UDC 547.536:631.42
DOI: 10.7562/SE2015.5.01.01
Original article
www.safety.ni.ac.rs

VESNA STANKOV JOVANOVIĆ[1]
VIOLETA MITIĆ[1]
JELENA CVETKOVIĆ[1]
MARIJA ILIĆ[1]
SLOBODAN ĆIRIĆ[1]
SNEŽANA NIKOLIĆ-MANDIĆ[2]
GORDANA STOJANOVIĆ[1]

[1]University of Niš,
Faculty of Science and Mathematics
[2]University of Belgrade,
Faculty of Chemistry

[1]*sjvesna@pmf.ni.ac.rs*
[1]*violetamitic@yahoo.com*
[1]*jelenacvetkovic7@gmail.com*
[1]*marija.fertico@gmail.com*
[1]*slobodanciric@yahoo.com*
[2]*snezananm@chem.bg.ac.rs*
[1]*gocast@pmf.ni.ac.rs*

AN INNOVATIVE APPROACH TO ENVIRONMENTAL SAMPLE PREPARATION FOR DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS BY GC-MS USING NEW SORBENTS IN QUECHERS TECHNIQUE

Abstract: *Polycyclic aromatic hydrocarbons (PAHs) have been considered as environmental pollutants of a great concern. Regardless of the method of quantitative analysis to be applyied, sample preparation is essential for the accurate determination of PAHs. Due to the extreme complexity of the soil samples, caused primarily by the presence of hundreds of compounds, many of them have similar physical and / or chemical properties as well as the analyzed compounds, and preparation of environmental samples for analysis is crucial for validity of the PAHs analysis. No matter which method will be applied for later analysis, sample preparation has to fulfill a number of conditions such as, adequate selectivity, efficiency, availability, easy to perform, short duration of the procedure. QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) method of sample preparation is a relatively new method that uses different sorbents and solvent systems. In this paper, the possibility of application of sorbents (diatomaceous earth, clinoptilolite and carbon black), which are not usually used in QuEChERS clean-up step of sample preparation, using 3 different solvent mixtures hexane / acetone (1:1, v / v) cyclohexane / acetone (1: 1, v / v) and acetonitrile / methanol (2:1, v / v) was investigated. Standard solutions of PAHs were treated with selected sorbents and solvent systems in all combinations, and then analyzed by GC-MS method. The overall accuracy of the method varied depending of compound and used sorbent/solvent system, while precision of the method was constantly good. Highest mean recovery for all PAHs (49.22%) was recorded for clinoptilolite, hexane / acetone combination. Diatomaceous earth showed lower recoveries in comparison with clinoptilolite, with all solvent systems, while recoveries for carbon black were almost zero. Among tested sorbents, clinoptilolite was identified as good starting sorbent which characteristics could be modified with aim to achieve higher accuracy, precision and selectivity of the method, and enable its new application in analytical chemistry.*

Key words: PAHs, QuEChERS, sorbents, GC-MC.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) because of its long degradation period in the environment and toxic effects, belong to the group of persistent organic pollutants (POPs), presenting one of the most widespread group of organic pollutants. PAHs are aromatic hydrocarbons with two or more fused benzene rings. They can be divided to light and heavy PAHs. Light PAHs are those who have up to 4 fused benzene rings, while heavy PAHs are those with more than 4 fused benzene rings. Heavy PAHs persist in the environment because of the low volatility, resistance to leaching and recalcitrant nature [1]. They consist mainly of carbon and hydrogen, but in this group there are also PAHs derivatives, in which carbon atoms are replaced by nitrogen, sulfur or oxygen, making it a heterocyclic aromatic compound. Although there are a number of different PAHs, European Commission (2005) defined 16 priority compounds, because of potential toxicity and frequency of occurrence (Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyren, Benzo[a]anthracene, Chrysene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Indeno[1,2,3-cd] pyrene, Dibenz[ah]anthracene, Benzo[ghi]perylene).

PAHs are produced in all processes of incomplete combustion of organic substances [2]. Sources of PAHs in the environment can be natural and anthropogenic. PAHs can originate from natural processes such as biomass burning, volcanic eruptions and diagenesis [3]. Significant amounts of PAHs in environment originate from anthropogenic activities, such as burning of fossil fuel, coal tar, wood, garbage, refuse, used lubricating oil and oil filters [4]. Due to higher volatility, amount of light PAHs will be higher in the air, but they will be more prone to degradation under the influence of the atmosphere. Similarly, these compounds are more soluble in water, so their concentration in water will be higher than heavy molecular PAHs. Heavy molecular compounds are found in water and atmosphere adsorbed into particulate matter. Large amounts of PAHs are adsorbed by soil organic matter and thus relatively unavailable for degradation process. However, certain amounts of light PAHs are lost over time due to evaporation, degradation and leaching. As molecular weight increases, PAH sorption on soil organic matter increases, due to higher lipophilicity.

Considering the increasing evidence of the ubiquitous presence of PAHs and health risk associated with their exposure, their analysis is of great importance. PAH analysis includes the procedure sampling and sample homogenization, extraction (in order to separate PAHs from matrix), clean up step (to remove impurities from obtained extract) and instrumental analysis (identification and quantification of these compounds). The extraction methods explored over the years include: Soxhlet extraction, sonication, liquid-liquid extraction, purge and trap, headspace, shaking, vortex, solid-phase extraction, supercritical fluid extraction, solid-phase micro extraction (SPME), stir-bar sorptive extraction (SBSE), miniaturized solid-phase extraction (SPE), liquid-phase micro extraction (LPME) and membrane-assisted solvent extraction techniques (MASE) [5]. Different solvents were used for extraction of PAHs like methylene chloride/acetone (1:1 v/v) [6], ethyl acetate/hexane (1:1 v/v), acetone/hexane (1:1 v/v) [7], n-butanol [8], methylene chloride/acetone (1:1), [9] but the preferred solvent system which gives the best recovery is methylene chloride [7]. The international standardization organization [10] recommended solvent extraction with acetone for soils with low contamination level, while Soxhlet extraction with toluene should be used in highly contaminated soils. An extraction technique is efficient if produces good results, within short time and not demand complicated operations. Clean up step include solid phase extraction (SPE) on cartridges with alumina, florisil, silica, C18, PS-DVB [11,12] or column chromatography with silica gel [13]. Analytical methods mostly used for PAH determination are HPLC with fluorescence detection [14,15] and GC –MS [16]. In 2003, Anastassiades et al. [17] proposed QuEChERS method, which consists of extraction with organic solvent miscible with water, in presence of salts or buffering agents and a clean-up step by dispersive solid-phase extraction (QuEChERS). This procedure offers much simpler, faster and low cost clean up of the samples than other techniques used, so there is interest in modification and development of QuEChERS technique.

The aim of this paper was to evaluate different sorbents and solvents which weren´t used in QuEChERS for sample clean up in PAH analysis in environmental samples, by assessing convenience of three different sorbents: clynoptilolite, diatomaceous earth and carbon black using three solvent mixtures (acetonitrile/methanol, hexane/acetone and cyclohexane/acetone). The usefulness of each sorbent and solvent mixture was verified based on recovery ratio of each compound. To the best of author's knowledge, this paper is very first one dealing with aplication of the new sorbents for environmental samples clean up QuEChERS procedure.

EXPERIMENTAL

Methods and materials

Chemical reagents

Acetonitrile (MeCN), hexane, cyclohexane, methanol HPLC–grade and $MgSO_4$ were purchased from Sigma Aldrich. PAH Kit 601–N containing acenaphthylene, anthracene, benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[g,h,i]perylene, benzo[k]fluoranthene, chrysene, dibenzo[a,h]anthracene, fluoranthene, fluorene, napthalene, phenanthrene, pyrene and internal standards (chrysene d_{10} and acenaphthene d_{10}) purchased from Supelco, Bellefonte, Pennsylvania. Working standard solution at concentration 17.95 µg/ml for each PAH was prepared in different solvent mixtures: hexane/acetone (1:1, v/v), cyclohexane/acetone (1:1, v/v) and acetonitrile/methanol (2:1, v/v).

In this study, a natural zeolite, from the mine Zlatokop (Vranjska banja), which contains about 92 % clinoptilolite phase, 3.4 % feldspar plagioclase and 4.6 % quartz was used as the starting material. Before modification, the zeolite samples (grain size 0.063–0.1 mm) were washed several times with distilled water to remove impurities and then dried at 60 °C.

Inert diatomaceous earth sorbent of a high purity, under commercial name Hydromatrix, was purchased from Varian (Harbor City, CA).

Carbon black with particle size of 100-1000 nm in diameter and >97% of carbon, was purchased from Centrohem, Belgrade.

Instrumentation

The Agilent 7000 Series Triple Quadrupole MS is a standalone triple quadrupole mass spectrometer for use with the Agilent 7890A GC system. The injector was PAL sampler, with injection volume of 2.5 µl in splitless mode. Chromatographic separations were conducted using a HP-5MS (5% Phenyl Methyl Siloxane) column (30 m x 250 µm x 0.25 µm). The GC oven was operated with the following temperature program: 75 °C for 3 minutes then 6 °C/minute to 300 °C for 10 minutes. The total run time was 50.5 minutes. Analyses were conducted in the selected ion monitoring (SIM) mode based on the use of one quantitative ions. Analyzed compounds were identified according to their qualitative ions and retention times (Table 1).

Table 1. *Retention time, quantification ion, calibation slope and correlation coefficient of the analyzed compounds*

PAH name	Retention time (min)	Quantification ion	Calibration slope	Correlation coefficient
Naphthalene	12.087	128.0	2.428	0.98
Acenaphthene	18.759	152.0	1.612	0.99
Fluorene	20.688	165.0	1.841	0.99
Phenanthrene	24.302	178.0	1.427	0.99
Anthracene	24.478	178.0	0.869	0.99
Fluoranthene	28.878	202.0	0.715	0.97
Pyrene	29.696	202.0	6.389	0.95
Benzo[a]anthracene	34.513	228.0	3.912	0.99
Chrysene	34.360	228.0	2.572	0.99
Benzo[b]fluoranthene	38.258	252.0	1.437	0.99
Benzo[k]fluoranthene	38.347	252.0	1.658	0.99
Benzo[a]pyrene	32.289	252.0	1.087	0.95
Dibenz[ah]anthracene	43.161	278.0	0.466	0.92
Benzo[ghi]perylene	43.964	276.0	0.536	0.91

Sample preparation

For construction of calibration curve, standard PAHs solutions in hexane, prepared by dilution of the PAH stock standard solution adjusting the concentrations to 0.38, 1.92, 3.85, 9.62, 19.23, 24.04, 28.85 and 38.46 µg/ml were used. The reagent blank pure hexane and corresponding mixtures of solutions were used. One milliliter of PAHs mixture standard solution, used as a model extract of environmental sample and in corresponding concentration as the standard solutions, was transferred into QuEChERS tube containing 50 mg of sorbent. Mixture was shaken for 1 minute and centrifuged at 8000 rpm for 10 minutes. Supernatant volume of 0.6 ml was transferred into GC vial, and 0.2 ml of internal standard solution was added. Standard solutions and solutions treated by above described procedure were then analyzed by GC-MS. The obtained results were presented as recoveries (ratio of concentration after QuEChERS treatment and corresponding standard solution concentration, in percents).

RESULTS AND DISCUSSION

Sample preparation step is the most difficult and time consuming task, including analyte extraction and extract purification. One of the most used techniques in clean up step is solid phase extraction (SPE), as it is fast, efficient and offering a large variety of purification sorbents and devices with possibility of automated on-line sample treatment. QuEChERS has advantage over classic SPE, because of less solvent and sorbent consumption but above all, simple and cheap technical demands and possibility of changing experimental conditions. However, sometimes commercially available sorbents do not have enough efficient capacity or selectivity to adequately clean up complex samples. Most of sorbents works on adsorption principle, thus some errors can appear due to analyte remnant on the sorbent surface, regardless it is a consequence of strong binding to the surface or usage of solvents with deficiencies in rinsing analyte from the surface.

Accuracy studies (presented as recovery) were conducted after adding PAH standard mixture to QuEChERS tube with the different sorbents and using various combinations of solvent mixtures. Acceptable recoveries within 50-120 % [18] should be provided in order to obtain accurate results. The results of recovery studies of 14 analyzed PAHs treated with three different sorbents and solvents are represented in Figures 1, 2 and 3.

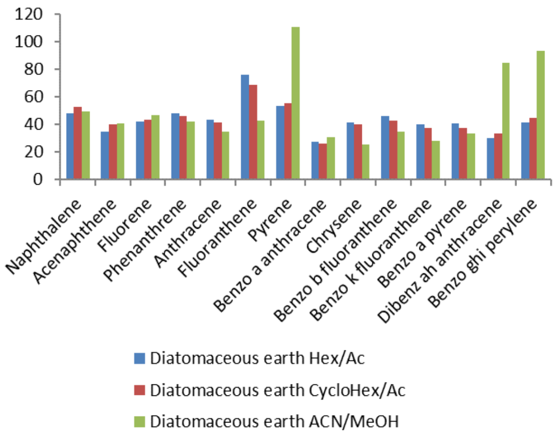

Figure 1. *Accuracy of PAHs determination using diatomaceous earth as the sorbent*

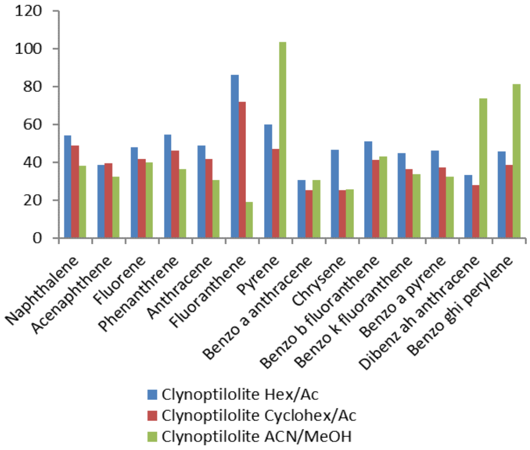

Figure 2. *Accuracy of PAHs determination using clinoptilolite as the sorbent*

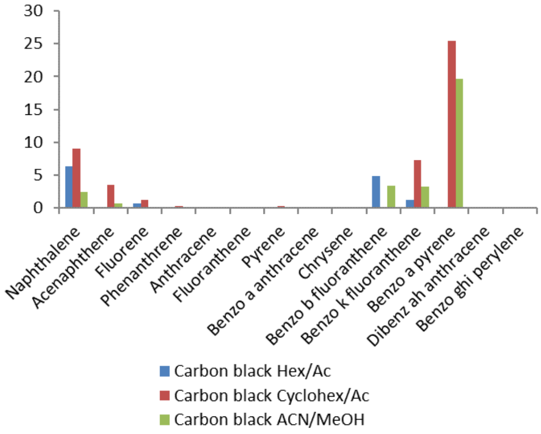

Figure 3. *Accuracy of PAHs determination using carbon black as the sorbent*

Diatomaceous earth typically consists of 87–91% silicon dioxide (SiO_2), with significant quantities of alumina (Al_2O_3) and ferric oxide (Fe_2O_3) [19]. Hexane/acetone mixture (1:1, v/v) is an effective extraction solvent for PAHs [20,21]. Mean recovery of PAHs, using diatomaceous earth and hexane/acetone mixture was 43.70%, with highest value for fluoranthene (75.97%), and lowest for benzo[a]anthracene (27.31 %) (Figure 1). Most of analyzed compounds gave recovery between 40% and 50%. It can be seen that recovery values, using this sorbent/solvent mixture were not satisfactory. Diatomaceous earth is a highly absorbent material due to its macroporous structure [22]. Other solvent combination used in this study was cyclohexane/acetone. Cyclohexane is used in PAHs extraction from highly polluted soils [23]. However, non-polar solvents were not recommended for lower PAHs, since they are not good soluble in nonpolar solvents. Combination of diatomaceous earth and cyclohexane/acetone gave mean recovery of 43.52%, with maximum recovery for fluoranthene (68.82%) (Figure 1). As in case with hexane/acetone, this sorbent gave poor average recoveries for analyzed compounds. Acetonitrile was used in original QuEChERS method proposed by Anastassiades et al. (2003) [17], used typically in QuEChERS method for pesticide extraction. According to Sadowska-Rociek et al. (2013) [24], acetonitrile is good solvent for PAH extraction, since it does not extract a lot of matrix. Using acetonitrile/methanol solvent mixture recovery values we got were between 25.50% and 111.06%, with mean recovery higher than other two combinations used (49.85%) (Figure 1). However, higher mean recovery is due to high recovery for fluoranthene (111.06%), benzo[ghi]perylene (93.69%) and dibenz[ah]anthracene (84.91%), while other compounds gave significantly lower recoveries. Comparing recovery values for all three solvent combinations used with diatomaceous earth we noticed that fluoranthene and pyrene gave higher recoveries than other compounds from this study, so it can be used in the analysis of these two compounds. Meesuk et al. (2009) [25] investigated benzo[a]pyrene adsorption on diatomaceous earth, and concluded that 73.92% of this compound has been adsorbed by diatomite. As far as we know, this sorbent hasn't been used in QuEChERS approach in PAH study. Arias et al. (2014) [26] evaluated various sorbents in QuEChERS clean up step, including diatomaceous earth, for pesticide analysis. Recovery values were between 60 and 120% for 15 out of 17 pesticides analyzed. Another group of authors suggested that diatomaceous earth could be used in pesticide analysis [27]. Since our results gave high recovery values for some compounds, further researches will be oriented in modification of diatomaceous earth in order to obtain higher recovery, since it has the advantage of its low cost and wide surface area [28].

Clinoptilolite is a natural, non-toxic zeolite (crystalline hydrated aluminosilicate) that has monoclinic crystal structure symmetry and strong adsorptive and ion exchange capacity [29]. It's general chemical formula is $Na_{0.1}K_{8.57}Ba_{0.04}(Al_{9.31}Si_{26.83}O_{72})\cdot 19.56H_2O$ [30], with capacity of Na^+, K^+ and Ba^+ ion-exchange. In case of clinoptilolite we used, these ions were naturally exchanged dominantly with Ca^{2+}. Employing hexane/acetone mixture, in combination with clinoptilolite, we have obtained recovery values between 30.61 and 86.44%, with highest recovery for fluoranthene (Figure 2). The combination of clinoptilolite with cyclohexane/acetone gave the values of the recovery in the range of 25.21% for chrysene to 71.99% for fluoranthene (Figure 2). As well as using hexane/acetone mixture, highest recovery is obtained for fluoranthene, using cyclohexane/acetone mixture. According to Lemić et al. (2007) [31], the adsorption of PAHs on unmodified zeolite was lower than 50%, except for benz[a]anthracene, where 75% of this compound remained on clinoptilolite, which is in agreement with our results. Using acetonitrile/methanol solvent mixture recovery values we got were between 18.98% (fluoranthene) and 103.40% (pyrene), with mean recovery 44.33% (Figure 2). Pyrene has been used as a model compound to study biodegradation of heavy PAHs, since it is structurally similar to several carcinogenic PAHs [32], so its analysis is of great importance. Clinoptilolite can be used in QuEChERS sample preparation technique in pyrene analysis, since highest recovery for this compound is obtained using this sorbent and acetonitrile/methanol solvent mixture. Zeolites are commonly used for removing undesirable heavy metal ions from industrial effluent waters [33]. Xie et al. (2012) [34] examined adsorption capability of modified zeolite for the removal of ionizable phenolic compounds and non-ionizable organic compounds, including naphthalene. As far as we know, clinoptilolite hasn't been used in PAH analysis. Since zeolites are natural occurring mineral and have lower price, they could be used in clean up step for PAH analysis. Some modifications of clinoptilolite could lead to higher recovery for analyzed compound, which could make this sorbent leading in extract clean up for PAH analysis.

Carbon black is a material produced by the incomplete combustion of heavy petroleum products which can be used in QuEChERS clean up step in order to remove pigments, which can be main interference in PAH analysis. Recoveries within 0-6.36% for 14 analyzed compounds were provided by using carbon black as sorbent an hexane/acetone as solvent mixture (Figure 3). Benzo[a]anthracene, chrysene, benzo[a]pyrene, dibenz[ah]anthracene and benzo[ghi]perylene gave 0% recovery, indicating their concentration were reduced more effectively than other compounds. Other two solvent mixtures also gave poor mean recovery values for carbon black as sorbent in clean up step (3.38% and 2.12%, for cyclohexane/acetone and acetonitrile/methanol mixture, respectively) (Figure 3). Nine of 14 analyzed compounds using cyclohexane/acetone and carbon black gave recovery lower than 1%, whereas 10 compounds gave less than 1% recovery using same sorbent and acetonitrile/methanol mixture. This indicates that carbon black cannot be used as sorbent in clean up step for PAH analysis. However, this indicates that carbon black could be used in PAH removal from environment. Low recovery values using carbon black were also obtained using other two solvent mixtures used in this study. Organic pollutants (PAH) strongly sorb to carbonaceous sorbents such as black carbon, unburned coal and kerogen [35,36]. Adsorption of PAHs on carbon black minimizes accumulation in plants and animals, lowering the risk for humans. Presence of black carbon in sediments will drastically limit the solubility and bioavailability of PAHs [37,38]. Black carbon has been found to have a large aromatic fraction and a surface area close to 100 $m^2\ g^{-1}$ [36], which can explain such a strong binding of PAHs to carbon black surface.

CONCLUSION

New sorbents were tested as alternative in clean up step in QuEChERS sample preparation technique. Diatomaceous earth, clinoptilolite and carbon black were tested with three different solvent mixtures, and results indicates that clinoptilolite and diatomaceous earth have promising characteristics in environmental sample clean-up for GC-MS analysis of PAHs, providing solid foundation for further investigations, including sorbent modifications, in order to obtain higher accuracy. Carbon black in the present form could not be used as sorbent in clean up step, because most of the analyzed of PAHs remained bound on its surface. However, this fact suggests that carbon black could be used as material in PAHs removal from the environment.

REFERENCES

[1] K. C. Jones, R. E. Alcock, D. L. Johnson, K. T. Semple, P. J. Woolgar: “Organic chemicals in contaminated land: analysis, significance and research priorities”, Land Contamination and Reclamation, Vol. 4(3), 1996, 189-198.

[2] S.R. Wild, K.C. Jones: “Polynuclear aromatic hydrocarbons in the United Kingdom environment: a preliminary source inventory and budget”, Environm. Poll. Vol. 88, 1995, p. 91.

[3] Z. Wang, J. Chen, P. Yang, X. Qiao, F. Tian: “Polycyclic aromatic hydrocarbons in Dalian soils: distribution and toxicity assessment”, Journal of Environmental Monitoring Vol. 9, 2007, pp. 199-204.

[4] C.P. Kaushik, A.K. Haritash: “Polycyclic aromatic hydrocarbons (PAHs) and environmental health”, Our Earth, Vol. 3, 2006, pp. 1–7.

[5] B. Tang, U. Isacsson: “Analysis of mono- and polycyclic aromatic hydrocarbons using solid-phase micro extraction”, State of the Art, Energy Fuels, Vol. 22, 2008, pp. 1425 -1438.

[6] O. N. Charles, K. Gauthreaux, J. Sneddon, J. N. Beck: “Determination of semivolatile organic compounds by gas chromatography-mass spectrometry in reclaimed marsh sediments in southwest Louisiana”, Microchem. J., Vol. 60, 1998, pp. 167-174.

[7] K. Juhani, J. Kettunen, K. Hartonen, R. Marja-Lissa: “Pressurised hot water extraction of nAlkanes and PAHs in soil and sediment from the oil shale industry district in Estonia”, J. Soils Sediments, 2004, pp. 1-8.

[8] L. Hans-Holger, M. Alexander: “Butanol extraction to predict bioavailability of PAHs in soil”, Chemosphere., Vol. 46(7), 2002, pp. 1011-1017.

[9] T. F. Guerin: “The extraction of aged polylcylic aromatic hydrocarbon(PAHS) residues from a clay soil using sonication and a Soxhlet procedure: A comparitive study”, J.Environ.Monit., Vol. 1, 1999, pp. 63-67.

[10] ISO 13877, “Soil quality – determination of polynuclear aromatic hydrocarbons, PAH - high performance liquid chromatographic (HPLC) Method”, 1994.

[11] S. A. V. Tfouni, C. S. Serrate, F. M. Leme, M. C. R. Camargo, CRA Teles, KMVAB Cipolli, RPZ Furlani: “Polycyclic aromatic hydrocarbons in coffee brew: influence of roasting and brewing procedures in two Coffea cultivars”, Food Sci Technol-Leb Vol. 50, 2013 pp. 526–530.

[12] J. K. Houessou, C. Benac, C. Delteil, R. V. Camel: “Determination of polycyclic aromatic hydrocarbons in coffee brews using solid-phase extraction”, J Agric Food Chem, Vol. 53, 2005, pp. 871-879.

[13] EPA METHOD 3630C SILICA GEL CLEANUP 1996.

[14] A. Barranco, R.M. Alonso-Salces, I. Crespo, L.A. Burreta, B. Gallo, F. Vicente, M. Sarobe: “Polycyclic aromatic hydrocarbon content in commercial Spanish fatty foods”, J. Food Prot., Vol. 67, 2004, pp.2786-2971.

[15] A. Dissanayake, T.S. Galloway: “Marine Environ. Res.”, Vol. 58, 2004, pp. 281.

[16] W. Jira: “A GC-MC methods for the determination of carcinogenic polycyclic aromatic hydrocarbons (PAH) in smoked meat products and liquid smokes”, Eur. Food Res. Technol., Vol. 218,2004 pp. 208-212.

[17] M. Anastassiades, S.J. Lehotay, D. Štajnbaher, F.J. Schenck: “Fast and easy multiresidue method employing acetonitrile extraction/partitioning and dispersive solid-phase extraction for the determination of pesticide residues in produce”, JAOAC Int. Vol. 86(2), 2003, p. 412-31.

[18] COMMISSION REGULATION (EU) No 836/2011 of 19 August 2011 Official Journal of the European Union

[19] K.R. Engh, in: (Ed.), Kirk–Othmer “Encyclopedia of Chemical Technology”, vol. 8, M. Howe-Grant, fourth ed., Wiley, 1993, New York, p. 108.

[20] M. T. Pena, M. C. Casais, M. C. Mejuto, R. Cela: “Optimization of the matrix solid-phase dispersion sample preparation procedure for analysis of polycyclic aromatic hydrocarbons in soils: comparison with microwave-assisted extraction”, Journal of Chromatography A, vol. 1165, no. 1–2,2007, pp. 32–38.

[21] Y. Y. Shu and T. L. Lai: “Effect of moisture on the extraction efficiency of polycyclic aromatic hydrocarbons from soils under atmospheric pressure by focused microwave-assisted extraction,”Journal of Chromatography A, vol. 927, no. 1–2, 2001, pp.131-141.

[22] H. Elden, G. Morsy, M. Bakr: “Diatomite: its characterization, modifications and applications”, Asian J. of Materials Sci., 2 (3), 2010, pp. 121-136.

[23] J. D. Berset, M. Ejem, R. Holzer, P. Lischer: “Comparison of different drying, extraction and detection techniques for the determination of priority polycyclic aromatic hydrocarbons in background contaminated soil samples”, Analytica Chimica Acta, vol. 383, no. 3, 1999, pp. 263–275.

[24] A. Sadowska-Rociek, M. Surma, E. Cieślik: “Comparison of different modifications on QuEChERS sample preparation method for PAHs determination in black, green, red and white tea”, Environmental Science and Pollution Research, 21(2): 2013, 1326–38.

[25] L. Messuk, P. Watthanakul, C. Attha-Aroon: “The use of low grade diatomite to recover repoeatingly used palm oil, Chemical, Biological and Environmental Engineering - Proceedings of the International Conference on Cbee 2009 edited by Li Kai, 2009, Singapore, International Conference on Chemical, Biological and Environmental Engineering

[26] J. L. d. Oliveira Arias, C. Rombaldi, S. S. Caldas, E. G. Primel: “Alternative sorbents for the dispersive solid-phase extraction step in quick, easy, cheap, effective, rugged and safe method for extraction of pesticides from rice paddy soils with determination by liquid chromatography tandem mass spectrometry”, Journal of Chromatography A, Vol. 1360, 2014, pp. 66–75.

[27] A. Di Muccio, P. Fidente, D. Attard Barbini, , R. Dommarco, S. Seccia, P. Morrica: (2006). “Application of Solid-Phase Extraction and Liquid Chromatography–Mass Spectrometry to the Determination of Neonicotinoid Pesticide Residues in Fruit and Vegetables”, Journal of Chromatography A, Vol.1108, No.1, 2006, pp. 1-6.

[28] L.d.C. Cabrera, M.L. Martins, E.G. Primel, O.D. Prestes, M.B. Adaime, R. Zanella: “Extrac¸ão em Fase Sólida Dispersiva na determinac¸ ão de resíduos e contaminantes em alimentos”, Sci. Chromatogr. Vol. 4, 2012, pp. 227–240.

[29] D.W.J. Breck: “Chem. Educ”, Vol. 41, 1964, 678.

[30] E. Galli, G. Gottardi, H. Mayer, A. Preisinger, E. Passaglia: “Acta Crystallogr. Sect. B”, Vol. 39, 1983, 189.

[31] J. Lemić, M. Tomašević-Čanović, M. Adamović, D. Kovačević, S. Milićević: “Competitive adsorption of polycyclic aromatic hydrocarbons on organo-zeolites”, Microporous and Mesoporous Materials, Vol. 105 (3), 2007, pp. 317-23.

[32] R. A. Kanaly, S. Harayama: “Biodegradation of high-molecular-weight polycyclic aromatic hydrocarbons by bacteria. J. Bacteriol”, Vol. 182, 2000, pp. 2059-2067.

[33] E. Erdem , N. Karapinar , R. Donat: “The removal of heavy metal cations by natural zeolites”, Journal of Colloid and Interface Science, Vol. 280, 2004, pp.309-314.

[34] J. Xie, W. Meng, D. Wu, Z. Zhang, H. Kong: “Removal of organic pollutants by surfactant modified zeolite: Comparison between ionizable phenolic compounds and non-ionizable organic compounds”, Journal of Hazardous Materials, Vol. 231-232, 2012, pp. 57–63.

[35] M.T.O. Jonker, A.A. Koelmans: “Sorption of polycyclic aromatic hydrocarbons and polychlorinated biphenyls to soot and soot-like materials in the aqueous environment mechanistic considerations”, Environ. Sci. Technol. Vol. 36, 2002, pp. 3725– 3734.

[36] G. Cornelissen, G.D. Breedveld, S. Kalaitzidis, K. Christanis, A. Kibsgaard, A.M.P. Oen: “Strong sorption of native pahs to pyrogenic and unburned carbonaceous geosorbents in sediments”, Environ. Sci. Technol. Vol. 40, 2006, pp. 1197-1203.

[37] O. Gustafsson, P.M. Gschwend: 1997. “Soot as a strong partition medium for polycyclic aromatic hydrocarbons in aquatic systems”, R.P. Eganhouse (ed.) Molecular markers in environmental geochemistry. American Chemical Society, Washington, DC, 1997, pp. 365–380.

[38] A. Accardi-Dey, P.M. Gschwend: 2002. “Assessing the combined roles of natural organic matter and black carbon as sorbents in sediments”, Environ. Sci. Technol. Vol. 36, 2002, pp. 21–29

BIOGRAPHY

Vesna Stankov Jovanović was born in Pirot 11.10.1968 and acquired following degrees: Graduated Chemist (1992) and Master of Chemistry (1999) Department of Chemistry, University of Niš, PhD in Chemistry (2007) at Faculty of Chemistry, University of Belgrade and Postdoctoral studies in Mass spectrometry (6 months) at University Pierre and Maria Curie, Paris (France) and PhD of biological sciences 2013).The areas of her research are analytical and bioanalytical chemistry, environmental chemistry, and phytochemistry.

She has participated in several international and national projects, both scientific and institutional capacity building.

Her present position is associate professor at Department of Chemistry, Faculty of Science and Mathematics, University of Niš. She is the head of the Section for Chemistry and Biology of the Center of Serbian Academy of Science and University of Niš.

INOVATIVNI PRISTUP PRIPREMI UZORAKA IZ ŽIVOTNE SREDINE ZA ODREĐIVANJE POLICIKLIČNIH AROMATIČNIH UGLJOVODONIKA METODOM GC-MS KORIŠĆENJEM NOVIH SORBENASA U QUECHERS TEHNICI

Vesna Stankov Jovanović, Violeta Mitić, Jelena Cvetković, Marija Ilić, Slobodan Ćirić,
Snežana Nikolić-Mandić, Gordana Stojanović

Rezime: *Policiklični aromatični ugljovodonici (PAH) se smatraju zagađivačima koji izazivaju veliku zabrinutost za životnu sredinu. Bez obzira na metodu kvantitativne analize, koja će biti primenjena, priprema uzorka je od suštinskog značaja za tačno određivanje PAHova. Zbog izuzetne složenosti uzoraka zemljišta, uslovljenim pre svega prisustvom više stotina jedinjenja, od kojih mnoga imaju slične fizičke i / ili hemijske karakteristike, kao i analizirana jedinjenja, priprema uzoraka iz životne sredine za analizu je od ključnog značaja za validnost analize PAH-ova. Svejedno koja će se metoda kasnije primenjivati za analizu, priprema uzorka mora da ispuni niz uslova kao što su adekvatna selektivnosti, efikasnost, dostupnost, laka izvodljivost, kratko trajanja postupka. QuEChERS (Brzo -quick,* ***Qu****, Lako-easy,* ***E****, Jeftino-cheap,* ***Ch****, Efikasno-effective,* ***E****, Robusno-rugged,* ***R*** *i Sigurno-safe,* ***S****) način pripreme uzoraka je relativno nova metoda koja koristi različite sorbense i kombinacije rastvarača. U ovom radu je istražena mogućnost primene sorbenasa (dijatomejska zemlja, klinoptilolit i aktivni ugalj), koji se obično ne koriste u koraku prečišćavanja kod pripreme uzoraka QuEChERS tehnikom, primenom 3 različite smeše rastvarača heksan / aceton (1: 1, v / v) cikloheksan / aceton (1: 1, v / v) i acetonitril / metanol (2: 1, v / v). Standardni rastvori PAHova su tretirani određenim sorbensima i sistemima rastvarača u svim kombinacijama, a zatim analizirani primenom GC-MS metode. Ukupna tačnost metode varira u zavisnosti od jedinjenja i primenjenog sorbens / rastvarač sistema, dok je preciznost metode bila konstantno dobra. Najveća srednja vrednost za rikaveri za sve PAHove (49,22%) je registrovana za klinoptiolit, heksan / aceton kombinaciju. Dijatomejska zemlja je pokazala niže rikaveri vrednosti u odnosu na klinoptiolit, sa svim sistemima rastvarača, a rikaveri vrednosti za aktivni ugalj su bile gotovo nula. Među testiranim sorbensima, klinoptiolit je identifikovan kao dobar polazni sorbens čije karakteristike mogu biti modifikovane, sa ciljem da se postigne veća tačnost, preciznost i selektivnost metode, koja će omogućiti njegovu novu primenu u analitičkoj hemiji.*

Ključne reči: *PAH, QuEChERS, sorbensi, GC-MS.*