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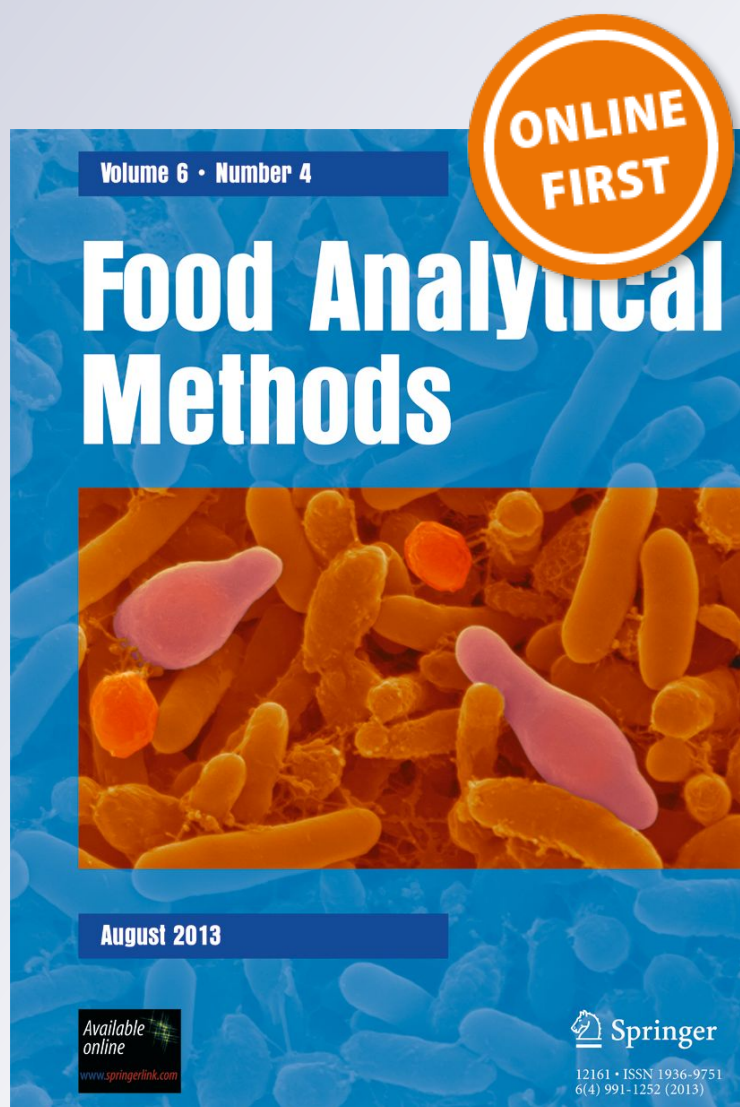
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Use of Sorbent-Based Vacuum Extraction for Determination of Volatile Phenols in Beer

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Abstract

A novel method based on vacuum-assisted sorbent extraction (VASE) used with gas chromatography-mass spectrometry (GC-MS) for isolation of volatile phenols was described. The method is based on extraction of analytes into sorbent traps (sorbent pen) filled with Tenax in a vacuum system—vials with traps from which air was evaluated. The method was applied for extraction of volatile phenols from aqueous matrix and smoked beer was used as a food example. Methyl-, dimethyl-, and trimethylphenols, along with 4-ethylphenol, 4-methylguaiacol, 4-ethylguaiacol, 4-propylguaiacol, and eugenol, were used in method development. Optimal extraction parameters were elaborated. For the analysis of volatile phenols in beer matrix, the method was characterized with satisfactory linearity ($r^2 \geq 0.99$) in a range of 0.005–0.5 mg/L. Limits of detection (LODs) for analyzed compounds ranged from 0.0006 to 0.018 mg/L and repeatability for majority of compounds was < 5% for a single trap extraction. The detected volatile phenols in beer samples ranged from 0.003 to 0.672 mg/L.

Keywords Vacuum-assisted sorbent extraction · VASE · Volatile phenols · Beer

Introduction

For the analysis of food flavor compounds, numerous extraction techniques are used (Augusto et al. 2003). Headspace analysis allows the determination of volatile compounds from simple liquid, as well as complex, often non-homogenous matrices. Though static headspace is the simplest extraction technique, it offers no preconcentration step and usually is characterized by relatively low sensitivity. Therefore, more popular are extraction techniques based on sorbents, especially in microscale (Baltussen et al. 2002). Among them, solid-phase microextraction (SPME) gained the highest popularity due to the method robustness, sensitivity, selectivity based on partition constants, and integration of extraction and preconcentration in one device that also allows the simple sample transfer to gas chromatograph (Jeleń et al. 2012). Headspace SPME is highly suitable for compounds that have high Henry's law volatility constant (K_H). However, compounds which are characterized with low K_H , for which gas-phase resistance controls more than

95% of the evaporation rate (Psillakis et al. 2012; Psillakis 2017), are not favored in SPME extraction. Usually, in water matrices, polar compounds of low volatility are the most difficult to analyze by SPME.

The effect of vacuum on SPME extraction was noted for the first time by Brunton and coworkers (Brunton et al. 2001), who noticed improved extraction efficiency when using Carboxen/PDMS fiber to extract volatile compounds from a cooked and raw turkey breast. A rotary vane pump was used by authors to reduce pressure (5×10^{-2} bar). Then, vacuum use for SPME was rediscovered by Psillakis group, who considered theoretical fundamentals for this process, developed various vessels for sampling, and provided protocol for the vacuum SPME analysis together with some applications (Psillakis 2017).

The idea of using vacuum to be utilized in sorbent extraction was also developed and commercialized based on specific sorbent traps (tubes), which are used with specially designed vial caps allowing evacuation of air from the vial by a membrane pump and special injection port, in which desorption of analytes into chromatographic column is performed (www.entechnst.com).

The goal of this paper was to develop extraction method based on vacuum-assisted sorbent extraction (VASE) to extract phenolic compounds from aqueous matrices. Developed method was used for extraction of volatile phenols from

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smoked beers. Volatile phenols represent a group of compounds that are highly polar and pose difficulties in their extraction from aqueous matrices. They are formed in foods in a thermal degradation of phenolic acids—in reactions such as malt kilning, wort boiling, or food smoking, but also in enzymatic reactions—among them is enzymatic decarboxylation of phenolic acids by *Saccharomyces* yeasts or others, sometimes contaminating microorganisms and playing a significant role in sensory qualities of various foods (Sterckz et al. 2011; Czerny et al. 2011; Kheir et al. 2013; Jeleń et al. 2005). Several methods were developed for the analysis of phenols in beers, majority of them being focused on the most often occurring compounds 4-ethyl phenol, 4-ethylguaiacol, and their vinyl precursors. They were analyzed usually by gas chromatography (GC) with different detectors and SPME (Pizarro et al. 2010; Pizarro et al. 2007; Sterckx et al. 2010) or stir bar sorptive extraction (SBSE) (Shou et al., 2015) used for their extraction; however, also HPLC is sporadically used for this purpose (Vanbeneden et al. 2006). There is relatively little information on the quantitative analysis of other phenolic compounds, especially those associated with the smoking process by GC (Scholtes et al. 2014). Therefore, the use of vacuum-assisted sorbent extraction provides a possible solution to this type of analyses.

Materials and Methods

Reagents and Samples

Standards of 2-methyl phenol (o-cresol), 3-methyl phenol (m-cresol), 4-methylphenol (p-cresol), 2-methoxyphenol (guaiacol), 2,6-dimethylphenol (2,6-xyleneol), 2,4-dimethylphenol (2,4-xyleneol), 4-ethylphenol, 2-methoxy-4-methylphenol (4-methylguaiacol), 2,4,6-trimethylphenol (mesitol), 2,3,5-trimethylphenol, 4-ethyl-2-methoxyphenol (4-ethylguaiacol), 2-methoxy-4-(2-propenyl) phenol (eugenol), and 2-methoxy-4-propylphenol (4-propyl guaiacol) of highest available GC purity (usually > 98%) were obtained from Sigma Aldrich (Poznań, Poland). Samples of craft smoked beers and light Pilsner-type beers were purchased at local beer shops.

Analytical Equipment

For extraction of volatiles and their subsequent analysis, the VASE 5800 system was used (Entech Instruments, Simi Valley, CA). The system consisted of sorbent pens filled with Tenax, a vacuum diaphragm pump, and 44-mL EPA vials with special gas tight screw on closures (Fig. 1) making gas tight connection with inserted sorbent pens and a specially designed desorption port mounted as an injector in the GC/MS system. The desorption port used electronic pressure control unit (EPC) from standard, already mounted split/splitless port



Fig. 1 Sorbent pens and vial closures used for extraction of phenols by VASE

of GC. Desorption process was manual and all operations as well as synchronization of desorption with GC/MS were provided by Entech 5800 controller and software. Sorbent pens (traps) were conditioned at 260 °C for 30 min before the first use in a sorbent pen conditioner (Entech Instruments) with a helium flow of 10 ml/min.

For analysis of volatiles, a single quadrupole GC/MS system was used (7890A/7895 TAD MSD; Agilent Technologies, Santa Clara, CA). GC/MS was equipped with DB-5MS column (30 m × 0.200 mm × 0.25 μm; Agilent Technologies). The column was connected with a desorption port with a precolumn (of 5 m length) via a tee connector, which enabled diverting flow at this point to vent. The following GC oven program was used for analysis: He flow 0.8 mL/min, initial temp. 40 °C for 5 min, then increase of 10 °C/min to 180 °C and 20 °C/min to 280 °C at which the system was kept for 3 min. Transfer line temp. was 290 °C. For method development, a mass spectrometer was working in a scan mode (m/z 33–233 range, 6.6 scan/s). Mass Hunter software (B.07.00) was used to control instrument. Quantitation of volatile phenols in beer was performed using SIM with set of seven ions monitored during the entire run— m/z 107, 121, 124, 137, 138, 164, and 166. Dwell time for each ion was 50 and cycle time—2.664 Hz.

Extraction Procedure and Parameters

For development of extraction parameters, a solution of mixture of analyzed volatile phenols (1 mg/L each) in water was used. In 44-mL EPA screw top vials, 10 mL of standards solution was placed and a vial was capped with a special cap allowing mounting of sorbent pen and air evacuation from the vial. A membrane pump was used to obtain a vacuum of 29" Hg. Sampling was performed at different temperatures and times. For quantitation of compounds in beer samples, the volume of beer was reduced to 5 mL (to avoid trap overloading with the most abundant beer volatiles (mainly esters)). The following parameters for desorption process were elaborated and used in analyses: preheat: duration 90 s, temp. 260 °C, and preinjection—splitless; desorption: standby temp

70 °C, duration 3 min, temp. 260 °C, and divert—no, split mode (180 s); bakeout: duration 21.3 min and temp. 260 °C; and post bake: duration 5 min and temp. 70 °C.

Results and Discussion

Desorption and Separation of the Compounds

Desorption of compounds from traps filled with sorbent (i.e., Tenax) due to a relatively high amount of sorbent requires often refocusing of desorbed compounds band, which is done usually by cryofocusing, the use of sorbent traps/liners of smaller volume or/and chromatographic precolumn. As the compounds are adsorbed by vacuum diffusion into the volume of a trap (unlike the purging through the trap in purge and trap (P&T) methods), they occupy mainly the zone near the bottom of the trap. Therefore, when desorbed, they form a relatively narrow band. The injection is performed in a desorber that has no traditional split/splitter mechanism, so the splitting is achieved by manipulating with split and divert valves and opening them for a certain period of time. Figure 2 shows the separation of standard mixture of extracted volatile phenols desorbed at parameters described in the “Materials and Methods” section. The separation of methyl phenol isomers is difficult especially for 3-methylphenol and 4-methylphenol and they appear as a coeluting peak in the chromatogram. Similarly, 2,3,5-trimethylphenol and 4-ethylguaiaicol were coeluting; however, they can be quantified based on unique ions.

Optimization of Extraction Parameters

For the extraction optimization parameters, standards stock solution (appr 1 mg/mL each) was diluted in water to get a working solution of 0.5 mg/L. The comparison of peak areas when compounds were extracted for 30 min at 50 °C by passive adsorption on the sorbent and vacuum-assisted diffusion is

shown in Fig. 3. When total peak areas were compared, there was over a sevenfold increase in peak areas. Contrary to vacuum SPME, the sample cannot be introduced into the vial, from which the air was evacuated (Psillakis 2017). Evacuation of air from the vial with sample and sorbent pen installed is performed at room temperature and lasts 15–30 s, so eventual loss of highly volatile compounds from headspace is minimized.

The influence of temperature on extraction efficiency was evaluated by comparing peak areas of extracted compounds at 40, 50, and 60 °C. In all cases, vials were shaken at a speed of 150 rpm in a vial heater/shaker and the extraction lasted for 20 min. Figure 4 shows the comparison of peak areas of particular phenols at examined temperatures. Increasing temperature rises the amounts of analytes in the headspace (vapor pressure dependence on temperature), especially those which are characterized with high partition coefficient (between liquid phase and headspace, i.e., polar compounds in aqueous solutions). However, increasing temperature decreases vacuum, so it decreases the effect it has on migration of high boilers (low K_H compounds) into the headspace. The additional factor to be considered is the increased water pressure in a vial, which results in more water in the trap used in a sorbent pen. The sorbent pens used were filled with Tenax, which is hydrophobic, and at examined temperatures and times, no increased water concentration that would influence the performance of MS was observed. The potential solution to above-described drawbacks could be periodical cooling of the headspace, to condense water vapors. Temperature of 50 °C was chosen for further experiments.

Figure 5 shows the extraction profile for the total (sum of) phenols used for method elaboration performed at 50 °C for time periods ranging from 5 to 60 min. The concentration of phenols used in this experiment was relatively high (0.5 mg/L). With a Tenax trap with 70 mg of sorbent, the examined times were too short to achieve an equilibrium. However, the results show the major influence of extraction time on the amount of analytes diffused into the trap under vacuum—the

Fig. 2 TIC chromatogram of volatile phenol standard mixture extracted using VASE. 2MP, 3MP, 4MP—o-cresol, m-cresol, p-cresol respectively; 2MeP—guaiaicol; 2,6DMP—2,6-xyleneol; 2,4DMP—2,4-xyleneol; 4EP—4-ethylphenol; 2Me4MP—4-methylguaiaicol; 2,4,6TMP—mesitol; 2,3,5TMP—2,3,5-trimethylphenol; 4E2MeP—4-ethylguaiaicol; 2Me4(2Pr)P—eugenol; 2Me4PrP—4-propylguaiaicol

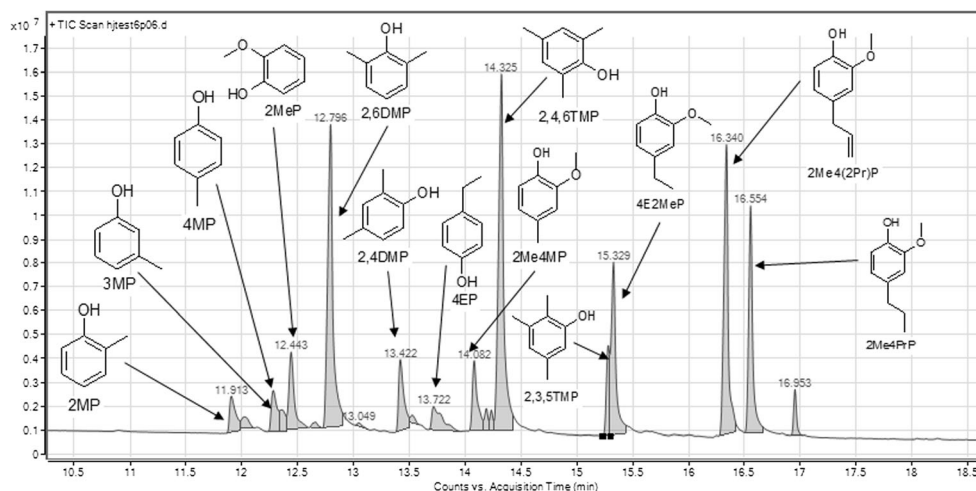


Fig. 3 Comparison of peak areas of volatile phenols extracted using passive diffusion (no vac) and vacuum-assisted diffusion (vac)

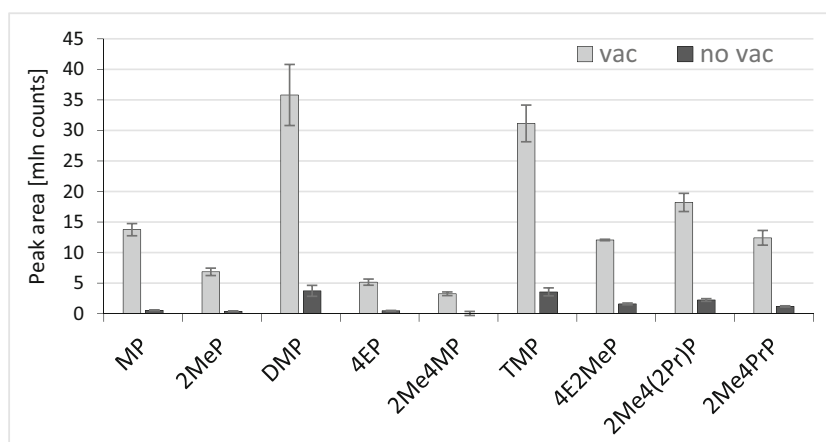
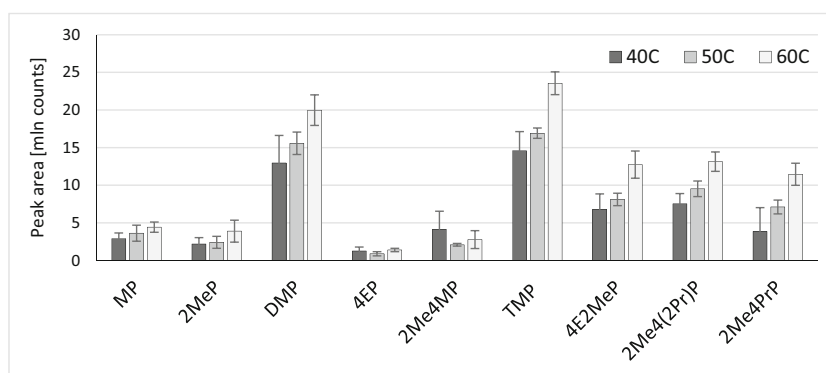


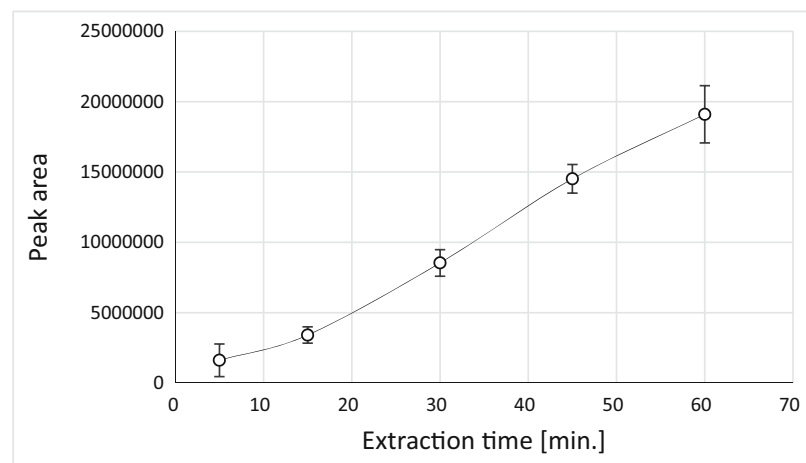
Fig. 4 Comparison of peak areas of volatile phenols extracted using VASE at different temperatures



total peak areas increase tenfold comparing extraction times of 5 and 60 min. The strategies for extraction with pen sorbents could be ranging from higher temperature and shorter time to low temperature and long time with all benefits and drawbacks of each approach and should be tested for a particular analyte/matrix setup. Extraction repeatability was evaluated for a single sorbent pen, as well as for different sorbent pens (Table 1). When the same sorbent pen was used for seven consecutive extractions of analytes, very good reproducibility was achieved with relative standard deviation (RSD) values ranging from 0.89 to 7.77%; for the majority of compounds,

the RSD values were less than 5%. When seven different sorbent pens were compared, the RSD values were higher, but also satisfactory. The lowest repeatability was noted in this case for 4-ethylphenol. The sorbent pens were also tested for carryover. In method parameters, there is a bakeout cycle after desorption in which the sorbent pen is heated for the time usually equal to GC runtime—preheat and desorption at a temperature which usually equals desorption temperature. To test the real carryover after desorption, the bakeout section of the method was canceled, so the compounds from sorbent pens were desorbed only during 3 min desorption time. The

Fig. 5 Extraction profile for total volatile phenols performed at 50 °C for 5–60 min



sorbent pen was desorbed for the second time after initial desorption. No compounds were detected in the second desorption. It proves the sufficient time and temperature for desorption of analyzed phenols. No carryover is probably also related to the diffusion of volatiles into the trap mainly to its first section (unlike in the purge and trap method). It also contributes to narrower bands of analytes during desorption.

Quantitative Analysis

The goal of experiments was to elaborate extraction parameters that would allow efficient extraction of volatile phenols from aqueous matrix and use it for their quantitation in smoked beers. Smoked beers which were prepared from smoked malt by microbreweries were examined to test the method performance for real sample analysis. Beer samples were initially ran in full scan mode to examine compounds that may interfere with analyzed phenols. The main volatiles that are extracted by sorbent methods from beer headspace are esters (mainly ethyl hexanoate, octanoate, decanoate) and also phenylethanol. The last compound with abundant molecular ion at m/z 122 is the main interference in volatile phenols analysis, sharing the same ion as some of phenols (i.e., 4-ethylphenol), also tropylium ions originating from aromatic alcohols (m/z 107, m/z 77) are potentially interfering compounds with analyzed phenols.

To minimize the influence of the matrix, especially the abundant esters and alcohol peaks, 5 mL of beer sample was analyzed. Extraction time was shortened to 30 min to avoid trap overloading. Calibration curves were prepared using light Pilsner type beer free from detectable analyzed phenols. Standard solutions in a concentration ranging from 0.005 to

Table 1 Basic method parameters for VASE determination of volatile phenols in beer

Compound	Ion m/z	LOD [mg/L]	LOQ [mg/L]	R^2	Rep ^a RSD [%]	Rep ^b RSD [%]
2-Methyl phenol	107	0.002	0.006	0.991	3.84	8.04
3+4-Methylphenol	107	0.005	0.015	0.987	7.77	12.76
Guaiacol	124	0.001	0.003	0.987	4.22	5.32
2,6-Dimethylphenol	107	0.001	0.003	0.987	2.81	13.08
2,4-Dimethylphenol	107	0.002	0.006	0.989	2.48	13.00
4-Ethylphenol	107	0.002	0.006	0.988	6.75	18.86
4-Methylguaiacol	138	0.002	0.006	0.997	4.41	9.49
2,4,6-Trimethylphenol	121	0.006	0.018	0.998	1.52	6.35
2,3,5-Trimethylphenol	121	0.006	0.018	0.989	2.43	8.48
4-Ethylguaiacol	137	0.001	0.003	0.998	6.25	10.87
Eugenol	164	0.001	0.003	0.990	0.89	15.30
4-Propylguaiacol	166	0.0002	0.0006	0.997	1.75	10.74

Ion m/z —ion used for quantitation, LOD based on $S/N=3$; R^2 —linearity in the concentration range 0.005–0.5 mg/L; Rep^a—repeatability for $n=7$ using one sorbent pen; Rep^b—repeatability for seven different sorbent pens

Table 2 Content of volatile phenols in smoked beers. Concentration range and median for smoked beers analyzed ($n=5$)

Compound	Range [mg/L]	Median [mg/L]
Methyl phenols	0.063–0.393	0.020
Guaiacol	0.059–0.672	0.329
Dimethylphenols	0.135–0.571	0.203
4-Ethylphenol	0.013–0.036	0.013
4-Methylguaiacol	0.006–0.471	0.023
Trimethylphenols	0.005–0.017	0.007
4-Ethylguaiacol	0.014–0.060	0.024
Eugenol	0.011–0.062	0.017
4-Propyl guaiacol	0.003–0.017	0.005

0.5 mg/L were used to create calibration curves. Quantitation was performed in a SIM mode with seven ions monitored simultaneously (m/z 107, 121, 124, 137, 138, 164, and 166). The high number of ions selected in SIM decreases sensitivity of the method, and therefore, usually three ions are used—target (quantitative) ion and two qualifiers. However, in tested volatile phenol's case, an option with monitoring seven ions was chosen due to the stable (not segmented) baseline and easier quantitation of particular peaks. The choice was based after a “classic” approach was used, i.e., quantifying methyl phenols using m/z 77, 107, and 108; methoxyphenol— m/z 81, 109, and 124; dimethylphenols and 4-ethylphenol— m/z 71, 107, and 122; 4-methylguaiacol— m/z 107, 123, and 138; trimethylphenols— m/z 107, 121, and 136; 4-ethylguaiacol— m/z 121, 137, and 152; eugenol— m/z 137, 149, and 164; and propyl guaiacol— m/z 137 and 166. Table 1 shows linearity of a method in examined concentration range, which was satisfactory, and in all cases, r^2 equalled or exceeded 0.99. The limits of detection estimated at $S/N=3$ were ranging from 0.0002 mg/L (for 4-propyl guaiacol) to 0.006 mg/L for trimethylphenols. The corresponding limits of

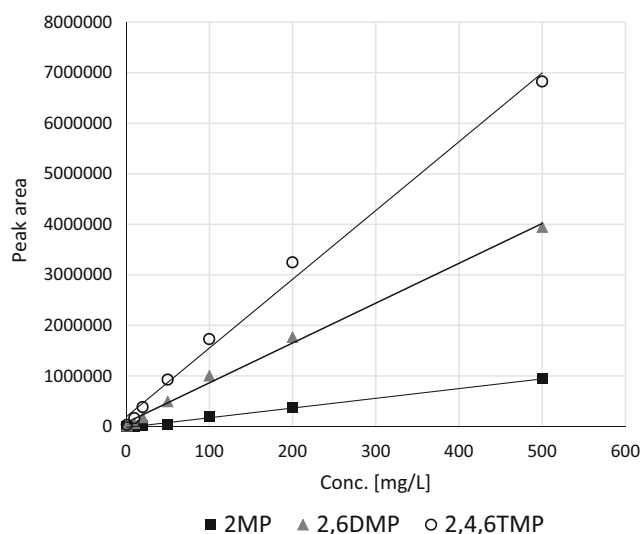


Fig. 6 Sensitivity comparison of VASE for extraction of alkylphenols

quantitation (LOQs) ranged from 0.0006 to 0.018 mg/L for these compounds. When literature data was examined for the LOQs for volatile phenols, most of the data refers to 4-ethyl phenol and 4-ethylguaiacol (from the set of analyzed compounds). When HPLC was used for the quantitative analysis of 4-ethylphenol and 4-ethylguaiacol, authors obtained LOQs of 0.05 and 0.126 mg/L respectively (Vanbeneden et al. 2006). When SPME was used for the extraction of 4-ethylphenol and 4-ethylguaiacol, the LOQs obtained were 0.00018 and 0.0002 mg/L using MHE-SPME (Pizarro et al. 2007) and surprisingly lower values—0.00006 and 0.00002 mg/L—using HS-SPME (Pizarro et al. 2010). However, in both cases, tandem mass spectrometry was used to detect these compounds. The benefits of tandem mass spectrometry are evident here minimizing influence of the matrix (background) on detected peaks (increasing significantly *S/N* ratio). When SBSE was used for direct extraction of 4-ethylphenol and 4-ethyl guaiacol from beer, the LODs were 0.47 and 0.25 µg/L respectively (Zhou et al. 2015).

Five craft smoked beers were analyzed using the described method and the range and medians of detected phenols are shown in Table 2.

When the sensitivity of sorbent pen extraction was compared for different phenols, it was noted that the slope of calibration curved increased from methyl phenols to trimethylphenols (Fig. 6). To eliminate the matrix effect, the comparison was made for solutions of standards in water. Similar effects were observed for guaiacols with increasing size of functional groups. It indicates the usefulness of sorbent pens to extract especially the heavier compounds of lower K_H .

Conclusion

This is, to our knowledge, the first or one of the first quantitative applications of vacuum-assisted sorbent extraction (VASE) to isolate volatile compounds from food matrix. The method has a promising potential, especially for extraction of more polar and less volatile compounds. The method is robust, reproducible, and sensitive and can be used for extraction of samples of different sizes and at different conditions, depending on a chemical character of analyte and the matrix.

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Compliance with Ethical Standards

Conflict of Interest Henryk Jeleń declares that he has no conflict of interest. Anna Gaca declares that she has no conflict of interest. Monika Marcinkowska declares that she has no conflict of interest.

Ethical Approval This article does not contain any studies with human participants or animals performed by any of the authors.

Informed Consent Not applicable.

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