



Trace level analysis of corky off-flavor compounds: Development of a new analytical method based on solid phase extraction and analysis by multidimensional gas chromatography with mass spectrometric detection[☆]

Hans-Georg Schmarr^{a,*}, Stefan Koschinski^{a,1}, Wei Sang^{a,b}, Petra Slabizki^{a,c,1}

^a Dienstleistungszentrum Ländlicher Raum (DLR) Rheinpfalz, Competence Centre for Wine Research, Breitenweg 71, D-67435 Neustadt an der Weinstraße, Germany

^b Fachhochschule Kaiserslautern – University of Applied Sciences, Fachrichtung Chemietechnik, Carl-Schurz-Str. 10-16, D-66953 Pirmasens, Germany

^c Landesbetrieb Hessisches Landeslabor (LHL), Glarusstraße 6, D-65203 Wiesbaden, Germany

ARTICLE INFO

Article history:

Available online 19 October 2011

Keywords:

Multidimensional gas chromatography–mass spectrometry
Solid phase extraction
Solid phase microextraction
Stable isotope dilution analysis
Haloanisoles

ABSTRACT

This work describes the development of a trace level ($<1 \text{ ng L}^{-1}$) analysis of haloanisoles in complex wine matrix. The suggested method involves sample preparation based on solid phase extraction, a clean-up to remove acidic compounds, concentration of the haloanisole fraction and large volume on-column injection into a multidimensional GC–MS system. Mass spectrometric detection in the selected ion mode allowed reliable quantification of 2,4,6-trichloroanisole (TCA) or 2,4,6-tribromoanisole (TBA), via their highly deuterated ($[^2\text{H}_5]$) isotopologues as internal standards (stable isotope dilution analysis; SIDA), which had prior been synthesized in house. The development of this new method had become necessary, as a one-dimensional HS-SPME–GC–ECD method, routinely applied for analysis of TCA in cork soaks, had to be extended for TeCA and TBA determination, but failed due to co-elutions within wine matrices. The newly developed SPE//MDGC–MS method provided detection limits well below olfactory thresholds of the analytes with 0.05 ng L^{-1} (LOD), 0.19 ng L^{-1} (LOQ) for TCA, 0.06 ng L^{-1} (LOD), 0.21 ng L^{-1} (LOQ) for TeCA, and 0.09 ng L^{-1} (LOD), 0.34 ng L^{-1} (LOQ) for TBA.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

The corky taint of wines is one of the most known off-flavors to the wine industry, and has recently been reviewed by several authors [1–3]. Although the compounds primarily important for this off-flavor, such as 2,4,6-trichloroanisole (TCA) or 2,4,6-tribromoanisole (TBA), are known for many years [4], their reliable trace level analysis still is a challenging task for the analytical chemist. This can be seen in method optimization steps found in numerous publications which are still produced on that topic [5–14], citing only a few. Sensory thresholds of haloanisoles have been reported to be extremely low [15,16] and cork taint in wine can easily be detected by consumers with TCA concentrations as low as a few ng L^{-1} , depending on wine style and alcohol content [17–19]. Therefore, analytical procedures for quality control have to work on concentration levels even down to the sub- ng L^{-1} level.

Reliable quantification can best be achieved using isotopic labeled internal standards [20,21], in a stable isotope dilution assay [22]. In our situation we started using highly deuterated $[^2\text{H}_5]$ -isotopologues of TCA and TBA for quantification, and a common sample preparation approach using headspace solid phase microextraction (HS-SPME) [21,23–31]. The $[^2\text{H}_5]$ -isotopologues provide good chromatographic separation from the non-deuterated target compounds, allowing the use of the selective and sensitive electron capture detector (ECD) for quantitative analysis [32]. However, the complex wine matrix caused co-elution problems in the classical (one-dimensional, 1D) HS-SPME–GC–ECD analysis (Fig. 1) which had to be overcome by an alternative approach.

Besides the fact that most recent applications found in literature use headspace SPME techniques for the analysis of haloanisoles in cork or wine matrix, alternative methods have been described. Static headspace with cryo-trapping [33] or dynamic headspace [34] have also been described in the literature. Supercritical fluid extraction (SFE) [35] or pressurized liquid extraction [36] have been described for direct cork analysis. An alternative method to SPME is stir bar sorptive extraction (SBSE), having the advantage of higher capacities of the sorbent material, suitable for trace level analysis and allowing multiple extractions in parallel [8,11,37–40]. Furthermore, Maggi et al. [41] compared immersion (IS) SPME,

[☆] Presented at the 35th International Symposium on Capillary Chromatography, Joint Congress, CASSS, May 01 to May 05, 2011, San Diego, CA, USA.

* Corresponding author. Tel.: +49 6321 671 289; fax: +49 6321 671 375.

E-mail address: hans-georg.schmarr@dlr.rlp.de (H.-G. Schmarr).

¹ These authors contributed equally to this work.

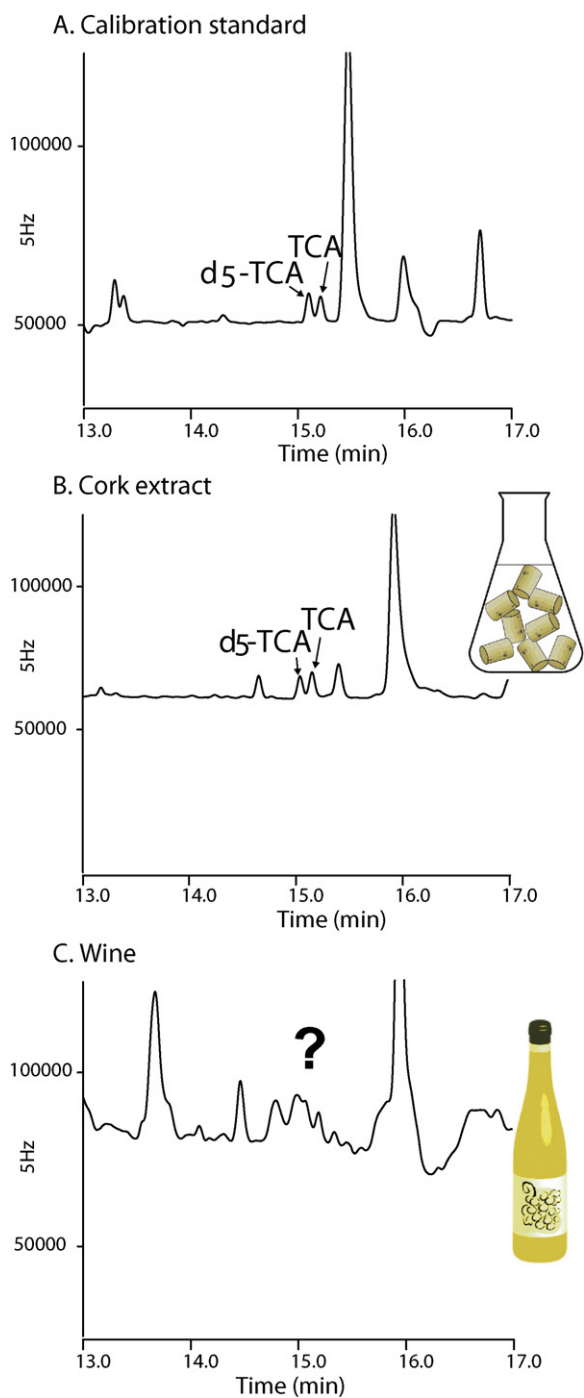


Fig. 1. HS-SPME-GC-ECD chromatogram of a calibration standard (A), a cork soak sample (B) and a wine sample (C).

HS-SPME and SBSE (usually applied in immersion mode) for the analysis of haloanisoles in different liquid matrices, and found best results for trace level analysis with SBSE. In their study, detection was performed with ion-trap tandem mass spectrometry (MS/MS).

Amongst the liquid extraction methods, solid phase extraction (SPE) is a good alternative, with applications for the analysis of haloanisoles in wine [13,42]. SPE materials can be made very selective, e.g. with the incorporation of immunosorbents as described recently [14]. SPE sorbents are available in various polarities suiting dedicated purposes, and liquid extracts obtained can be further processed and concentrated for trace level analysis.

Still, wine matrix problems encountered with target component analysis, are common and may be further resolved by more specific detection [43] or increased separation efficiency, e.g. by multidimensional gas chromatographic (MDGC) separation [44]. The latter has been successfully applied for trace level determination of methoxypyrazines [45] or 2-aminoacetophenone [46] in our laboratory before. Therefore, we wanted to develop a reliable method for trace level analysis of some important haloanisoles based on SPE and MDGC and compare its suitability particularly for wine and cork soak analysis with a 1D HS-SPME-GC-ECD method.

2. Experimental

2.1. Chemicals and reagents

Acetonitrile and 2,3,4,6-tetrachloroanisole (TeCA) were from LGC Promochem (Wesel, Germany), calcium hypochlorite (technical), 2,4,6-trichloroanisole (TCA), [$^2\text{H}_6$]-phenol were from Sigma-Aldrich (Steinheim, Germany), [$^2\text{H}_3$]-iodomethane, dichloromethane, N,N-dimethylformamide (anhydrous), tetrabutyl ammoniumbromide were from Fluka (Buchs, Switzerland), diethylether, ethanol (absolute) (30%) hydrogen peroxide, sodium hydroxide, sodium chloride, sodium carbonate (anhydrous), sodium hydrogencarbonate, vanadium(V) oxide, silica gel and LiChrolut[®] EN solid phase extraction cartridges (200 mg, 3 mL) were from VWR (Darmstadt, Germany), magnesium sulfate (anhydrous) and phosphoric acid were from Riedel de Hen (Seelze, Germany). Aluminum oxide (basic) was from J.T. Baker (Griesheim, Germany). A vacuum manifold from Agilent (Waldbronn, Germany) was used for SPE preparation. Commercial chemicals were usually of analytical grade. Method calibration data were calculated with DINTEST, vers. 2005 DE software (Georg Schmitt, Inst. f. Rechtsmedizin, Universitatsklinikum Heidelberg, Germany; www.analytiksoft.de) according to DIN 32645.

2.2. Cork soaks and wine samples

Cork samples (100 individual corks) were submersed in an ethanol/water solution (10% vol.). The flasks were covered with aluminum foil and left at room temperature over night. Samples were from routine quality control, or when sensory analysis of cork samples suggested chemical analysis.

Wine samples were taken from tanks, respectively barrels or from bottled wines, when a cork taint was suspected during quality control or sensory evaluation.

2.3. Synthesis of deuterated reference substances

Whereas deuterated [$^2\text{H}_5$]-TCA is available from various suppliers in mg amounts, no source for the deuterated [$^2\text{H}_5$]-TBA was listed in the chemical abstracts database (CAS). This prompted us to synthesize the standards in-house, as outlined hereafter.

2.3.1. Synthesis of [$^2\text{H}_2$]-2,4,6-trichlorophenol ([$^2\text{H}_2$]-TCP)

Basically following the procedure described earlier [47], 3.24 g calcium hypochlorite were added to a solution of 300 mg [$^2\text{H}_6$]-phenol in 60 mL water and 30 mL 0.1 M NaOH. The solution was then stirred for 18 h at room temperature. Then, 20 mL of an aqueous solution of sodium thiosulfate (250 g L^{-1}) were added and pH was brought to 3.5 with 0.45 M phosphoric acid. This mixture was extracted 3 times with 30 mL diethyl ether and once with 30 mL dichloromethane. The combined organic extracts were washed with half saturated sodium hydrogen carbonate solution and brine, and finally dried with anhydrous magnesium sulfate. After filtration, the solvent was evaporated using a rotavapor and the product was dried in an exsiccator, yielding 304 mg (51%) [$^2\text{H}_2$]-TCP (CAS

Download English Version:

<https://daneshyari.com/en/article/1206815>

Download Persian Version:

<https://daneshyari.com/article/1206815>

[Daneshyari.com](https://daneshyari.com)