Exploring analytical methods for the detailed chemical profiling of old Vine Chenin blanc wine volatiles

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Introduction

Chenin blanc is a cultivar that lends itself to the production of wide variety of popular styles. Traditionally used in the production of bulk wines, this cultivar is recently being recognised for the production of premium wines. Chenin blanc wines produced from old vines (older than 35 year) are considered superior due to their unique sensory attributes. While sensory studies confirm this, very little is known about the aroma chemistry of South African Chenin blanc wines in general, and old vine wines in particular.

In the present work, we report on evaluation of different analytical methods for the elucidation of the unique volatile composition of old vine Chenin blancs compared to wines produced from younger vineyards. Different sample preparation techniques in combination with gas chromatography-mass spectrometric (GC-MS) analysis are shown to provide complementary information on the volatile composition of these samples, while preliminary comprehensive 2-dimensional GC×GC-MS analysis showed promise for more detailed investigation of volatile constituents of this cultivar. Liquid-liquid extraction (LLE) in combination with GC-MS and multivariate statistical data analysis is then used to differentiate young from old vine Chenin blanc wine samples based on their volatile composition.

Sample preparation

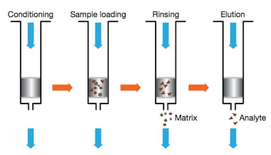
Liquid-liquid extraction (LLE)

Wine:	5 mL
Solvent:	1 mL dichloromethane (DCM)
Time:	15 min

Headspace solid phase micro-extraction (HS-SPME)

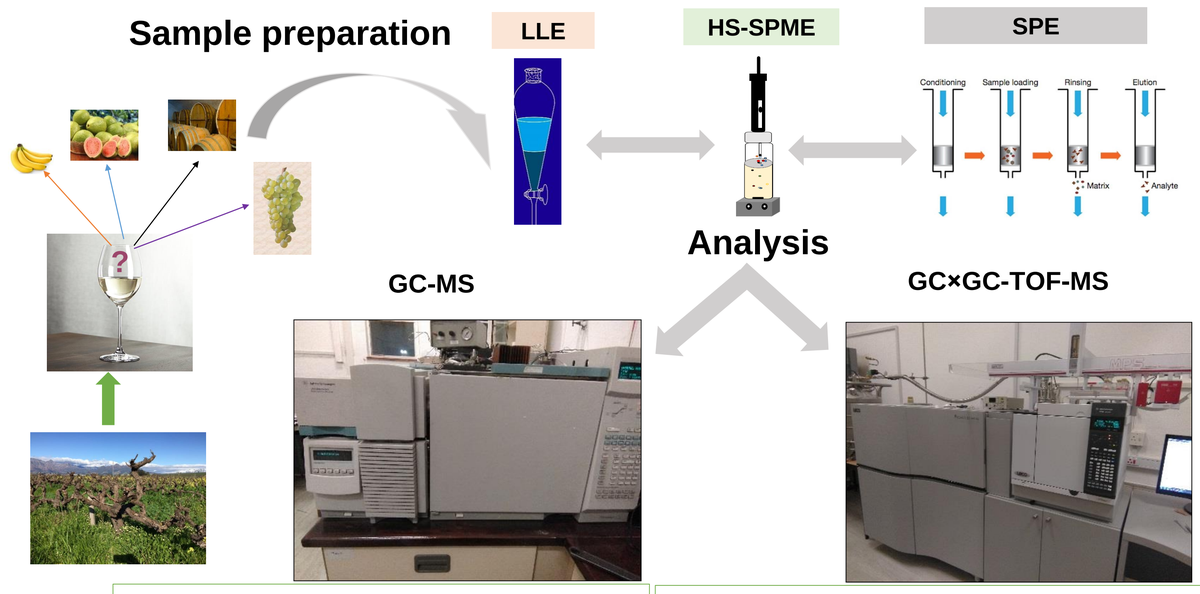
Fiber:	DVB/CAR/PDMS
Temperature:	50°C
Wine sample:	11% wine/water (v/v)
Extraction time:	30 min
Salt content :	30% NaCl

Solid phase extraction (SPE)



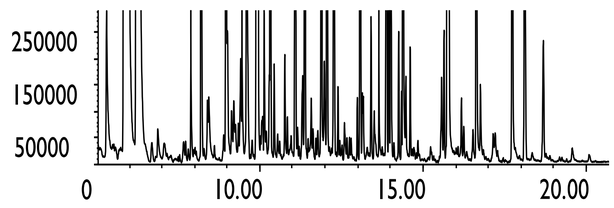
Cartridge:	SDB-L (500 mg/ 3mL)
Wine:	40 mL
Rinse:	20 mL 1% $NaHCO_3$ in 50% MeOH/H_2O
Elution:	1.5 mL DCM

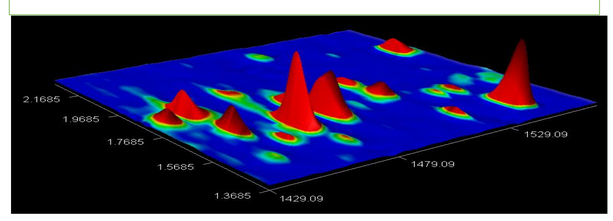
Instrumental conditions



Column:	30 m × 0.25 mm × 0.25 µm HP-FFAP
Carrier gas:	He (1 mL/min)
Injection:	230°C split 1:10 for LLE and SPE, splitless 2 min for HS-SPME
Oven:	40°C (2 min), 5°C/min to 230°C (5 min)

Columns:	^{1}D: 30 m × 0.25 mm i.d. × 0.25 µm d_f Rxi-5Sil MS
	^{2}D: 0.6 m × 0.25 mm i.d. × 0.25 µm d_f StabilWax
Carrier gas:	He (1 mL/min)
Injection:	240°C, split 1:10 (HS-SPME)
Modulation:	4 sec, cryogenic cooling (liquid N_2)
Oven:	40°C (2 min), 5°C/min to 220°C (5 min)
Detection :	HR-TOF-MS , 50-500 m/z, 200 Hz





Results and discussion

Sample preparation method comparison

Different sample preparation methods were optimised and compared in terms of the volatile constituents which could be analysed using each by GC-MS. 128 volatile compounds could be tentatively identified in Chenin blanc using LLE-, HS-SPME- and SPE-GC-MS. Significant differences in terms of the compounds identified using each of these methods were observed (**Fig. 1A**). LLE was found to be suitable for the analysis of major volatile compounds such as esters, acids and alcohols, whereas SPE was suited to the extraction of trace-level compounds such as terpenes, aldehydes and ketones and HS-SPME provided a good compromise for a wide range of Chenin blanc volatiles.

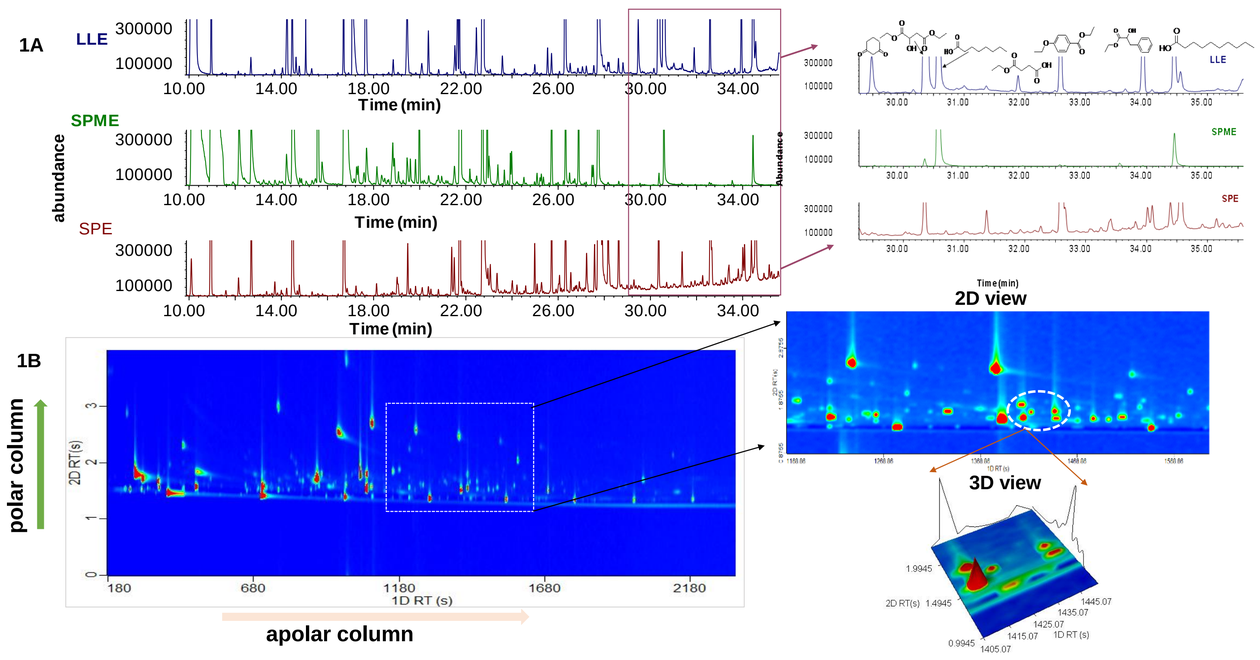


Fig. 1: 1 A Comparison of GC-MS chromatograms obtained for the analysis Chenin blanc volatiles using LLE, HS-SPME and SPE; **1B** Contour plot obtained for Chenin blanc by HS-SPME-GC×GC-TOF-MS.

Initial HS-SPME-GC×GC-TOF-MS experiments demonstrate the improved separation obtained using this technique (**Fig. 1B**). In combination with high resolution MS, more than 200 compounds could be tentatively identified in this manner.

Conclusions

This work showed that for the comprehensive characterisation of Chenin blanc volatiles, complementary sample preparation methods are required. Preliminary HS-SPME-GC×GC-MS analysis confirm the power of this method for improved analysis of Chenin blanc volatiles; further work is required using different sample preparation methods. Using LLE-GC-MS in combination with multivariate statistical data analysis, we were able to differentiate between Chenin blanc wines produced from old and young vines, and to identify volatile compounds responsible for this differentiation. Detailed statistical analysis using quantitative data for the compounds identified in the studied wines is currently underway.

Differentiation between old and young vine Chenin blanc wines based on volatiles

To investigate differences in the volatile composition between Chenin blanc wines produced from old and young vines, LLE-GC-MS analysis was used. Similar compounds were detected in both sample groups, with differences mainly observed in terms of their relative abundance (**Fig. 2A**).

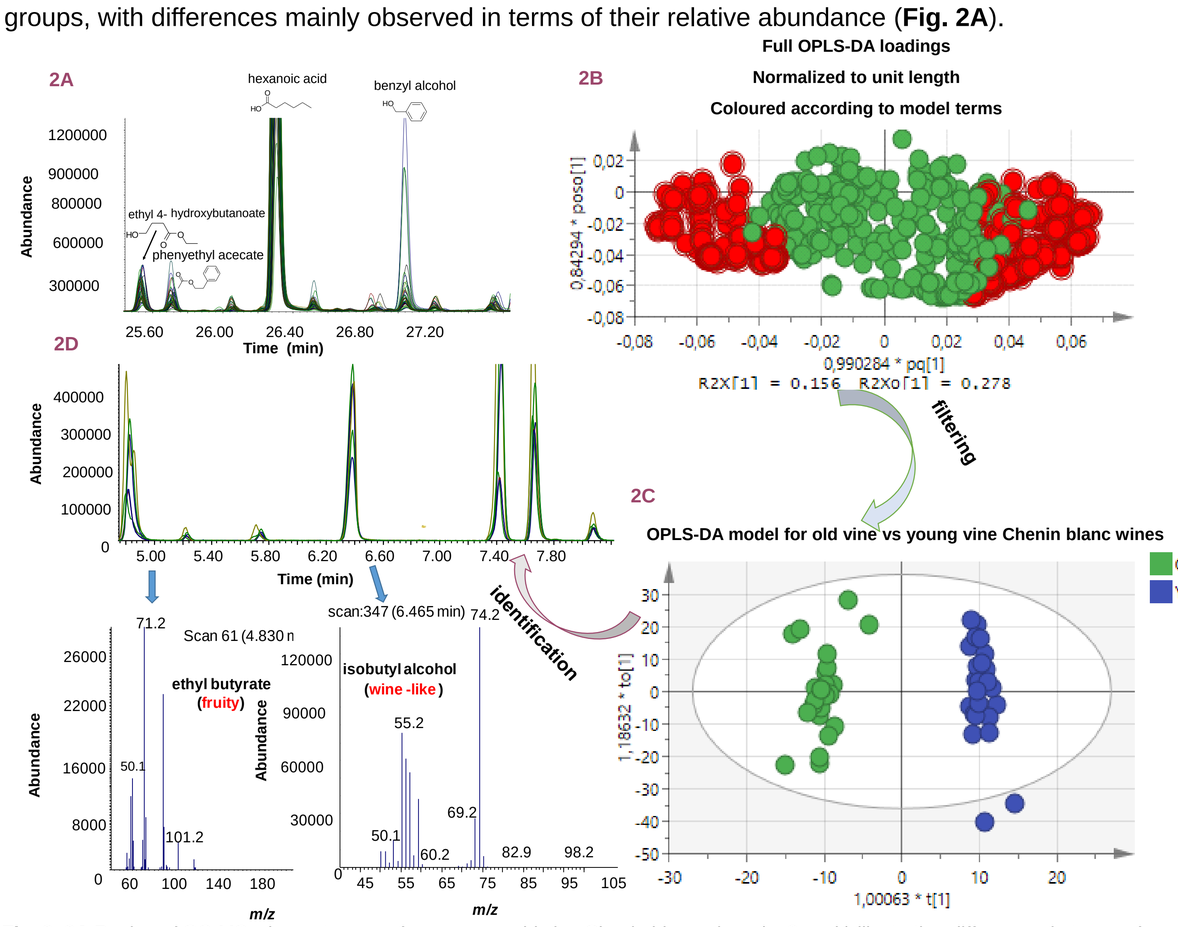


Fig. 2: 2A Region of GC-MS chromatograms for young an old vine Chenin blanc wines (n=8 each) illustrating differences in terms of relative abundances of volatiles; **2B** Full OPLS-DA loadings plot illustrating features in young and old vine Chenin blancs; **2C** OPLS-DA plot obtained for both sets (O=old vine; Y=young vines) based on volatile content; **2D** Overlaid GC-MS chromatograms illustrating different levels of two compounds responsible for the differentiation between old and young vine Chenin blancs: ethyl butyrate and isobutyl alcohol as examples.

GC-MS data were subjected to principal component analysis (PCA) (**Fig. 2B**) to identify distinguishing features, and orthogonal partial least square-discriminant analysis (OPLS-DA) was used to identify compounds responsible for differences between the young and old vine Chenin blancs (**Fig. 2C**). Using the output from this model, individual compounds responsible for the observed differentiation could then be identified (selected examples in **Fig. 2D**).

Acknowledgements

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