Assessment of Sauvignon Blanc Aroma and Quality Gradings Based on Static Headspace-Gas Chromatography-Ion Mobility Spectrometry (SHS-GC-IMS): Merging Analytical Chemistry with Machine Learning

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ABSTRACT

The analytical scope of static headspace-gas chromatography-ion mobility spectrometry (SHS-GC-IMS) was applied to wine aroma analysis for the first time. The method parameters were first fine-tuned to achieve optimal analytical results, before the method stability was demonstrated, in terms of repeatability and reproducibility. Succinct qualitative identification of compounds was also realised, with the identification of several volatiles that have seldom been described previously in wines. Using the SHS-GC-IMS data in an untargeted approach, computer modelling of large data sets were applied to link aroma chemistry via prediction models to wine sensory quality gradings. Six machine learning models were compared, and artificial neural network (ANN) returned the most promising prediction performance. Despite its inherent complexity, the ANN model offered intriguing insights on the influential volatiles that correlated well with higher and lower sensory gradings. These findings could, in the future, guide winemakers in establishing wine quality, particularly during blending operations prior to bottling.

1 INTRODUCTION

New Zealand Sauvignon Blanc wines are widely appreciated for their fresh and fruity aroma, often described as herbaceous, vegetative, grassy, in addition to gooseberry, grapefruit, and passion fruit notes, while being delicately balanced by its vibrant acidity.[1] The chemical composition of Sauvignon Blanc wines has been systematically reviewed by Coetzee and du Toit.[2] Multiple researchers have reported that the varietal thiols (3-mercaptohexan-1-ol, 3-mercaptohexyl acetate and 4-mercapto-4-methylpentan-2-one) play a major role in the typicality of Sauvignon Blanc wines.[3-4] Other researchers have examined the organoleptic influences that esters and green leaf volatiles have on Sauvignon Blanc wine aroma.[4-5] These volatiles, either individually, synergistically, or antagonistically, contribute to the overall sensory perception of Sauvignon Blanc wines.

Given the enormously complicated biochemical processes that occur on grapevines and in fermentation tanks, subtle yet tangible variations can be present among wines made from grapes sourced from different vineyards.[4, 6] It is a critical job for winemakers to judge the quality grading of wines, usually during the annual post-harvest tasting and blending session, held internally at wineries, and prior to further wine processing. Subjectively, seasoned winemakers will have their very own style preferences and "gold standards" in mind to determine the quality grading of wines, which are often difficult to articulate.[6] Objective guidelines, such as the presence of agreed-upon sensory faults and perceived sweetness, are also important in the decision-making for wine quality gradings. Not all of these guidelines, however, are supported by measurable parameters.[6] Therefore, the wine industry would benefit from analytical methods that could establish a relationship between measurable wine attributes and their perceived quality. In red wines, for example, tannins have been demonstrated to positively correlate with red wine quality from both flavour and colour perspectives.[7-8] Additionally, volatile compounds, especially those expressing the varietal character, may also be used to indicate wine quality.[9-10] The methods employed in these publications, however, all involve expensive instruments such as GC-MS and often elaborate sample handling, which renders them impractical for use in a commercial winery lab setting. A cost-effective, easy-to-use alternative, which could quickly and reliably produce information regarding wine quality, would be more useful to assist winemakers and complement their empirical insights in assigning wines with appropriate gradings.

Due to the inherent complexity of wine aroma, it is suitable to employ a non-targeted method that indifferently analyses the total headspace composition. Furthermore, the non-targeted search would produce a multitude of data, which requires advanced statistical tools to identify patterns, either explicit or latent, contained within the data. This can lead to the construction of quality prediction models to assist winemakers with their decision-making process.

A promising technology that may provide the long-desired solution to the wine industry is ion mobility spectrometry (IMS), employed in volatile compound analyses. Initially developed for military purposes during the Vietnam War, the use of IMS has recently been extended to other fields, such as the screening of explosives at airports, the detection of chemical warfare agents, proteomics, clinical samples, human breath volatiles, manufacturing process control, and more recently food research.[11] The IMS device is comprised of three components: an ionisation chamber, a drifting tube, and a Faraday Plate detector. Unlike conventional mass spectrometric techniques, IMS includes a separation dimension based upon the mobility of ions, in addition to the separation achieved on any GC column placed before it. Volatiles in the sample mixture are firstly transformed into gas phase ions, which are then driven, in a matter of milliseconds, by a weak electric field across the drifting tube towards the detector situated at the end of tube.[12] A drifting gas, usually nitrogen, flows in a direction against the ion current, and thus differentially lowers the velocity of ions depending on their physical characteristics.[13-14] As a result, gas phase ions can be differentiated depending on their travel time in the IMS drifting tube.[12, 15]

Independent IMS units have already been successfully applied in food volatile analysis.[16-17] However, competitive ionisation can pose a problem when a complex array of volatiles, as often found in food matrices, is simultaneously introduced into the instrument, which can result in lowered IMS selectivity.[18-19] A pre-fractionation step is hence crucial in maintaining the IMS analytical capability. Appending a gas chromatographic (GC) column prior to IMS has been extensively used when studying complex food samples, such as olive oil, honey, egg, and dry foods.[11] Not only does the orthogonal combination of GC and IMS improve overall selectivity, but the two analytical dimensions can also complement each other to achieve better separation outcomes.

Despite the aforementioned advantages of the GC-IMS instrument, research publications regarding using this technology in the aroma analyses of wine and other alcoholic beverages are still rare.[20] Therefore, the current study focuses on the application of static headspace GC-IMS (SHS-GC-IMS) in Sauvignon Blanc wine aroma analysis using a global fingerprint approach. Moreover, machine learning techniques have been utilised to produce wine grading prediction models based on the aroma analyses, without the need for prior knowledge of the aroma composition.

2 MATERIALS AND METHODS

2.1 Sauvignon Blanc wine samples

For method development purposes, two commercial Sauvignon Blanc wines from the 2014 and 2020 vintages were used. For the precision studies, one bottle of 2018 commercial Sauvignon Blanc wine was used. All of the wines were produced in Marlborough, New Zealand, and had been stored in their original packaging and away from direct sunlight at room temperature before analysis.

A total of 143 Sauvignon Blanc end-ferment wine samples were sourced from Constellation Brands NZ. These samples were obtained directly from fermentation tanks after fermentation had concluded and prior to blending. Each wine sample was assigned a quality grade (from 1 to 3) by an internal tasting panel consisting of six experienced winemakers, to give a total grade score for each wine between 6 and 18. These samples were subsequently divided into three gradings:

- Grade A: scores 13-18 (inclusive), 36 samples in total;
- Grade B: scores 10, 11 and 12, 74 samples in total;
- Grade C: scores 6-9 (inclusive), 33 samples in total.

All end-ferment wine samples were analysed in duplicates using the SHS-GC-IMS method, which produced 286 measurements. After these samples were retrieved from fermentation tanks, and prior to instrumental analysis, they were stored in a commercial freezer at -20°C.

2.2 Chemicals and reference standards

Reference standard compounds were used for the identification of a number of the peaks detected on the SHS-GC-IMS instrument. 24 compounds were procured from Sigma-Aldrich (Taufkirchen, BY, Germany). These standards included ethyl formate, ethyl acetate, ethyl butyrate, isobutyl acetate, ethyl 2-methylbutyrate, ethyl isovalerate, isoamyl acetate, ethyl hexanoate, hexyl acetate, (*Z*)-3-hexenyl acetate, ethyl octanoate, ethyl decanoate, 1-propanol, isobutanol, 1-butanol, isoamyl alcohol, 1-hexanol, methyl acetate, ethyl propionate, ethyl pentanoate, ethyl heptanoate, ethyl nonanoate, propyl acetate, and amyl acetate. All standard compounds were of a minimal of ≥ 98% purity and were stored in a 5°C cool room prior to use.

Stock solutions of standards were prepared by carefully dispensing one drop (approximately 0.01 g) of the standard compound into 10 mL of 99% Absolute ethanol (Ajax Finechem, Australia). The qualitative identification sample (5 mL total volume) was made from diluting the stock solution with a model solution (12% *v/v* ethanol in Type 1 water, pH = 3.23 adjusted by tartaric acid) using a dilution factor of 1 in 50. These samples were then analysed on the SHS-GC-IMS instrument using the same program as for the actual wine samples.

2.3 Volatile compound analysis using SHS-GC-IMS

2.3.1 Optimisation of static headspace, GC and IMS parameters

As the analytical method did not involve any extraction steps, the availability of volatile compounds dissociable from the liquid fraction of wine, and subsequently introduced into the GC column, can be optimised by manipulating three factors: the injection volume (µL), the sample incubation time (s), and the sample incubation temperature (°C). Although the "salting-out" technique using sodium chloride is often used in GC-MS based methods for enhancing volatile dissociation, it was not considered in the current SHS-GC-IMS method, due to the high sensitivity of the IMS component.[21] The absence of the "salting-out" step also improved method simplicity

and increased sample throughput. The injection volume was tested at three different levels: 500, 1000 and 1500 µL. Sample incubation time was set to 5, 10 and 15 minutes, whereas four incubation temperatures were compared, namely, 30°C, 40°C, 50°, and 80°C. The parameters optimised for the GC and IMS component included the GC column and IMS drifting tube temperatures. The GC column temperature was evaluated at 40°C, 55°C and 70°C, whereas the IMS drifting tube temperature was tested at 45°C, 60°C and 75°C.

2.3.2 General analytical procedures

Analyses of volatile compounds were conducted using a gas chromatograph coupled to an ion mobility spectrometry detector (SHS-GC-IMS, FlavourSpec, Gesellschaft für Analytische Sensorsysteme mBH, Dortmund, Germany). The instrument was fitted with a MXT-WAX polar GC column (30 m length × 0.53 mm internal diameter × 0.5 µm film thickness, 100% crossbond Carbowax polyethylene glycol stationary phase) procured from RESTEK (Bellefonte, PA, USA). The instrument was also connected to an autosampler (CTC Analytics AG, Zwingen, Switzerland) with headspace sampling unit for automated sample introduction onto the SHS-GC-IMS.

For each sample, 5 mL of wine were carefully transferred into a 20 mL headspace glass vial using a micropipette. Each wine sample was spiked with 50 µL of internal standard (3-octanol, absolute amount = 63.35 µg per sample) as a quality control. Samples were subsequently incubated at 40°C for five minutes, before 500 µL of the headspace sample was introduced into the SHS-GC-IMS using a heated syringe (80°C) through a heated injection port. Nitrogen (purity: 99.95%) was used as both carrier gas for GC and drift gas for IMS. On the GC, the carrier gas flow rate was programmed as follows:

- 0 min → 1 min: maintained at 2 mL/min;
- 1 min → 20 min: increasing from 2 mL/min to 40 mL/min at a rate of 2 mL/min^2;
- at 20 min: immediately increased to 150 mL/min;
- 20 min → 50 min: maintained at 150 mL/min;
- at 50 min: immediately decreased to 2 mL/min;
- 50 min → 52 min: maintained at 2 mL/min;
- at 52 min: program completion.

The GC column was set to operate in isothermal mode at 40°C. Analytes were ionised in the IMS chamber using a tritium (^{3}H) source. Ionised volatile compounds then entered the 98 mm long IMS drifting tube, where an electric field (strength: 500 V/cm) was applied. The ionisation chamber and the drifting tube were programmed at 75°C. The drift gas was set at a constant flow rate of 150 mL/min counter-current of the analyte ion flow. Each IMS spectrum was acquired as the average of six scans.

In order to minimise memory effects and ensure the optimal performance of the instrument, two air-blank samples were always placed as the first and the last vial in the sequence for each day before and after the wine samples. Also, an intermittent 4-hour thermal cleaning was performed at the conclusion of each sequence and a 24-hour thermal cleaning was performed each week over the weekend.

Peak identification was achieved by comparing the signals of the stock solutions to the signals revealed in actual wine samples. Additionally, an ethyl ester series (straight-chain C_1-C_9, ethyl formate to ethyl nonanoate) was used as an external reference for calculation of the retention indices of the wine volatiles. The retention index was used as an auxiliary tool for crosschecking the GC×IMS database and to ascertain peak identity.

The analytical results acquired from the SHS-GC-IMS were visualised using the Laboratory Analytical Viewer (LAV) software suite (version 2.2.1). The GC×IMS Library Search software (version 1.0.3) was also used for peak identification. Both software packages were supplied by the instrument manufacturer (G.A.S., Dortmund, NW, Germany).

2.4 Multivariate data analysis and machine learning

The raw results obtained from the instrument were pre-processed using the LAV software (Laboratory Analytical Viewer, Dortmund, Germany). Initially, each peak was manually defined as a box on the 2-D contour plot, with the *x*-axis being the IMS drift time and the *y*-axis the GC retention time. A total of 65 peaks (excluding the internal standard) were accordingly defined with their retention times (s) and drift times (RIP rel., relative to RIP position), and then collated into the area-set file as a template for future analyses. The pre-defined peaks were acquired with their *volume-under-the-shape* calculated automatically in subsequent wine samples. Acquisition of peaks was realised by the LAV main program, while peak *volume-under-the-shape* calculations were conducted using the in-built LAV – quantitation module.

Given the complicated nature of the aroma compounds present in the wines, a large array of data was expected to be collected, as the non-targeted approach was to be applied. As the major aim of the current research was to establish a classification tool, which would make use of the SHS-GC-IMS volatilomic data to predict wine gradings, basic statistical tools such as linear regression would fail to cope with data with highly complex structure. Therefore, the research adopted approaches from the fast-growing machine learning community and made use of advanced classification algorithms to build the prediction model. In total, five machine learning models were fitted to the SHS-GC-IMS data. These includes PCA-LDA (principal component analysis coupled to linear discriminant analysis), PLS-DA (partial least squares discriminant analysis), *k*NN (*k* nearest neighbour), SVM (support vector machine), XGBoost (eXtreme Gradient Boosting), and ANN (artificial neural network). Furthermore, SHAP values were utilised to explain the structures of the trained models to explore potential marker volatile compounds to predict wine grading.

Microsoft Excel 2019 (Redmond, WA, USA) was used to collate and organise raw data. Both Python (version 3.8.3, Fredericksburg, VA, USA) and R (version 4.0.2, Vienna, Austria) languages were used for data handling and statistical analyses. A comprehensive list of all the programming languages and packages used in the current project is shown in **Supplementary Table S1**.

3 RESULTS AND DISCUSSION

3.1 Optimisation of HS-GC-IMS analytical parameters

Prior to analysing wine samples on the SHS-GC-IMS instrument, a set of five instrumental parameters associated with the headspace, GC, and IMS components were optimised to achieve desirable instrument responses, namely, GC selectivity and IMS signal intensity. The final parameters and the range within which they were optimised, are summarised in **Supplementary Table S2**.

The three optimisable parameters in the headspace were incubation temperature, incubation time, and injection volume. Initially these parameters were set at 30°C, 10 min, and 500 µL, to align with the manufacturer recommended defaults. Firstly, an increase in incubation temperature of wine samples, from 30°C to 80°C, raised the signal intensities of most peaks. An excessively high sample incubation temperature, however, suppressed the intensities of certain peaks and cause existing peaks to distort and agglomerate into indistinguishable clusters. Additionally, some abundant signals, such as ethanol, competitively bound to all available reactant ions in the ionisation chamber, thereby masking the presence of other minor compounds with similar retention times and resulting in false peak identifications (theoretical principles discussed in detail in **Section 3.3**). Given the side effects of a high incubation temperature, the incubation temperature was selected at 40°C, which is also suitable to best mimic human body temperature involved in orthonasal and retronasal olfaction.[22] Changes in incubation time from 5 min to 15 min, on the other hand, barely had any impact on the instrument response, and 600 s was selected to streamline the GC-IMS process. Increasing the injection volume from 500 to 1500 µL increased signal intensities. However, problems such as compound overload, peak shape distortion, and a noisy baseline also occurred, which rendered compound identification and future quantification more difficult. The injection volume was therefore chosen as 500 µL.

The temperatures of GC and IMS components were also optimised across different ranges. A higher GC column temperature, from 40°C to 70°C, accelerated the elution process, but also led to severe resolution loss such as peak tailing, shouldering, and peak shape distortion, rendering it nearly impossible to differentiate peaks with close retentions times. Thus, the column temperature was set at 40°C. On the contrary, increasing the IMS drifting tube temperature from 45°C to 75°C was beneficial with little side effects, and improved instrument sensitivity immensely, resulting in the detection of peaks that were otherwise barely visible under lower IMS temperatures. Such effects were also reported by Gerhardt et al. in their study of olive oils.[23] Hill and Simpson noted that high a IMS temperature helps with the declustering of excessively hydrated analyte ions as heated drift gas collides with analyte ions and remove water molecules, thereby reducing moisture interference to achieve better signal response and a less noisy baseline.[24] Therefore, the IMS temperature was set at 75°C. These optimised parameters ensured the balance between the number of detectable peaks and desirable instrument response, resolution, and sensitivity.

3.2 Precision study of SHS-GC-IMS

Both repeatability (intra-day variation) and reproducibility (inter-day variation) were examined by analysing a moderately aged (vintage 2018) Sauvignon Blanc wine, each day as quadruplicates over a five-day period. Variations in terms of the retention time, drift time, and signal intensity were monitored. Relative standard deviation (RSD) ranges of these parameters are summarised in **Table 1**. All RSD values were below 10%, which indicate a desirable level of precision for the SHS-GC-IMS method.

It was noted that severe retention time shifts were observed when the instrument had not been thermally cleaned for a prolonged period of time (data not shown), which could result in inaccurate results. This problem, fortunately, was remedied by frequently applying the cleaning program at the end of each run. The instrument

should be thermal cleaned at least once every 24 hours for a minimum of four hours to ensure consistent analytical outputs.

Table 1. Precision study (RSD, %) for wine samples and quality control mix tested using SHS-GC-IMS. The data are presented in ranges.

Type of measurement	Repeatability (RSD%, n=4)	Reproducibility (RSD%, n=20, days=5)
Retention time (s)[a]	0.03 – 0.35	0.11 – 0.32
Drift time (ms)[b]	0.00 – 0.12	0.67
Signal intensity (a.u.)[c]	0.36 – 5.38	0.79 – 6.27

a) Values were based on 13 identified compounds: ethyl propionate, ethyl butyrate, ethyl isobutyrate, isobutyl acetate, ethyl 2-methylbutyrate,ethyl isovalerate, isobutanol, isoamyl acetate, isoamyl alcohol, ethyl hexanoate, hexyl acetate, ethyl octanoate,1-hexanol;
b) As all peak areas were defined relative to the RIP, the repeatability and reproducibility values of drift time were measured according to the RIP ;
c) volume-under-the-shape.

3.3 Fingerprint aroma profiling and peak identification in Sauvignon Blanc wine

Following the method optimisation and precision study, the developed HS-GC-IMS method was used to establish aroma profiles for Sauvignon Blanc wines. The current study features a non-targeted approach, in which all peaks on the chromatogram were used to construct a detailed aroma profile, regardless of the actual identity of each peak. Such a non-targeted approach enables subsequent chemometric analyses to exploit potential variations across different samples using the maximum amount of raw information captured by the instrument.

An initial visual inspection of the chromatograms generated by the SHS-GC-IMS instrument revealed that most volatiles appeared from retention time 3 to 21 min and drift time 1.21 RIP rel. to 2.12 RIP rel. A comparative chromatogram showing currently identified peaks of a young and an aged Sauvignon Blanc wine is presented in **Figure 1**. An illustration showing the 3D structure of an example SHS-GC-IMS peak is shown in **Supplementary Figure S1**. Also, the chromatogram showing all unidentified peaks is presented in **Supplementary Figure S2**. Multiple volatiles appeared to the right side of the ethanol peak. These compounds that coelute with ethanol normally require further mass spectral investigation to confirm their identity when analysed on conventional GC-MS equipment.[25] However, they were easily separated by the SHS-GC-IMS instrument, due to their different ion mobilities.

When an analyte is present at an excessively high concentration, it can exhaustively bind all available reactant ions, thereby driving the signal intensity towards the theoretical maximum (i.e. equal to the RIP intensity when IMS is idle), and hence interfering with quantification of the compound.[26-27] This characteristic of IMS dictates an upper limit for the quantitative analysis of volatiles.[27] Certain analyte peaks in the chromatogram produced a strong instrument response, in that the reactant ion peak was completely substituted (e.g. peak 2: ethyl acetate), which exemplifies the aforementioned SHS-GC-IMS upper limit for accurate quantification.

Among the 65 recognisable signals, a total of 32 peaks were identified using reference standards. Information related to peak identification is summarised in **Supplementary Table S3**. The majority of the identified aroma compounds were esters, along with some alcohols. The information regarding unidentified peaks is also collated in **Supplementary Table S4**.

Some of these identified compounds have rarely before been reported in Sauvignon Blanc grapes and wines, including methyl acetate, ethyl formate, propyl acetate, and amyl acetate. For example, a study published in 1964 determined the presence of ethyl formate, and the tentative presence of methyl acetate, in Sauvignon Blanc grapes.[28] Propyl acetate has been quantitatively assessed by Antalick, Perello and de Revel, although their wine samples consisted of Sauvignon Blanc blended with other white wine varieties.[29] By innovatively applying SHS-GC-IMS to wine analysis, these compounds were clearly identified. Their explicit peak shapes will also enable further quantitative analyses in the future.

In addition to GC retention index, IMS provides another metric for compound identification, namely the reduced ion mobility (K_0, with units of $cm^2 \cdot V^{-1} \cdot S^{-1}$). In IMS, the time span for ions to traverse the drifting tube (drift time, t_D) is directly measured, and can subsequently be used to calculate K_0 using equation (1):

$$K_0 = \frac{L}{E \cdot t_D} \cdot \frac{p}{p_0} \cdot \frac{T_0}{T} \quad (1)$$

where L = drifting tube length (cm), E = strength of electric field in the ionisation chamber ($V \cdot cm^{-1}$), t_D = drift time (s), p = drift gas pressure (kPa), p_0 = normal pressure (101.3 kPa), T = drift gas temperature (K), T_0 = normal temperature (273.2 K). As K_0 is normalised against normal pressure and normal temperature, it becomes device-independent and comparable on different drift-time IMS instruments. Hence, the K_0 values were determined for all of the identified compounds, and are listed in **Supplementary Table S3**.

A number of compounds, depending on their concentration, are able to form dimer ions in the IMS, which adds extra confidence in compound identification.[30] According to Gerhardt et al., dimer ions tend to completely replace monomer ions as the compound concentration increases.[31] Although theoretically, trimer ions could also be formed in the IMS, their instability means that they have a relatively short survival time and can rarely be observed in IMS spectra.[30]

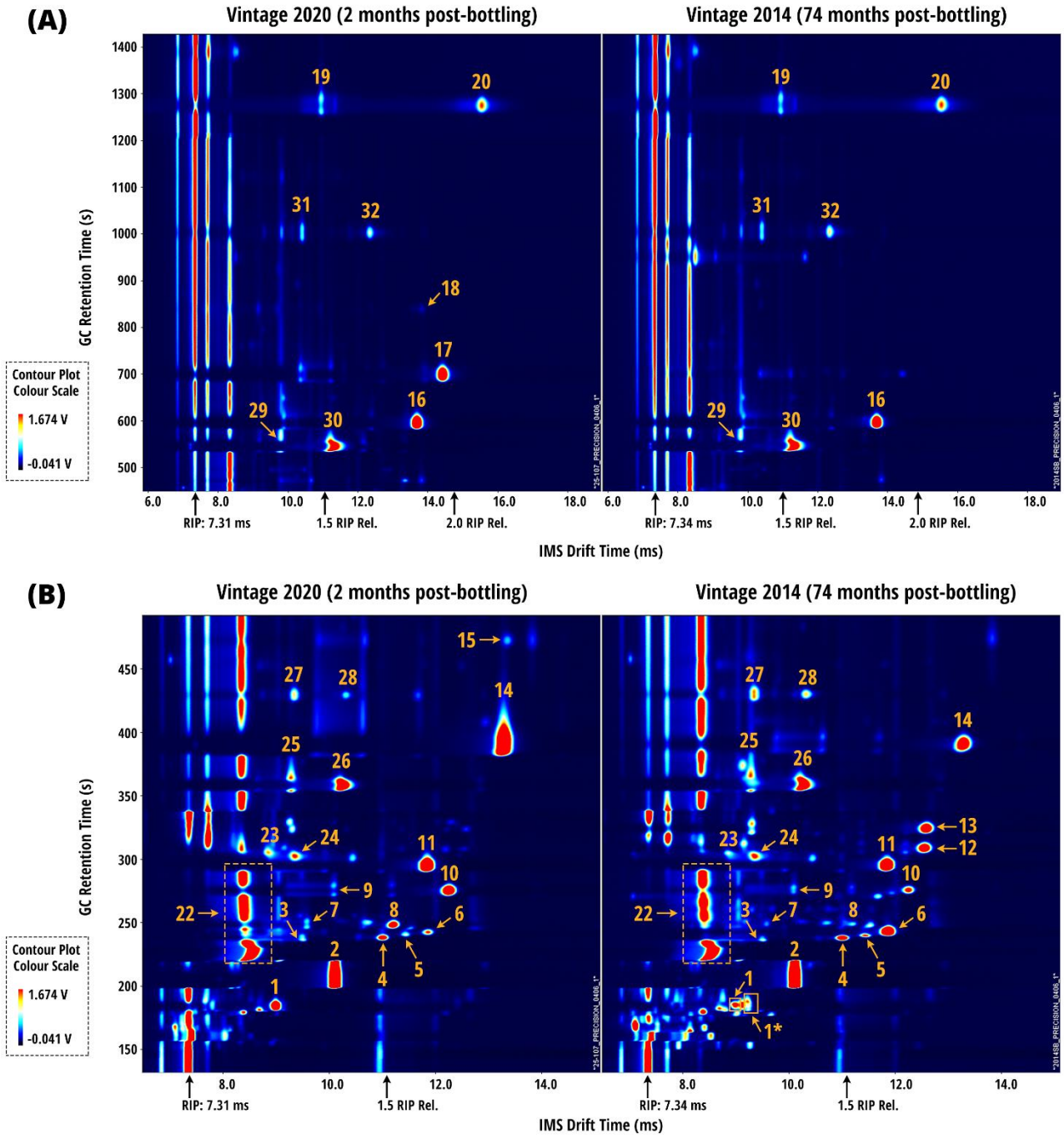


Figure 1. Chromatograms of two NZ Sauvignon Blanc wines analysed using SHS-GC-IMS. (A) The upper half of the chromatogram with retention time 8.33 – 23.33 min. (B) The lower half of the chromatogram with retention time 2.5 – 7.5 min. The numberings of peaks are as follows: (1) methyl acetate, (1*) ethyl formate, (2) ethyl acetate, (3) ethyl propionate (monomer), (4) ethyl propionate (dimer), (5) ethyl isobutyrate (monomer), (6) ethyl isobutyrate (dimer), (7) propyl acetate (monomer), (8) propyl acetate (dimer), (9) isobutyl acetate (monomer), (10) isobutyl acetate (dimer), (11) ethyl butyrate, (12) ethyl 2-methylbutyrate, (13) ethyl isovalerate, (14) isoamyl acetate, (15) amyl acetate, (16) ethyl hexanoate, (17) hexyl acetate, (18) (*z*)-3-hexenyl acetate, (19) ethyl octanoate (monomer), (20) ethyl octanoate (dimer), (21) ethyl decanoate (not shown), (22) ethanol, (23) 1-propanol (monomer), (24) 1-propanol (dimer), (25) isobutanol (monomer), (26) isobutanol (dimer), (27) 1-butanol (monomer), (28) 1- butanol (dimer), (29) isoamyl alcohol (monomer), (30) isoamyl alcohol (dimer), (31) 1-hexanol (monomer), (32) 1-hexanol (dimer).

3.4 Grading prediction of Sauvignon Blanc wines with chemometric methods

The chemometric tools employed in the current study were inspired by the research published by Vega-Márquez et al. in 2019[32] and the fast-growing machine learning community. In summary, an unsupervised principal component analysis (PCA) was conducted first to inspect clustering of the samples based on the SHS-GC-IMS data. Then, six different classification models, namely, PCA-LDA, PLS-DA, *k*NN, SVM, XGBoost, and ANN, were tested for their capabilities to correctly assign samples to their corresponding gradings. Lastly, the model with the highest discriminatory power, together with its validation results, was interpreted and visualised using SHAP values for intuitive delineation.

3.4.1 Principal Component Analysis (PCA) of SHS-GC-IMS data

Since the SHS-GC-IMS instrument was programmed to operate under isothermal conditions, and compound separation was facilitated with the carrier gas flow ramp, a crucial first step of data cleaning was the alignment of chromatograms to ensure peaks were well placed within pre-defined areas. Then, a principal component analysis (PCA) was conducted on all 65 peaks arising for the 143 Sauvignon Blanc end-ferment samples, regardless of their identities. The PCA was used as an exploratory method on the discriminatory power of SHS-GC-IMS data, before supervised classification methods were implemented.

However, as seen in the PCA score plot shown in **Supplementary Figure S3**, no clear clustering could be identified, with the first two principal components (PCs) merely explaining 36.48% of all variance in the data. Moreover, neither PC1 nor PC2 could explicitly separate a certain wine grading from the others. A high degree of intra-grading variability of samples could also be observed. Since PCA functions as a linear projection of high dimensional data into a lower dimensional space, it lacks the ability to explain complex non-linear relationships that are likely present in the SHS-GC-IMS data.[33] Hence, advanced methods that could recognise non-linear variable relationships were tested.

3.4.2 Advanced chemometric methods for wine grading classification: the introduction

As previously described in **Section 2.4**, a collection of six advanced methods (PCA-LDA, PLS-DA, *k*-NN, SVM, XGBoost, ANN) were used in the classification of wine gradings. Each of the six methods possesses distinctive principles of discriminating the possible grading for a specific sample.

Although the underlying principles of these chemometric methods are essential in understanding how the models could transform the input data into classification results, they will not be discussed elaborately in this article for the sake of conciseness. Interested readers are encouraged to refer to the publications listed in **Supplementary Table S5** for more detailed information.

3.4.3 Advanced chemometric methods for wine grading classification: the implementation

The six chemometric models were tested using k-fold cross validation for their efficacy in wine grading classification. Model efficacy was represented by prediction accuracy and the area-under-curve (AUC) of the receiver operating characteristic (ROC) curve. Readers are recommended to consult Rodriguez, J. D., Perez, A. and Lozano, J. A. (2010)[34] for details regarding k-fold cross validation, and Brown, C. D. and Davis, H. T. (2006)[35] for information regarding the AUC or ROC.

The cross validation accuracy and AUC of ROC figures are summarised in **Table 2**. It can be seen that simple statistical models such as PCA-LDA and PLS-DA, where linear correlations are inferred between the input (peaks) and the output (classes), demonstrated less desirable performance. As the model structure became more

complicated (ensemble algorithm and neural network), the accuracy and AUC of ROC rose accordingly. This points to the inherent complexity of not only standalone correlations, but also high-order interactions between volatile compounds, which result in the depth of wine aroma as perceived by humans. The most complex model of all, the artificial neural network (ANN), also achieved the highest average classification accuracy of 89.5% with the highest AUC of ROC (0.983). Hence, this model was chosen for the subsequent model prediction test, which was based on the 85%/15% train/test split of the original dataset.

Table 2. Robustness of different chemometric algorithms using SHS-GC-IMS data based on 10-fold cross validation.

Classification algorithm	Classification accuracy [d]	AUC of ROC
PCA-LDA [a]	65.7% (7.3%)	0.552
PLS-DA [b]	58.7% (1.5%)	0.729
k nearest neighbour (*k*-NN) [c]	60.8% (7.9%)	0.787
Support vector machine (SVM)	51.8% (1.1%)	0.703
eXtreme Gradient Boosting (XGBoost)	81.8% (8.0%)	0.940
Artificial neural network (ANN)	89.5% (6.0%)	0.983

a) The first five principal components were used;
b) The first five latent variables were used;
c) k was set to five;
d) Represented as average of 10 cross validated results, with the standard deviation shown in parentheses.

In the complete set of 268 wine samples (143 wines tested in duplicates), a total of 225 samples was firstly used to train the ANN model. During the training process, the neurons from both hidden layers were activated to study the patterns in the data, and attempt to minimise the prediction error using stochastic gradient descent. After the training process was completed, a collection of 43 wine samples (11 Grade A, 22 Grade B, 10 Grade C) was passed onto the trained model to predict their gradings. The model performed excellently and was able to return a prediction accuracy of 95.4%. Only two samples were mislabelled, both of which were Grade A and were incorrectly assigned Grade C by the model. The prediction results are summarised in **Supplementary Table S6**. The combination of SHS-GC-IMS and powerful classification tools such as the artificial neural network can thus deliver highly satisfactory outcomes, despite the large amount of volatile compounds involved.

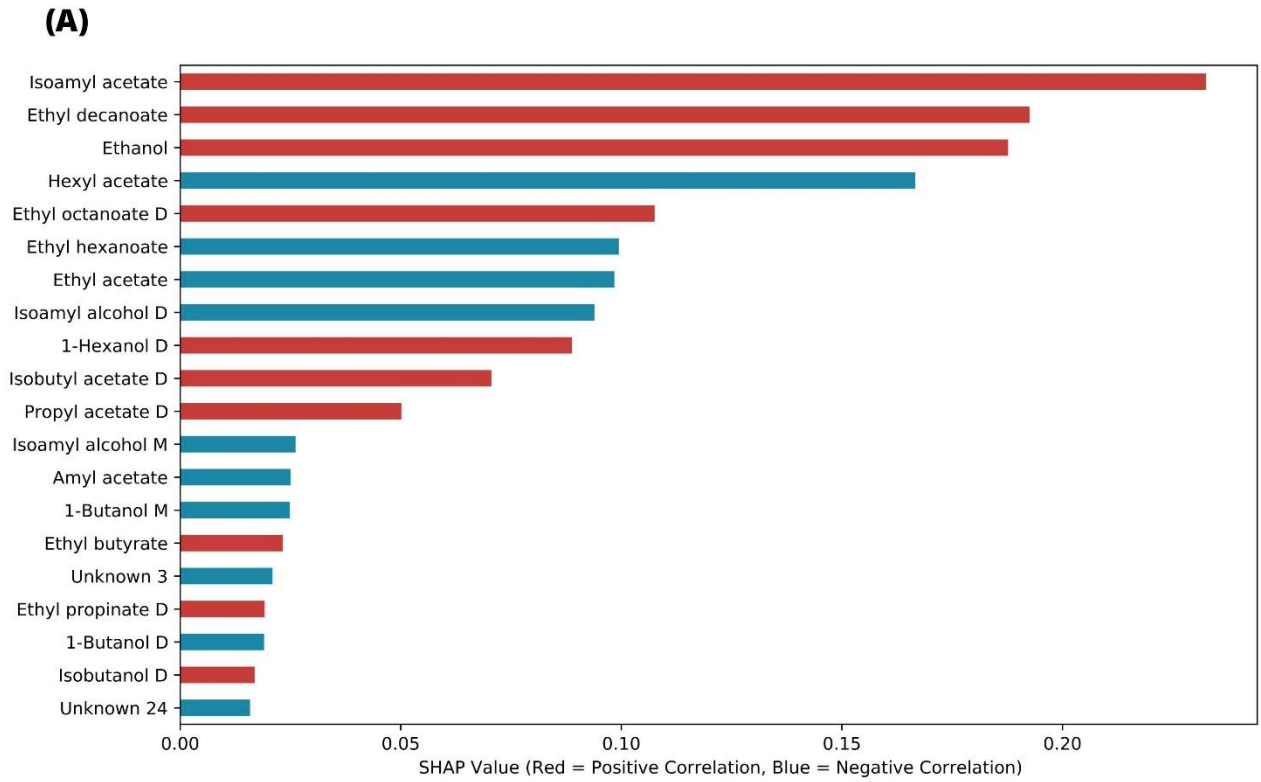
3.4.4 Advanced chemometric methods for wine grading classification: the interpretation

Although desirable classification results were achieved using sophisticated algorithms such as XGBoost and ANN, these models have been traditionally regarded as "black-boxes" compared to conventional, more straight-forward classification methods such as LDA. These later methods accept data input and produce a classification output, whereas the decision process in between is excessively complicated for humans to comprehend (see **Supplementary Figure S4**).[36] Hence, such algorithms also lack the important attribute of interpretability and the possibility to feedback the analytical discoveries to guide upstream operations.

A powerful tool named SHapley Additive exPlanations (SHAP) values was developed by Lundberg and Lee in 2017, which inherits an idea from coalitional game theory and aims to uncover the marginal contribution of each feature in a statistical model, regardless of its complexity.[37] The SHAP values method was used in the current

study to differentiate the contributions of each peak on the final model output for the purpose of global model interpretations.

The SHAP values for the high grading A and the low grading C wines are shown in **Figure 2**. Compared to the medium grading, both the higher and the lower ends of the grading spectrum are of more interest, as they indicate potential future directions to optimise winemaking.



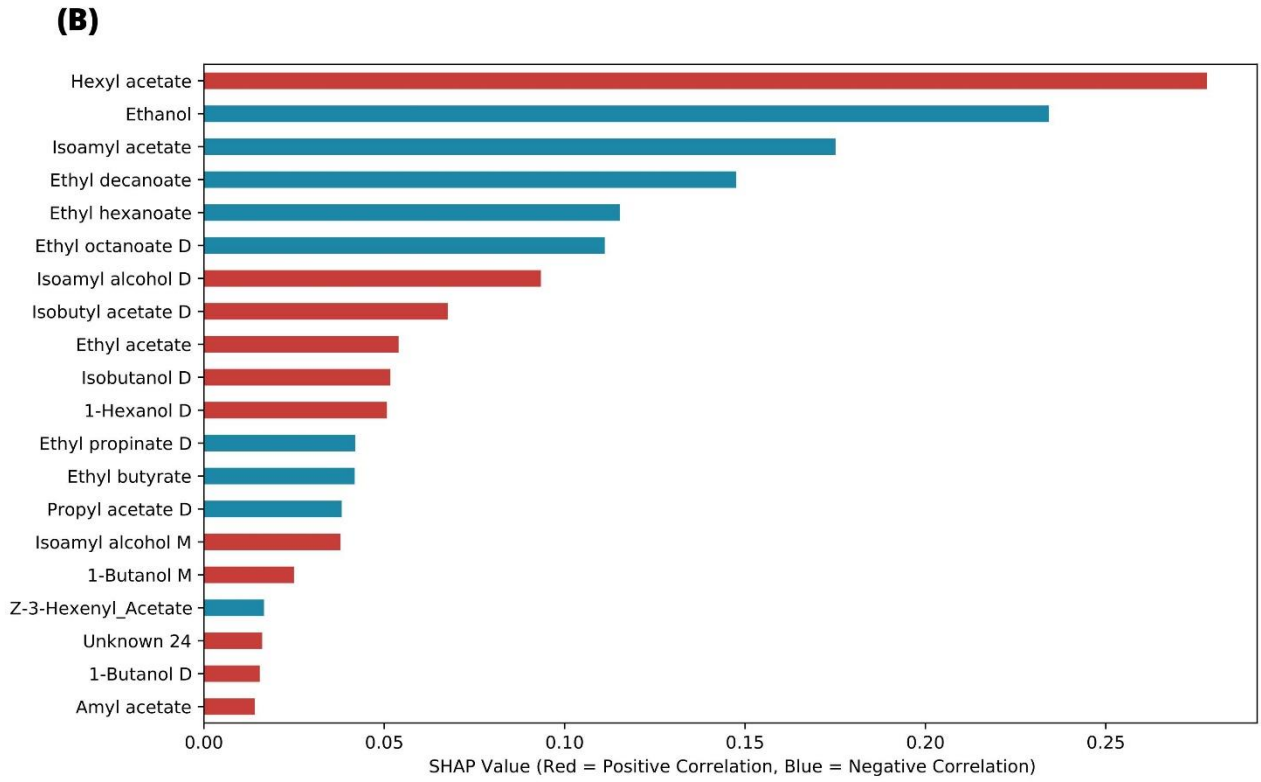


Figure 2. (A) SHAP values for samples pertaining to grading A (high grading); and (B) SHAP values for samples pertaining to grading C (low grading). Compounds with bars in red indicate a positive correlation with the particular grading, whereas compounds with blue bars indicate a negative correlation. The SHAP value is also proportional to the influence on model output. Hence, the compounds have been sorted according to their descending order of influence on the ANN model.

It can be seen from the SHAP values that isoamyl acetate, ethyl decanoate, ethanol, ethyl octanoate and 1-hexanol are the top five most influential compounds that drive the model prediction towards the Grade A category. Among these compounds, isoamyl acetate and ethyl octanoate have been previously shown to have strong positive effects on young white wine bouquet, with banana and pear notes, respectively.[38] Also, thanks to the wide use of machine harvesting in the Marlborough region, 1-hexanol has been typically found in concentrations higher than its sensory threshold, which imparts green, grassy, and bourbon characters.[38-39] Indeed, in the article published by Benkwitz et al. in 2012, isoamyl acetate, ethyl decanoate, ethyl octanoate and 1-hexanol are among the most important volatiles that contributed to the characteristic NZ Sauvignon Blanc aroma.[38] These compounds, due to their higher abundance in NZ Sauvignon Blanc wines, are also responsible for separating them from their international counterparts.[40] Hence, it is not unexpected that these compounds would correlate positively with the highest sensory grading for quality NZ SB wines, as assessed by experienced winemakers.

The influence of ethanol, on the other hand, is more complex. An increase in ethanol content has been demonstrated to lower the availability of various volatiles in the headspace of wine, including the aforementioned four compounds.[41] This could be revealed by the SHS-GC-IMS, since no pre-concentration steps were involved. However, a study published recently pointed out that 10% alcohol in a low-polyphenol rosé wine tended to increase the persistence of fruity esters in the mouth, compared to the same wines after dealcoholisation, which enhances the retronasal olfaction of these volatiles.[42] Since the grading of wines in this study involving both smelling and tasting of the wines, the desirable effects of ethanol on the wine palate, together with the retronasal enhancement of esters, likely outweighed the detrimental effects, thereby contributing to a positive correlation with wine grading.

By contrast, the most prominent factor that led the classification model to favour grading C predictions, was hexyl acetate. This compound has been shown to be derived from C_6 alcohols and aldehydes such as 1-hexanol, hexanal, (*E*)-2-hexen-1-ol, and (*E*)-2-hexenal, during alcoholic fermentation.[43] Although C_6 compounds are normally unappreciated when present in wines, in NZ Sauvignon Blanc wines these volatiles can provide green and grassy notes that are desired by consumers.[44] Hence, the high levels of hexyl acetate could be related to the loss of green characters in young wines, which is likely to lead to a lower grading. Moreover, (*E*)-2-hexen-1-ol and (*E*)-2-hexenal have been confirmed as precursors of two varietal thiols (3-mercaptohexanol, 3-mercaptohexyl acetate) that are of critical importance to the sensory profile of Sauvignon Blanc wines.[45-46] Therefore, their conversion into hexyl acetate could in turn lower the concentration of varietal thiols, which are greatly favoured by consumers and winemakers alike. Additionally, the high concentration of hexyl acetate was previously reported to be present in heavily pressed grape juices.[39] Such juice fractions have been shown to inherently contain less varietal thiols and could subsequently undergo advanced polyphenol oxidation during, which negatively impacts the mouthfeel and the aroma release from the finished wine.[47] Hence, it can be concluded that hexyl acetate functions as a suppressor of desirable Sauvignon Blanc sensory traits which results in the model drifting towards lower grading predictions.

Furthermore, as reported by Cameleyre et al., isoamyl alcohol and 1-butanol was able to impose suppressive effects on the fruity notes perceived in a simulated wine matrix, which contained 13 esters, including those previously show to correlate positively with higher grading (isoamyl acetate, ethyl hexanoate, ethyl octanoate).[48] These findings were further investigated by the same research group, using static headspace low pressure GC-MS. It was shown that such suppressive effects could be due to the reductions to the partition coefficients of

fruity esters in the wine system in the presence of higher alcohols.[49] Such conclusions are highly applicable to the current study, as the SHS-GC-IMS method also utilised a static headspace unit for sample extraction. The "fruity" attribute, as described by Lund et al., contributes considerably to the typicality of New Zealand Sauvignon Blanc wines.[50] Therefore, the positive correlation between lower quality grading and higher alcohols, as revealed by the SHAP value, could be due to the deleterious effect of higher alcohols on fruity esters.

Despite the succinct information revealed using the SHS-GC-IMS method, the neural network model and the SHAP values, it must also be noted that the aroma profile of wines is highly complex, and includes many other volatile compounds that were not observed in the present study. For example, the varietal thiols, which play a major role in the characteristic NZ Sauvignon Blanc wines, could not be detected, and were thus were not part of the model-building. Other non-polar compounds are also not within the scope of analysis due to the polar MXT-WAX GC column fitted to the instrument.

The SHS-GC-IMS method can thus serve as a fast screening technique to provide winemakers with possible gradings of end-ferment wines prior to tank blending, which could be used as an extra reference based on objective measurements. Also, as higher grading wines need consensus from winemakers for extra confirmation, using the SHS-GC-IMS method to pre-sort and filter out lower-grade wines could reduce the workload of winemakers, and allow them to concentrate more on wines with potentially higher gradings.

4 CONCLUDING REMARKS

The current study has demonstrated the use of SHS-GC-IMS as a fast and reliable method for the untargeted screening of volatile compounds in wines. In addition to the stability and comprehensiveness manifested by the method itself, the succinct information gained can be fed into sophisticated machine learning models to produce a powerful tool for the prediction of wine quality, with high levels of accuracy and confidence.

Regardless of the inherently complicated structure of machine learning models, useful, human-comprehensible information was also extracted using SHAP values. Such information could be a starting point for winemakers to investigate the effects of winemaking operations on the expression of the volatiles shown to correlate with higher gradings, in order to enhance the quality of wines.

In a commercial laboratory setting, where cost-efficiency and high turnover are favoured over more detailed analytical information, SHS-GC-IMS functions impressively as a benchtop alternative to instruments such as GC-MS. However, more research should be conducted to fully explore the potential of the instrument to produce quantitative results in addition to the semi-quantitative data provided by signal intensities.

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CONFLICT OF INTEREST

The authors declare no conflict in competing financial interest.

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