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Use of synthetic wine for models transfer in wine analysis by HS-MS e-nose

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ABSTRACT

A method to verify the feasibility of the calibration transfer technique in HS-MS wine analysis is proposed. PLS multivariate calibration models, whose elaboration and prediction quality are fully discussed, have been built for the quantitative determination of three of the most common volatiles found in wine aroma: ethyl hexanoate (EH), isoamyl acetate (IA) and 2-methyl butanol (MB). The method involves the use of a fortified synthetic wine to overcome the instability drawbacks related to the natural evolution of real wines. The results showed a decrease of the prediction error through the time for the three compounds when the calibration transfer is applied.

1. Introduction

Aroma is a fundamental parameter to define the quality of wines. It is composed by hundreds of volatile chemical compounds which belong to very heterogeneous groups such as alcohols, esters, acids, aldehydes, ketones, etc. and that are present at very different concentration levels (from several mg/L to a few ng/L). Due to this complexity, the most widely used technique to determine the aroma composition has been the conventional gas chromatography (GC) [1], which, although slow, is very effective in this kind of analysis, especially when it is coupled to a mass detector. However, to evaluate the aroma properties, sensory analysis becomes imperative, although it is time consuming and requires a trained panel of tasters, which implies subjectivity on the response and variability between individuals [2]. To overcome these limitations and obtain fast and objective aroma information, in the last 25 years new techniques have been studied, such as electronic noses, whose main advantage over other techniques is that they give analytical responses in a few minutes and, as in GC methods, from the overall volatile composition of the samples [2–11].

The most common type of electronic noses is the one based on the interaction of compounds of the headspace with a series of gas sensors whose physic-chemical properties determine the instrumental response, giving a "fingerprint" of the samples analyzed that can be used, by means of suitable chemometric tools, to characterize and classify wines. However, when dealing with spirits, these gas sensors are not suitable enough because ethanol, due to its predominance in the headspace, overlaps the response of other volatiles. For this reason, some sample pretreatments must be carried out [12], which slow down the analysis. In addition, sensor passivations cause a great variability on the responses and, as a consequence, the reliability of the models must be continuously checked.

At the end of the 90s, a new type of e-noses appeared, based on coupling the headspace (HS) with mass spectrometry (MS) technique. In HS-MS systems, the volatile compounds in the headspace of the sample are injected directly in the ionization chamber of the mass spectrometer, where they are fragmented. The result is a global mass spectrum for each sample analyzed that constitutes, as in gas sensor e-noses, a sample fingerprint. When dealing with HS-MS e-noses, no sample pretreatment is needed because the interference of the ethanol can be skipped by instrumentally avoiding the spectra fragments resulting from the ethanol ionization. Furthermore, the run times are usually very fast (1–5 min/sample), mainly when an autosampler is used. Many applications of HS-MS e-noses can be

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found in literature, especially related to wine characterizations [13–18].

However, this technology (also called chemical sensor), exhibits a great problem of instability due to loop HS autosampler contaminations and to the MS itself, as a result of the fouling of the ion source, the vacuum instability or the aging of the ion multiplier [24]. If these effects are not corrected, a high irreproducibility, a gradual drift and a loss of sensitivity [19,20] eventually lead to unsuitable calibration models.

In order to solve the signal instability problems of the HS-MS e-nose, different strategies have been proposed: (a) addition of He–Xe [21] to normalize the abundances of each ionic fragment with respect to ^{129}Xe; (b) use of an internal standard [22] to rate each mass intensity to the intensity of the fragment corresponding to the internal standard; (c) and calibration transfer [23], in which transfer samples (samples of known properties) are processed together with the samples used to build the calibration models.

The principal advantage of the calibration transfer method is that it allows the correction of the signal variations in an independent way in each mass-to-charge ratio (m/z). This overcomes the problem when a signal increases for a fragment and decreases for another one. Moreover, the analysis of an additional sample set is not a problem for a fast technique like HS-MS and it avoids the interference caused by the addition of a standard to the samples. These advantages have favoured the use of the transfer calibration method in many applications [24–29].

However, in the HS-MS e-nose calibration step, one of the most important drawbacks found when preparing the wine aroma transfer samples is that these samples are intrinsically unstable and usually irreproducible, since wines evolve continuously, even being bottled. So, to get reliable results it is important to have a standardized method for preparing and using these standards.

In the present work we propose the use of synthetic wines as transfer samples. To verify the reliability of the calibration transfer, the methodology has been applied to the quantification of three of the most characteristic volatile compounds in wine aroma.

2. Materials and methods

2.1. Instrumental

All analyses were performed with an HS-MS e-nose comprising an HP 7694 static headspace sampler, an HP 6890 gas chromatograph and an HP 5973 quadrupole mass spectrometer from Hewlett–Packard (Waldbronn, Germany). With this setup, the function of the gas chromatograph was to transfer the volatiles to the MS and not to chromatographically resolve the peaks. So, the analytical column (HP-5MS) was always used in temperature conditions that guarantee the total sample transference in less than 5 min. The softwares used for data collection and analysis were Pirouette 4.0 from Infometrix, Inc. (Woodinville, WA, USA) and PARVUS [30].

2.2. Samples and standards

To build and validate the different models, we selected three wines: a red, a rosé and a white wine, all of them with neutral aroma, that is, wines with no predominant note. All the samples were stored under nitrogen atmosphere, in darkness and at 4 °C to guarantee their stability.

For the calibration transfer, we elaborated five different synthetic wines by diluting 3.5 g of tartaric acid and 120 mL of ethanol in a suitable amount of Milli-Q quality water to give 1 L of solution and adjusting the pH to 3.5. Moreover, to obtain a matrix as similar as possible to a real wine sample, we added 25 of the main wine volatiles at different concentrations inside the usual range of concentration of these compounds in real wine [31] (Table 1). These samples were also stored in darkness, under nitrogen atmosphere and at 4 °C.

The different aroma chemicals (purity >97%) added to the synthetic wine were supplied by Sigma–Aldrich (Madrid, Spain) and Fluka (Madrid, Spain). All the other chemicals and reagents used were of analytical grade.

Stock solutions of the standards chosen for the calibration transfer (ethyl hexanoate (EH), isoamyl acetate (IA) and 2-methyl butanol (MB)) were prepared in ethanol to give final concentrations

Table 1
Concentration (mg L^{-1}) of the different chemical added to the 5 synthetic wines and usual range (mg L^{-1}) of these compounds in real wines [30].

Compound	Range	Wine A	Wine B	Wine C	Wine D	Wine E
Methanol	40–120	70	110	90	100	50
1-Propanol	10–50	15	30	45	25	40
2-Methyl 1-propanol	45–140	60	85	130	105	90
2-Methyl 1-butanol	50–80	55	50	65	60	75
3-Methyl 1-butanol	120–320	140	300	270	160	220
2-Phenylethanol	20–130	90	65	110	55	30
Ethyl butyrate	0.01–4.0	0.9	3.0	2.5	1.5	3.5
Ethyl 2-methylbutyrate	0.05–1.0	0.1	0.6	0.8	0.2	0.1
Ethyl 3-methylbutyrate	0.01–0.04	0.02	0.01	0.04	0.03	0.02
Ethyl hexanoate	0.02–2.0	1.0	1.5	0.5	0.1	0.1
Ethyl octanoate	0.05–3.0	0.5	2.0	2.5	1.5	0.1
Ethyl decanoate	0.0–2.0	0.5	1.5	1.0	1.2	0.01
Ethyl acetate	30–150	130	90	100	45	70
Methyl 2-propyl acetate	0.01–1.0	0.1	0.6	0.5	0.1	0.03
Methyl 3-butyl acetate	0.03–10	2.0	6.0	0.7	8.0	3.0
Hexyl acetate	0.0–0.5	0.4	0.4	0.1	0.1	0.2
Phenylethyl acetate	0.01–2.0	1.0	1.8	0.1	0.5	0.7
Ethyl lactate	10–300	250	160	55	90	200
Acetic acid	50–600	550	420	95	160	310
2-Methyl propanoic acid	1.0–6.0	5.0	2.0	5.5	3.0	4.3
Butyric acid	1.5–4.0	1.9	2.5	2.2	3.5	3.0
3-Methyl butyric acid	0.5–5.0	4.0	1.0	3.0	5.0	2.0
Linalool	0.001–0.01	70	110	90	100	50
Ethanal	5.0–100	15	30	45	25	40
Dicacetyl	2.0–3.0	60	85	130	105	90