

OPTIMIZATION OF A HEADSPACE-SPME-GC-ECD FOR THE DETERMINATION OF CHLOROANISOLE IN WINE AND CORKS

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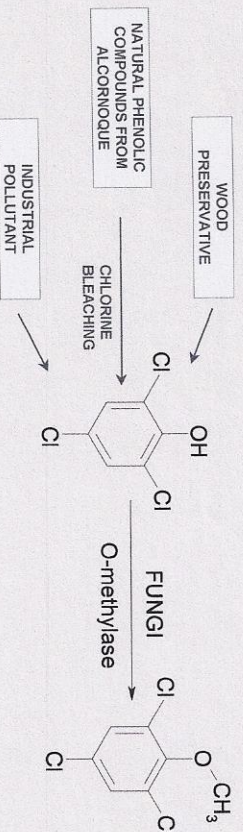
INTRODUCTION

Cork has been used as closures for wine bottles since the 17th century because of its unique physical properties, including long-lasting flexibility, hydrophobicity, and gas impermeability.

"Cork taint", a musty-moldy off-odor, represents one of the most serious problems in wine industry. 2,4,6-Trichloroanisole (TCA), along with other compounds, is known to be responsible for this effect. Wine industry is losing an estimated \$100 million annually in the U.S. alone, due to TCA contamination. The problem could be in the billions of dollars world-wide.

The present work reports an optimized method for rapid TCA determination based on headspace solid-phase microextraction (HS-SPME) followed by gas chromatographic (GC) separation and electron capture mass detection (ECD). The method was validated after a lawsuit had filed against a stopper manufacturing firm, claiming that the agglomerate corks had ruined 80,000 liters of red wine with a retail value of more than \$2,500,000

Formation of 2,4,6-Trichloroanisole



OBJECTIVE: move from sensory to chemical analysis

ANALYTICAL PROCEDURES

SAMPLE PREPARATION: 10mL of wine or ethanol/water (10%) were piped into 20mL screw-cap headspace vials, sealed with a PTFE septum. For cork materials, 100mg of matrix was moistened with 5mL of deionized water and filled into 20mL vials. Samples were saturated with NaCl and allowed 5 min of equilibration time before SPME analysis.

EXTRACTION TEMPERATURE / TIME: was controlled by an oven system maintained at constant temperature (30°C) for 20 min. Stirring rate 1100 rpm.

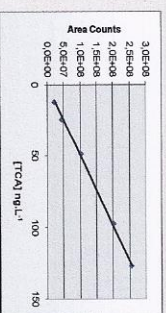
EXTRACTION SPME FIBER: Supelco Polydimethylsiloxane (PDMS, 100 µm)

DESCRIPTION TIME: 5 min at splitless mode, 42mm injector penetration

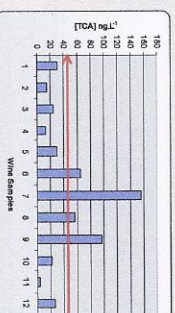
INSTRUMENTATION: HP 5890 Series II Plus chromatograph equipped with an ECD Detector. Column: SUPELCO SPBx.5 Fused silica capillary column (30m x 0.25mm i.d. x 0.25mm film thickness). The conditions were as follows: the initial oven temperature was 80 °C for 2.0 min, then programmed from 80 to 250 °C at 10 °C/min, to a final holding time of 1.0 min. The detector temperature was 280 °C. The injector temperature was 260 °C.

SENSORY ANALYSIS: The level of the musty/moldy off-flavor in the red wines was studied by the magnitude estimation method, performed by four experienced assessors.

METHOD DEVELOPMENT



Linearity/range: 0.5 to 150 ng L⁻¹
 Correlation coefficient: 0.9982
 Accuracy: recovery mean value: 83 – 104 %
 Precision: RSD %: 3.3 (spiked level 20 ng L⁻¹)
 LOD: 1.0 ng L⁻¹ LOQ: 4.0 ng L⁻¹
 Repeatability (n=5): 2.5%



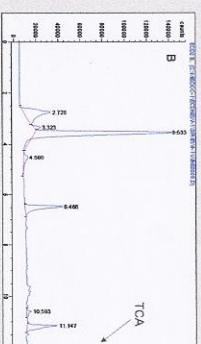
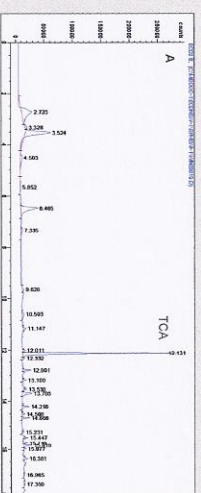
TCA determination of different commercial red early wine (varietal Malbec from Lujan de Cuyo - Argentina)

LABORATORY THRESHOLD
 20 ng/L TCA (red wines)
 19 ng/L TCA (white wines)



Stripped Cork from an Alcornoque Tree, Quercus suber

CHROMATOGRAPHY



CONCLUSIONS

- ✗ The combination of techniques (HS-SPME-GC/ECD) has created an accurate system measuring TCA well below the human identification threshold .
- ✗ The adjustment of method parameters like salt addition, stirring rate and mild temp 30 °C) are relevant variables affecting the TCA extraction.
- ✗ According to our experience, each wine sample is unique showing high matrix effect
- ✗ The entire methodology is "environmentally friendly" due to the absence of any org involved in the analysis and is a real solution for oak chips/shavings screening prior to
- ✗ The availability of reliable, quantitative methods for TCA extraction from both wines allow further investigation into the chemical / physical behavior of TCA in bottled wine
- ✗ A good knowledge of the complex behavior of TCA and the related taint compounds the development of methods to reduce the incidence of cork taint in all wine produc

CORK INDUSTRY

QUALITY CONTROL
 REAL PROBLEMS



U.S. Wine Industry Statistics	
Statistics	Cost Per Year
Value of wine lost to cork taint	\$650 million
Est. cork taint rate	2-5 percent of