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Modifying PTR-MS operating conditions for quantitative headspace analysis of hydro-alcoholic beverages. 2. Brandy characterization and discrimination by PTR-MS

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ABSTRACT

The characterization of the release of aroma compounds from beverages can bring pertinent information that can help in better understanding aroma perception. However, this kind of measurement is complex for high ethanol-containing beverages and needs to be adapted or optimized. Increasing the mean collision energy in the drift tube *via* the E/N ratio can be an interesting solution to prevent H_3O^+ depletion when high ethanol-containing samples, as distilled beverages for instance, are analyzed. However, the higher collision energy induced by these conditions impacts ionization reactions due to an increased number of fragmentation mechanisms, which could make data analysis difficult. The aim of the present study was to highlight the pertinence of using strong operating conditions ($E/N = 454$ Td) compared to reference conditions ($E/N = 120–140$ Td) for the analysis of 40% (v/v) ethanol-containing beverages. The first step was to better understand product ion distributions of 11 aroma compounds, known to be important for the overall flavor of brandies and prepared in 40% (v/v) ethanol/water solutions, at both operating conditions. As a validation, eight commercial brandies from different brands and with different aging times were analyzed under the two operating conditions. It appeared that the E/N value did not impact product ion distribution, but changed their relative abundances: increasing the E/N ratio increased fragmentation mechanisms, resulting in the detection of a greater proportion of low mass fragments to the detriment of protonated ions issued from aroma compounds. The response linearity of the PTR-MS was not modified at strong operating conditions. The application of these conditions to the analysis of brandies highlighted that, in spite of modifications on ionization mechanisms, products can be correctly discriminated, mainly according to their aging time.

1. Introduction

Proton Transfer Reaction Mass Spectrometry (PTR-MS) has been widely used in recent years as a pertinent analytical technique to characterize the release of volatile organic compounds (VOCs) from foods and beverages. This very powerful tool enables online monitoring of VOC releases during the consumption of food and represents a first step to better understand the construction of the dynamic aromatic perception, which needs to be considered in alcoholic beverages [1]. Its principle is based on the chemical ionization of VOCs under appropriate energetic conditions: H_3O^+ reagent ions, produced in the source, perform a proton transfer reaction with VOCs in the drift tube according to the following reaction: $H_3O^+ + VOC \rightarrow H_2O + VOC^{\bullet}H^+$ [2,3]. One advantage of using H_3O^+ ions as the reagent species is that they do not react with most of the natural components of air (CO_2, N_2, O_2) due to their proton affinities, lower than the one of water. In addition, the soft ionization conditions favor a non-dissociative process: only one product ion is formed for each analyte and it generally corresponds to the protonated molecule, which can be detected at the m/z (mass/charge) ratio equal to its molecular mass plus one [2,4,5]. Ionization conditions are determined by the value of the mean collision energy between VOCs and neutrals in the drift tube, which can be controlled by the modification of the E/N ratio: E represents the electric field strength and N the buffer gas density in the drift tube [2]. Standard drift tube conditions (E/N ratio = 120–140 Td)

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ensure low compound fragmentation and low water cluster formation, thus leading to stable analysis conditions [2,6,7]. However, in practice, fragmentation mechanisms can be observed for some molecules: for example, it is well know that alcohols and aldehydes, after being protonated by H_3O^+ reagent ions, easily loss a water molecule even under standard operating conditions [2,8]. In the case of alcoholic beverages like brandies, hundreds of volatile compounds are present and can lead to difficulties in interpreting the mass spectrum: several isobaric ions can be formed from different parent compounds, especially when analyzing complex mixtures [9]. Besides, as reported by Boscaini et al. (2004) and Spitaler et al. (2007), the main problem concerning the analysis of ethanol-containing beverages concerned the depletion of H_3O^+ reagent ions by ions from ethanol, which led to unstable analysis conditions and modifications of ionization mechanisms [10,11]. To overcome these limits, Boscaini et al. (2004) proposed to dilute sample headspace with a flow of ethanol-saturated nitrogen, which led to the total replacement of H_3O^+ reagent ions by protonated ethanol and protonated ethanol clusters [10]. Another solution proposed by Spitaler et al. (2007) consists in sample dilution with a nitrogen flow in order to minimize the ethanol content transmitted to the drift tube and to maintain H_3O^+ reagent ion abundance at an acceptable level [11]. The main drawback of these solutions is that an important dilution of sample headspaces, and thus of VOCs, can be needed according to the ethanol content in the beverage liquid phase. From a practical point of view, both solutions require the setting up of an additional dilution/saturation upstream system. Also, when H_3O^+ reagent ions are replaced by protonated ethanol and protonated ethanol clusters, several ethanol-based product ions are detected. The overlapping effect of ions issued from the ethanol can lead to a complication of the final mass spectrum and its interpretation. As far as we know, most PTR-MS studies in literature dealing with alcoholic beverages focused on wine or on samples with ethanol content around 10–15% in the liquid phase [10,11]. No study has yet focused on the characterization of distilled beverages by PTR-MS due to the problem of ethanol content and of the high number of ions detected. In consequence, the PTR-MS analyses of alcoholic beverages such as liquors and spirits still represent a challenge to overcome. In the case of ethanol-containing samples, it could be interesting to work with higher E/N values in the PTR-MS drift tube to avoid the depletion of H_3O^+ reagent ions: the application of appropriate operating conditions could help in analyzing samples with high ethanol content [12]. However, working at increased values of E/N has major consequences on product ion distribution: compound fragmentation patterns and product ion distribution can be modified by the variation of the mean collision energy. At increased E/N ratios, the high mean collision energy between ions produced by the reaction between H_3O^+ and the buffer gas leads to collision-induced dissociations (CID) [7,13,14]. For example, Hansel et al. (1995) showed that the reaction between H_3O^+ reagent ions and isopropanol ions C_2H_7OH can produce both protonated molecular ions $C_2H_7OH^{\bullet}H^+$ and fragment ions $C_3H_7{}^+$ in varying proportions, depending on the applied kinetic energies [15]. More recently, Demarke et al. (2010) showed that the product ion distributions of some unsaturated biogenic alcohols (2-methyl-3-buten-2-ol, 1-penten-3-ol, cis-3-hexen-1-ol, trans-2-hexen-1-ol, 1-octen-3-ol, DL-6-methyl-5-hepten-2-ol, linalool) were influenced by the E/N ratio [16]. On the basis of these observations, the objective of this study was to evaluate the applicability of applying high mean collision energy in the drift tube ($E/N = 454$ Td), previously defined as appropriate operating conditions for 40% (v/v) ethanol-containing sample, for the analysis of high ethanol-containing beverages such as brandies [12]. The approach involved the analysis of the fragmentation patterns of 11 VOCs commonly found in brandies [17], prepared in 40% (v/v) ethanol/water solutions at strong PTR-MS operating conditions. As a validation, these conditions were applied to discriminate eight different brandies from their headspace characterization. Results were compared to the ones obtained with standard operating conditions to highlight the interest of such an approach.

2. Materials and methods

2.1. Samples

2.1.1. Hydro-alcoholic solutions

Forty percent (v/v) hydro-alcoholic solutions were used to study VOC fragmentation patterns, product ion distributions and PTR-MS response linearity. They were prepared with mineral water (Evian, Danone, France) and food grade anhydrous ethanol with purity higher than 99.5% (Carlo Erba Reagents, France). Eleven VOCs with purity of 98% or better (Sigma–Aldrich) were selected for their known contribution to the aromatic profile of brandies [17–21]. They were individually added to hydro-alcoholic solutions (nos. 1–11) (Table 1). VOC concentrations were increased compared to levels usually found in brandies in order to have a good signal response (PTR-MS sensitivity was taken into account). Solutions nos. 6, 6^1, 6^2, 6^3 and 6^4, containing different amounts of ethyl hexanoate, were used to determine the response linearity of the PTR-MS instrument. Solution no. 12 contained only ethanol and water and was used as a control to determine ions issued from ethanol. Three replicates were tested for each solution.

Table 1
VOC molecular weights and concentrations (g/L) in hydro-alcoholic solutions.

Solution number	Name	IUPAC[a] nomenclature	Molecular weight (g/mol)	VOC concentration (g/L)
1	Isoamyl alcohol	3-Methylbutan-1-ol	88	9.0
2	Phenethyl alcohol	2-Phenylethanol	122	3.5
3	Linalool	3,7-Dimethylocta-1,6-dien-3-ol	154	2.5
4	Trans-3-hexen-1-ol	Trans-3-hexen-1-ol	100	3.0
5	Ethyl acetate	Ethyl acetate	88	8.0
6	Ethyl hexanoate	Ethyl hexanoate	144	0.02
6^1	Ethyl hexanoate	Ethyl hexanoate	144	0.2
6^2	Ethyl hexanoate	Ethyl hexanoate	144	0.6
6^3	Ethyl hexanoate	Ethyl hexanoate	144	1.1
6^4	Ethyl hexanoate	Ethyl hexanoate	144	2.2
7	Isoamyl acetate	3-Methylbutyl acetate	130	3.0
8	Diacetyl	Butane-2,3-dione	86	4.5
9	Whisky lactone	5-Butyl-4-methyldihydrofuran-2(3H)-one	156	12.5
10	Furfural	Furan-2-carbaldehyde	96	8.0
11	Acetaldehyde	Ethanal	44	7.5
12	Water–ethanol 40% (v/v) (control)			

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