Quantification of chrysene and benzo(a)pyrene in surface water samples by fluorescence measurement

Quantificação de cristão e benzo (a) pireno em amostras de água de superfície por medição de fluorescência

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Jaldair Araújo e Nógrega
Doutor em Física pela Universidade Federal de São Carlos
Instituição: Universidade Federal da Grande Dourados
Endereço: Rod. Dourados-Itahum, Km 12 - Cidade Universitaria, Dourados - MS, 79804-970
E-mail: jaldair@gmail.com

Lucilene dos Santos Rosa
Doutoranda do programa de pós-graduação em ciência e tecnologia ambiental pela Universidade Federal da Grandes Dourados
Instituição: Universidade Federal da Grande Dourados
Endereço: Rod. Dourados-Itahum, Km 12 - Cidade Universitaria, Dourados - MS, 79804-970
E-mail: lenesrosa@yahoo.com.br

Higor de Nar Rigon
Doutorando do programa de pós-graduação em ciência e tecnologia ambiental pela Universidade Federal da Grandes Dourados
Instituição: Universidade Federal da Grande Dourados
Endereço: Rod. Dourados-Itahum, Km 12 - Cidade Universitaria, Dourados - MS, 79804-970
E-mail: higor.rigon@gmail.com

Rosemeire Aparecida Nunes de Oliveira
Doutorando do programa de pós-graduação em ciência e tecnologia ambiental pela Universidade Federal da Grandes Dourados
Instituição: Universidade Federal da Grande Dourados
Endereço: Rod. Dourados-Itahum, Km 12 - Cidade Universitaria, Dourados - MS, 79804-970
E-mail: rosimeire.nunes3@gmail.com

Carlos Fabiano Capato
Doutorando em Biologia Celular e Molecular pela Universidade de São Paulo
Instituição: Universidade de São Paulo
Endereço: Avenida bandeirantes, 3900, Monte Alegre. Riberão Preto -SP
E-mail: capato.fab@gmail.com

Evaristo Alexandre Falcão
Doutor em Física pela Universidade estadual de Maringá
Instituição: Universidade Federal da Grande Dourados
Endereço: Rod. Dourados-Itahum, Km 12 - Cidade Universitaria, Dourados - MS, 79804-970
E-mail: evaristo.falcao766@academico.ufgd.edu.br
ABSTRACT
Polycyclic aromatic hydrocarbons, or PAHs, are compounds of organic nature derived from burning other organic compounds. They are common in nature, but in high concentrations are a sign of pollution and have harmful effects on human health. Therefore, techniques to identify and quantify these compounds in environmental samples, especially water samples, become essential. In this paper we apply the technique of synchronous fluorescence spectroscopy to identify and quantify types of PAH in water samples, showing the simplicity of execution and low cost of the technique over other ones conventionally used and reported. For this study, we choose two PAH which seem to be the most common in the environment and are associated with several diseases, including cancer. Analytical curves were constructed, and analytical parameters for their determination collected; limits of detection and quantification were 2.0 and 6.7 ng.mL⁻¹ for chrysene and 1.7 and 5.7 ng.mL⁻¹ for benzo[a]pyrene, respectively. To study the validity of the proposed method, water samples collected from a stream in the city of Dourados (MS, Brazil) were studied. At each of the collection points, significant concentrations of chrysene and benzo[a]pyrene was detected, mostly at levels above those permitted by international regulatory organizations.

Keywords: Polycyclic Aromatic Hydrocarbons; Synchronous Fluorescence Spectroscopy; Environmental Monitoring; Pollution; Water; Chrysene and benzo[a]pyrene.

RESUMO
Os hidrocarbonetos aromáticos policíclicos, ou PAHs, são compostos de natureza orgânica derivados da queima de outros compostos orgânicos. Eles são comuns na natureza, mas em altas concentrações são um sinal de poluição e têm efeitos prejudiciais à saúde humana. Portanto, técnicas para identificar e quantificar esses compostos em amostras ambientais, especialmente amostras de água, tornam-se essenciais. Neste artigo, aplicamos a técnica de espectroscopia de fluorescência síncrona para identificar e quantificar tipos de HAP em amostras de água, mostrando a simplicidade da execução e o baixo custo da técnica em relação a outras convencionalmente usadas e relatadas. Para este estudo, escolhemos dois HAP que parecem ser os mais comuns no ambiente e estão associados a várias doenças, incluindo câncer. As curvas analíticas foram construídas e os parâmetros analíticos para sua determinação foram coletados; os limites de detecção e quantificação foram de 2,0 e 6,7 ng.mL⁻¹ para o criseno e 1,7 e 5,7 ng.mL⁻¹ para o benzo [a] pireno, respectivamente. Para estudar a validade do método proposto, foram estudadas amostras de água coletadas em um riacho na cidade de Dourados (MS, Brasil). Em cada um dos pontos de coleta, foram detectadas concentrações significativas de criseno e benzo [a] pireno, principalmente em níveis acima dos permitidos pelas organizações reguladoras internacionais.

Palavras-chave: Hidrocarbonetos aromáticos policíclicos; Espectroscopia de fluorescência síncrona; Monitoramento ambiental; Poluição; Água; Criseno e benzo [a] pireno.
1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds formed by two or more conjugated aromatic rings (Nuria; Vera; Martinez-Mecnhon; Navarro. G; Lucas; Navarro.S,2012; Shemer; Linden,2007). Depending on the concentration, these compounds have toxic properties, thus they represent a threat to the health of living beings (Shemer;Linden 2007). In studies reported, it was noted that rates of lung cancer and cardiovascular diseases in humans have increased since exposure to high levels of PAHs. This occurrence is related to the fact PAHs possess toxic properties that make them cancerous and mutagenic to humans with daily life exposure to these chemicals (Nuria; Vera; Martinez-Mecnhon; Navarro.G; Lucas; Navarro.S, 2012; Xu; Cook; Ilacqua; Kan; Talbottt; Kearney,2010; Xu; Hu; Kearney; Kan; Sheps,2013;Kamal;Qamar; Gulfraz; Anwar; Malik,2015).

Human contact with these compounds occurs by air inhalation, food and water intake and by direct contact of the skin with soil and dust (USEPA,2014; Wogan; Hecht; Felton; Conney; Loeb, 2004) and they have great environmental mobility by air, soil and by water. Once PAHs are found mainly in bodies of water (Kim; Jahan; Kabir; Brown,2013), they are a large problem for human. Their hydrophobic character allows aggregation with surrounding particles and accumulation in the environment (Jajoo; Mekala; Tomar; Grieo; Tikkanen; Aro, 2014).

There are environmental agency regulations to protect human health concerning the concentration of PHAs in drinking water by establishing the maximum content of then (USEPA, 2014). The existence of regulations comes up against the need to monitor and control pollutants in the environment, and the development of techniques and measurement protocols for the identification and quantification of PAHs has become a goal of several studies. Among the techniques described to characterize, determine and monitor the compounds, gas and liquid chromatography and fluorescence spectroscopy stand out (Brown,A.S; Brown, R.J.C, 2012).

This study aims to show the capabilities of the synchronous fluorescence spectroscopy (SFS) technique in the determination of two PAHs, chrysene and benzo[a]pyrene in surface water samples from the Rego D’Água, Água Boa and Paragem stream in the region of Dourados, Mato Grosso do Sul (MS), Brazil. These two PHAs were choose since then are abundant in this area and are associated to several diseases in some reports (Xu; CooK; Ilacqua; Kan; Talbottt; Kearny, 2010; Xu; Hu; Kearney; Kan; Sheps,2013; Kamal; Qamar; Gulfraz; Anwar; Malik, 2015). The collection points covered urban and rural regions of the stream, whose water is used for waste disposal, for bathing and for agricultural activities.

2 MATERIALS AND METHODS

2.1 CHEMICALS
For the calibration curve, 1 mL of a mixture of PAHs diluted in acetone (EPA PAH Mix-B-Aldrich), composed of pyrene (Pyr), benzo[a]pyrene (BaP), anthracene, benzo[k]fluoranthene, dibenzo[a,h]anthracene, phenanthracene, chrysene, acenaphthylene, benzo[b]fluoranthene, benzo[g,h,i]perylene, fluorene, and infeno[1,2,3-c,d]pyrene were used with methanol 99.9% UV/HPLC VTEC® Spectroscopic (Sigma-Aldrich). Hexane 99.5% UV/HPLC (mixture of isomers) Sigma Aldrich® Spectroscopy and Milli-Q ultrapure water were also used to extract the PHAs from the samples water.

2.2 FLUORESCENCE MEASUREMENT

Fluorescence spectroscopic measurements were performed on a Cary Eclipse Spectrofluorometer (Varian) coupled to a photomultiplier tube (R928), in synchronous mode. The measurement interval was from 200 to 600 nm with a wavelength interval (Δλ) of 40 nm. The excitation and emission slots were calibrated to 2.5 nm and 5 nm, respectively (Patra; Mishra, 2001).

2.3 SAMPLE COLLECTION AND STORAGE

The study area is a stream, located in Dourados, in Brazil’s Midwestern Region, located at the south of Mato Grosso do Sul state. The population of the city is 210,218 and has an estimated population density of 51.443 inhabitants per km² (IBGE, 2013).

The stream is characterized as extremely polluted by domestic waste water, since most of its route is in the middle of the city. Its course continues to the rural area until its waters flow into the Dourados River, which is the main source of drinking water for the population (Gomes; Silva, 2012; Silva, 2010). The stream’s route passes through several neighborhoods like Vila São Pedro, Jardim Água Boa, BNH 4º Plano, Vila Cachoeirinha and Parque dos Coqueiros. These neighborhoods, among others in the county, are considered densely populated.

Water samples were collected at specific points on the stream, where the Point 1 is located is in the Rego D’Água; Point 2 is in the Rego D’Água and Água Boa; Point 3 is in the Rego D’água in Vila Cachoeirinha; and Point 4 is located is in the Paragem in Parque dos Coqueiros.

The collected samples were surface water, consisting of samples taken from 0 to 30 cm water depth. At each collection point two samples of 1000 mL were collected, at very close intervals. The sample collections were made in successive intervals, in different climatic periods, following the reference protocols (Xia; Pignatello, 2001; Rockne; Shor; Taghon; Kosson, 2002). After collection, the samples were immediately sent for further analysis.
2.4 PYRENE AND BENZO[A]PYRENE EXTRACTION

It is observed that in aquatic systems, organic pollutant compounds are spontaneously dissolved, and it is noted that in rich organic matter systems the adsorption of PAHs occurs with the dissolved organic matter (Hong; Garnier; Zhong; Bergheaud; Fei; Liang, 2014). Knowing that organic matter from environmental samples may have a complex chemical structure, and that they have portions of non-polar substances which allow interaction with hydrophobic molecules such as PAHs (Xia; Pignatello, 2001; Xing; Pignatello, 1997), it is necessary to segregate such materials into different mediums.

The process of liquid-liquid extraction (LLE) is the most common procedure for the separation of compounds with different polarities in a liquid medium (Brum; Cassella; Neto, 2008). This process is based on partitioning a sample between two immiscible phases, where one is organic and the other is aqueous. This type of procedure is used in water sample analysis (Olkiewicz; Caporgno; Fortuny; Stüber; Fabregat; Font; Bengoa, 2014).

In this study we applied the process of LLE modified as previously described (Brum; Cassella; Netto, 2008; Abdel-Shafy, Mansour, 2015). In order to do this, aliquots of 100 mL were taken from the collected water samples. Each aliquot was transferred to a 250 mL Erlenmeyer flask, and then 20 mL of hexane was added. This mixture was stirred for 20 min at room temperature. Due to the insolubility of the medium, part of the hexane extract was removed. This procedure was performed four times for each aliquot. The result of this washing process (about 80 mL of hexane) was transferred into the round bottom flask of the retro evaporator (IKA-RV10) and mixed with 10 mL of methanol. The solution was then heated to a temperature close to 40ºC and retro evaporated, resulting in a final extract of ~2 mL. To complete preparation of the sample for analysis, this extract was diluted in an equal volume of methanol-water solution (1:1 v/v) using a 5 mL volumetric flask.

3 RESULTS AND DISCUSSION

3.1 STUDY OF THE APPLIED ANALYTICAL METHODS

Figure 1(a) and 1(b) shows the normalized fluorescence spectrum of the PAH mixture solution, dissolved in methanol and Milli-Q ultrapure water with $\Delta \lambda = 40$ nm. Under these measurement conditions, it is possible to identify the peaks related to the maximum fluorescence of Chy and BaP at wavelengths of 265 and 366 nm, respectively (Brum; Cassella; Netto, 2008; Abdel-Shafy, Mansour, 2015).
Figure 1. (a): Standard sample fluorescence spectrum (PAH Mix) for a ∆λ = 40 nm, with the identification of peaks for BaP λ<sub>Max</sub> = 366 nm. HPLC grade methanol used as solvent.

Figure 1. (b): Standard sample fluorescence spectrum (PAH Mix) for a ∆λ = 100 nm, with the identification of peaks for Chy λ<sub>Max</sub> = 265 nm. HPLC grade methanol used as solvent.

In Figure 2 the curves of fluorescence intensity as a function of the concentration of Chy(a) and BaP (b) are represented, for the concentration range between 5 ng.mL<sup>-1</sup> and 25 ng.mL<sup>-1</sup>. In this range, the dependence of fluorescence intensity on the concentration of each HPA is apparently linear; setting coefficients, agreement ratios, detection limit values and quantification limit values are described in Table 1.
Figure 2. (a): Analytical curve for Chy determination.

Figure 2. (b): The analytical curve for BaP determination. The red line represents the linear fit performed for each PAH (n = 3).
Table 1. Adjustment coefficients, concordance rates, limits of detection and quantification of Chy and BaP, obtained by analytical curve adjusted by a line without linear coefficient.

| HPA | Angular coef | R²   | LOD (ng.mL⁻¹) | LOQ (ng.mL⁻¹) | Reference                  |
|-----|--------------|------|---------------|---------------|----------------------------|
| Chy | 3.73         | 0.99 | 0.11          | 0.36          | This study                 |
|     |              |      | 0.13          | 0.45          | Molina et all, 2013        |
|     |              |      | 0.09          | 0.34          | Sanchez et all, 2012 and Gonzalez et all, 2007 |
| BaP | 4.96         | 0.99 | 0.05          | 0.17          | This study                 |
|     |              |      | 0.06          | 0.20          | Molina et all, 2013        |
|     |              |      | 0.03          | -----         | Tor et all, 2010           |
|     |              |      | 0.06          | 0.19          | Ferretto, 2014             |

The strong correlation index of the measurements is justified by linear regression coefficient (R²) values of 0.9960 for Chy and 0.9970 for BaP (INMETRO, 2010). We found limits of detection (LOD) and quantification (LOQ) of 2.0 and 6.7 ng.mL⁻¹ for Chy and 1.7 and 5.7 ng.mL⁻¹ for BaP, respectively. The LOD and LOQ values found were very close and, in most cases, lower than the respective values found in the literature (Molina; Lopez; Reyes; Diaz, 2013; Sánchez; Gomez; Malagón; Vilchez, 2012; Gonzalez; Grana; Lorenzo; Mahía; Redon; Goutx, 2007; Tor; Ozcan; Aydin, 2010; Ferretto; Tedetti; Guigue; Mounier; Redon; Goutx, 2014), as shown in Table 1, which shows that in this study, using this technique it is possible to obtain results as accurate and selective as the current literature.

3.2 ENVIRONMENTAL SAMPLE ANALYSIS

After LLE, we were able to identify the spectra of absorption and emission of the PAHs Chy and BaP, with maximum absorption intensity close to 265 nm and 366 nm for the respective compounds. A systematic study of the concentration of these PAHs at selected points of the stream during different seasonal conditions was carried out using the SFS technique.

Figure 3 and 4 shows the dates of collection and the concentrations obtained at each collection point on different days. The concentrations found for Chy at all data for all collection dates ranged between 0.03 ng.mL⁻¹ and 20.12 ng.mL⁻¹, and the concentrations for BaP varied between 0.09 ng.mL⁻¹ and 15.05 ng.mL⁻¹.
Figure 3: Concentration values obtained for PAH Chy at every point for all collection dates.

Figure 4: Concentration values obtained for PAH BaP at every point for all collection dates.
For both PAHs studied, the concentration depended on the rainfall rate. The higher values of the lower level of PHAs, were obtained on rainy days, showing the influences of the seasonal conditions on the quality of the water. The Chy concentrations on dry days ranged from 0.03 to 17.86 ng.mL$^{-1}$, and on rainy days from 2.05 to 3.58 ng.mL$^{-1}$. The concentrations found for BaP on dry days ranged from 0.09 to 15.06 ng.mL$^{-1}$, and on rainy days from 0.58 to 3.75 ng.mL$^{-1}$.

Studies using other techniques show the same tendency to find higher values on rainy days compared to dry days. This tendency is mainly related to the fact that PAHs are hydrophobic and are adsorbed by dust (Varnosfaderany; Bakhtiari; Z. Gu; G.Chu, 2014). Research results suggest that the street dust size and the topographical and hydrological characteristics of the landscape in the flow network are important factors that influence the concentration of PAHs in surface water (Hongtao; Chengqing; Meixue; Weidong; Chris; Baoqing, 2009). The contribution of urban runoff significantly influences the concentration of this chemical in tap water, and for this reason, rain provides the flow of particulate material from the streets to running water, significantly increasing its concentration after rainy periods (Varnosfaderany; Bakhtiari; Z. Gu; G.Chu, 2014; Hongtao; Chengqing; Meixue; Weidong; Chris; Baoqing, 2009). According to the USEPA, the maximum permitted concentration level of the contaminant BaP in drinking water is 0.2 ng.mL$^{-1}$ (Liao; Ma; Chen; Yang, 2015). In this study we measured minimum and maximum concentration values for BaP, which is a major contaminant regulated by USEPA. The minimum value we measured on a dry day with elevated temperature was 0.6 times of the permitted concentration, and on a rainy day the amount of the contaminant was 5.7 times higher than allowed.

4 CONCLUSION

In this study it was possible to identify and quantify the PAHs Chy and BaP in water samples from the natural aquatic environment using the technique of SFS and the sample fortification method of LLE. To validate this analytical procedure, analytical curves for both PAHs were built. Good results of the regression coefficients allow to obtain excellent results of LD and LQ.

Each sample, collect in different day forecast present significant concentrations of the PAHs Chy and BaP. Concentrations found for Chy ranged from 0.03 to 20.12 ng.mL$^{-1}$ and for BaP ranged between 0.09 and 15.05 ng.mL$^{-1}$. The differences of such concentrations can be attributed to the rainfall rate due to the PHAs hydrophobicity. By the way in some points of study, high level of contaminant was found, which may cause damage to living beings.
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REFERENCES

V. Nuria, N. Vera, M.M Martínez-Mecnhon, G.Navarro, G.P. Lucas, S.Navarro. Removal of polycyclic aromatic hydrocarbons (PAHs) from groundwater by heterogeneous photocatalysis under natural sunlight, Journal of Photochemistry and Photobiology A: Chemistry. 2012, 232, 32-40.

H. Shemer, K.G.Linden, Photolysis, oxidation and subsequent toxicity of a mixture of polycyclic aromatic hydrocarbons in natural waters. Journal of Photochemistry and Photobiology A: Chemistry. 2007, 187, 186-195.

X.Xu, R. L. Cook, V. A. Ilacqua, H. Kan, E. O. Talbott, G. Kearney. Studying associations between urinary metabolites of polycyclic aromatic hydrocarbons (PAHs) and cardiovascular diseases in the United States. Science of the total Environment. 2010 v. 408, p. 4,943-4948.

X.Xu, H.Hu, G. D. Kearney, H.Kan, D.S.Sheps. Studying the effects of polycyclic aromatic hydrocarbons on peripheral arterial disease in the United States. Science of the total Environment. 2013, 461, 341-347.

A. Kamal, K. Qamar, M. Gulfraz, M. A. Anwar, R. N. Malik. PAH exposure and oxidative stress indicators of human cohorts exposed to traffic pollution in Lahore city (Pakistan). Chemosphere. 2015, 120, 59-67.

USEPA. UNITED STATES ENVIRONMENTAL PROTECTION AGENCY. National Primary Drinking Water Regulations. Accessed February 05, 2014. Available at: http://water.epa.gov/drink/contaminants/upload/mcl-2.pdf.

G. N.Wogan, S. S. Hecht, J. S. Felton, A. H. Conney, L. A. Loeb. Environmental and chemical carcinogenesis Seminars in Cancer Biology. 2004, 14, 473-486.

K.H. Kim, S.A. Jahan, E. Kabir, R.J.C. Brown. A review of airborne polycyclic aromatic hydrocarbons (PAHs) and their human health effects. Environment International. 2013, 60, 71-80.

A. Jajoo, N. R. Mekala, R. S. Tomar , M. Grieco , M. Tikkanen , E.M. Aro. Low pH-induced regulation of excitation energy between the two photosystems. Febs Letters, 2014, 588, 970-974.

A.S. Brown, R.J.C. Brown. Correlations in polycyclic aromatic hydrocarbon (PAH) concentrations in UK ambient air and implications for source apportionment. Journal of Environmental Monitoring, 2012, 14, 2072-2082.
S. Valência, JM. Marín, G. Restrepo. FH. Frimmel, *Evaluation of natural organic matter changes from Lake Hohloh by three-dimensional excitation–emission matrix fluorescence spectroscopy during TiO$_2$/UV process*. Water Research. 2014, 51,124-133.

D. Patra, A. K Mishra. Talanta. *Concentration dependent red shift: qualitative and quantitative investigation of motor oils by synchronous fluorescence scan*. 2001,53,783-790.

IBGE – Brazilian Institute of Geography and Statistics. Dourados Mato Grosso do Sul. 2014. Access: 07.07.2015 at: http://cidades.ibge.gov.br/xtras/perfil.php?codmun=500370.

S.T. GOMES, A.C. SILVA, *DOURADOS: URBANIZAÇÃO E DINÂMICA CLIMÁTICA*. Geonorte magazine, Special Edition. 2012, v.3, 844-856.

SILVA E. A. Socio-Environmental Policies: Municipal Government Action in the city of Dourados-MS. Proceedings XVI Meeting of Geographers, Crisis, praxis and autonomy: spaces of resistance and hope Dialogues and Practices space. Porto Alegre - RS. 2010.

G.S.Xia, J.J.Pignatello, *Detailed Sorption Isotherms of Polar and Apolar Compounds in a High-Organic Soil*. Environmental Science and Technology. 2001, 35,84-94.

K. J. Rockne, L.M. Shor, L.Y.Young, G.L. Taghon, D.S.Kosson. *Distributed Sequestration and Release of PAHs in Weathered Sediment: The Role of Sediment Structure and Organic Carbon Properties*. Environmental Science and Technology. 2002,36, 2636-2644.

Y.X.Hong, P.Garnier, W.S.-Zhong, V.Bergheaud, H.X.Fei, Q. R.Liang. *PAHs Sorption and Desorption on Soil Influenced by Pine Needle Litter-Derived Dissolved Organic Matter*. Pedosphere,2014,24,575-584.

B.Xing, J. Pignatello. *Dual-Mode Sorption of Low-Polarity Compounds in Glassy Poly(Vinyl Chloride) and Soil Organic Matter* Environmental Science and Technology. 1997, v. 31, 792-799.

D.M. Brum, R.J. Cassella, A.D.P. Netto. *Multivariate optimization of a liquid–liquid extraction of the EPA-PAHs from natural contaminated waters prior to determination by liquid chromatography with fluorescence detection*. Talanta. 2008, 74. 1392-1399.

M.Olkiewicz, M.P.Caporgno,A.Fortuny,F.Stüber,A.Fabregat, J.Font, C. Bengoa. *Direct liquid–liquid extraction of lipid from municipal sewage sludge for biodiesel production*. Fuel Processing Technology. 2014, 128, 331-338.

Hussein I. Abdel-Shafy, Mona S.M. Mansour, *A Review on Polycyclic Aromatic Hydrocarbons: Source, Environmental Impact, Effect on Human Health and Remediation*. Egyptian Journal of Petroleum. 2015, p. 1 - 17.

INMETRO - National Institute of Metrology, Standardization and Industrial Quality. Orientation to Chemical Test Methods Validation. Revision 03 - Feb / 2010.
J.R. Molina, B.G. Lopez, J.F. G. Reyes, A.M. Diaz. Gas chromatography triple quadrupole mass spectrometry method for monitoring multiclass organic pollutants in Spanish sewage treatment plants effluents. Talanta. 2013, 111, 196-205.

F.J. C. Sánchez, A. Z. Gómez, S.C.Malagón, J.L.Vilchez. Validation of a method for the analysis of 77 priority persistent organic pollutants in river water by stir bar sorptive extraction in compliance with the European Water Framework Directive. Talanta. 2012 89,322-334.

V. F.Gonzalez, E.C.Grana, S.M.Lorenzo, P.L.Mahía, D.P.Rodríguez. Solid-phase microextraction–gas chromatographic–tandem mass spectrometric analysis of polycyclic aromatic hydrocarbons: Towards the European Union water directive 2006/0129 EC. Journal of Chromatography A. 2007,1176, Ed. 1-2, 48-56.

S. TOR, OZCAN, M. E. A. AYDIN. Determination of polycyclic aromatic hydrocarbons in waters by ultrasound-assisted emulsification-microextraction and gas chromatography–mass spectrometry Analytica Chimica Acta. 2010,665, 193-199

N.Ferretto, M.Tedetti, C.Guigue, S.Mounier,R.Redon, M.Goutx. Identification and quantification of known polycyclic aromatic hydrocarbons and pesticides in complex mixtures using fluorescence excitation–emission matrices and parallel factor analysis. 2014, 107, 344-353.

M. N. Varnosfaderany, A.R.Bakhtiari, Z. Gu, G.Chu. Vertical distribution and source identification of polycyclic aromatic hydrocarbons (PAHs) in southwest of the Caspian Sea: Most petrogenic events during the late Little Ice Age. Marine Pollution Bulletin. 2014,87,152-163.

Z.Hongtao, Y. Chengqing, C.Meixue, W. Weidong, J. Chris, S. Baoqing, Size distribution and diffuse pollution impacts of PAHs in street dust in urban streams in the Yangtze River Delta. Environmental Sciences. 2009, 21,162-167.

W.Liao, Y.Ma, A.Chen, Y.Yang. Preparation of fatty acids coated Fe₃O₄ nanoparticles for adsorption and determination of benzo(α)pyrene in environmental water samples. Chemical Engineering Journal. 2015, 271,232-239.