MEPS: A NEW TECHNIQUE FOR THE ANALYSIS OF SMALL BROMINATED AND CHLORINATED AROMATIC COMPOUNDS

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Introduction

The wine industry has long suffered from TCA (2,4,6-trichloroanisole) and TBA (2,4,6 tribromoanisole) contamination or "cork" taint. These compounds more recently has been found to be present in corks, packaging material, cardboard boxes, wooden products and many other materials. Only 1-2 ng/l of TCA or TBA is required to give wine the "musty" aroma associated with cork taint. It has been proposed that chlorophenols are the precursor for TCA (Fig1). As dioxins are known to be present as contaminants in chlorophenol formulations (1) they might therefore also be present in the wine corks, a hypothesis that needs further invesitigation. In this work, the analysis of TCA and TBA is performed by a new technique for sample preparation called Microextraction by Packed Sorbent (MEPS). This technique in combination with different GCMS techniques is described below and compared with other methods.

Methods and Materials

All stock solutions were prepared in methanol, and all working solutions were prepared by dilution of the stock solution with methanol. Wine was spiked with the working solution to a final concentration of 0.001-100 µg/L. The wine used in the study (Sangiovese and Sauvignon Blanc) was purchased from the Swedish Alcohol Retailing Monopoly. MEPS was performed using a 100 µL gas-tight syringe filled with 4 mg of C18; it was conditioned using 30 µL MeOH and 30 µL water. Extraction was performed by drawing 100 µL or 10 × 100 µL of the sample through the syringe and the C18 solid phase. The C18 sorbent bed was dried by 3 × 80 µL of dry air. The analytes were then eluted with 10 µL solvent into a GC-vial with conical insert and injected using a standard GC autosampler.

Method	Extraction volume	LOD		Ref.
		TCA (ng L^{-1})	TBA (ng L^{-1})	
MEPS-GC-EI-MS (red wine)	100 µL	490	450	(1)
MEPS-GC-EI-MS (white wine)	100 µL	270	170	(1)
MEPS-GC-ECNI-MS (red wine)	10 × 100 µL	20	5.0	(1)
MEPS-GC-HRMS (red wine)	10 × 100 µL	0.75	0.23	(1)
MEPS-GC-HRMS (white wine)	10 × 100 µL	0.67	0.22	(1)
HS-SPME-GC-NCI-MS (red wine)	3 mL	0.3 [a]	0.2 [a]	(2)
HS-SPME-GC-HRMS (red wine)	3 mL	0.03 [a]	0.03 [a]	(2)
SPE-PTV-GC-ITMS (five wines)	50 mL	0.2	0.4	(3)
HS-SDME-GC-ECD (synthetic wine)	20 mL	8.1	6.1	(4)
MHS-SPME-GC-MS-MS	5 mL	10	10	(5)

Table 1. Comparison of limits of detection (S/N = 3) for TCA and TBA using MEPS with GC-EI-MS, GC-NCI-MS or GC-HRMS from the present work and the literature.

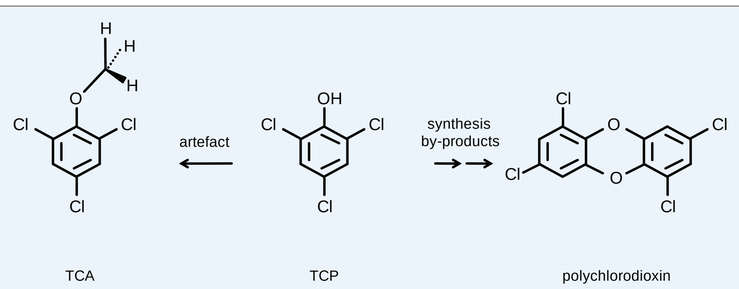

Fig 1. Chlorophenols have been proposed as the source of trichloroanisole responsible for 'cork' taint in wine. Chlorophenols are also associated with the formation of dioxins.

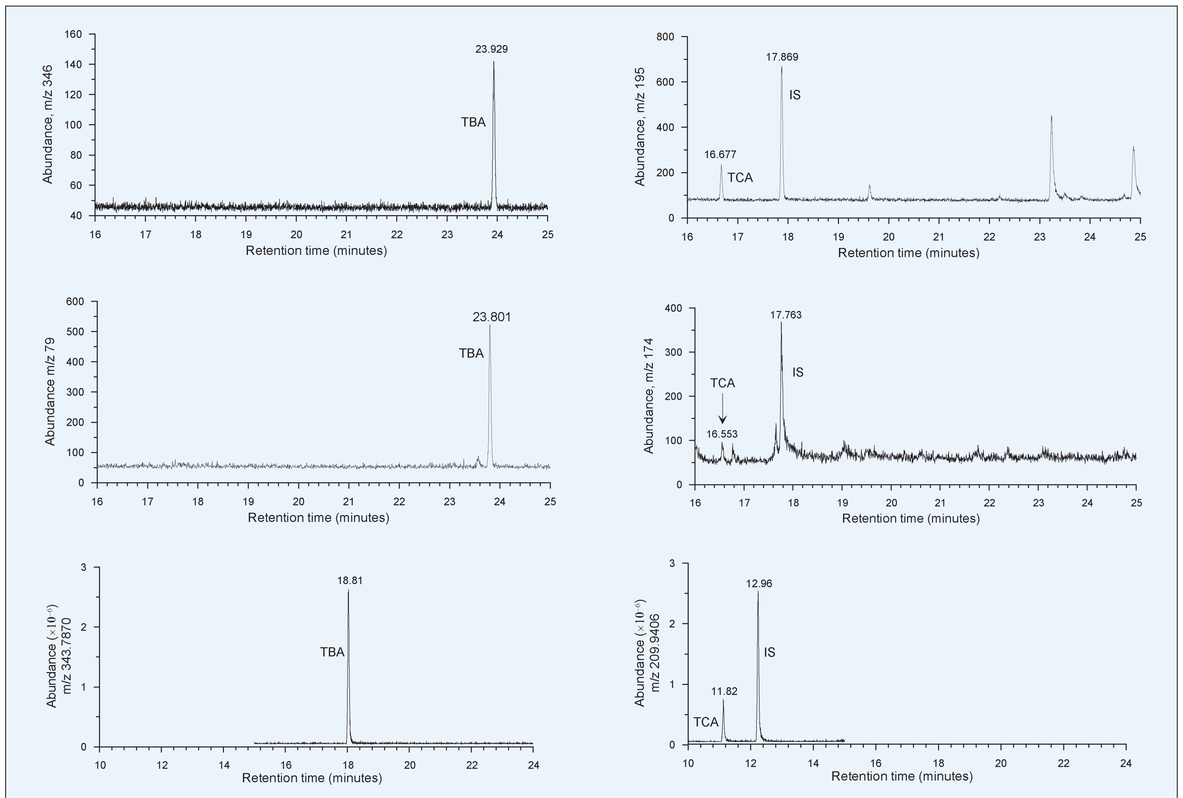

Fig 2. Extracted ion chromatograms for EI-(top), NCI-(middle) and HR-GCMS (bottom) for red wine spiked with 1 ng/mL of TBA (left) and TCA (right) and 10 ng of internal standard using BPX5 (30 m, 0.25 mm i.d., 0.25 um film thickness).

Conclusion

The reproducibility of the method was increased by the usage of an internal standard (2, 3, 6 - TCA) for quantification. LODs were extremely low for GC-NCI-MS and GC-HRMS and TCA and TBA can be detected in the wine before it is sensorially noticed as cork tainted. The MEPS based method is comparable to both SPME and SPE based methods, but the sample preparation time is reduced.

Acknowledgments

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