions from $C_2H_5OH_2^+(C_2H_5OH)_{n=1,2}$ ions [15]. An additional advantage of working with absolute ethanol is that its vapor pressure depends only on temperature and pressure, which are easily controlled and reproduced with the described experimental set-up. Concentrations of solutions may not be exactly reproducible and will change in time. Wine samples are thus optimally analyzed by diluting analyte wine headspace into an absolute ethanol/nitrogen gas stream. The $C_2H_5OHH^+(C_2H_5OH)_{n=1,2}$ distribution is not altered by the sample ethanol content and changes in the mass spectra are only due to proton transfer reactions and ligand switching reactions to other trace VOCs. Samples with different ethanol content can thus be directly compared and mass spectral fingerprints of different wine samples can be generated. Identification of VOCs would require a detailed $C_2H_5OHH^+(C_2H_5OH)_{n=1,2}$ + VOC ion chemistry study. This is beyond the scope of this paper and will be subject of forthcoming research. Absolute quantification of VOCs would require calibration, which will also be addressed in a future study.

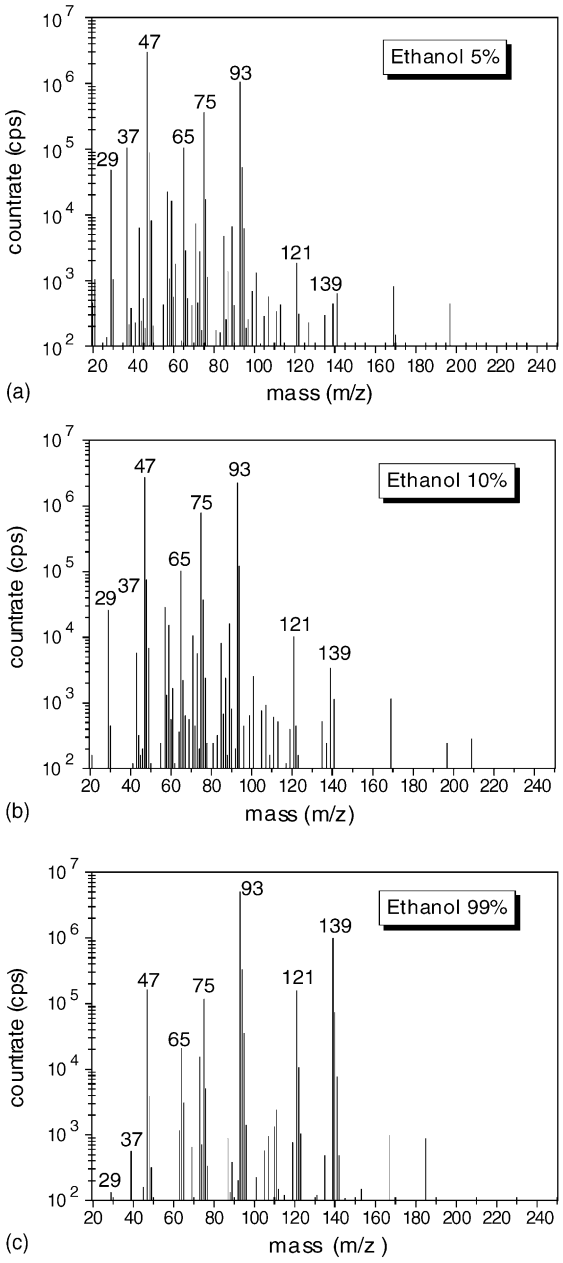

Fig. 2. PTR-MS mass spectra for a 5% ethanol/water solution (a), a 10% ethanol/water solution (b) and absolute ethanol (c).

3.2. Wine discrimination by PCA

PCA discriminates the investigated four wine varieties (Fig. 3). Different varieties are well separated and in the case of CV samples from the three bottles are discriminable. GV has a clearly distinct volatile profile compared to the other investigated wines. MA and CF, both red wines, have a closer volatile profile than the two white wines. By inspecting the associated loadings specific correlations between selected ions and wine varieties can be found. GV correlates with a large number of ions: *m*/*z* = 163, 115, 237, 71, 191, 83, 223, 177, 145, 131. CV has a high correlation with *m*/*z* = 81, 247 and

Table 1
Intensities of the major ions for ethanol solutions at 5%, 10% and 99.8%

m/*z*	Ion formula	cps			Relative percentage		
		Ethanol 5%	Ethanol 10%	Ethanol 99.8%	Ethanol 5%	Ethanol 10%	Ethanol 99.8%
19	H_3O^+	520,000	80,000	0	10.0	1.3	0.0
37	$H_3O^+(H_2O)$	105,453	35,840	0	2.0	0.6	0.0
29	$C_2H_5^+$	47,787	25,720	133	0.9	0.4	0.0
47	$C_2H_5OHH^+$	3,019,427	2,684,720	163,640	57.9	45.2	2.6
65	$C_2H_5OHH^+(H_2O)$	104,427	101,960	3,053	2.0	1.7	0.0
75	$C_2H_5^+(C_2H_5OH)$	360,827	773,680	117,520	6.9	13.0	1.8
93	$C_2H_5OHH^+(C_2H_5OH)$	1,051,613	2,223,800	4,960,427	20.2	37.4	77.6
121	$C_2H_5^+(C_2H_5OH)_2$	1,827	10,080	155,733	0.0	0.2	2.4
139	$C_2H_5OHH^+(C_2H_5OH)_2$	440	3,360	988,827	0.0	0.1	15.5

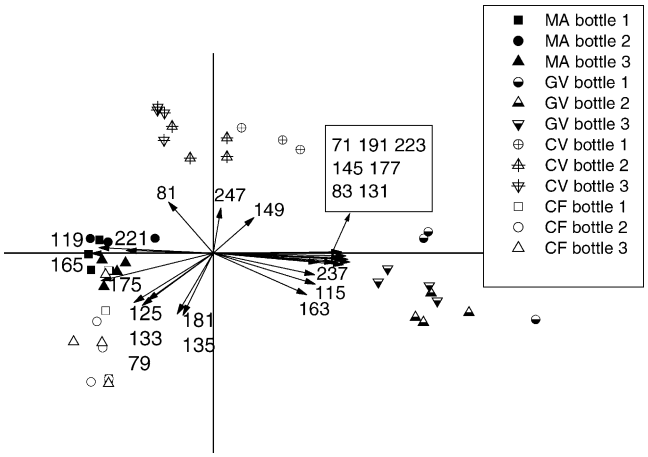

Fig. 3. PCA of PTR-MS wine data. Scores on wine samples and loadings of discriminant ions on the first (horizontal) and the second (vertical) principal component axes.

149. MA highly correlates with *m*/*z* = 119, 211, 165 and 175. CF correlates with *m*/*z* = 125, 133, 79, 181 and 135. As mentioned above, the identification of the ions is beyond the scope of this paper. No effort has been done in this direction but will be subject of forthcoming research.

Fig. 4 displays abundances of ions which show significant differences between various wine varieties. A characteristic pattern for each variety is observed. In particular, signals on *m*/*z* = 131, 71, 145, 191, 219, 173, 223, 115 are significantly enhanced for GV with respect to the other three varieties. This confirms the results obtained by PCA.

4. Conclusions

A new method to measure VOC profiles of alcoholic beverages (or other ethanol-containing analytes, e.g., perfumes or herbs) has been developed. Characteristic mass spectral fingerprints of different wine varieties have been

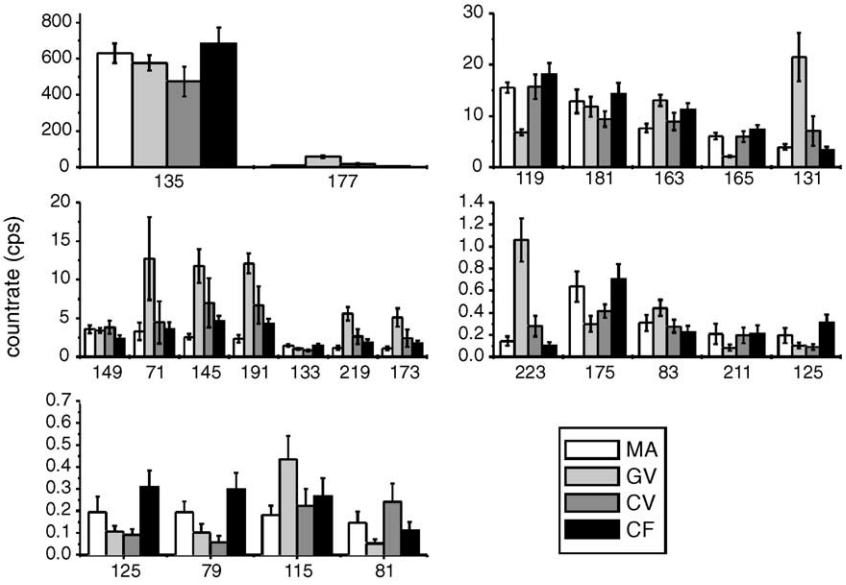

Fig. 4. Abundances (in decreasing order) of ions with significant differences between investigated wine varieties.

obtained. Possible future applications include quality control and production monitoring. Further research is needed to explore the possibilities of VOC identification and quantification.

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