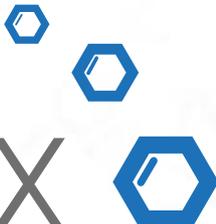
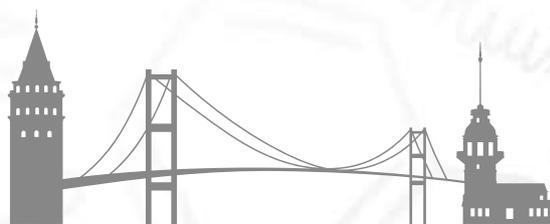




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ABSTRACTS & PROCEEDINGS



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(RNS) take part in cell signalling under various physiological conditions and also provide host defense against bacterial and fungal pathogens (Kumar et al., 2013). While neither $\cdot\text{NO}$ nor $\text{O}_2\cdot^-$ are strong oxidants, ONOO^- is highly reactive. They can cause damage to proteins, DNA, and lipids contributing to diseases ranging from atherosclerosis and aging to neurodegenerative disorders such as Parkinson's and Alzheimer's disease (Dowding et al., 2012). Sodium

nitroprusside is stable in a dry environment, but it produces nitric oxide radicals in aqueous solution at physiological pH. Nitric oxide radicals are scavenged in the presence of antioxidant materials, and the excess of this radical is converted into nitrite by molecular oxygen (Ignarro et al., 1993). A novel nanomaterial-based colorimetric method was developed for sensitive and selective determination of nitrite by our laboratory. A literature search reveals that there is no useful gold nanoparticles-based method for measuring either $\cdot\text{NO}$ or its scavengers. In the developed method, some parameters were optimized such as temperature, solvent medium, sodium nitroprusside concentration and reaction time. Before being scavenged with thiol type antioxidants, the nitric oxide blank absorbance (according to the proposed nano-colorimetric method) of the reference solution was stabilized at $A \sim 1.100$ after optimization of reaction parameters. The developed method was carried out between 7.27×10^{-5} – 3.64×10^{-4} mol L⁻¹ final concentration range for L-cysteine, N-acetyl-L-cysteine, and cysteamine. As a result, nitric oxide radical scavenging activity of L-cysteine was found higher than N-acetyl-L-cysteine, and cysteamine.

Keywords: Thiol-type antioxidants, nitric oxide radical, modified gold nanoparticles

Acknowledgements:

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Keywords: Thiol-type antioxidants, nitric oxide radical, modified gold nanoparticles

[Abstract:0531] P1-089

Determination of semi-volatile additives in wines by vacuum-assisted headspace solid-phase microextraction method

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Abstract

For determination of semi-volatile components in wine samples was used HSSPME and vacuum-assisted HSSPME methods forward to compare the results of analysis. Focal point of this study was non-volatile additives in wine, such as sorbic acid, benzoic acid, polypropylene glycol. In sample preparation procedure wine samples were transferred into vials and evaporated up to removing volatile components, after these samples were equilibrated by freezing. Subsequently, equilibrated sample with air-evacuation step and without this technique analyzed by HSSPME and vacuum-assisted HSSPME methods following by parameters in gas chromatography mass-spectrometry equipment. Comparison of extracted semi-volatile constituents between two methods confirmed the hypothesis. Extracted benzoic acid, sorbic acid and polypropylene glycol by vacuum-assisted HSSPME method presented less extraction time and higher extraction capability than HSSPME. In this study for the first time, screening and quantitative possibilities of vacuum-assisted HSSPME method for the determination of semi-volatile components in wine have been evaluated.

Keywords: Wine, semi-volatile additives, vacuum-assisted headspace solid-phase microextraction

1. Introduction

Wine fragrances contain different classes of compounds such as hydrocarbons, alcohols, terpene alcohols, esters, aldehydes, ketones, acids, ethers, lactones, bases, sulfur-compounds, halogenated compounds and nitriles. Most of these constituents are volatile; also some of these compounds have low volatility. Semi-volatile organic compounds are fundamental to wine quality, deciding their aroma and varietal attributes. Some of the volatile compounds providing to wine property are produced from semi-volatile compounds by the yeasts during fermentation. In the present wine manufacturing preserving agents such as sorbic acid, benzoic acid, polypropylene glycol etc. often used. Sorbic acid and its salts are preservatives which are used in food industry as additives E200-E203. Maximum permissible quantity of sorbic acid according to technical regulations varied from 0.2 to

5 g/kg depending on the type of product and for wine amount of component must not exceed 0.3 g/kg. Sorbic acid is often used in winemaking mainly to prevent the proliferation of yeast and molds. Benzoic acid and its sodium salts are actively used due to concentrations of 0.05–0.1% in an acidic environment are active on yeast and molds. Used in limited quantities for the procurement of semi-finished juices and non-alcoholic beverages. To profile and quantify semi-volatile compounds, they can be extracted from wines using different techniques. A few extraction-concentration techniques have been used in prior studies, for instance, liquid-liquid extraction, liquid-liquid extraction with ultrasound, simultaneous distillation-extraction, solid phase extraction and other techniques. Solid-phase microextraction is a standout method among the most commonly used techniques. It is quick and economical method, which doesn't need the use of solvents, is also able to detect low concentration of components. The SPME is procedure permits the procurement of intriguing results when gas chromatography is combined with mass spectrometric detection, making the concurrent investigation of tens or many unstable compounds conceivable.

Most of components in wine are volatile, but also there are semi-volatile components, which impact to the quality and aroma of wine. More suitable and effective method for identification of compounds in wine is HS-SPME. But for headspace SPME, the extraction of volatile analytes was always faster than semi-volatiles and analyzes needs higher temperature. That is inappropriate method to analyze nonvolatile components in wine with SPME. Also vacuum-assisted HSSPME (Vac-HSSPME) were constantly found to yield high extraction efficiencies and great sensitivities within short sampling times and at low temperatures. Vac-HSSPME was successfully used to identify various groups of semi-volatile compounds in water samples. All published Vac-HSSPME methods yielded, within shorter sampling times and at lower sampling temperatures, limits of detection similar or lower than those attained with regular HSSPME [2].

II. Material and method

All wine samples were purchased from local market. 3 types of wine samples were chosen for screening and quantitative analysis. The main semi-volatile additives in wine propylene glycol, sorbic and benzoic acids were identified by gas chromatography-mass spectrometry combined with HSSPME and vacuum-assisted HSSPME method after evaporation of water, ethanol and most polar volatile wine components at 90°C. For identification of these and other supplements was chosen optimized parameters - 85 µm CAR/PDMS fiber coating, extraction time 2 min for white and 3 min for red wines, 85 °C 15 min temperature, 15 min pre-incubation time [1].

Sample preparation: 1 and 5 ml samples of wine was transferred into 20 ml vials and water, ethanol and most polar volatile wine components were evaporated in 90°C temperature 4-6 hours depending on the wine type. After these technique evaporated samples were stored in freezer for 24 hours up to equilibrium condition of components. In half part of samples air vacuumed for 2 min. Collection of samples divided into two HSSPME and vacuum-assisted HSSPME methods analyzed by gas-chromatography mass-spectrometer. Analysis was conducted three times.

III. Results and discussion

Wine flavor contain various classes of volatile and semi-volatile compounds. There are lot of suitable methods for determination of volatile components. But these methods are inappropriate for identification of nonvolatile components. Solid-phase microextraction is a standout method among the most commonly used techniques. It is quick and economical method, which doesn't need the use of solvents, is also able to detect low concentration of components. The SPME is procedure permits the procurement of intriguing results when gas chromatography is combined with mass spectrometric detection, making the concurrent investigation of tens or many unstable compounds conceivable. Vac-HSSPME was effectively used to identify various groups of semi-volatile compounds in water samples, because of it is provide better extraction. The propose of this study is to develop Vac-assisted HSSPME GC/MS, due to evaporation and optimize parameters for determination semi-volatile components in wine. Extracted polypropylene glycol in (5 ml wine sample) by vacuum-assisted HSSPME method presented less extraction time and higher extraction capability than HSSPME. However extracted polypropylene glycol in 1 ml sample by HSSPME method presents the more peak area. Consequently extraction of benzoic acid following by two methods showed the same results. The peak area of sorbic acid in both amount of sample volume presents positive results approving the effectiveness of vacuum-assistant HSSPME method.

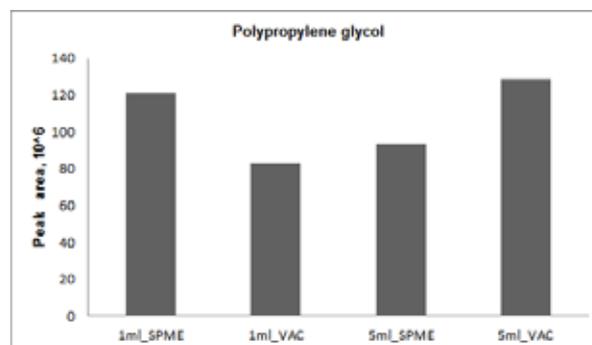


Fig. 1: Comparison of the extracted polypropylene glycol by HSSPME and vacuum-assisted HSSPME methods

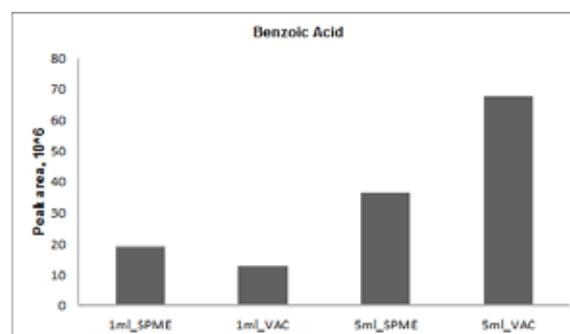


Fig. 2: Comparison of the extracted benzoic acid by HSSPME and vacuum-assisted HSSPME methods

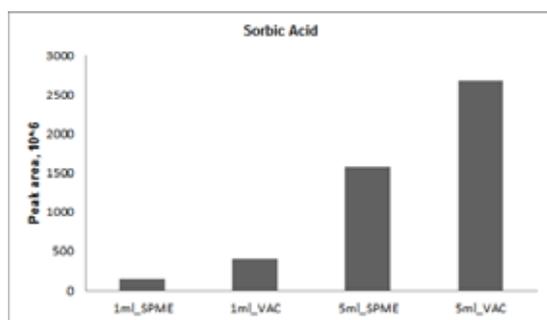


Fig. 3: Comparison of the extracted sorbic acid by HSSPME and vacuum-assisted HSSPME methods

IV. Conclusion

More than half of components of wine are volatile. Most of semi-volatile constituents in wine composition can be found as preservatives and other additives. For determination of semi-volatile components in wine samples was used HSSPME and vacuum-assisted HSSPME methods forward to compare the results of analysis. Focal point of this study was non-volatile additives in wine, such as sorbic acid, benzoic acid, polypropylene glycol. In sample preparation procedure wine samples were transferred into vials and evaporated up to removing volatile components, after these samples were equilibrated by freezing. Subsequently, equilibrated sample with air-evacuation step and without this technique analysed by HSSPME and vacuum-assisted HSSPME methods following by parameters [1] in GC/MS equipment. Comparison of extracted semi-volatile constituents between two methods confirmed the hypothesis. Extracted benzoic acid, sorbic acid and polypropylene glycol by vacuum-assisted HSSPME method presented less extraction time and higher extraction capability than HSSPME. In this study for the first time, screening and quantitative possibilities of vacuum-assisted HSSPME method for the determination of semi-volatile components in wine have been evaluated. Consequent investigation will be the optimization of vacuum-assisted headspace solid-phase microextraction method for analysis of semi-volatile additives in wines following by the results.

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[Abstract:0666] P1-091

Determination of Furosine Concentrations at Royal Jelly Samples Using Ion Exchange Separation Coupled with UV Detection

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Abstract

Royal Jelly (RJ) is a natural product secreted by the hypopharyngeal and mandibular glands of worker bees. RJ contains many components such as water, sugars, amino acids, proteins, fatty acids and vitamins [1]. Nevertheless, there is no international regulation concerning RJ harvest, production. Because of the poor storage conditions, royal jelly may be spoiled or lose its health-promoting properties [2]. These changes occur due to the Maillard Reaction (MR). It is crucial to detect the MR from the early stages and furosine is commonly chosen as freshness indicator. Furosine is commonly quantified by liquid chromatography with UV detection. A purification step by SPE (Solid Phase Extraction) is usually conducted and long elution and acid hydrolysis times are general. Our main purpose was to develop a sensitive, rapid method using cation exchange separation that is coupled with UV detection (HPCE-UV). The novel method has been applied to the analysis of 10 Turkish RJ.

RJ sample corresponding to about 30–70 mg of protein, was hydrolyzed with 20 mL of HCl 8N at 110°C for 4h. The solution was filtered through 0.45 µm syringe filter. We have to note that a purification of the hydrolyzate by SPE is indispensable to decrease matrix interferences for the usual determination of furosine. Here it is not necessary as the chromatographic conditions were specific to furosine. The HPLC analysis was carried out on an Thermo Accela UHPLC-UV system. The analytical separation was performed on a Grace Spec Furo column maintained at 40 °C. The flow was 1,2 mL/min and 10 µL sample were injected. The mobile phases were composed of 4% acetic acid and 0.34% KCl. The total run time was about 24 min.

To assess the linearity, working standard solutions of 5, 10, 20, 50, 100 and 200 ppm of furosine were injected in eight replicates. Calibration curves gave good fits ($R^2 > 0.99$). The LOD and LOQ were determined at 0,5 ppm and 1 ppm, respectively. The percent recovery was calculated it is found with 93% rate. To investigate the repeatability, 8 replicates of 3 calibration concentrations (5,20,50 ppm) were injected. The repeatability obtained were lower than 8%. After hydrolysis, the LC-UV method allowed