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Detection and Quantification of Natural Contaminants of Wine by Gas Chromatography−Differential Ion Mobility Spectrometry (GC-DMS)

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ABSTRACT: Rapid and direct, in situ headspace screening for odoriferous volatile organic compounds (VOCs) present in fresh grapes and in wines is a very promising method for quality control because the economic value of a wine is closely related to its aroma. Long used for the detection of VOCs in complex mixtures, miniature differential ion mobility spectrometry (DMS) seems therefore adequate for in situ trace detection of many kinds of VOCs of concern appearing in the headspace of selected foodstuffs. This work aims at a rapid detection, identification, and quantification of some natural and volatile contaminants of wine such as geosmin, 2-methylisoborneol (2-MIB), 1-octen-3-ol, 1-octen-3-one, and pyrazines (2-isopropyl-3-methoxypyrazine, IPMP, and 3-isobutyl-2-methoxypyrazine, IBMP). In the present study, these compounds were spiked at a known concentration in wine and analyzed with a hyphenated trap-GC-DMS device. The detection of all target compounds at concentrations below the human olfactory threshold was demonstrated.

KEYWORDS: *headspace analysis, wine, geosmin, 2-methylisoborneol (2-MIB), pyrazines (IPMP, IBMP), 1-octen-3-ol, 1-octen-3-one, differential ion mobility spectrometry (DMS)*

INTRODUCTION

The high sensitivity of ion mobility spectrometry (IMS) toward compounds having a high electronegativity or proton affinity, fast response time, and hand-held portability make IMS analyzers ideally suitable for detecting trace amounts of certain chemicals.[1] The first instruments were developed in early 1970, mainly for military applications[1−3] or for the detection of toxic compounds in industrial environments.[4−6] With the end of the Cold War, the IMS technology became applicable also in other fields such as medical diagnostic and control of bioprocesses (environmental and biological applications).[7] Thus, IMS also appears to be a promising tool in biomedical analysis, especially for the rapid and noninvasive diagnosis of respiratory diseases. In this context, the detection of volatile biomarkers in exhaled breath for the early detection of lung, kidney, or liver disorders by conventional IMS has been reported.[8,9]

Another type of IMS is differential ion mobility spectrometry (DMS). The advantages over conventional IMS include higher sensitivity, simpler construction, and excellent scaling for microfabricated devices.[3,10] A prominent example of field deployment of this analytical technique is the recent validation trial of a gas chromatography−differential ion mobility spectrometer (GC-DMS) installed on the International Space Station. In these tests, the on-board real time analysis was validated against grab-samples obtained within the space station and returned to Earth for analysis by gas chromatography−mass spectrometry (GC-MS). Most of the investigated volatile organic compounds were correctly identified and accurately quantified by the GC-DMS.[11]

Although the use of IMS for detecting organic compounds in aqueous samples has rarely been reported in the literature, this approach seems very promising because most of the other analytical methods involve time-consuming sample preparation and treatment steps, including the use of organic solvents prior to the analysis. With IMS methods, no sample pretreatment steps are usually required and, ideally, the analyte is separated from the aqueous matrix without using any organic solvent.

With regard to foodstuffs and beverages, the pioneering application of ion mobility spectrometry for industrial processing and quality testing purposes was the monitoring of the beer fermentation process using GC-UV-IMS.[12] By using the implemented method, it was possible to perform online process control and optimization, which allowed the fermentation duration to be shortened. Besides, the potential of GC-UV-IMS instruments to perform qualitative analysis of white and red wines has been mentioned in the context of food quality and safety assessments.[13] A recent paper has focused on qualitative wine headspace analysis and demonstrated a successful discrimination of white wines issued from four wine-growing regions.[14] In this study, a large data set collected with a portable UV-IMS spectrometer (GAS GmbH, Dortmund, Germany) has been postprocessed by the combined use of principal component analysis (PCA), linear discriminant analysis (LDA), and *k*-nearest neighbor classifier (kNN), resulting in a successful discrimination with a very high score. Some attempts to analyze the direct headspace of liquid foodstuffs and beverages have also been demonstrated with a

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stand-alone, chip-based field asymmetric ion mobility spectrometer (FAIMS, from Owlstone Nanotech Inc., Cambridge, UK). The authors focused on achieving a rapid detection of the industrial trace contamination of milk[15] and also a detection of 2,4,6-trichloroanisole (TCA) in wine, responsible for highly undesirable cork taint.[16] More recently, an investigation employing a nonpolar gas chromatographic column coupled to a portable Tourist (Owlstone Nanotech Inc.) detector incorporating a multichannel FAIMS chip identical to that used in the previous study aimed at the detection of ethyl acetate in wine.[17] Whereas ethyl acetate is the most common ester in wine and contributes to the perception of depth and richness of its body, excessive amounts are considered to be a wine defect, resulting in estery and solvent notes.

Because of the large number of volatile organic compounds (VOCs) and microbial volatile organic compounds (MVOCs) present, assessing the quality and the subsequent commercial value of must or wine is challenging when carried out directly in the field or in the cellar (i.e., outside an analytical laboratory). Organoleptic deviations in wines have been identified a few years ago in several wine-growing regions. They have been attributed to the presence of fungi such as *Botrytis cinerea* and *Penicillium expansum* on the grapes, the incidence of which increases under conditions of high humidity and high grape density.[18] Among these organoleptic deviations are off-flavors for which geosmin and 2-methylisoborneol (2-MIB) are the main responsible molecules of the muddy-earthy smell in wine.[19,20] Some unsaturated aliphatic compounds with alcohol or carbonyl functional groups such as 1-octen-3-one and 1-octen-3-ol have also been identified as the cause of fresh mushroom odor in foodstuffs and beverages including wines.[21] These functional groups are metabolites of many fungal species and orchids and may particularly occur in grapes during rainy vintage and after hail damage.[20,22,23] The methoxypyrazines are heterocyclic compounds formed by micro-organisms or naturally present in some plants.[24] It has been observed that the fruits produced in cold climates are more often contaminated by those compounds than the ones cultivated in tropical regions. The two most widely distributed methoxypyrazines in foodstuffs are 2-isopropyl-3-methoxypyrazine (IPMP) and 3-isobutyl-2-methoxypyrazine (IBMP).[25] Whereas IPMP is also responsible for earthy off-flavors, IBMP is characteristic of the "green" flavor in Sauvignon blanc wines, although higher concentrations of the compound may have undesirable aromatic effects. Generally, these compounds are detected and quantified using gas chromatography coupled with olfactometric detection (GC-O) or mass spectrometry (GC-MS), associated with a preconcentration using headspace-solid phase microextraction (HS-SPME).[26−28] Despite their high precision, these methods are quite complex and cannot be directly implemented in the field. They are also time-consuming because of the sample preparation requiring the control of a wide range of parameters such as adsorption time, temperature, and sample pH and volume, among others.

Rapid and early detection of these off-flavors is of paramount importance to winegrowers. Indeed, it may already interfere at the inspection and preselection stage of the incoming, fresh grape must and may also assist at the postvinification level in deciding for the adequate fining procedures on problematic wines, in which muddy-earthy or fresh mushroom smells are expressly perceptible. Although SPME-GC-MS is an accurate method for the detection of off-flavors, it would be of great benefit to employ additional, fast, and in situ methods of detection. In this context, a transportable and ubiquitous, integrated trap-GC-DMS detector of sufficiently high sensitivity and selectivity and capable of detecting positive and negative ions of various species seems to be an attractive solution.

The present paper describes the detection and quantification of some natural contaminants (geosmin, 2-MIB, 1-octen-3-ol, 1-octen-3-one, IPMP, and IBMP), directly in the headspace of wine samples, using a hyphenated trap-GC-DMS analyzer. This rapid, transportable device will be of use for the winegrowers for an in situ evaluation of must quality and decision on further oenological practices for optimal wine production.

MATERIALS AND METHODS

Differential Ion Mobility Spectrometry (DMS). *Theory of IMS.* The term IMS refers to the principles, methods, and instrumentation for characterizing chemical species on the basis of velocity of gas phase ions in an electric field.[1,29−31] In traditional IMS, compounds are introduced into the ionization region of an ion mobility spectrometer, where they are converted to gas phase ions. These ions are then exposed to a weak homogeneous electric field applied in the drift cell and attain a constant velocity through the electric field (drift velocity) at ambient pressure in gas (usually air). They can then be separated according to their different mobilities through the drift cell.[1,32,33] The IMS is basically composed of an ion source (ionization region), a drift cell (separation region), and a detector (detection region). The two most current types of IMS are (1) conventional IMS such as time-of-flight (TOF) using lengthwise low electric fields (<10 kV/cm) and (2) DMS or field asymmetric ion mobility spectrometry (FAIMS) based on transverse high electric fields (>10 kV/cm).

Principle of DMS. DMS, also called FAIMS, is a detection technique based on differences in mobilities through a high field drift cell. In DMS/FAIMS with a high field-based drift tube, carrier gas flow is used to move ions through the drift region, where an asymmetric electric field, $E(t)$, is applied perpendicular to the gas flow. The amplitude of the asymmetric waveform under high-field conditions is >10000 V/cm. At this field strength, ions rapidly move toward the top plate (or electrode), according to the formula $V_{\perp} = K(E) \times E(t)$, where $V_{\perp}$ refers to the ion velocity perpendicular to the gas flow; $K(E)$ is the field-dependent mobility, and $E(t)$ is the electric field strength.[5,6,29]

During the low-field portion of the radio frequency (RF) waveform, the ion moves toward the bottom plate at a slower velocity (which is about 4 times weaker than the high-field portion). The ion is drawn by a net amount Δh toward one plate for each RF period. The average value of Δh for an ion species is determined by the duty cycle of the oscillating, radio frequency field and the field dependence of the mobility $K(E)$. Thus, for a number n of RF periods, the ion experiences a total displacement of $n\Delta h$. Only ions with a total transverse displacement less than the distance between the plate width will reach the detector, whereas all other ions will be driven to the drift-tube wall. These ions are neutralized or annihilated and swept from the drift region by the gas flow. Ions of a given value of $n\Delta h$ can be kept from striking the plates (allowing a stable passage to the detector) by applying a low-voltage dc field (separation voltage SV) across the plates in opposition to the net oscillating transverse motion of the ion. A sweep of the SV will provide a measure of all the ions in the analyzer and results in a mobility scan[33] (Figure 1). One link between ion behavior under low-field and high-field regimens is given by the equation $K(E) = K_0(1 + \alpha(E))$, where $K(E)$ is the ion mobility for any field, K_0 is the mobility constant at low field, E is the electric field strength, and α is the specific mobility coefficient depending on the electric field.

In conventional time-of-flight-type IMS, the separation of ion molecules is based on the absolute value of coefficient mobility K_0, whereas in DMS, the separation phase is led by the specific mobility coefficient α, which shows a dependence between the coefficient mobility and the electric field.[31] Hand-held ion mobility spectrometers such as those based on DMS have several practical advantages such as high portability, convenient operation, simultaneous detection of

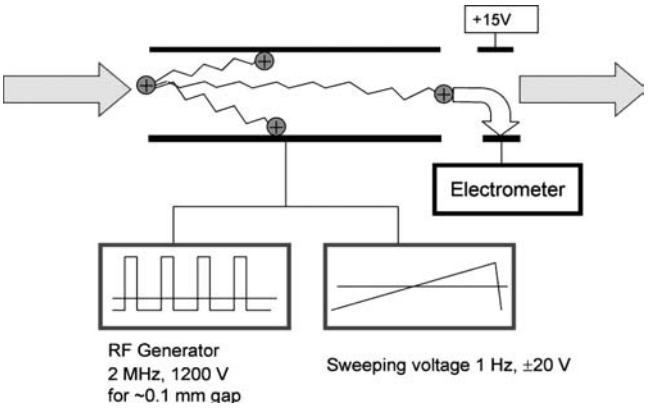

Figure 1. Schematic of drift tube for high-field, asymmetric, ion mobility spectrometry.[33]

positive and negative ions, and continuous monitoring or selective ion filtering. Contrary to conventional IMS devices, DMS/FAIMS detectors do not require any ion shutters, voltage dividers, or aperture grids. That is why the manufacturing of drift tubes from DMS detectors is less complex than the ones from conventional IMS devices.[30,31]

Several groups have attempted to miniaturize this design; the shutter pulse width must be reduced as the drift lengths are shortened. Fundamentally, this miniaturization is limited by the instrumental noise leading to a lower sensitivity. Ion shutters, aperture grids, and discrete drift rings have been barriers for a truly successful miniaturization and commercialization of IMS, as they imply costs for both manufacture and maintenance. These components are dispensable for the new high-field drift tubes (FAIMS) for which at least three designs are available: the first one was designed at the National Research Council in Canada;[34] another one, developed as part of a collaboration between Draper Laboratory and New Mexico State University, is based on a planar micromachined drift tube;[31,35] and a third one, which is being developed by Owlstone Nanotech Inc., is based on interdigitated electrodes.[36,37]

Sionex Trap-GC-DMS. The integrated trap-GC-DMS microanalyzer (mDMx type, Sionex Corp., Bedford, MA, USA) used in this study was equipped with a ^{63}Ni ionization source (5 mCi) enabling the simultaneous formation of both positive and negative product ions. This apparent redundancy helps in identifying the analytes of concern in the spectra, whereas in this paper only the positive spectrum has been chosen for the quantitative analysis. The analyzer was supplied with an XLB 10 m × 0.25 mm × 1 μm gas chromatographic column (Agilent Technologies) and a carbon trap preconcentrator (Sionex Corp.). The column was eluted at a flow rate of 1.5 mL/min by the ambient air, cleaned and dried through the analyzer's internal carbon and molecular sieve scrubber system. The DMS dispersion field (DF) was pulsed by the asymmetric, half-sinusoidal (fly back) 1.25 MHz separation waveform defined by f1, f2, f3, and f4 moments, respectively, of 0.1606, 0.0981, 0.0955, and 0.0844. The gap of the analytical region of the DMS sensor was of 50 mm and spanned from 500 to 1500 V, resulting in the asymmetric DF from 10 to 30 kV/cm. The RF waveform's duty cycle of the dispersive field was of 25%, with a positive pulse duration of 0.2 μs. The analyzer was operated at room temperature (21 °C) and at atmospheric pressure of ca. 760 Torr, both in the scanning mode (fixed DF value and SV swapped from −40 V to +10 V) and in the GC mode (fixed DF value and fixed narrow SV window).

Trap-GC-DMS Setting Parameters. The DMS scanning mode experiments were conducted at a DF ranging from 18 to 23 kV/cm (or V_{RF} from 900 to 1150 V) with SV swapping from −30 to +10 V. The value of the optimal DF is related to the target compound and was determined following the results of initial tests. For example, the experiments with geosmin and pyrazines were conducted with a fixed value of DF of 23 kV/cm, whereas 1-octen-3-ol and 1-octen-3-one were calibrated with a DF of 21 kV/cm. The analyzer was mostly operated in the screening mode with SV swapped from −30 to +10 V with 0.40 V steps of 10 ms each. All spectra were collected within a 30 s sampling time. The carbon trap preconcentrator of the analyzer was initially kept at 25 °C and was charged with headspace probes sampled at the rate of 100 mL/min over a 30 s sampling period. After charging, samples were finally released by flash desorption at 250 °C directly into the incorporated GC column. A GC thermal profile covering a temperature range of 40−150 °C with a heating ramp of 20 °C/min was found to give the highest selectivity of wine constituents, except for the experiments with geosmin, which were carried out at a constant GC temperature of 110 °C. The duration of each analysis was typically <10 min, including the analyzer self-cleaning cycle.

Sample Preparation. The chemical standards used in this study were purchased as certified standard solutions or pure compounds from Sigma-Aldrich (Bornem, Belgium). The calibration solutions were prepared from representative Moselle Vineyard region white wines purchased in a local shop, in which the target analytes were spiked at the desired concentrations for external calibration. The water used for blanks and dilutions was produced from a Milli-Q water purification system (Millipore, Billerica, MA, USA).

The sampling receptacle was a vial of 60 mL containing 3 μL of the wine sample previously prepared (i.e., spiked with the required amount of standard solution). The vials were purged with synthetic air (N60 POL, purity of 99.99%, containing 2.0 ppm of H_20 and 0.1 ppm of CO_2, from Air Liquide, Luxemburg) and closed with a rubber septum, allowing the sampling through a punch-through needle connected to the mDMx analyzer. To increase the occurrence of cluster formations during the sampling phase, a dry, synthetic air was continuously injected into the vial. The low pressure of injection was set at 4 psi and was controlled through a pressure regulator (HBS 240-0.1-0.5, Air Liquide).

Quantification Procedure. The DMS measurements obtained in scanning and GC modes were visualized in two or three dimensions (2D or 3D) using IGOR software (IGOR Pro version 6.12A, WaveMetrics, Inc., Lake Oswego, OR, US). The chromatographic traces (obtained in GC mode) were obtained by plotting the measured voltage versus the retention time. In 2D scanning mode, spectra were obtained by plotting the measured voltage versus both the retention time and the SV. The raw chromatographic traces, which displayed a strong baseline distortion, were corrected by fitting a higher order polynomial with coefficients derived from the minimization of a truncated quadratic cost function.[38] The offset of the ion abundance was also eliminated during the postprocessing. Furthermore, all chromatograms collected in the GC mode were denoised by appropriate wavelet filtering. We employed pseudocoiflets,[39] Coifman's wavelets with interpolating scaling functions, well preserving the smoothness of the Gaussian peaks. For the scanning mode spectra recorded in the SV swapping mode experiments, carried out at fixed DF, our attention was exclusively focused on compounds' protonated monomers. The baseline distortion observed at this single peak was insignificant, and only a limited intensity offset correction was required. Furthermore, the peak amplitude of the target species was retrieved for quantitative calibration purposes. Whenever possible, errors associated to every point of the calibration curve were roughly estimated from three repetitions of the previous trials conducted with similar compounds and concentrations.

RESULTS AND DISCUSSION

Geosmin. Rapid and direct headspace screening for the presence of geosmin in fresh grape must and in white and red wines by using the GC-DMS technique has been successfully demonstrated in our previous paper.[40] Sufficiently high detection selectivity and sensitivity levels below the human olfactory threshold of 50 ng/L were achieved and confirmed by parallel SPME-GC-MS measurements. Interestingly, despite the high viscosity and the presence of suspended solid matters in wine must as well as the multitude of flavors in wines, geosmin was successfully detected and calibrated in both wine must and

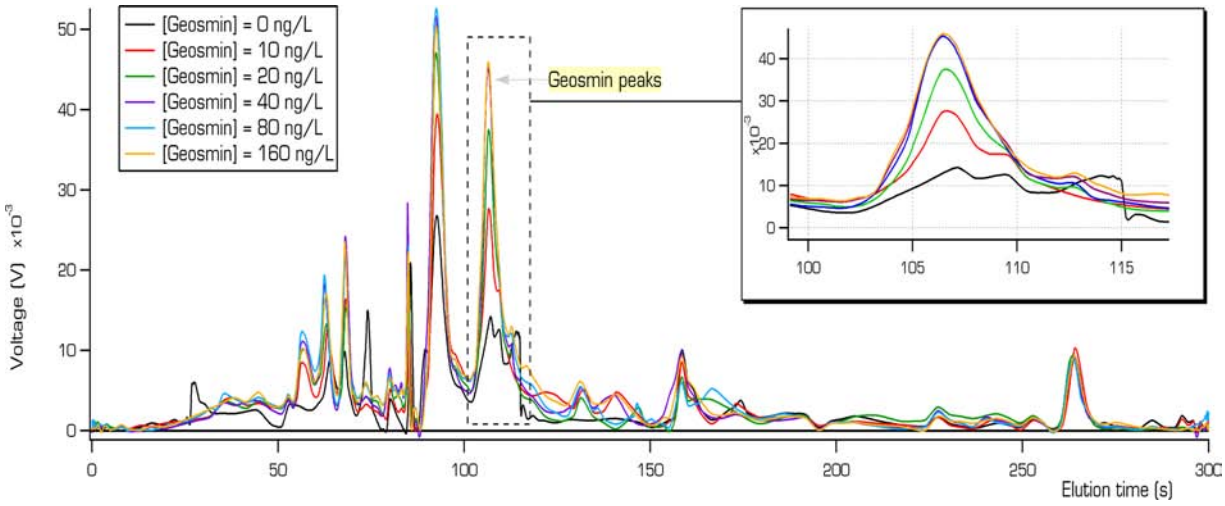

Figure 2. Geosmin in Elbling wine: GC-DMS smoothed chromatograms collected at dispersion field of 23 kV/cm (V_{RF} of 1100 V) with separation voltage of −1.72 V and steady GC temperature at 110 °C.

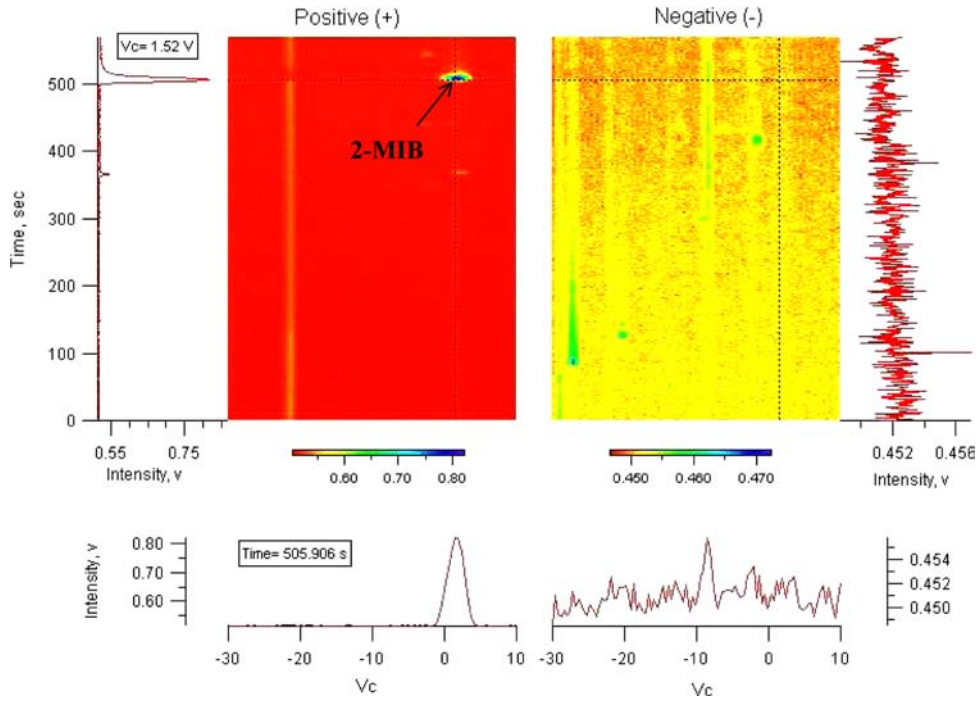

Figure 3. Scan mode GC-DMS spectrum of 2-MIB collected after 30 s of sampling and with GC ramp of 20 °C/min. Dispersion field was set to 21 kV/cm, and separation voltage was swapped in [−30, +10 V] range.

red and white wines over a range of concentrations from 10 to 160 ng/L (Figure 2). Despite a short sampling time (30 s), geosmin was still detectable at a concentration as low as 7 ng/L, which is significantly below the human olfactory threshold of 50 ng/L.

2-Methylisoborneol. As noted above, 2-MIB was located and calibrated using a standard solution at a concentration of 100 μg/mL in methanol. The identification of the 2-MIB peak over the other peaks of DMS spectrum was challenging because of the background related to the standard solution containing the target compound. The precise peak position has been elucidated thanks to the extraordinarily persistent smell of 2-MIB. Indeed, as shown in Figure 3, the response of the DMS to 2-MIB remained intense even 15 min after the experiment, whereas the response of other background compounds present in the standard solution (methanol and probably some traces of contaminants) was decreasing with time, thus facilitating the peak attribution and calibration of 2-MIB.

Moreover, one can see that 2-MIB is not represented by any peak in the negative spectrum (Figure 3). This is related to the fact that these tests were performed with sampling vials containing little oxygen, whereas production of negative product ions depends mainly on oxygen contained in the carrier gas ($M + (H_2O)_m O_2^- \Leftrightarrow (H_2O)_{m-1} MO_2^- + H_2O$, with M the target compound).[1] In opposition to negative product ions, positive product ions, characteristic of the positive spectrum of DMS, mainly come from water molecules not only in the carrier gas but also in the sample ($M + (H_2O)_m H^+ \Leftrightarrow (H_2O)_{m-1} MH^+ + H_2O$, with M the target compound).[1] The richness of the wine sample headspace, in terms of humidity

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and target compounds, often leads to additional displacement reactions, where proton-bound dimers are formed. However, because the target analytes are in trace level, the probability of dimer formation is negligible compared to monomers, which were the only ions used for qualitative and quantitative analysis in the present study.

Given the persistent smell of 2-MIB and the high sensitivity of the detector for this compound, the 2-MIB calibration was performed at low concentrations, ranging from 0.5 to 5 ng/L. The results obtained for three consecutive experiments demonstrated an increase of the mean peak amplitude with the concentration of 2-MIB in Riesling white wine (Figure 4).

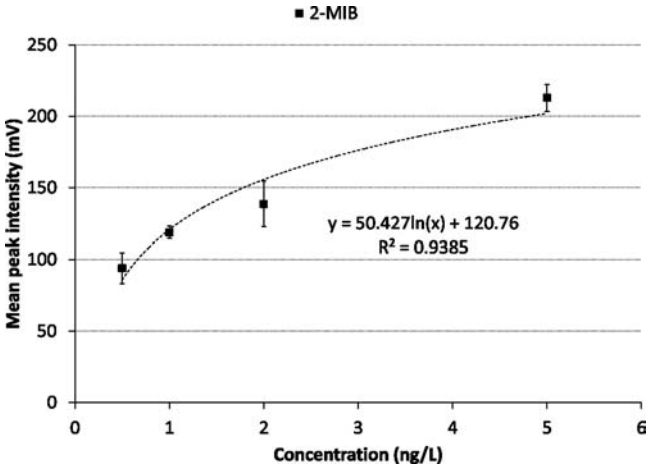

Figure 4. Calibration curve of 2-MIB in Riesling wine collected after 30 s sampling and with GC heating rate of 20 °C/min: concentration versus peak intensity from GC-DMS.

The calibration curve appears to be best fitted by nonlinear models, rather than by a linear model, which would had led to a too narrow dynamic range. By extrapolation of the calibration curve toward very low concentration (<0.5 ng/L), we can estimate the detection limit of 2-MIB to be a few hundred picograms per liter. This high sensitivity of DMS toward 2-MIB molecules could be attributed to a high proton affinity of 2-MIB compared to other VOC species.

1-Octen-3-one and 1-Octen-3-ol. The detection and direct separation (without any specific extraction) of the pair 1-octen-3-ol−1-octen-3-one is a major challenge in the control of wine quality. Although 1-octen-3-one and 1-octen-3-ol are separately detectable by GC-MS techniques, their extraction protocol and analysis are very complex and time-consuming. In the case of the GC-DMS method, no pretreatment is required for both compounds to be separately identified in wine samples. Because of their structural similarity, 1-octen-3-ol and 1-octen-3-one peaks were located close to each other in the positive spectrum: they respectively eluted at 328 and 331 s with SVs of 1.92 and 2.73 V during the GC-DMS analysis (Figure 5). These results confirmed our previous measurements, for which these compounds were spiked separately.

Because the representative peaks of 1-octen-3-ol and 1-octen-3-one tended to overlap on each other, the heating profile has been set so as to optimize their separation along retention time. With a GC heating profile ranging from 40 to 150 °C at a rate of 20 °C/min, we were able to identify both 1-octen-3-ol and 1-octen-3-one in Auxerrois Moselle wine.

1-Octen-3-one. The quantitative calibration of 1-octen-3-one in Auxerrois wine, carried out between 3 and 83 ng/L, showed an increase of the monomer peak intensity versus headspace concentration (Figure 6). We noted that the wine used in these experiments, namely, the Auxerrois wine, naturally contained some traces of 1-octen-3-one, which made difficult the calibration of low concentrations below 2 ng/L. Despite this, we can estimate the detection limit of our detection system to be in the range of 1−2 ng/L, as the monomer signal remains very strong even at 2 ng/L.

1-Octen-3-ol. Unlike the other compounds, 1-octen-3-ol was calibrated in Auxerrois wine at much higher concentrations, up to 500 ng/L, because of a relatively low sensitivity of our detector to this particular analyte (Figure 7). This high threshold of detection may be due to a significantly lower proton affinity than in the case of 1-octen-3-one, detectable below 5 ng/L. Because the alcohol (ethanol) naturally contained in wine is eluted from the GC column at very different times, this lack of sensitivity toward 1-octen-3-ol can be explained by competitive depletion of reactant ions prior to the formation and detection of product ions. The 1-octen-3-ol calibration curve showed a logarithmic increase of peak

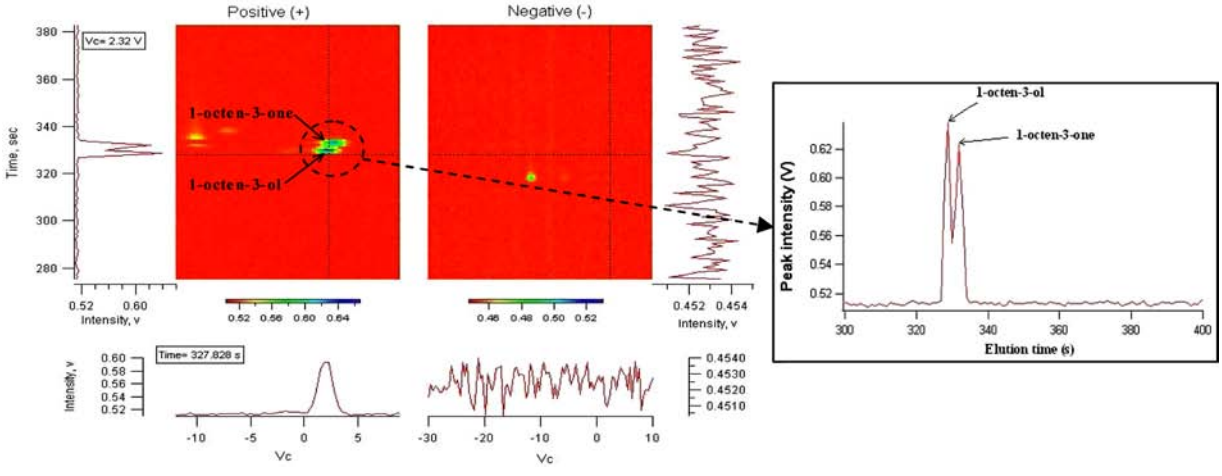

Figure 5. GC-DMS analysis of 1-octen-3-ol and 1-octen-3-one mixture collected after 30 s of sampling and with GC ramp of 20 °C/min: (a) DMS scan mode with a RF of 21 kV/cm and SV swapped in [−30, +10 V] range; (b) smoothed GC mode with RF of 21 kV/cm and SV of +2.32 V.

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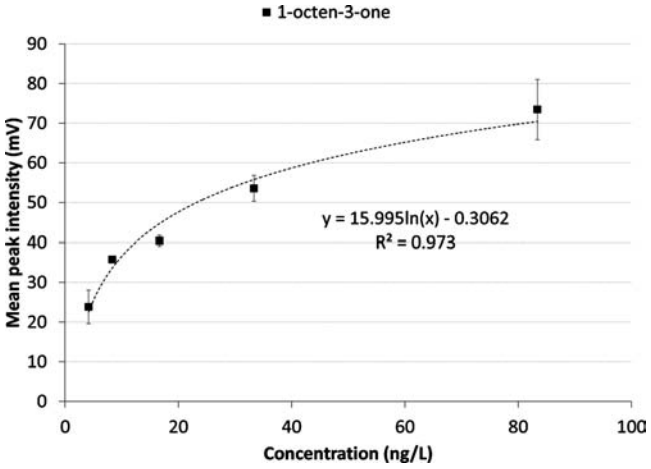

Figure 6. 1-Octen-3-one spiked in Auxerrois wine collected after 30 s of sampling under low pressure of dry air and with GC heating rate of 20 °C/min: headspace concentration versus peak intensity from GC-DMS.

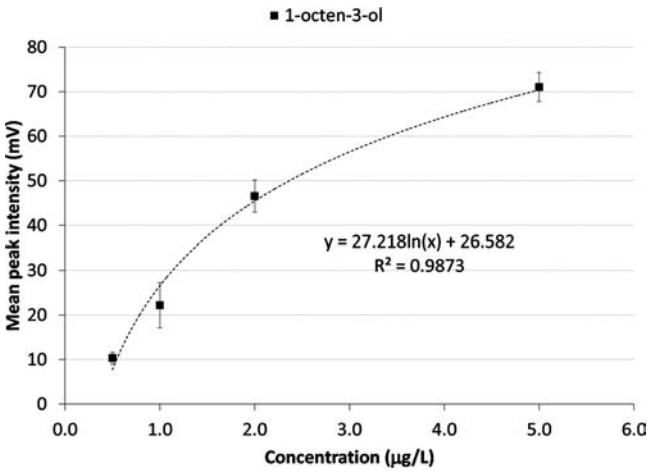

Figure 7. 1-Octen-3-ol spiked in Auxerrois wine collected after 30 s of sampling and with GC heating rate of 20 °C/min: concentration versus peak intensity from GC-DMS.

intensity versus concentration, with a detection limit estimated below 500 ng/L in wine.

Pyrazines. Pyrazines (1,4-diazines) are aroma compounds found in many green vegetables. The two predominant pyrazines in foods and water are IPMP and IBMP. Because these two pyrazines could have a negative impact on the value of a wine, their detection and quantification are needed not only for tracking the source of contamination but also to define the acceptable level of contamination.

Initially, the respective positions (elution time and SV voltage) of two pyrazines were located by injecting them separately in the sampling vial of DMS under a low-pressure flow of synthetic air. The IPMP was first eluted from the GC column at a retention time of 377 s and at an SV of 0.71 V; IBMP appears at exactly the same SV but was eluted 71 s later than IPMP (Figure 8). This time gap is sufficient to avoid any possible overlap of monomer peaks from both species, thus ensuring their nonambiguous attribution. The observed time gap is in line with our expectations, because for species displaying similar polarity, the elution time quickly increases with molar mass (152.19 and 166.22 g/mol, respectively, for IPMP and IBMP).

Following the procedure described above, two pyrazines (IBMP and IPMP) were quantitatively calibrated by spiking them into Auxerrois wine at concentrations ranging from 2 to 100 ng/L. Three successive experiments were performed at each concentration to assess the reproducibility of the method.

2-Isopropyl-3-methoxypyrazine and 3-Isobutyl-2-methoxypyrazine. The calibration curve of monomer ion peak intensity versus headspace concentration of IPMP and IBMP in wine showed a logarithmic behavior (Figure 9).

Following the method developed for calibration experiments, we can estimate the detection limit of the IPMP and IBMP in wine to <1 ng/L, because of the high sensitivity of the DMS detector for pyrazines, shown by the intense peak obtained at 2 ng/L (29 mV) despite the low concentration.

As a summary of the presented study, the benefits of using field-deployable DMS for fast and in situ VOCs screening in wine have been successfully demonstrated. The applied technique associates a micro-DMS with a sample preconcentrator and a short gas chromatography column (trap-GC-DMS)

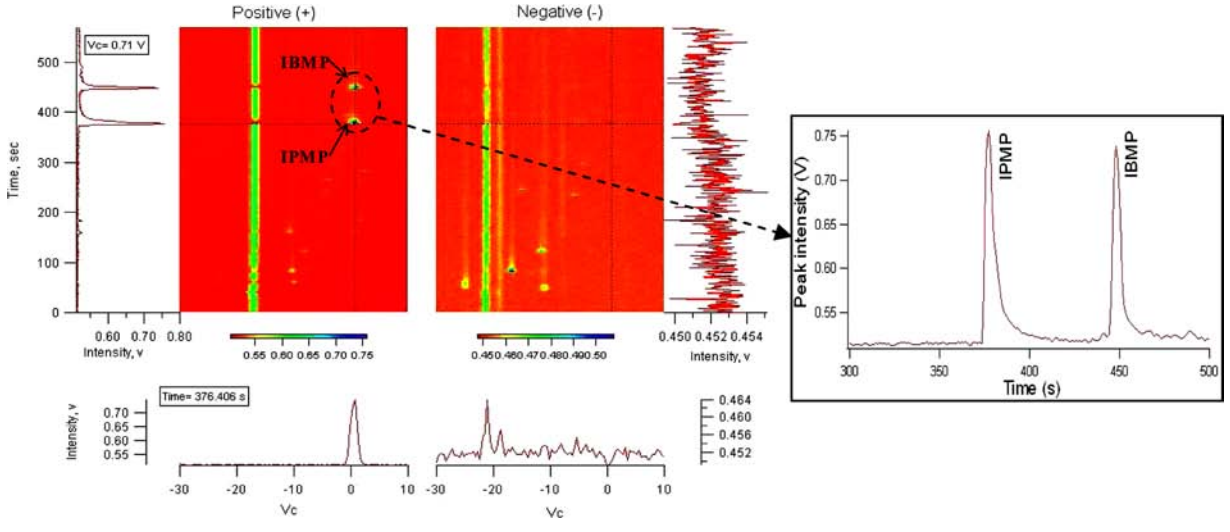

Figure 8. GC-DMS analysis of IPMP and IBMP mixture collected after 30 s of sampling and with GC ramp of 20 °C/min: (a) DMS scan mode with RF of 23 kV/cm and SV swapped in [−30, +10 V] range; (b) smoothed GC mode with RF of 23 kV/cm and SV of +0.71 V.

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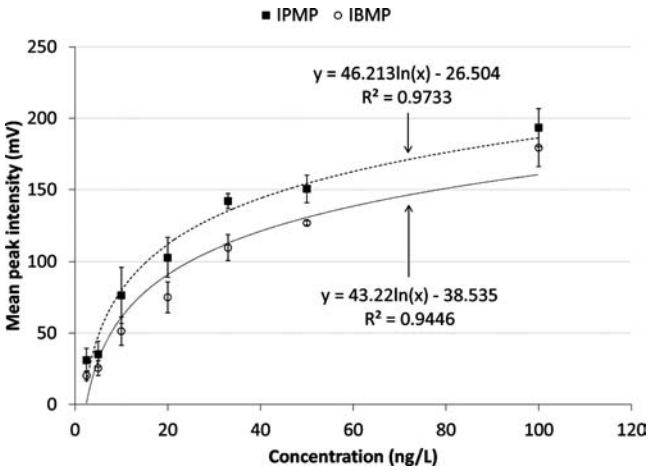

Figure 9. IPMP and IBMP spiked in Auxerrois wine and collected after 30 s of sampling under dry air flow and with GC heating rate of 20 °C/min: concentration versus peak intensity from GC-DMS.

for direct headspace detection. This innovative approach can be considered as an alternative and complementary technique to the conventional SPME-GC-MS method, which requires a specialized laboratory facility.

Direct headspace detection and fast quantification of many kinds of VOCs (geosmin, 2-MIB, 1-octen-3-one, 1-octen-3-ol, pyrazines) known as natural contaminants of wine (when present at too high concentrations) have been carried out with a sufficiently selective and sensitive GC-DMS, without any preliminary treatment of samples. The multidimensional separation (depending on retention time and SV) offered by the Sionex mDMx analyzer allowed us to perform quantitative analyses of most of the wine off-flavors, at very low concentration levels below 5 ng/L (except 1-octen-3-ol calibrated at 500 ng/L), typically below the human olfactory thresholds (close to 50 ng/L for most of target compounds and 40 μg/L for 1-octen-3-ol) through a very fast run cycle (including sample preparation, analysis, and self-cleaning of DMS) in <10 min.

As a perspective to the present work, the forthcoming task will be to develop a multicomponent method allowing the simultaneous detection of the different contaminants investigated so far. This will involve an optimization of the GC heating rate and the use of common detection parameters. In addition, kinetic studies on the evolution of the VOCs during the maturation period of the wine are envisaged, by the regular monitoring of off-flavors using GC-DMS, from the grape must to the final wine.

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Notes

The authors declare no competing financial interest.

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