

9. simpozijum
Hemija i zaštita životne sredine
EnviroChem2023
sa međunarodnim učešćem



9th Symposium
Chemistry and Environmental Protection
EnviroChem2023
with international participation

KNJIGA IZVODA
BOOK OF ABSTRACTS

Kladovo 4-7. jun 2023. godine

ENVIROCHEM2023

KNJIGA IZVODA

9. simpozijum Hemija i zaštita životne sredine

Kladovo, 4-7. jun 2023.

BOOK OF ABSTRACTS

9th Symposium Chemistry and Environmental Protection

Kladovo, 4-7th June 2023

Izdaje/Published by

Srpsko hemijsko društvo/Serbian Chemical Society

Karnegijeva 4/III, 11000 Beograd, Srbija

tel./fax: +381 11 3370 467; www.shd.org.rs, E-mail: office@shd.org.rs

Za izdavača/For Publisher

Dušan Sladić, predsednik Srpskog hemijskog društva

Urednici/Editors

Sanja Živković, Branka Lončarević, Minja Bogunović, Gordana Gajica

Slika sa naslovne strane/Photo from cover page

Foto Video Boce

Priprema za štampu i štampa/Prepress and printing

Razvojno-istraživački centar grafičkog inženjstva Tehnološko-metalurškog fakulteta,
Beograd

Tiraž/Circulation

150 primeraka/150 copies

ISBN 978-86-7132-082-5

Informacije i stavovi izneti u ovoj publikaciji su provizorni. Srpsko hemijsko društvo, urednici i naučni odbor nisu odgovorni za interpretacije, eventualne posledice i štamparske greške. The information and the opinions given in this publication are provisional. Serbian Chemical Society, Editors or Editorial Board are not responsible for any interpretations, their consequences or typographical errors.

Development of a method based on solid-phase extraction and ultra-high performance liquid chromatography coupled with mass spectrometry for simultaneous analysis of compounds of emerging concern in water matrices

I. Antić^{1,*}, J. Živančev¹, D. Rakić¹, M. Buljovčić¹, N. Đurišić-Mladenović¹

(1) University of Novi Sad, Faculty of Technology Novi Sad, Bulevar cara Lazara 1, Novi Sad, Serbia;

*antic@tf.uns.ac.rs

The contamination of fresh water is a global concern. Continuous release of natural and anthropogenic organic substances, among them compounds of emerging concerns (CECs), into the aquatic environment pose a threat to aquatic organisms and humans. CECs represent the specific organic pollutants not considered under the European Union Directives (e.g. Directive 2013/39/EU) with the exception of substances and/or classes of substances listed under Watch Lists [1]. These compounds include “life-style” products, industrial chemicals, food additives, personal care products, active pharmaceutical ingredients, pesticides in current use, etc. Mass spectrometry in combination with liquid and gas chromatography represents the method of choice for CECs analysis due to the specificity and sensitivity and consequent undoubted identification and quantification with very low method detection limits [2]. For the CECs extraction and efficient reduction of interferences and matrix effects solid-phase extraction (SPE) is the most widely used technique [3].

The aim of this study was the development and validation of sample preparation and instrumental analysis method based on SPE and ultra-high performance liquid chromatography coupled with tandem mass spectrometry (UHPLC-MS/MS) for simultaneous analysis of selected CECs from water. For this purpose, the model water solution containing CECs was prepared - 20 pharmaceutically active compounds belonging to the groups of analgesics and antipyretics, antibiotics, non-steroidal anti-inflammatory drugs (NSAIDs), diuretic drugs as well as 16 pesticides in current use belonging to the group of herbicides, insecticide, fungicides, etc. Sample preparation was based on universal polymeric reversed-phase sorbent (Oasis HLB cartridges, 200 mg) that was developed for the extraction of a wide range of acidic, basic, and neutral compounds from various matrices. Conditioning of SPE cartridges was carried out with methanol (MeOH) and water followed by the application of 200 mL CECs model solution. After the sorbent washing and drying steps, compounds of interest were eluted with 8 mL of MeOH. The eluent was evaporated to dryness and reconstituted in 1 mL of the first gradient phase used for chromatographic separation. For the efficient chromatographic separation of matrix components including CECs, a Hypersil GOLD column (500 mm × 2.1 mm i.d., 1.9 μm particle size) was used. For the chromatographic separation, the used mobile phases were water containing 5 mM ammonium acetate and 0.1% (v/v) formic acid and methanol (without the addition of salts and acids), operated at a flow rate of 400 μL/min. MS detection was performed with a TSQ Vantage™ triple-stage mass spectrometer connected to UHPLC by heated electrospray (HESI) probe operated in both positive and negative ionization modes. Optimization of MS parameters (finding the parent and product masses, collision energies, S-lens) in multiple reaction monitoring (MRM) mode was carried out by direct MS infusion of working standard solutions of each compound at the concentration of 1 μg/mL.

During the method validation the following validation parameters were evaluated, instrumental linearity of calibration curves (R^2), method quantification limits (MQLs), the efficiency of extraction (recovery), and precision (intra- and inter-day precision).

In total, 36 CECs were investigated. Satisfactory instrumental linearity of calibration curves ($R^2 > 0.990$) was obtained for all investigated compounds. Method quantification limits were in the range from 0.20 to 10 ng/L (for the majority of the analytes MQLs were lower than 1 ng/L) which are reliable results for the application of the method for CECs quantification in environmental matrices [3]. For 25 compounds the efficiency of extraction was in the range from 60 to 120 % while only 5 compounds showed an efficiency of extraction lower than 20 %. The lower recoveries for some compounds were expected as the model water solution consisted of CECs belonging to the different classes of pharmaceutically active compounds and pesticides with different physicochemical properties. This is clearly visible by observing the retention times of compounds which were in the range from 1.09 (for the most polar compound) to 4.70 min (for the most nonpolar compound). Repeatability and reproducibility of the method were proved as the intra- and inter-day precision was in all cases lower than 15 %.

Based on the obtained results, the developed method can be used for selected CECs determination in water matrices as the validation parameters were in the same range as the previously published results from similar studies. Additionally, the validation parameters must be checked by analysis of real water samples (surface and wastewaters) spiked with CECs where the influence of matrix components is more pronounced than in ultra-pure water used for the preparation of the CECs model solution.

References

1. Sousa, J.C.G., Ribeiro, A.R., Barbosa, M.O., Fernando, M., Pereira, R., Silva, A.M.T. *J. Hazard. Mater.* 344 (2018) 146-162.
2. Farré, M., Kantiani, L., Petrović, M., Pérez, S., Barceló, D. *J. Chromatogr. A* 1259 (2012) 86-99.
3. Petrović, M., Škrbić, B., Živančev, J., Ferrando-Climent, L., Barcelo, D. *Sci. Total Environ.* 468–469 (2014) 415-428.

Acknowledgement - Funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or EU executive agency. Neither the European Union nor the granting authority can be held responsible for them. This study is conducted under the project TwiNSol-CECs that has received funding from Horizon Europe programme under grant agreement no.101059867.