University of Glasgow

Papageorgiou, M., Lambropoulou, D., Morrison, C. , Namieśnik, J. and Płotka-Wasylka, J. (2018) Direct solid phase microextraction combined with gas chromatography – mass spectrometry for the determination of biogenic amines in wine. *Talanta*, 183, pp. 276-282.(doi:10.1016/j.talanta.2018.02.006)

This is the author's final accepted version.

There may be differences between this version and the published version. You are advised to consult the publisher's version if you wish to cite from it.

http://eprints.gla.ac.uk/156646/

Deposited on: 02 February 2018

Enlighten – Research publications by members of the University of Glasgow
http://eprints.gla.ac.uk

Direct solid phase microextraction combined with gas chromatography – mass spectrometry for the determination of biogenic amines in wine

Myrsini Papageorgiou[1], Dimitra Lambropoulou[1], Calum Morrison[2], Jacek Namieśnik[3], Justyna Płotka-Wasylka[3]*

[1]*Department of Chemistry, Environmental Pollution Control Laboratory, Aristotle University of Thessaloniki, 54 124 Thessaloniki, Greece*

[2] *Forensic Medicine and Science, School of Medicine, Dentistry and Nursing, College of Medical, Veterinary and Life Sciences, University of Glasgow, Glasgow G12 8QQ, United Kingdom*

[3]*Department of Analytical Chemistry, Faculty of Chemistry, Gdańsk University of Technology, 11/12 Narutowicza Street, 80-233 Gdańsk, Poland*

**Corresponding author: plotkajustyna@gmail.com; juswasyl@pg.gda.pl*

Abstract

A direct method based on immersion solid phase microextraction (DI-SPME) gas chromatography mass-spectrometry (GC-MS) was optimized and validated for the determination of 16 biogenic amines in Polish wines. In the analysis two internal standards were used: 1,7-diaminoheptane and bis-3-aminopropylamine. The method allows for simultaneous extraction and derivatization, providing a simple and fast mode of extraction and enrichment. Different parameters which affect the extraction procedure were studied and optimized including ionic strength (0-25%), fiber materials (PDMS/DVB, PDMS/DVD+OC, Polyacrylate, Carboxen/PDMS and DVB/CAR/PDMS) and timings of the extraction, derivatization and desorption processes. Validation studies confirmed the linearity, sensitivity, precision and accuracy of the method. The method was successfully applied to the analysis of 44 wine samples originating from several regions of Poland and 3 wine samples from other countries. Analysis showed that many of the samples contained all examined biogenic amines. The method, assessed using an Eco-Scale tool with satisfactory results, was found to be green in terms of hazardous chemicals and solvents usage, energy consumption and production of waste. Therefore the proposed method can be safely used in the wine industry for routine analysis of BAs in wine samples with a minimal detrimental impact on human health and the environment.

Keywords: biogenic amines, DI-SPME, derivatization, GC-MS, wine, (green chemistry or Eco-Scale)

1. Introduction

Biogenic amines (BAs) are of worldwide importance as they are naturally formed compounds from the decarboxylation of amino acids, and may be used as markers for quality and freshness of products that are consumed in a regular human diet. Although they are involved in important metabolic and physiological functions in every living organism, consumption at high concentrations may cause undesirable physiological effects [1].

Biogenic amines occur in many matrices worldwide including alcoholic beverages such as wine [2-7]. Since ethanol and acetaldehyde can increase the risk effects on human health by inhibiting the enzymes responsible for detoxification, the presence and the levels of BAs in wine has received much attention [1,8-10].

Several methods for the determination of BAs in food and alcoholic beverages [5,6] have been reported, with the determination of amines in complex matrices, such as wine, being particularly difficult as a result of the low concentrations involved (1-50 mg/L). The quantification of this group remains challenging due to the variation in the physicochemical properties (Table SM1, Supplementary Materials) and potential matrix effects from polyphenols and other substances present within the sample. This problem has been addressed using a derivatization process, with pre- and post-column approaches in high-performance liquid chromatography most widely employed at present [7]. Many derivatization processes reduce polarity and reactivity, and increase volatility of the amine compounds thereby making gas chromatographic analysis a viable option [9]. A further increase in the sensitivity and selectivity may be achieved with the use of mass spectrometric detection. .

Derivatization may cause the loss of the analytes, introduce additional impurities and extend the sample preparation time, but is often required to complement the analysis. A further challenge is the need for the derivatization process to be in accordance with green chemistry [10] and green analytical chemistry [11], under the principles of sustainable development. It has been shown that miniaturization and automation are key elements that should be taken into account during optimization of "green" analytical procedures involving a derivatization step [12], with the aim of reducing reagent use and overall waste. The application of microextraction techniques in conjunction with the derivatization procedure here has an excellent fit with these specified requirements. There are a large number of reports in the literature for the determination of biogenic amines in the wine industry, but these tend to

focus on the use of liquid-liquid extraction or solid phase extraction rather than solid phase microextraction techniques [13,14,15].

Therefore, an SPME procedure involving either immersion of the derivatization agent in a suitable solution or direct contact with the fiber [14, 15] allows determination of the target BAs without the use of toxic organic solvents with GC-MS affording additional sensitivity. In summary, this approach has many advantages when compared with conventional derivatization procedures, including ease and speed of use, relatively low cost (per sample) and low solvent use.

The main objective of this study was to optimize and validate a reliable DI-SPME/GC-MS method for the simultaneous determination of common BAs present in wine samples (Table SM1, Supplementary Materials). During the optimization of the DI-SPME procedure, attention was given to a careful evaluation of the SPME fiber type, time of extraction and desorption processes, pH, ionic strength, and three parameters (type, quantity, reaction time) associated with the derivatizing reagent (DR). Thereafter, the optimized method was used to assess the occurrence of selected biogenic amines in wine samples originating from different regions of Poland.

To the best of our knowledge, there is no data concerning BA analysis in wine samples using DI-SPME method with simultaneous isobutyl chloroformate derivatization, therefore, this study enriches knowledge in the field of wine analysis and provides a green method applicable for routine analysis of BAs in the wine industry.

2. Materials and methods

2.1. Reagents and materials

Sixteen biogenic amines standards were used : 1.7 diaminoheptene, bis-3-aminopropyl amine, butylamine, cadaverine hydrochloride, diethylamine hydrochloride, dimethylamine hydrochloride, hexylamine, histamine dihydrochloride, isobutylamine, isopentylamine, methylamine hydrochloride, propylamine hydrochloride, putrescine dihydrochloride, tryptamine hydrochloride, tyramine hydrochloride and 2-phenylethylamine hydrochloride. All were purchased from Sigma–Aldrich (Steinheim, Germany) and diluted in ultrapure water for the preparation of stock solutions (1000 mg/L). All the standards were >99% purity except for cadaverine hydrochloride, 1-7 diaminoheptane and bis (3-amino propyl) amine (98%). Two

internal standards were used: 1-7 diaminoheptane (IS1) and bis-3-aminopropyl amine (IS2). Isobutyl choroformate (IBCF) was used as the derivatization agent and supplied by Sigma-Aldrich (Steinheim, Germany). Ultrapure water (resistivity at 25°C: 7 MΩ•cm) was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA).The stock solutions of BAs were stored in a refrigerator (4°C) and working solutions prepared daily from dilution of the stock solutions with ultrapure water.

2.2. SPME fibers and materials

The SPME fiber assembly kit assortment, Stableflex 24Ga, manual holder, 4pk fibers and PDMS/DVB (divinylbenzene), fused silica 24 Ga, SPME holder and SPME manifold were supplied by Supelco. The fibers selected were PDMS/DVB and PDMS/DVD+OC (organic carbon) with film thickness diameter 65 μm, polyacrylate 85 μm, Carboxen™/PDMS 85 μm and DVB/CAR/PDMS 50/30 μm. Fibers were conditioned with the set up parameters and tested without further modification. To eliminate potential problems with carry over and baseline noise, blank injections were performed between runs.

2.3. GC-MS equipment

A gas chromatograph 7890A (Agilent Technologies) equipped with an electronically controlled split/splitless injection port was interfaced to a mass selective detector (5975C, Agilent Technologies) with an electron impact ionization chamber. The temperature of the injector and the interface were set at 250ºC. Chromatographic separation was achieved using a ZB-5MS capillary column (30 m × 0.25 mm I.D., 0.25 μm) (Zebron Phenomenex) with the following temperature program: 100ºC held for 1.2 min, increased to 160ºC at 10ºC/min and finally ramped to 280ºC at 25ºC/min and held for 12 min giving a total run time of 25 min. The sample injection volume was 2 μL and helium was used as the carrier gas at a 1.0 mL/min flow rate. Mass Spectra were obtained at 70 eV.

For improved selectivity and sensitivity, the analysis was performed in selected ion monitoring (SIM) mode. The ion fragments of BAs detected are given in Table 1. All the ion fragments with their relative intensities at the specific retention times were considered as valid confirmation criterion and used for the identification of the specific BAs. Agilent Chemstation software was used for data collection.

2.4. Sampling

A total of 44 samples (red, white and rose) originating from vineyards located in different parts of Poland (Figure SM1) were collected. Additionally, three samples from other countries located in Europe were examined. All samples were stored at room temperature (21^{o}C) and protected from light. Information on the samples is presented in Table SM2.

2.5. Direct immersion-solid phase microextraction (DI-SPME) procedure

The direct-immersion solid phase microextraction procedure was as follows: 10 mL of the sample solution (5 mL of wine and 5 mL of deionized water) was adjusted to pH 12 with sodium hydroxide (NaOH) and immersed in screw top vials with phenolic caps and PTFE/silicon septa. The derivatization agent, isobutyl chloroformate (50 μL) was added to the solution along with sodium chloride (15% NaCl) and the solution was stirred with a magnetic stirrer for 2 min. After the derivatization, the extraction occurred by immersing the polyacrylate SPME fiber in the solution for 40 min. All procedures were performed at room temperature. The fiber was then carefully removed and inserted directly into the GC-MS with a 10 min desorption time. The schematic representation of this procedure is illustrated in Figure SM2.

2.6. Optimized extraction conditions

In the combined SPME and derivatization procedure, a number of parameters require optimization, including the sorbent material of the fiber, the ionic strength and pH of the solution, extraction time and derivatization reaction time. In addition, the appropriate dilution of the sample is required in order to minimize matrix effects affecting the analysis of the BAs. The most commonly used derivatizing reagents for BAs are: dansyl chloride, o-phthalaldehyde, benzoyl chloride and isobutyl chloroformate [7,16,17]. In this study, isobutyl chloroformate was chosen, which has been previously used with successful results [18]. Optimization of experimental parameters is discussed in Section 3. Each experiment was conducted in triplicate, and average results are discussed.

2.7. Quality assurance/ quality control of DI-SPME

The optimized method was evaluated using linearity, precision, sensitivity and accuracy according to quality assurance and quality control (QA/QC) protocols. Linearity was tested using six different concentrations. Sensitivity was estimated in terms of limit of detection (LOD) and limit of quantification (LOQ). The LODs and LOQs were calculated from spiked samples (n=6) and the minimum detectable amount of the target compound with a signal to

noise ratio of 3 and 10, respectively, was established. Recovery rates of the analytical method were calculated using the ratio of the peak areas of the spiked samples of known concentration of BA to those of spiked aqueous solutions. Six measurements were taken for each and the lowest and highest concentrations were obtained. The intra-day (RSD_r) and inter-day (RSD_R) precision was determined using six replicates of wine samples spiked at six levels (10, 100, 250, 500, 750, and 1000 µg/L); each replicate was submitted to the overall method.

3. Results and discussion

3.1. Fiber selection

Supelco guidelines [14] were followed for selection of stationary phase type, thickness and polarity. The fibers chosen were: 65 µm polydimethylsiloxane/divinylbenzene with stable flex and fused silica (pink and blue) designed for volatiles, amines and nitro-aromatic compounds; 85 µm polyacrylate for polar semi-volatiles compounds; 85 µm Carboxen™/polydimethylsiloxane for gases and low molecular weight compounds; and 50/30 µm divinylbenzene/Carboxen™/polydimethylsiloxane. All fibers were tested at basic pH (8). A comparison between peak intensities for each stationary phase type is presented in Figure 1a. The 65 µm polydimethylsiloxane/ divinylbenzene with stable flex and fused silica fiber (pink and blue) showed better results for dimethylamine and hexylamine, but demonstrated poor peak intensities for tyramine, putrescine, cadaverine and 2-phenylethyl amine. No significant differences were noted for 85 µm Carboxen/polydimethylsiloxane (light blue) and 50/30 µm divinylbenzene/Carboxen/polydimethylsiloxane (grey), while 85 µm polyacrylate (white) demonstrated improved results for all other compounds and was therefore selected.

3.2. Derivatization process

The process for isobutyl chloroformate derivatization is outlined in Fig. 2 and provides a fast and stable derivatization [18]. Furthermore, an in-solution derivatization procedure was followed, since in-fiber derivatization is potentially harmful to the fiber. Volumes of IBCF from 25 to 100 µL were chosen for optimisation experiments with the highest peak intensities for all BAs obtained with 50 µL. The effect of the volume of IBCF on peak intensity is depicted in Fig. 1b.

Derivatization times were studied between 1 and 20 min. In the first 2 min all compounds reached the highest peak intensities, thereafter a decrease in intensity and derivatization by-

products were apparent. Optimal derivatization time was therefore 2 min with detailed results from the study shown in Fig. SM3a.

3.3. Ionic strength

The peak intensity improves by increasing the ionic strength of the aqueous solution, favouring extraction of analytes into the fiber and solubility of the extracted compounds [20-22]. The impact of ionic strength on the uptake of BAs after exposure to the fiber was investigated at NaCl concentrations ranging between 0 and 25 % (w/v). While the response of the fiber was slightly affected, recovery was increased by the addition of NaCl (Fig. SM3b). The extraction was conducted with 15% addition of salt to guarantee good extraction efficiency.

3.4. pH

When physicochemical properties (pKa and pKow) of the analyte are important, consideration of the pH of the sample is vital to obtain reproducible results. The variations of peak intensities in different pH values were tested within the range 2-12 with adjustments made using NaOH and HCl. Lower peak intensities were evident in the pH range from 2 to 6, while peak intensities increased for the pH range 8 to 12. This is due to the suppression of dissociation of BAs in alkaline conditions to the non-ionic form [19]. Peak intensities compared to pH value is given in Fig. 1c. A pH of 12 was selected for further studies.

3.5. Extraction time

After optimization of the previous parameters, the time between 10-60 min with stirring (magnetic stirrer) was investigated, concluding that the BAs showed the highest peak intensity at 40 min (Fig. 1d). An attempt to reduce the equilibrium time between the BAs and the fiber using a different agitation method (vortex) increased destruction of the fiber.

3.6. Wine sample preparation

The wine samples were stored in the dark before analysis. The dilution effect was studied using three scenarios: 1:2, 1:10 and without dilution. In Fig. SM3c the peak intensities with the different ratios of dilution presented. Clearly the best results were obtained using a 1: 2 dilution.

3.7. Method validation

The linearity achieved for BAs in the concentration range from 1 to 1000 µg/L was good as shown by the correlation coefficients (0.991–0.999). The average recovery values varied from 65 to 107% as can be seen in Table 2. The relative standard deviation ranged from 1% to 15% for intra-day precision (RSD_r) and from 5.2 to 12.8% for inter-day precision (RSD_R) (<20%) (Table 2). LODs and LOQs were in the ranges 0.009–0.859 µg/L and 0.028– 1.634 µg/L, respectively. All validation criteria are shown in Table 2.

3.8. Application to real samples

The reliability of the proposed procedure was evaluated by analysis of a set of 44 Polish wine samples (24 white, 2 rose and 18 red wines) and 3 wines originating from other European countries. Samples of interest were analysed with three replicates. Information on biogenic amines content (µg/L) in samples with standard deviation (n=3) are given in Table SM4. Fig. 3 represents a chromatogram obtained after analysis of sample W1 demonstrating good separation for compounds of interest.

The BAs were determined in all samples except 5R, with the type and quantity varying depending on the sample analysed.

Five primary biogenic amines were examined. In the samples a toxic primary amine, methylamine, was determined in two white Polish wines (W2, W10) and one white wine from another country (Z2W), with levels ranging from 179±31 to 298±12 µg/L. A volatile compound, propylamine, was determined in two white Polish wines (W1, W2) and one red wine coming from another country (Z1R), with levels ranging from 8.01±0.11 to 67.2±1.0 µg/L. Hexylamine was determined in 3 Polish wines (1.002±0.011 to 175.3±1.6 µg/L) and all samples from other countries (1.003±0.012 to 719±17 µg/L). Two biogenic amines, namely butylamine and isobutyl amine, were not detected in any sample.

Dimethylamine, a secondary amine important as a potential precursor of the carcinogen dimethylnitrosamine, was found in two white wines (W9 and Z1W) and 6 Polish red wines with levels ranging from 3.00±0.21 to 77.0±1.1 µg/L. The other secondary amine quantified was diethylamine, with levels ranging from 24.01±0.35 to 80.2±1.2 µg/L, and was found in two samples (W1, W2).

When considering the aromatic and heterocyclic amines (2-PE, TRP, TYR, HIST) found in the analyzed wines, histamine is described as the most toxic for humans. This BA is the causative agent of physiological distress experienced by some individuals following wine

ingestion [1]. Histamine was present in 44 of the 47 samples analyzed, with levels ranging from 10.09±0.11 to 1639±48 µg/L. 2-Phenylethylamine, tyramine and tryptamine can elevate blood pressure and cause migraines [1]. 2-Phenylethylamine was determined in 14 white wines (two not from Polish origin) and 10 red wines, with levels ranging from 3.023±0.065 to 192±10 µg/L (white) and from 9.09±0.16 to 127.1±1.4 µg/L (red). This compound was not detected in rose wines. Tryptamine was found in 17 white (from 1.012±0.011 to 134.0±1.3 µg/L) and 5 red (from 1.020±0.008 to 22.10±0.21 µg/L) Polish wines and detected in all samples from countries other than Poland. Tyramine was determined in 6 white wines (from 10.21±0.10 to 432±10 µg/L) including sample Z1W (62.11±0.32 µg/L) and 2 red wines (from 35.05±0.10 to 54.01±0.27 µg/L) including Z1R (54.01±0.27 µg/L). It should be mentioned that the toxic effects of this group of amines are potentiated in the presence of alcohol, acetaldehyde and other amines. According to Ganic et al. [23], the toxic dose of BA in alcoholic beverages varies between 8 and 20 mg/L for histamine, between 25 and 40 mg/L for tyramine, and 3 mg/L for phenethylamine and therefore none of the examined samples exceeded toxic doses of these BAs.

The amines associated with sanitary conditions (putrescine and cadaverine) were also found in the analysed samples, however, the levels were different depending on the compounds. Additionally, putrescine was determined in 43 samples, with levels ranging from 37.00±0.24 to 1148±29 µg/L for samples coming from Poland and from 13.12±0.20 to 417±13 µg/L for other samples, while cadaverine was found in 23 samples**,** with levels ranging from 12.00±0.12 to 397±10 µg/L.

The total amount of biogenic amines determined in wine samples varied widely with higher total levels for red wine numbered as sample R1 (2544 µg/L) followed by samples R10 (2265 µg/L) and R2 (1505 µg/L), compared to white wines where the highest total levels are noted for samples W11 and W1 (1387 and 1317 µg/L, respectively). The total level of BAs in rose wines ranges from 774 to 971 µg/L. The total level of BAs in samples coming from countries other than Poland ranges from 823 to 1545 µg/L. Putrescine and histamine contributed the most to total levels.

3.9. Environmental assessment of the method

The analytical community is currently focused on eliminating or at least reducing the usage of hazardous chemicals and solvents in its methodologies. In this context, green, eco-friendly, or clean practices have been implemented across research areas, including analytical chemistry.

As previously stated, the determination of BAs in wine samples is mainly performed by application of liquid-liquid extraction and liquid chromatography techniques [24-28]. Gas chromatography is rare and generally requires solvent-based techniques at the sample preparation stage. This study presents a greener alternative for existing methods for the simultaneous determination and quantitative analysis of biogenic amines in wine, using DI-SPME coupled with derivatization and GC-MS. The method demonstrates a short run time without solvents and minimal amount of waste production. This approach was feasible without compromising method performance criteria, such as separation efficiency, peak symmetry, and chromatographic retention. The greenness profile of the proposed method was estimated and compared with reported conventional methods using the analytical Eco-Scale as an assessment tool (Table 3)[28]. The Eco-Scale tool is based on assigning penalty points (PPs) to parameters of an analytical process that are not in agreement with the ideal green analysis. The basis for the concept of an analytical Eco-Scale is that the ideal green analysis has a value of 100.

The proposed method was found to be greener in terms of usage of hazardous chemicals and solvents, energy consumption and production of waste (84 PPs). The method can be safely used for the routine analysis of BAs in wine samples with a minimal detrimental impact on human health and the environment. It should be noted that although, in this work, the helium was used as a carrier gas for GC due to its inertness, good purity, and excellent performance, the proposed methodology could be greener if hydrogen was used instead of helium as a carrier gas. Hydrogen has a wide range of applicability, provides good efficiency, and, for the most part, separations are faster than with other popular carrier gases like helium and nitrogen. In addition, it is much cheaper to purchase than helium and can be generated easily and cheaply by using hydrogen generators with a very high level of purity.

4. Conclusion

The levels of fourteen biogenic amines in Polish wines were investigated using DI-SPME-GC-MS and reported for the first time. The method enables extraction and derivatization processes to be carried out simultaneously with acceptable enrichment factors. This approach has advantages when compared with conventional derivatization procedures, such as ease of use, rate, and low solvent use, all desirable when considering GAC principles. However, the SPME fiber is an expensive element and can be destroyed under some circumstances when

immersed in a wine sample. This can be avoided with careful operation and therefore not considered to be a significant limiting factor.

The levels of biogenic amines found in the Polish wines were very low suggesting that high quality vinification practices are used by producers. Further studies following the whole process, including grapes characterization should be undertaken to ascertain the influence of specific vinification steps on amine formation. Finally, biogenic amine content can be used to indicate or assess the quality of wine and therefore the method in this study could be applied in wine industry quality and testing procedures.

Acknowledgments

The research is funded by the Polish Ministry of Science and Higher Education within the "Iuventus Plus" program in years 2015-2018, project no: IP2014 037573. The authors would like to thank Zodiak Vineyard, Przy Talerzyku Vineyard, Kozielec Vineyard, Pod Orzechem Vienyard, Stok Vineyard, Spotkaniówka Vineyard, and Dwór Kombornia Vineyard for the samples of wine. The authors are grateful to Ailsa Morrisons for assistance with proof reading and constructive comments.

References

[1] S.C. Souza, K.H. Theodoro, É.R. Souza, S.d. Motta, M.B.A. Glória, Bioactive amines in Brazilian wines: types, levels and correlation with physico-chemical parameters, Brazilian Archives of Biology and Technology, 48 (2005) 53-62.

[2] V. Andruch, M. Burdel, L. Kocúrová, J. Šandrejová, I.S. Balogh, Application of ultrasonic irradiation and vortex agitation in solvent microextraction, TrAC Trends in Analytical Chemistry, 49 (2013) 1-19.

[3] F. Gardini, Y. Ozogul, G. Suzzi, G. Tabanelli, F. Ozogul, Technological Factors Affecting Biogenic Amine Content in Foods: A Review, Front Microbiol. 7 (2016) 1218-1236.

[4] M.R. Loizzo, F. Menichini, N. Picci, F. Puoci, U.G. Spizzirri, D. Restuccia, Technological aspects and analytical determination of biogenic amines in cheese, Trends in Food Science & Technology, 30 (2013) 38-55.

[5] M. Papageorgiou, D. Lambropoulou, C. Morrison, E. Kłodzińska, J. Namieśnik, J. Płotka-Wasylka, Literature update of analytical methods for biogenic amines determination in food and beverages, TrAC Trends in Analytical Chemistry, 98 (2018) 128-142.

[6] J.L. Ordonez, A.M. Troncoso, C. Garcia-Parrilla Mdel, R.M. Callejon, Recent trends in the determination of biogenic amines in fermented beverages - A review, Analytica chimica acta, 939 (2016) 10-25.

[7] A. Onal, S.E. Tekkeli, C. Onal, A review of the liquid chromatographic methods for the determination of biogenic amines in foods, Food chemistry, 138 (2013) 509-515.

[8] S.C. Cunha, R. Lopes, J.O. Fernandes, Biogenic amines in liqueurs: Influence of processing and composition, Journal of Food Composition and Analysis, 56 (2017) 147-155.

[9] S.C. Cunha, M.A. Faria, J.O. Fernandes, Gas chromatography-mass spectrometry assessment of amines in Port wine and grape juice after fast chloroformate extraction/derivatization, J Agric Food Chem, 59 (2011) 8742-8753.

[10] J. Płotka, M. Tobiszewski, A.M. Sulej, M. Kupska, T. Górecki, J. Namieśnik, Green chromatography, Journal of Chromatography A, 1307 (2013) 1-20.

[11] A. Gałuszka, Z. Migaszewski, J. Namieśnik, The 12 principles of green analytical chemistry and the SIGNIFICANCE mnemonic of green analytical practices, TrAC Trends in Analytical Chemistry, 50 (2013) 78-84.

[12] L.H. Keith, L.U. Gron, J.L. Young, Green Analytical Methodologies, Chemical Reviews, 107 (2007) 2695-2708.

[13] J. Płotka-Wasylka, N. Szczepańska, M. de la Guardia, J. Namieśnik, Miniaturized solid-phase extraction techniques, TrAC Trends in Analytical Chemistry, 73 (2015) 19-38.

[14]Sigma-Aldrich, SPME Application Guide 7th Edition, Sigma-Aldrich, sigma-aldrich.com, 2009.

[15]F. Aflaki, V. Ghoulipour, N. Saemian, M. Salahinejad, A simple method for benzoyl chloride derivatization of biogenic amines for high performance liquid chromatography, Analytical Methods, 6 (2014) 1482.

[16] H. Kataoka, H.L. Lord, J. Pawliszyn, Applications of solid-phase microextraction in food analysis, Journal of Chromatography A, 880 (2000) 35-62.

[17] J. M. Płotka-Wasylka, C. Morrison, M. Biziuk, J. Namieśnik, Chemical Derivatization Processes Applied to Amine Determination in Samples of Different Matrix Composition, Chem. Rev. 115 (2015) 4693−4718.

[18] J. Plotka-Wasylka, V. Simeonov, J. Namiesnik, An in situ derivatization - dispersive liquid-liquid microextraction combined with gas-chromatography - mass spectrometry for determining biogenic amines in home-made fermented alcoholic drinks, Journal of chromatography. A, 1453 (2016) 10-18.

[19] R. Parchami, M. Kamalabadi, N. Alizadeh, Determination of biogenic amines in canned fish samples using head-space solid phase microextraction based on nanostructured polypyrrole fiber coupled to modified ionization region ion mobility spectrometry, Journal of chromatography. A, 1481 (2017) 37-43.
[20] Z. Zhang, M.J. Yang, J. Pawliszyn, Solid-Phase Microextraction. A Solvent-Free Alternative for Sample Preparation, Solid Anal. Chem. 66 (1994) 844A-853A.
[21] D. Djozan, T. Baheri, Preparation and evaluation of solid-phase microextraction fibers based on monolithic molecularly imprinted polymers for selective extraction of diacetylmorphine and analogous compounds, Journal of chromatography. A, 1166 (2007) 16-23..
[22] X.-Y. Song, Y.-P. Shi, J. Chen, A novel extraction technique based on carbon nanotubes reinforced hollow fiber solid/liquid microextraction for the measurement of piroxicam and diclofenac combined with high performance liquid chromatography, Talanta, 100 (2012) 153-161.
[23] K.K. Ganic, L. Gracin, D. Komes, N. Curko, T. Lovric, Changes of the content of biogenic amines during winemaking of Sauvignon wines, Croat. J. Food Sci. Technol. 1 (2009) 21-27.
[24] C. Proestos, P. Loukatos and M. Komaitis, Determination of biogenic amines in wines by HPLC with precolumdansylation and fluorimetric detection, Food Chem. 106 (2008) 1218-1224.
[25]H. Wu, G. Li, S. Liu, Z. Ji, Q. Zhang, N. Hu, Y. Suo, J. You, Simultaneous Determination of Seven Biogenic Amines in Foodstuff Samples Using One-Step Fluorescence Labeling and Dispersive Liquid–Liquid Microextraction Followed by HPLC-FLD and Method Optimization Using Response Surface Methodology, Food Analytical Methods, 8 (2014) 685-695.
[26] M.L. Latorre-Moratalla, J. Bosch-Fustéa, T. Lavizzaria, S. Bover-Cidb, M.T. Veciana-Noguésa, M.C. Vidal-Caroua, Validation of an ultra high pressure liquid chromatographic method for the determination of biologically active amines in food, J. Chromatogr. A, 1216 (2009) 7715-7720.
[27] K. Nalazek-Rudnicka, A. Wasik, Development and validation of an LC-MS/MS method for the determination of biogenic amines in wines and beers, Monatsh Chem. 148 (2017) 1685.
[28]A. Gałuszka, Z.M. Migaszewski,P. Konieczka,J. Namieśnik, Analytical Eco-Scale for assessing the greenness of analytical procedures, Trends Anal. Chem. 37 (2012) 61-72.