Comparative SPDE and SPME Studies for Analysis of Off-Flavors in Wines

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Abstract

An off-flavor in wine known as “cork taint” is of concern to the wine industry. Cork taint imparts a musty flavor to the wine and is primarily due to the presence of 2,4,6 – trichloroanisole (TCA). The olfactory threshold of TCA ranges from 4 to10 ppt in wines. Comparative studies have been carried out using solid phase dynamic extraction (SPDE) and solid phase microextraction (SPME) techniques.

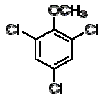

Fig. 1: 2,4,6 TCA

Introduction

A very efficient enrichment technique is needed for the detection of TCA since the complexity of wine matrices often precludes the detection of TCA even with full-scan MS at the low levels required in this application. Studies published in literature show that TCA in this range is commonly determined with GC/MS in SIM mode [2,3].

In this comparative study, SPME and an automated extraction technique called SPDE (also known as the “*magic needle*”, developed by CHROMTECH GmbH, Germany) were used with a CTC Combi PAL Autosampler (Fig. 3) to detect TCA in red wine using GC-FID.

Both techniques used the principle of solventless extraction of partitioning organic compounds, sorption on the stationary phase, followed by thermal desorption, analytes separation and quantification.

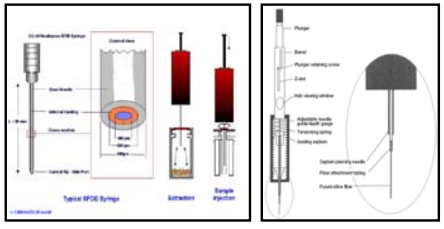

Fig. 2: Schematic diagrams of commercial SPDE and SPME devices

Experiment

Sample Preparation: 10% Ethanol – water (saturated with NaCl) was used for sample preparation. The above solution was then spiked with the diluted standards to final concentrations of 100 ppt to 10 ppb. Sample aliquots of 5mL were piped into 20mL screw-cap headspace vials.

Extraction: The sample extraction was carried out with a SPDE syringe (CHROMTECH GmbH, Germany) and SPME fiber, and was fully automated by the CTC Combi PAL Autosampler. The SPDE syringe was internally coated with PDMS polymer, while SPME had a fiber outside coating containing the same polymer (Fig. 2).

For SPDE, dynamic headspace extraction was carried out using 25 pumping cycles at a vial temperature of 65º C. Desorption was performed in splitless mode with hydrogen at 280º C.

SPME extraction was carried out for 8 min. at a vial temperature of 65º C and was desorbed in the inlet at 280º C.

Commercially bought wines -- Cabernet Sauvignon (2002 California) and Pinot Noir (California 2004) -- were saturated with NaCl and subjected to SPDE and SPME extraction.

SPDE Automation

Fig. 3: GC equipped with CTC Combi PAL Autosampler and SPDE options

Fig. 4: SPDE Kit

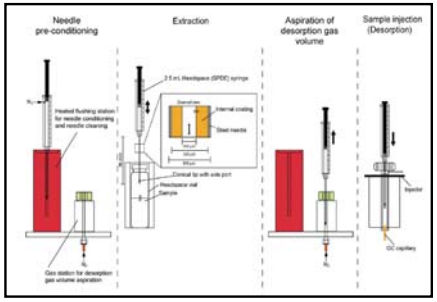

Fig. 5: Schematic view of Solid Phase Dynamic Extraction

Method Development

Table I: SPDE Method Parameters

SPDE Parameters	Units	Values
Preincubation Time*	[m:ss]	5:00
Syringe Temp*	[°C]	65
Incubation Temp*	[°C]	65
Agitator Speed*	[rpm]	600
Agitator On-Time	[m:ss]	0:00
Agitator Off-Time	[m:ss]	0:02
Sample Penetration*	[mm]	30
Extraction Strokes*	--	25
Extraction Fill Speed*	[µl/s]	100
Extraction Eject Speed*	[µl/s]	100
Desorption Gas Volume*	[µl/s]	1000
Injector Penetration	[mm]	42
Pre-Desorption Time	[m:ss]	0:00
Desorption Flow Speed*	[µl/s]	25

Table II: SPME Method Parameters

SPME Parameters	Units	Values
Preincubation Time*	[m:ss]	5:00
Agitator Speed*	[rpm]	600
Agitator On-Time	[m:ss]	0:00
Agitator Off-Time	[m:ss]	0:02
Sample Penetration*	[mm]	22
Extraction Time*	[m:ss]	8:00
Extraction Temp*	[°C]	65
Injector Penetration	[mm]	42
Desorption Time*	[m:ss]	2:00

An Agilent 6890N GC equipped with a CTC Combi PAL Autosampler was used to perform analysis.

Combi PAL Autosampler method parameters signed with asterisk (*) were modified step by step for optimizing the extraction of TCA.

GC – Parameters:

Initial Column Temp: 40° C

Initial hold time: 0 min

Temp ramp 1: 20° C/min to 180° C

Temp ramp 2: 2° C/min to 186° C

Temp ramp 3: 50° C/min to 300° C

Final hold time: 1 min

Column: 30 m HP 5 MS, 0.25 mm ID, 0.25 µm film

SPDE Syringe: PDMS, 50 µm x 56 mm (2.5 mL)

SPME Syringe: 100 µm PDMS fiber

Chromatograms and Calibration

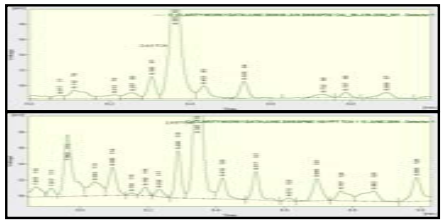

Fig. 6: Chromatogram of 2,4,6 TCA with sensitivity and selectivity, and positive identification by GC-FID

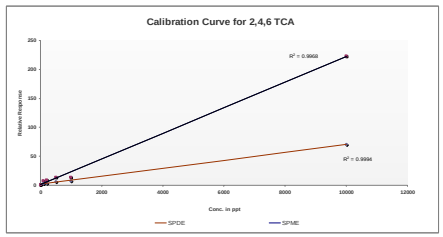

Fig. 7: Excellent linearity was observed in the studied concentration range of 0-10 ppb.

Results and Discussion

Both SPDE and SPME techniques worked highly effectively for qualitative and quantitative analysis of TCA in wines. Fig. 5 shows the good selectivity of 2,4,6 TCA in a wine spiked with TCA.

Calibration curves were run ranging from 100 ppt to 10 ppb. Both techniques are comparable, while SPME has a higher sensitivity under tested parameters. SPDE showed better performance with excellent linearity of $R^2 = 0.9994$ while still good linearity was obtained for SPME with $R^2 = 0.9968$. The method was precise with RSD (%) < 5% at 100 ppt for SPDE compared to RSD(%) of 9% with SPME.

The method is sensitive with detection limit of around 100 ppt. Although SPME had higher sensitivity, a two fold higher sensitivity can be attained by using a longer extraction time with SPDE. During the studies three SPME fibers were consumed compared to one SPDE syringe.

The adjustment of method parameters like salting out, temperature dependence, sorption and desorption conditions had a significant influence on the overall performance – with temperature dependence being most significant.

Conclusions

- SPDE and SPME turned out to be extremely sensitive tools for the determination of TCA in wine – but MSD detector is necessary to reach olfactory threshold factor of up to 2 ppt.
- The methods are comparable showing good stability and reproducibility.
- The entire methodology is “environmentally friendly” due to the absence of any organic solvents involved in the analysis.
- The linearity of both procedures is satisfactory.
- SPDE is promising in providing higher sensitivity attributing to higher sorption capacity and therefore less competition at the active sites of the polymer. This is particularly helpful with samples with difficult matrices.
- Advantage with SPDE has a longer lifetime due to robust stainless steel support with SPDE syringe lifetimes > 1500 samples.
- The SPDE technique represents a economical alternative to SPME.

References

1. C. Bicchi, C. Cordero, E. Liberto, P. Rubiolo, B. Sgorbini, Automated headspace solid-phase dynamic extraction to analyse the volatile fraction of food matrices. J. Chromatogr. A, 1024 (2004) 217-226.
2. C.E. Butzke, T.J. Evans, and S.E. Ebeler, Detection of cork taint in wine using automated solid-phase microextraction in combination with GC/MS-SIM. ACS Symp. Ser. (1998), 714 (Chemistry of Wine Flavor)
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Further Information

Please contact *info@chromsys.com*. More information and application notes can be obtained at http://www.chromsys.com/application_notes.htm.