

INTRODUCTION

Port wine is a fortified wine produced in the Douro Demarcated Region (DDR) of Portugal, widely known throughout the world. This type of wine is produced from authorized grape varieties grown in the DDR and by a specific winemaking practice. Particularly, Tawny Port wines are stored in small wood barrels during several years and bottled at commercialization time [1]. The extent of this aging process is essential to the quality of the final product. In this oxidative aging process, Tawny Port wine undergoes through many changes in colour and aroma, with the levels of some compounds decreasing over time while other increase or appear [2]. Some of the compounds formed or accumulated over the aging time can be considered age markers being the wine aging process a complex system [3], so it is important to know more about the evolution of the aroma composition of Tawny Port wines. In line with that, it is necessary the optimization of a method to identify the compounds present in Tawny Port wines aroma. Some parameters like sample dilution, extraction temperature and time and ionic strength effect from adding different amounts of NaCl were optimized using a four three-level box blocks design to factorial with three determine the optimal experimental conditions the volatile for analysing compounds in Tawny Port wine aroma by HS-SPME-GC/MS (headspace solid phase microextraction – gas chromatography mass spectrometry) using a DVB/CAR/PDMS fibre. The optimal conditions were as follows: sample dilution of 5 mL of wine to 5 mL of water with 3.5 g of NaCl and the extraction during 90 min at 30 °C. In order to eliminate possible matrix interferences, MHS-SPME (multiple headspace solid phase microextraction) was performed to analyse Tawny Port wine samples. .

CONCLUSIONS

A four three-level box factorial design was used to determine the optimal experimental conditions for analysing the volatile compounds in Tawny Port wine aroma by MHS-SPME-GC/MS using a DVB/CAR/PDMS fibre. The optimal conditions were as follows: sample dilution of 5 mL of water to 5 mL of wine with 3.5 g of NaCl and the extraction during 90 min at 30 °C.

REFERENCES

[1] S. C. Cunha, M. A. Faria, J. O. Fernandes. J. Agric. Food Chem. 2011, 59, 8742-8753.

[2] A. C. S. Ferreira, J.-C. Barbe, A. Bertrand. J. Agric. Food

Chem. 2003, 51, 4356-4363.

[3] D. Jacobson, A. R. Monforte, A. C. S. Ferreira. J. Agric. Food

Chem. 2013, 61, 2513-2521.

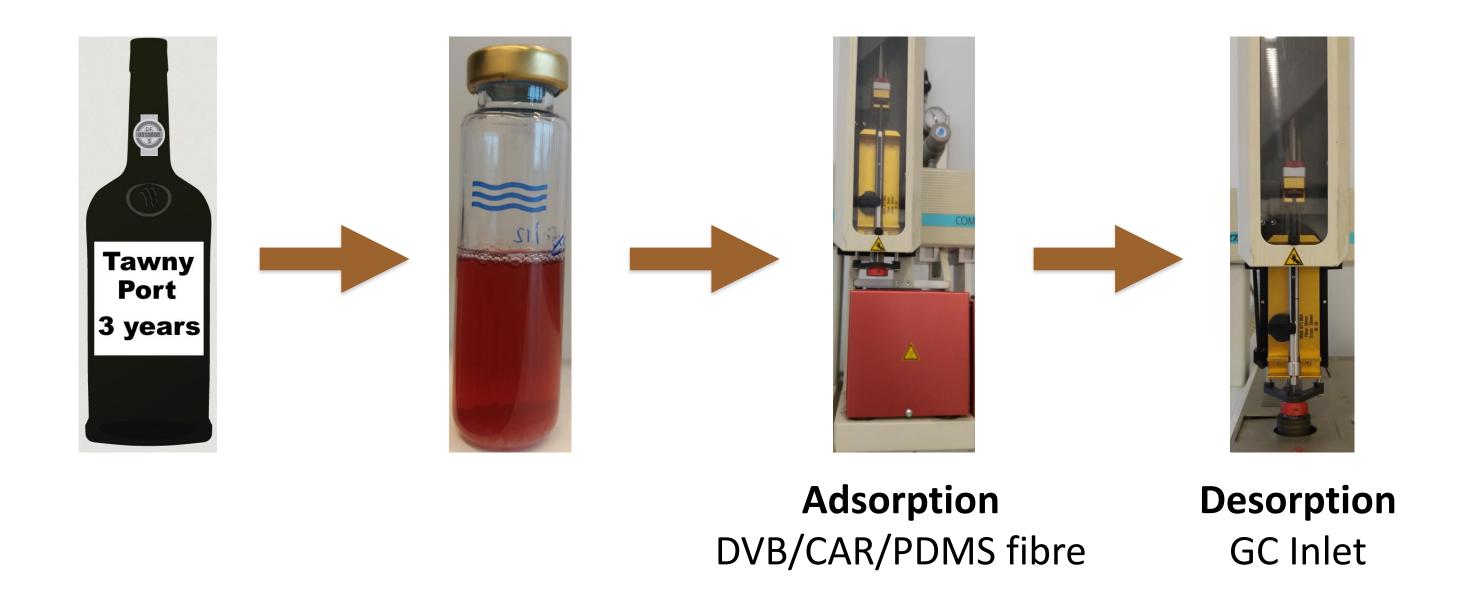
DEVELOPMENT OF A MHS-SPME-GC/MS METHOD FOR THE ANALYSIS OF VOLATILE COMPOSITION OF TAWNY **PORT WINE**

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MATERIALS AND METHODS

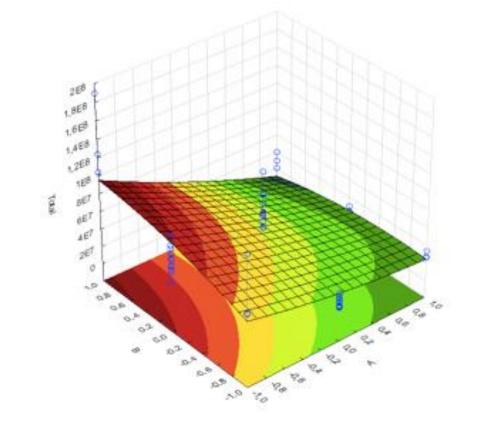


MHS-SPME-GC/MS – Five extractions

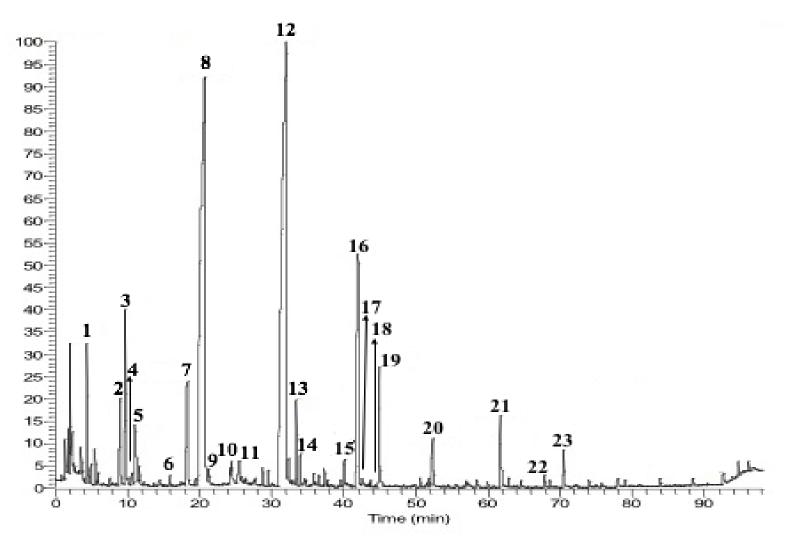
RESULTS

Four three-level box factorial with three blocks design

Factor	-1	0	1
A – Sample dilution (mL)	5 wine + 5 H ₂ O	7.5 wine + 2.5 H ₂ O	10 wine (no dilution)
B – NaCl (g)	0	1.75	3.5
C – Extraction time (min)	30	60	90
D – Extraction temperature ($^{\circ}$ C)	30	40	50



The interaction between the factors sample dilution (A) and amount of NaCl (B) appears statistically significant (p < 0.05). The addition of NaCl has a positive effect when sample is diluted. The total extracted quantity is higher when sample is



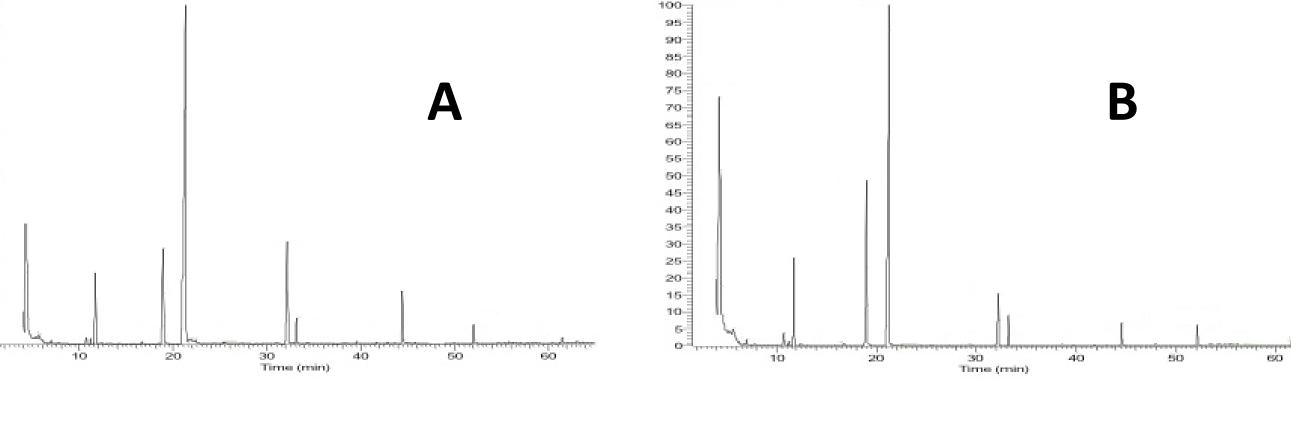
and the extraction during 90 min at 30 ° C.

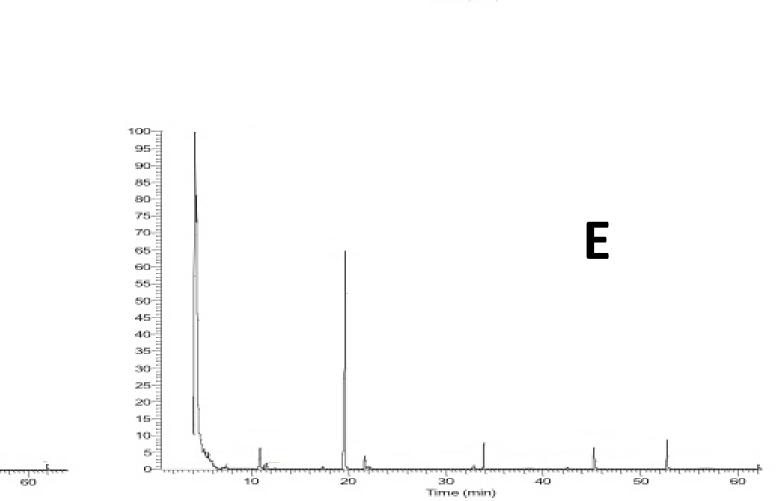
HS-SPME-GC/MS chromatogram of a Tawny Port Wine under optimal conditions of extraction.

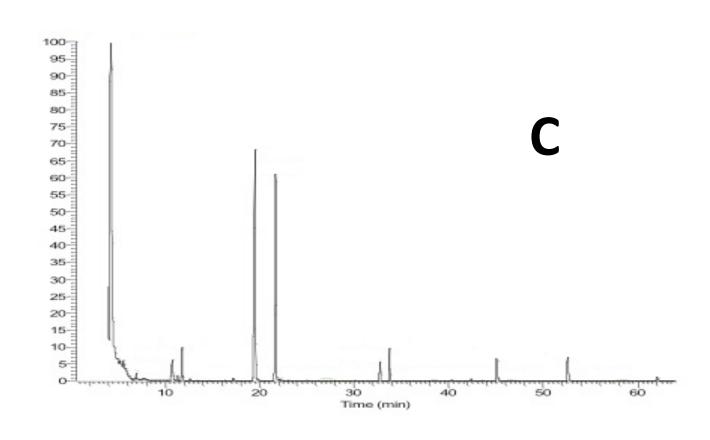
- 1 isoamyl acetate
- 2 3-methyl-1-butanol
- 3 ethyl hexanoate
- 4 p-cymene
- 5 1-hexyl acetate
- 6 1-hexanol
- 7 3-octanol (Internal Standard)

diluted and with NaCl. So, the optimal conditions are: sample dilution of 5 mL of wine to 5 mL of water with 3.5 g of NaCl

- 8 ethyl octanoate
- 9 furfural
- 10 vitispirane 11 – benzaldehyde
- 12 ethyl decanoate
- 13 butanedioic acid, diethyl ester
- 14 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN)
- 15 2-methylbenzyl acetate
- 16 ethyl laurate
- 17 isoamyl decanoate
- 18 ethyl 3-methylbutyl butanedionate
- 19 2-phenylethanol
- 20 octanoic acid
- 21 decanoic acid 22 – benzoic acid
- 23 dodecanoic acid

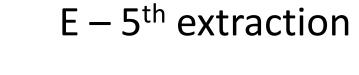






MHS-SPME-GC/MS chromatograms extractions of Tawny Port Wine under optimal conditions of extraction.

- A 1st extraction
- B 2nd extraction
- C 3rd extraction $D - 4^{th}$ extraction





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