CrossTOX® SPE Clean-up of *Phenolic Compounds* and *Polyphenols* as a Tool for Identifying Mislabelling in Wine and Spirits (food fraud)

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Introduction

Fig. 1: Barrel aged red wine

Polyphenols are known for their claimed positive impact on human health in general nutrition. In addition to this, polyphenols and phenolic components are valuable parameters to evaluate the authenticity of vinification and ageing of spirits in wooden barrels as well as to identify the usage of such substances as additives for flavouring by an analyte specific profiling. For this purpose, a clean-up to bind specific phenolic compounds to SPE cartridges was established in order to reduce matrix compounds that might negatively effect the analytical results. The easy and fast clean-up allows an increase in sample throughput and saves costs and time. The characterisation of the target analyte binding activity of the SPE cartridge and the corresponding applicability to identify food fraud/mislabelling regarding any non-declared usage of polyphenols/phenolic compounds as additives to mimic the more cost intensive wood barrel ageing of wine and spirits is the aim of this study. This aspects becomes a more important issue to food testing laboratories and is a permanent task in food and beverage analysis.

Method

Liquid Samples were diluted with water or applied directly onto the CrossTOX® cartridge (Fig. 2). Sample volumes of 1-5 mL (1 gr sample) were chosen depending on the experimental setup. After washing with 2 mL water, analytes were eluted with methanol and prepared for analysis either by further concentration, or injected directly into the LC-MS/MS. For binding studies polyphenols samples containing different methanol contents (0-50 %) were tested. Polyphenols (100 ng each) were loaded on the SPE cartridge at a flow rate of 1.5 mL/min. After washing with water, elution was performed using 1 mL methanol with a 5 minutes incubation of the elution solvent in the bed material. For the binding tests resveratrol, coniferylaldehyde, syringaldehyde and vanillin were used. Furthermore, additional analytes (coumarin, 6-methyl-coumarin, ethyl vanillin and sinapinaldehyde) for sample testing of various wine samples as well as for testing of spirits and whiskey profiling were investigated.

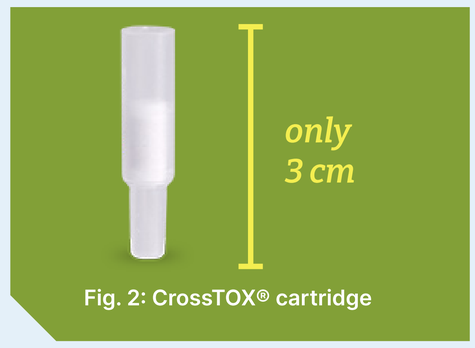

Fig. 2: CrossTOX® cartridge

Results

The binding of different polyphenols revealed an analyte specific binding depending on the methanol concentration. Up to 15 % of methanol was tolerated for a specific binding of polyphenols to the SPE material, whereas the matrix interferences were removed efficiently. The specific binding (Fig. 3). allows a clean-up of all tested polyphenols with recoveries >80 %.

The loading capacity of the individual polyphenols were tested at 15 % methanol and a sample volume of 5 mL. Up to 500 ng of each polyphenol (2000 ng in total) could be recovered with recovery rates ranging from 84-97 %.

The matrix interferences from wine samples (Fig. 4 A) could be easily reduced by the clean-up procedure (Fig.4 B) by more than 80% (tested by chromatography and UV analysis). This clean-up approach significantly reduces the costs for device cleaning, analytical downtime and internal standards for compensating matrix effects.

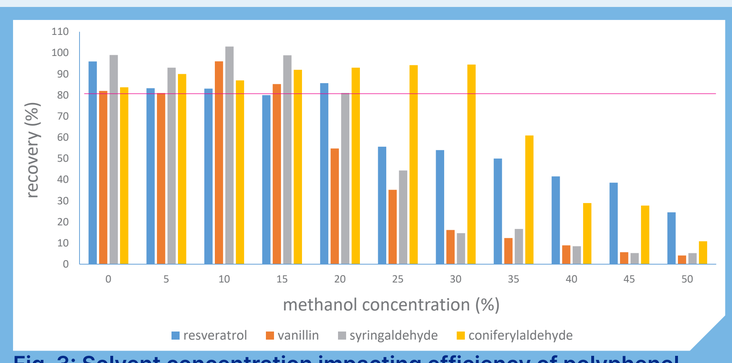

Fig. 3: Solvent concentration impacting efficiency of polyphenol binding to CrossTOX® cartridge (cut-off 80 % recovery).

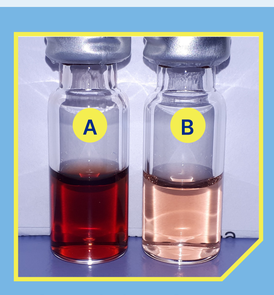

Fig. 4: Removal of matrix interferences by CrossTOX® clean-up. Red wine sample (A), after clean-up with CrossTOX® contains less matrix interferences (B).

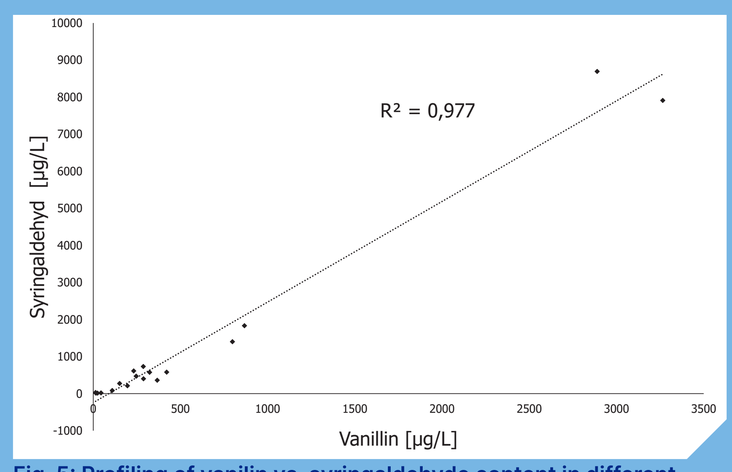

Fig. 5: Profiling of vanilin vs. syringaldehyde content in different spirits, which are claimed to be matured in wooden barrels.

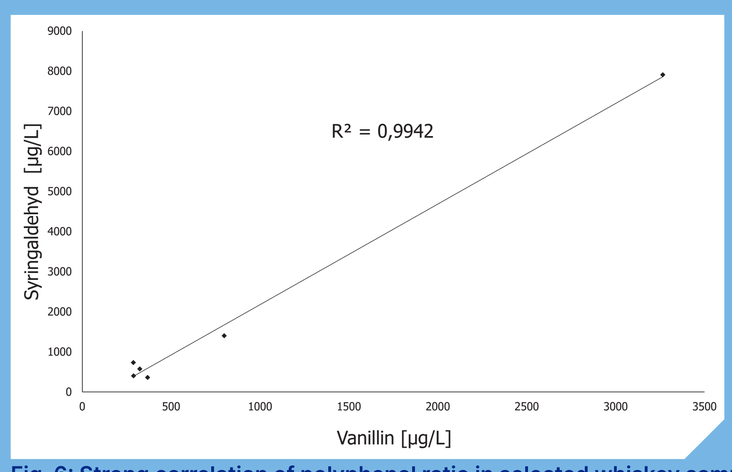

Fig. 6: Strong correlation of polyphenol ratio in selected whiskey samples, indicating the analytical proof for wood barrel maturation.

Testing of various spirits (as well as wines) indicate, that the profiling of vanillin, syringaldehyde and coniferylaldehyde could be a tool to detect food fraud and non-labelled aromatization to mimic the quality of wood barrel matured spirits or wine (Fig. 5). The correlation between syringaldehyde and vanillin becomes even stronger when focusing on specific spirit categories (e.g. Whiskey, Fig. 6). With a sufficient database size for specific spirit categories, this method also appears to be suitable for the identification of prohibited addition of vanillin to such wood barrel-aged spirits, e.g. Whiskey. Spirits mislabelled and aromatized could be identified during this study as well based on the identification of phenolic components and the suspicious ratio of polyphenols in the tested samples.

Conclusion

The CrossTOX® cartridge could be used to selectively concentrate polyphenols from various vines and spirits. This approach could be used to facilitate the analysis of wine and spirit regarding mislabelling and food fraud and for polyphenol clean-up and quantification in various matrices. Spirits flavoured with polyphenols, mimicking the quality of wood barrel aged products could be detected by the analysis and the ratio determination of individual polyphenols (e.g. vanillin, syringaldehyde) after clean-up with CrossTOX ® SPE cartridges and LC-MS/MS analysis. Thus a new, fast and easy to perform analytical approach was established that allows to identify possible mislabelling and food fraud in spirits and wine maturation and saves the analytical device from matrix burden impurities.

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