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Coupling gas chromatography and electronic nose for dehydration and desalcoholization of alcoholized beverages Application to off-flavour detection in wine

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Abstract

Aroma characterization of alcoholic beverages with sensor array electronic noses is a difficult challenge due to the masking effect of ethanol. Back-flush gas chromatography is proposed as a novel tool for the pretreatment of vapour samples before analysis in the electronic nose. The dehydration and desalcoholization step can be conducted in parallel with electronic nose detection, reducing significantly the analysis overall duration. As demonstration application, five molecules responsible for off-flavours in wines have been detected with a FOX 4000 system, after total dehydration and desalcoholization. Principal component analysis showed that discrimination between the control wine and off-flavour doped-wines became easy, even at concentrations corresponding to the human expert perception threshold.

Keywords: Electronic nose; Gas chromatography; Desalcoholization; Dehydration; Wine; Off-flavour

1. Introduction

Volatile compounds define the nature and quality of a particular food and contribute to consumer preferences. They are also invariably liable for off-flavour and taint occurrences, which arise due to chemical or biochemical changes, microbial action or contamination. Currently, there are two basic techniques available to assess flavour quality: first, the use of a panel of trained experts who carry out sensory analysis based on flavour, taste and colour. The expert panel may be affected by problems concerning the standardization, the training quality of the panel members and the stability and reproducibility of the evaluation. The second method is the Gas Chromatography/Mass Spectrometry (GC/MS) coupling, which enables identification and quantification of volatile compounds in most foods and beverages. The drawback of this method is the time required for a single analysis.

Electronic noses are thought to emerge as a third possibility for aroma profile analysis. According to the usually accepted definition [1], an electronic nose is a device composed of an array of gas sensors, with non-specific responses, having pattern recognition ability from the multivariate data analysis of the whole set of responses. These systems usually give comparative rather than quantitative or qualitative informations. They have been developed since the early 1980s [2], principally using metal-oxide semiconductor sensors [2,3], surface acoustic wave (SAW) sensors [4] and quartz resonators [5]. In the case of metal oxyde semiconductor (MOS) sensors, adsorption of volatile molecules on the sensor surface induces an oxido-reduction reaction, which affects the electric conductivity of the sensors.

The analysis of alcoholic beverages with semiconductor-based electronic noses is a difficult challenge due to the non-specificity of the sensor arrays and principally to the presence of high ethanol and water concentrations in the samples. Indeed, in a wine sample, the aroma compounds amount only

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to about 1 g/l, while water and ethanol amount to about 100 and 900 g/l, respectively. Water contributes to the shortening of the sensor span life and increases the signal drift with time, while ethanol masks the presence of other volatile compounds [6].

Although alcoholic beverages discrimination using electronic noses has been already reported in the scientific literature, it is believed that this discrimination most often reflects mere variations in the sample alcohol content and not true differences in the aroma profiles [7–10].

To overcome this problem, various desalcoholization procedures have been proposed [11], such as thermal techniques (distillation), adsorption methods (trap and purge, and non-polar resins), membrane systems (reverse osmosis and pervaporation) and liquid–liquid extraction. None of these methods allowed a complete removal of alcohol.

In this study, the aim was to develop a method for the detection of off-flavours in wine using an electronic nose, based on a new pre-treatment technique for complete sample desalcoholization and dehydration using gas chromatography

2. Materials and methods

A FOX 4000 from AlphaMOS (Toulouse, France) was used as the electronic nose system. The instrument consists principally in eighteen different MOS sensors, disposed in three temperature-controlled chambers, and software for hardware monitoring, data pre-processing, and statistical analysis.

The MOS sensors consisted of a ceramic substrate (round or flat), heated by means of a resistor and coated by a metal-oxide semi-conducting film (mainly zinc oxide, tin dioxide, titanium dioxide or iron (III) oxide), which responds to oxidizing compounds, or of the P-type (mainly nickel oxide or cobalt oxide), which responds to reducing compounds. A generator of purified air (Whatman), with a $CaCl_2$ post-dehydration column was used to provide clean dry air to the system.

Gas samples with standardized aroma composition were generated from 10-ml wine samples (Table 1), maintained at equilibrium at 50 (±0.2) °C in a 30-ml-mixing vessel. A 1 ml volume of head-space was introduced in a GC (Intersmat IGC 121C) equipped with a Porapak Q column (1 m × 0.32 cm). Three multi-way electro-valves were used respectively for automatic injection in the GC, column back flush and automatic injection in the electronic nose. Figs. 1 and 2 presented a schematic view of the experimental set-up and of the back-flush system, respectively.

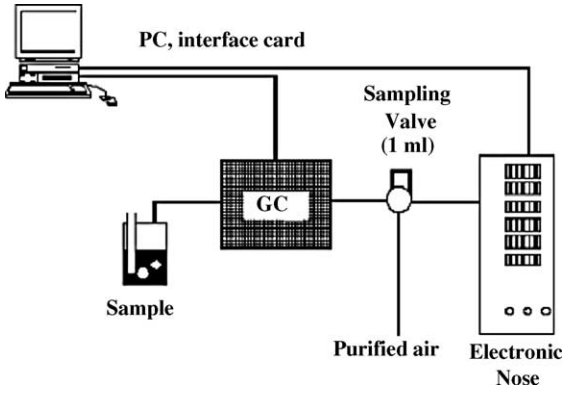

Fig. 1. Overview of the coupling GC and electronic nose system.

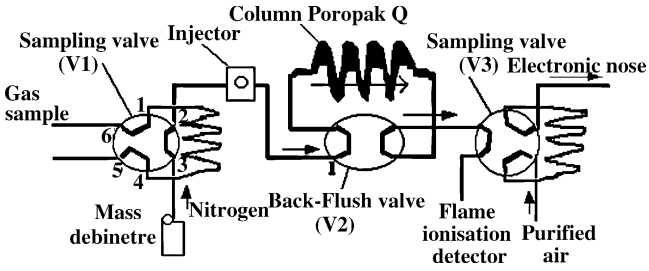

Fig. 2. Back-flush system used for headspace desalcoholization and dehydratation: V1—automatic injection in the GC; V2—dehydration–desalcoholization (back-flush) and V3—automatic injection in the electronic nose.

The GC and the FOX were interfaced using LabVIEW (National Instruments) with a computer that collected the chromatographic data using an analog to digital converter board (National Instruments) and the gas sensor array signals via an RS-232 communication port. The treatment and analysis of the samples were run simultaneously, the electronic nose measuring the dealcoholized sample while the GC was dealcoholizing the next sample.

Table 1
Theoretical head-space composition of solutions equilibrated at 50 °C, containing ethanol at 12% (v/v) and various aroma compounds at their off-flavour threshold concentrations

Compounds	Liquid		Gas	
	Concentration (g/l)	Relative mass (%)	Mass (%)	Relative mass (%)
Ethyl acetate	20×10^{-3}	0.021	0.013	0.085
Hexan-1-ol	4×10^{-3}	0.0042	0.00084	0.0056
Oct-1-en-3-ol	20×10^{-9}	0.00002	0.000022	0.00015
2,4,6-Trichloroanisole	12×10^{-9}	0.00001	0.000018	0.00012
4-Ethyl phenol	4×10^{-3}	0.0042	0.0064	0.042
Ethanol	96	100	15.1	100
Water	878	–	84.9	–