XVIII EDICIÓN DE LOS PREMIOS "JOSÉ ANTONIO GARCÍA DOMÍNGUEZ"

Como en ocasiones anteriores, dentro de la XXII Reunión Científica de la SECyTA (51ª Reunión Científica del GCTA) celebrada en Mallorca del 16 al 18 de octubre de 2023, se concedieron los premios *José Antonio García Domínguez* en su XVIII edición. Estos premios están patrocinados por la empresa Bruker y se otorgan a las dos mejores comunicaciones orales y las dos mejores en formato de póster de las presentadas por jóvenes investigadores. Una vez se reunieron los jurados encargados de fallar los premios en sus respectivas modalidades, unánimemente se tomaron los acuerdos con las siguientes concesiones:

1er Premio a la mejor comunicación oral (800 €)

ANALYSIS OF SARS-CoV-2 NUCLEOCAPSID PROTEIN BY ON-LINE APTAMER AFFINITY SOLID-PHASE EXTRACTION CAPILLARY ELECTROPHORESIS-MASS SPECTROMETRY

Laura Pont[(1,2)], Hiba Salim[(1)], Estela Giménez[(1)], Suttinee Poolsup[(3)], Maxim V. Berezovski[(3)], Fernando Benavente[(3)]*

[(1)] Department of Chemical Engineering and Analytical Chemistry, Institute for Research on Nutrition and Food Safety (INSA·UB), University of Barcelona, Spain; [(2)] Serra Húnter Program, Generalitat de Catalunya, Spain; (3) Department of Chemistry and Biomolecular Sciences, University of Ottawa, Canada. *laura.pont@ub.edu

Severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2) is a virus that causes an infectious respiratory disease called coronavirus disease 2019 (COVID-19), which has originated a major health crisis on a global scale in recent years [1]. The nucleocapsid protein (N protein, relative molecular mass ~51,000) is one of the most abundant structural proteins in SARS-CoV-2. Despite it is an immunodominant antigen in host immune responses that can be used as a good diagnostic biomarker [2], more information on this protein is needed to better understand the mechanisms of the disease, as well as for designing novel vaccines and drugs for COVID-19 prevention and treatment. In this work, an aptamer affinity sorbent was prepared for clean-up, preconcentration, separation, and characterization of N protein by on-line aptamer affinity solid-phase extraction capillary electrophoresis-mass spectrometry (AA-SPE-CE-MS) [3]. AA-SPE microcartridges were packed with a sorbent based on magnetic bead particles modified with an aptamer against the N protein. After a very challenging optimization of several parameters of the AA-SPE-CE-MS method, which needed the use of lab-made hydroxypropyl cellulose (HPC) coated capillaries to prevent protein adsorption on the inner capillary wall, the sample was loaded in separation background electrolyte (BGE, ammonium acetate 10 mM, pH 7.0), while the retained protein was eluted with acetic acid 1 M, pH 2.3. The developed method with N protein standards was repeatable in terms of migration times and peak areas, satisfactorily linear between 2.5 and 25 mg·L-1, and the limit of detection (LOD) was 0.5 mg·L-1, leading to a sensitivity enhancement of 500 times compared to CE-MS. The AA-SPE-CE-MS method was applied to the analysis of N protein in human saliva, pointing out its great potential for the development of accurate and reliable SARS-CoV-2 complementary analytical methods.

Acknowledgements
This study was supported by grant PID2021-127137OB-I00 funded by MCIN/AEI/10.13039/501100011033 and by "ERDF A way of making Europe". H. Salim thanks Generalitat de Catalunya for a FI (Ajuts per a la contractació de personal investigador novell)

fellowship. The Bionalysis group of the UB is part of the INSA-UB Maria de Maeztu Unit of Excellence (Grant CEX2021-001234-M) funded by MCIN/AEI /10.13039/501100011033.

References
[1] P. Haas, M. Muralidharan, N.J. Krogan, R.M. Kaake, R. Hüttenhain, J. *Proteome Res*. **20** (2021) 1133-1152.
[2] L.H. Cazares, R. Chaerkady, S.H. Samuel Weng, C.C. Boo, R. Cimbro et al., *Anal. Chem*. **92** (2020) 13813-13821.
[3] R. Pero-Gascon, F. Benavente, Z. Minic, M.V. Berezovski, V. Sanz-Nebot, *Anal. Chem.* **92** (2020) 1525-1533.

2º Premio a la mejor comunicación oral (600 €)

APPLICATION OF HOMEMADE SILICA-BASED ZWITTERIONIC ION-EXCHANGE MATERIALS FOR THE EXTRACTION OF PHARMACEUTICALS FROM ENVIRONMENTAL WATER SIMPLES

A. Moral[(1)], F. Borrull[(1)], K. G. Fourton[(2)], A. Kabir[(2)], R. M. Marcé[(1)], N. Fontanals[(1)]*

[(1)] Departament of Analytical and Organic Chemistry, Univestitat Rovira i Virgili, Sescelades Campus, Marcel·lí Domingo s/n, 43007 Tarragona, Spain; [(2)] International Forensic Research Institute, Department of Chemistry and Biochemistry, Florida International University, Miami, FL 33199, USA. *alberto.moral@urv.cat

The use of sorptive techniques is the preferred way to extract analytes from liquid samples, being the solid-phase extraction the common technique. The development of new materials that can be applied to solid-phase extraction is one important research area [1]. One problem is the extraction of ionic and ionizable compounds, there are commercial solutions that allow the extraction of cationic or anionic analytes (Oasis MCX, Strata X-AW…), however, the simultaneous extraction of both type of analytes is not possible with commercial sorbents. In this sense, in the present study, three homemade silica-based zwitterionic ion-exchange materials were synthesized through sol-gel reactions. After the functionalization, the sorbents had quaternary amines and sulfonic groups, allowing them to perform strong anion and cation-exchange interactions.
The three sorbents were evaluated for the SPE of acidic and basic pharmaceuticals at different pH. The best performing sorbent was the one functionalized with 2-(methacryloxy) ethyl dimethyl-3 (sulfopropyl) ammonium hydroxide. This sorbent was selected and its SPE method was optimized in terms of pH, loading volume and elution conditions, being the optimal conditions pH 5, a variable volume depending on the matrix and 5 mL of 1% NH4OH in MeOH.
The optimized method was applied for the extraction of the pharmaceuticals from river, effluent wastewater and influent wastewater samples. The method was validated in terms of apparent recovery, matrix effect, intra-day and inter-day precision and detection and quantification limits. The pharmaceuticals were quantified in several samples of each matrix, ranging the concentration of the compounds from <MDL to 401 ng/L in river samples, from <MDL to 2938 ng/L in effluent wastewater samples and from <MQL to 9542 ng/L in influent wastewater samples.

Acknowledgement
The authors would like to thank the Ministerio de Economía, Industria y Competitividad and the Agencia Estatal de Investigación (Project: PID2020-114587GB-I00) for the financial support and Universitat Rovira i Virgili for A. Moral grant (2020PMF-PIPF-33).

References
[1] E.V.S. Maciel, A.L. de Toffoli, E.S. Neto, C.E.D. Nazario, F.M. Lanças, New materials in sample preparation: recent advances and future trends, *TrAC, Trends Anal. Chem*. **119** (2019). 115633. https://doi.org/10.1016/j.trac.2019.115633.

1er Premio al mejor póster (400 €)

DEVELOPMENT OF A HPLC-DAD-TOF MS METHODOLOGY FOR THE AUTHENTICATION OF DAMIANA (*TURNERA DIFFUSSA*) EXTRACTS

Adal Mena[(1,2)], M. Luz Sanz[(1)], Marina Díez-Municio[(2)], Ana I. Ruiz-Matute[(1)]*

[(1)] Instituto de Química Orgánica General (CSIC), Spain; [(2)] Pharmactive Biotech Products, S.L.U. Spain. *adal.mena@pharmactive.eu

Damiana (*Turnera diffussa*) is an endemic shrub from Mexico, that has been historically used in traditional herbal medicine throughout the world, mainly as a sexual stimulant or aphrodisiac, being one of the most used herbs in this type of formulations [1]. Moreover, it has been also described as a traditional remedy against stomachache, lung diseases related to tobacco abuse, bladder and kidney infections, etc. [2] and it is now widely consumed as food supplement (FS). FS for sexual enhancement are some of the most adulterated at present using drugs intended for the treatment of erectile dysfunction [such as phosphodiesterase-5 (PDE-5) inhibitors] [3]. However, the development of analytical methods to detect such adulterations in damiana formulations has hardly been addressed. Therefore, in this work, a new analytical method to detect these potential frauds has been proposed.
Firstly, different solvents (water, methanol and hydroalcoholic mixtures) were evaluated as extractants of damiana leaf compounds, selecting the most appropriate one to allow a comprehensive characterization of these samples. A methodology based on liquid chromatography with diode array detector coupled to time of flight mass spectrometry (HPLCDAD-ToF MS) using a C18 reverse-phase column under both positive and negative ionization modes was proposed. In addition, PDE-5 inhibitors (sildenafil, tadalafil and analogues) as well as different simulated additions at different concentrations of these drugs to Damiana extracts were also analyzed by the developed methodology.
Methanol:water (50:50) extracts of damiana showed the highest number of extracted compounds; the untargeted analysis of these samples allowed the detection of 3000 molecular features in negative ionization mode and 4000 features in positive mode. Phenolic compounds such as flavonoids glycosides and catechins, cyanogenic glycosides such as tetraphyllin B and terpenoids such as tehuetenone A were detected in damiana leaf extracts. HPLC-DAD-ToF MS methodology allowed the analysis of PDE-5 inhibitors and the successful detection of their presence in the intentionally adulterated damiana extracts.

Acknowledgements
This work was funded by MCIN/AEI (PID2019-106405GB-I00/AEI/10.13039/501100011033) and by CSIC (project 202280I058). A.M.G. thanks the MICINN for an Industrial Doctorate grant

(DIN2019-010849/AEI/10.13039/501100011033) awarded to Pharmactive Biotech Products S.L.U.

References
[1] D.L. Rowland, W. Tai, *J. Sex & Marital Therapy* **29** (2003) 185-205.
[2] K. Szewczyk., C. Zidorn, *J. Ethnopharmacology* **152** (2014) 424-443.
[3] K. Skalicka-Wozniak, M.I. Georgiev, I.E. Orhan, *Food Chem. Tox.* **108** (2017) 355-364.

2º Premio al mejor póster (300 €)

OCCURRENCE AND SPATIAL DISTRIBUTION OF PHARMACEUTICALS IN MEDITERRANEAN INTERMITTENT RIVER BASINS

Olga Gómez Navarro[(1)], Sergio Santana[(1,2)], Sandra Pérez Solsona[(1)]*

[(1)] ONHEALTH, Department of Environmental Chemistry, IDAEA-CSIC, Barcelona Spain; [(2)] Instituto Universitario de Estudios Ambientales y Recursos Naturales (i-UNAT), Universidad de Las Palmas de Gran Canaria, 35017 Las Palmas de Gran Canaria, Spain. *ognqam@cid.csic.es

Most river basins are subjected to several anthropogenic inputs, including wastewater treatment plant (WWTPs) discharges and urban and storm runoff waters, affecting wáter quality. Even though WWTPs are used to manage and treat wastewater, the WWTP effluent may still contain several wastewater borne pollutants including several contaminants of emerging concern (CECs), as conventional WWTP do not fully elimate these. In these cases, pharmaceuticals and personal care products (PPCPs) are often prevailing, as they are continuously introduced in surface water and hence are seen as pseudo-persistant contaminants in the aquatic environment where their contamination profiles are often quite constant in concentration [1]. In this study the presence of several CECs was analysed in five countries; Spain, France and Italy, located in Southern Europe and Algeria and Tunisia, located in Northern Africa. In Tunisia and Algeria, WWTPs are sometimes over-exploited and many industries directly release their wastewater to the river basins. In addition to this, the lack of regulations regarding CECs concentration in surface water and the limited monitoring makes it interesting to investigate their presence and impact. Hence, different intermittent rivers from each site were sampled and possible differences between Southern Europe and Northern Africa were investigated. Samples were extracted by means of a solid pase extraction procedure using a homemade multilayer mixed-bed cartridge containing a mixture of four different sorbents with different selectivity to cover a wide range of polarities. A total of 81 target CECs, selected based on their occurrence and ubiquity in the aquatic environment were screened and quantified using high-resolution mass spectrometry Q-Exactive Orbitrap. For the separation of the analytes, liquid chromatography was performed using Acquity UPLC HSS T3 column [2]. The presence and potential differences in contamination levels across the five countries was investigated. The studied river basins from France and Algeria reported lowest concentrations and statistical analysis were performed to study the potential differences per CECs class between countries, and the most remarkable class were the industrial compounds where significant differences between Tunisia and the other four countries were observed. Regarding specific contaminants, caffeine concentrations were outstanding in Tunisia compared to the rest of countries, and Italy presented remarkable concentrations of antihypertensives, with ibersartan and valsartan acid concentrations being statistically different from the rest of the studied countries.

Acknowledgements
This study has been financially supported by the EU through the PRIMA project (INWAT 201980E121).
References
[1] A.J. Ebele, et al., *Emerging Contaminants* **3** (2017) 1-16.
[2] O. Gómez-Navarro, et al., *MethodsX* **10** (2023) 102093.