



## Comparison of silica gel modified with three different functional groups with C-18 and styrene–divinylbenzene adsorbents for the analysis of selected volatile flavor compounds

Mariusz Dziadas<sup>a</sup>, Magdalena Nowacka<sup>b</sup>, Teofil Jesionowski<sup>b</sup>, Henryk H. Jeleń<sup>a,\*</sup>

<sup>a</sup> Faculty of Food Science and Nutrition, Poznań University of Life Sciences, Poznań, Poland

<sup>b</sup> Faculty of Chemical Technology, Poznań University of Technology, Poznań Poland

### ARTICLE INFO

#### Article history:

Received 16 February 2011

Received in revised form 5 May 2011

Accepted 8 May 2011

Available online 14 May 2011

#### Keywords:

Solid phase extraction

Grape

Wine

Flavor compounds

Silica

### ABSTRACT

A comparison of SPE cartridges produced in authors laboratory containing silica modified by addition of three functional moieties with standard C-18 and SDVB cartridges was made in terms of their applicability for the isolation of flavor compounds. Compounds found in wine and grapes were used for model mixture, which was spiked into a grape juice. Functionalized phases for SPE were prepared modifying silica gel with alkoxyxilanes with different functional groups: (3-(phenylamino)-propyltrimethoxysilane, octyl-triethoxysilane and octadecyl-silane. The functionalization was carried out by the dry method, which resulted 5, 10 and 20 weight parts of initial support. Functionalized phases were characterized using FT-IR, elemental analysis and NMR.

Performance for new phases compared to “standard” ones (C-18 and SDVB (styrene–divinylbenzene) varied, depending on the group or type of analyzed compound. They were more efficient in extraction of methyl anthranilate and vanilins. For extraction of terpenes, C-6 alcohols, isoprenoids, benzene derivatives and phenols their efficiency was comparable to that of C-18.

Functionalized laboratory-made mixed phases are suitable for extraction of flavor compounds from grape juice. They are suitable for extraction of compounds belonging to different chemical classes with the efficiency comparable to C-18 and SDVB phases. The production of such functionalized phases can be easily performed in the laboratory, at a very low cost, comparing to C-18 or SDVB cartridges. This makes the proposed functionalized phases an interesting alternative, in sample preparation for analysis and particularly in preparative/flash chromatography.

© 2011 Elsevier B.V. All rights reserved.

### 1. Introduction

Wine volatiles are a group of several hundred compounds. Many of them influence wine flavor and are present in the concentration equal or exceeding their odor thresholds. They are present in grapes, but are also formed during fermentation processes and during wine ageing and storage [1]. Concentration of volatile compounds in wine range from mg/L down to ng/L. Apart from compounds that are present in a free form, many, especially terpenes, isoprenoids and volatile phenols can be present also in a bound form. Volatile/odoriferous aglycon is bound with mono or disaccharide. They are present in both forms in wine as well as in grapes [2–4]. Glycosides can undergo hydrolysis as a result of low pH environment in wine during its storage and of enzymatic hydrolysis [5]. Flavor aglycons released from glycosidally bound precursors influence wine flavor and in grapes flavor potential. Therefore, the

analysis of grapes and wine aroma compounds comprise of analysis of free and bound odorants.

For the analysis of food aroma compounds—their extraction and preconcentration, headspace methods based on compounds volatility, solvent extraction and methods based on adsorption/absorption mechanisms are used. The extraction methods determine often the profile of isolated compounds [6,7].

Among sorbents used in extraction of food aroma compounds several groups can be distinguished: silica gels (polar due to their hydroxyl groups), activated aluminas (polar), activated carbon (apolar), zeolites and polymers, such as polystyrene, polyacrylic esters, PDMS and phenolic resins [8]. Extraction and preconcentration of wine flavor volatile compounds are challenging tasks for the analyst, therefore various isolation techniques are used: liquid–liquid extraction, solid phase microextraction (SPME), stir bar sorptive extraction (SBSE) and solid phase extraction (SPE). For an overview of extraction methods used for wine and other oenological products a recent review by Castro et al. [9] can supply more insight into these applications.

\* Corresponding author. Tel.: +48 61 8487273; fax: +48 61 8487314.  
E-mail address: [henrykj@up.poznan.pl](mailto:henrykj@up.poznan.pl) (H.H. Jeleń).

Due to the nature of wine and grape volatile compounds—their presence in free and bound forms—extraction methods based on sorption are commonly used. The SPE approach allows fractionation of free forms of volatiles from nonvolatiles and their bound forms and also permits a concentration of volatiles. Pre-concentration is an important step, as many of the odoriferous volatiles occur in low concentrations. Generally, sample introduced into SPE cartridge is eluted with a nonpolar solvent, which elutes free compounds. Glycosidally bound flavor compounds, which are polar fraction are retained on the column and eluted from it using methanol or methanol/water. To analyze aglycons in bound form fast acid hydrolysis is usually performed and aglycons separated from sugars on a second SPE cartridge and subsequently analyzed by GC/MS [10]. Due to the range of concentrations in which flavor compounds of wine are present sometimes a fractionation using solvents of different polarities is advised. Compounds present usually in very high concentrations such as ethyl esters are separated from those occurring in trace amounts, though important from the sensory point of view [11].

For the extraction of small molecules from aqueous solution chemically bonded sorbents having large surface areas with long alkyl chains and high phase loading maximize their retention. Macroreticular porous polymers represented by copolymers of styrene–divinylbenzene (SDVB)—particles consisting of agglomerates of randomly packed microspheres with a network of holes and channels. They are usually more retentive than chemically bonded phases and have a high sample capacity.

The SPE analysis of free and bound flavor compounds in grape and wine is usually done using reversed phase SPE [12–14] or Amberlite XAD-2 resins [15]. The latter one and Lichrolut EN is the most effective for the extraction of acids, benzene derivatives and volatile phenols [10], whereas RP SPE proved to be the most effective for extraction of terpenes [10]. When Piñeiro et al. [16] tested various C-18 and SDVB cartridges for the extraction of terpenes from wine when using dichloromethane for compounds elution noticed better recoveries for these compounds for SDVB cartridge. Macroporous polydivinylbenzene–N-vinylpyrrolidone copolymer tested for the extraction of chloroanisols from water and 12% ethanol was much more efficient than C-18 [17]. As observed by Cullere et al. [11] silica sorbents present low capacity and some compounds can bind irreversibly, whereas styrene divinylbenzene have better loading capacity, stability and ability to be used in normal as well as reversed mode. Lopez et al. [18] found SDVB copolymer (LiChrolut-EN) satisfactory for analysis of 27 volatiles from wine. Extraction of polar compounds together with mid polar and nonpolar in alcoholic beverages often cannot be performed satisfactory due to the different interactions of these compounds with SPE beds. As tested by Lukic [19] higher alcohols (butanols) and some short chain esters provided low recoveries on C-18.

As the aroma volatiles in wine comprise compounds of different mechanism of binding, ranging from polar to nonpolar, aromatic and aliphatic, the development of functionalized adsorbents with different mechanisms of volatiles binding can provide more efficient extraction of volatiles. Our goal was to develop a SPE phases, containing one cartridge different functional groups to enhance spectrum of extracted compounds and use it for extraction of compounds of different characters that are found in wine, grapes and other fruit in a model system of grape juice spiked with mixture of 53 aroma compounds. To verify the effectiveness of modified silica produced in our lab in aroma compounds extraction they were compared with the two most popular phases commercially available for this type of analysis—C-18 and styrene–divinylbenzene cartridges.

## 2. Materials and methods

### 2.1. Volatile compounds

All standards of volatile compounds used for method performance evaluation were purchased from Sigma–Aldrich, Poznań, Poland and were of highest available purity. Compounds were selected to reflect those present in grape juice and wine, but also in other fruits that could influence their flavor. Compounds analyzed represented the following classes: monoterpenes ( $\alpha$ -pinene,  $\beta$ -pinene, limonene,  $\alpha$ -*trans*-ocimene,  $\gamma$ -terpinene,  $\alpha$ -*cis*-ocimene, terpinolene, *trans*-rose oxide, *cis*-rose oxide, *trans*-linalool oxide, *cis*-linalool oxide, citronellal, linalool, linalyl acetate, menthyl acetate, geranyl acetate, terpinyl acetate, terpinen-4-ol, menthol,  $\alpha$ -terpineol, citral,  $\beta$ -citronellol, nerol, myrtenol, geraniol); isoprenoids ( $\beta$ -damascenone,  $\beta$ -damascone,  $\alpha$ -ionone,  $\beta$ -ionone, *cis*-pseudoionone, *trans*-pseudoionone); benzene derivatives (benzaldehyde, benzyl alcohol, benzeneacetaldehyde, phenylethan-2-ol, 1,2-methyl-4-propenyl benzene); volatile phenols (guaiacol, 2,6-dimethylphenol, o-cresol, p-cresol, m-cresol, ethylguaiacol, eugenol, 4-ethyl phenol, *trans*-isoeugenol, 2,6-dimethoxy phenol); and miscellaneous compounds not included in previously mentioned classes (methyl anthranilate, vanillin, methylvanilin,  $\gamma$ -decalactone,  $\gamma$ -nonanactone, *cis*-3-hexene-1-ol, *cis*-hexene-2-ol). As internal standards [ $^2\text{H}_7$ ]-geraniol, [ $^2\text{H}_3$ ]- $\beta$ -ionone and [ $^2\text{H}_8$ ]-naphthalene were used. Deuterated geraniol was synthesized in authors laboratory according to procedure described by Pedersen et al. [20] and deuterated  $\beta$ -ionone—according to procedure described by Kotseridis et al. [21]. Deuterated naphthalene was purchased at Sigma (Poznań, Poland).

### 2.2. Preparation of sorbents

For the experiments reference sorbents were purchased from Biotage, Sweden (ISOLUTE cartridges). They were 500 mg/6 mL cartridges filled with C-18 and SDVB. For the preparation of selective adsorbents two silica gels—CCH Silica gel 60, 0.05–0.2 mm, and HR Silica gel 60, TLC HR “high purity” Merck, Darmstadt, Germany were purchased.

The adsorbent's silica surface was modified with selected alkoxy silanes with different functional groups (3-(phenylamino)-propyltrimethoxysilane, octyltriethoxysilane and octadecyl-silane purchased from Fluka. The appropriate modifying agents were separately hydrolyzed with methanol/water solutions (4:1, v/v) and sprayed onto silica gel surface applying “dry method” described in detail in [22,23]. The silane coupling agents were deposited in the amount of 5, 10, and 20 weight parts by mass of initial support (CCH-5, CCH-10, CCH-20, HR-5, HR-10, HR-20). The solvents were subsequently removed by distillation. Scheme of adsorbents preparation is shown in Fig. 1.

The degree of modification and the type of reaction between modifiers and silica surface were evaluated using FT-IR EQUINOX 55 spectrophotometer made by Bruker. Elemental analysis of the samples studied (C, H, N contents) was performed on an instrument Elementar model Vario EL III, Germany. NMR analysis of unmodified and modified silicas was conducted in DSX spectrometer (Bruker). For the determination of NMR spectra a sample of about 100 mg was placed in a rotator made of  $\text{ZrO}_2$  with 4 mm of diameter, which permitted spinning of the sample. Centrifugation at the magic angle was performed at the spinning frequency of 8 kHz.  $^{29}\text{Si}$  CP MAS NMR spectra were recorded at the pulse duration of 4.5  $\mu\text{s}$ , contact time of 1.5 ms and pulse spacing of 6 s. The  $^{13}\text{C}$  CP MAS NMR spectra were recorded at 100.63 MHz in a standard 4 mm MAS probe by application of single pulse excitation with high power proton decoupling (pulse repetition 10 s and spinning speed 8 kHz).

Download English Version:

<https://daneshyari.com/en/article/1166851>

Download Persian Version:

<https://daneshyari.com/article/1166851>

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