VIII Edición Premios José Antonio García Domínguez

En el marco de la XII Reunión Científica de la Sociedad Española de Cromatografía y Técnicas Afines (SECyTA) celebrada en Tarragona del 14 al 16 de noviembre de 2012 se otorgaron los premios José Antonio García Domínguez a las mejores comunicaciones orales y tipo cartel presentadas en dicha reunión. Al igual que en años anteriores, esta VIII edición de los premios ha sido patrocinada por Bruker. El jurado encargado de fallar los premios correspondientes a las mejores comunicaciones orales estaba formado por Jordi Díaz (Presidente), Francesc Borrull, Mercedes de Frutos, María Teresa Galcerán y Begoña Jiménez, que tras debatir los méritos científicos de las presentaciones, tomó por unanimidad los siguientes acuerdos:

1er Premio a la mejor Comunicación Oral (800 euros)

Comunicación: OP-13

Título: UNAMBIGUOUS CONFIRMATION OF CYCLIC IMINES AS EMERGING TOXINS IN SHELLFISH HAVERSTING AREAS OF CATALONIA (NW MEDITERRANEAN SEA)

Autores: M. García-Altares[1], V. Bane[2], A. Casanova[1], J. Diogène[1], A. Furey[2], P. de la Iglesia[1]

[1] IRTA, Sant Carles de la Ràpita, Spain

[2] Department of Chemistry, Proteobio, Mass Spectrometry Centre for Proteomics and Biotoxin Research, Cork, Ireland

2º Premio ex-aequo a la mejor Comunicación Oral (300 euros)

Comunicación: OP-14

Título: TRANSIENTS ISOTACHOPHORESIS OF PROTEINS ON GLASS MICROCHIP WITH LASER INDUCED FLUORESCENCE DETECTION

Autores: A.G. Crevillén, M.M. Barrios-Romero, M. de Frutos, J.C. Díez-Masa

Institute of General Organic Chemistry, CSIC. Madrid, Spain

2º Premio ex-aequo a la mejor Comunicación Oral (300 euros)

Comunicación: OP-38

Título: EVALUATION OF DIFFERENT POLAR COATINGS FOR STIR BAR SORPTIVE EXTRACTION OF EMERGING POLLUTANTS FROM ENVIRONMENTAL WATER SAMPLES

Autores: N. Gilart, N. Miralles, P.A.G. Cormack, R.M. Marcé, F. Borrul, N. Fontanals

Department of Analytical Chemistry and Organic Chemistry, Faculty of Chemistry, Rovira i Virgili University. Tarragona, Spain

En el caso de los premios a las mejores comunicaciones tipo cartel presentadas en la XII Reunión Científica de la SECyTA, el jurado estuvo constituido por: Fco. Javier Santos (Presidente), Belén Gómara, Elena Ibáñez y Yolanda Picó. Este jurado tomó por unanimidad los siguientes acuerdos:

1er Premio al mejor Póster (400 euros)

Comunicación: NDE-05

Título: ANALYSIS OF ANABOLIC STEROIDS IN URINE BY GC-APGC-MS/MS (QqQ AND QTOF). POTENTIAL USE FOR DOPING CONTROL

Autores: M. Raro[1], T. Portolés[1], J.V. Sancho[1], E. Pitarch[1], F. Hernández[1], J. Marcos[2], R. Ventura[2], O.J. Pozo[2], J. Segura[2]

[1] Research Institute for Pesticides and Water, University Jaume I. Castellón, Spain

[2] Bioanalysis Research Group. IMIM, Hospital del Mar. Barcelona, Spain

2º Premio al mejor Póster (300 euros)

Comunicación: ENV-42

Título: DETERMINATION OF ILLICIT DRUGS IN WATER SAMPLES BY COUPLING IN-LINE SOLID-PHASE EXTRACTION AND CAPILLARY ELECTROPHORESIS

Autores: T. Baciu, F. Borrull, M. Calull, C, Aguilar

Department of Analytical Chemistry and Organic Chemistry, Faculty of Chemistry, Rovira i Virgili University. Tarragona, Spain

La entrega de los premios tuvo lugar el 16 de noviembre de 2012, durante la ceremonia de clausura de la XII Reunión Científica de la SECyTA.

Belén Gómara
Secretaria de la SECyTA

1er Premio a la mejor Comunicación Oral (800 euros): comunicación OP-13

UNAMBIGUOUS CONFIRMATION OF CYCLIC IMINES AS EMERGING TOXINS IN SHELLFISH HARVESTING AREAS OF CATALONIA (NW MEDITERRANEAN SEA)

M. García-Altares[1], V. Bane[2], A. Casanova[1], J. Diogène[1], A. Furey[2], P. de la Iglesia[1]

[1]IRTA, Carretera de Poble Nou, km 5.5, 43540, Sant Carles de la Ràpita, Spain.

[2]Department of Chemistry, Proteobio, Mass Spectrometry Centre for Proteomics and Biotoxin Research, CIT, Bishopstown, Cork, Ireland.

pablo.delaiglesia@irta.cat

Cyclic imines are a group of lipophilic marine toxins that can be bioaccumulated in seafood. They comprise three main types of toxins (spirolides, gymnodimines and pinnatoxins) that have several spiro-linked functional groups and an imino group in their structure [1]. Although their fast-acting neurotoxicity in mice, there are no regulatory limits for cyclic imines in shellfish because these toxins have not been directly linked to human intoxication. Therefore, the European Food Safety Authority (EFSA) performed a risk assessment to human health related to the consumption of shellfish contaminated with cyclic imines, but it was not conclusive due to the lack of data about the occurrence of these toxins in seafood [2].

This work presents the first detection of spirolides and pinnatoxins in shellfish sampled in Catalonia (Spain, NW Mediterranean Sea). Spirolides were first detected in the Atlantic coast of Spain (Galicia region) in 2006 [3], but to the best our knowledge, the presence of pinnatoxins in Spanish shellfish has never been reported. These two toxins have been also detected in sea water using solid-phase adsorption toxin tracking devices (SPATTs) [4]. The detection by LC-MS/MS of spirolides and pinnatoxins was performed under alkaline chromatographic conditions using a QTrap 3200 hybrid triple quadrupole (AB/Sciex). The further identification of the compounds was performed in an 6340 Ion Trap (Agilent) and in an Orbitrap Discovery (Thermo Scientific). The complementation of these mass spectrometric techniques provided the optimum sensitivity, resolution and mass accuracy to quantify, characterize and unequivocally identify these new emerging marine toxins in Catalonian samples. The results of this work support the requests of EFSA to include cyclic imines in the shellfish safety monitoring programs to collect exposure data of cyclic imines to consumers, required to perform accurate assessments of the risk posed by cyclic imines in seafood.

[1] A. Otero, M.-J. Chapela, M. Atanassova, J.M. Vieites, A.G. Cabado, Chemical Research in Toxicology 24(11) (2011) 1817.

[2] EFSA Panel on Contaminants in the Food Chain (CONTAM), EFSA Journal 8 (6) (2010) 1628.

[3] A. Villar Gonzalez, M. L. Rodriguez-Velasco, B. Ben-Gigirey , L. M. Botana, Toxicon 48(8) (2006)1068.

[4] L. A. MacKenzie, Current Opinion in Biotechnology 21(3) (2010) 326.

2º Premio ex-aequo a la mejor Comunicación Oral (300 euros): comunicación OP-14

TRANSIENT ISOTACHOPHORESIS OF PROTEINS ON GLASS MICROCHIP WITH LASER INDUCED FLUORESCENCE DETECTION

A.G. Crevillén, M.M. Barrios-Romero, M. de Frutos, J.C. Diez-Masa
Institute of Organic Chemistry, Spanish National Research Council (IQOG-CSIC). C/ Juan de la Cierva, 3, 28006, Madrid, Spain, diez-masa@iqog.csic.es

Capillary electrophoresis (CE) is a powerful separation technique for protein analysis that has been successfully used in targeted proteomics and biomarker discovery [1]. Its implementation on microchip format (MCE) has grown in the last two decades because its promising features; integration of several analytical steps, portability, high speed, high efficiency, reduced reagent consumption, low waste generation and high throughput (multiple/parallel separations) [2]. However, due to the small injection plug and the short optical path, detection sensitivity is a drawback in MCE. For that reason, laser induced fluorescence (LIF) is the most widely used detection method for MCE, due to its superior selectivity and sensitivity [2, 3].

On the other hand, proteins of interest in biological samples, i.e., as molecular makers for illnesses, are often present in trace amounts so the development of preconcentration strategies, both outside and inside the microchips is necessary. In this sense, isotachophoresis (ITP), that is a separation technique, has also been successfully applied in conjunction with CE for sample preconcentration. ITP can be carried out in CE in several modes. In one of the ITP modes, called transient isotachophoresis (tITP) [3, 4], the same capillary is employed for both the ITP pre-concentration and the electrophoretic separation, thus enabling an in-line approach which is easily adaptable to microchip format, By on-chip tITP, 20000-fold concentration of BSA was reported by Baba's group under SDS-denaturing conditions [5]. It is worth mentioning that in the majority of works that use on-chip tITP for protein concentration, the separation is carried out by gel electrophoresis mode in SDS-denaturing conditions [4]. At this condition, proteins are highly charged and possess high electrophoretic mobility so it is very easy to find a terminating ion. However, the excellent selectivity achieved in CZE is usually lost when gel electrophoresis is used as a separation mode.

In this communication, we present preliminary results about the preconcentration and separation of three proteins (α-lactalbumin, β-lactoglobulin and carbonic anhydrase) by on-chip tITP using zone electrophoresis as separation technique. This methodology was carried out in a glass microchip with laser induced fluorescence detection. A commercial polyacrilamide derivative, EOTrol® (Target Discovery, Palo Alto, CA), was used as dynamic coating to avoid protein adsorption on the channel surface and to reduce the electroosmotic flow (EOF). This latter point is crucial in the analytical strategy developed because EOF disturbs ITP process brodening the stacked protein bands. Proteins were labeled off-chip with the fluorogenic reagent ChromeoTM P-503 (Active Motif, Carlsbad, CA). We chose chloride ion and 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) as leading and terminating anions, respectively. Several parameters such as the composition of leading electrolyte (LE) and terminating electrolyte (TE), injection time and separation distance were optimized to get the maximum concentration index (CI) along with acceptable peak resolution. Using the optimized methodology, CI close to two orders of magnitude and limit of detections below nM range were obtained for the studied proteins.

[1] X. Fang, B.M. Balgley, C.S. Lee, Electrophoresis 30 (2009) 3998.
[2] F. Shang, E. Guihen, J.D. Glennon, Electrophoresis 33 (2012) 105.
[3] N.T. Tran, I. Ayed, A. Palandre, M. Taverna, Electrophoresis 31 (2010) 147.
[4] T. Stroink, E. Paarlberg, J.C.M. Waterval, A. Buly, W.J.M. Underberg, Electrophoresis 22 (2001) 2375.
[5] J. Wang, Y. Zhang, M.R. Mohamadi, N. Kaji, M. Tokeshi, Y. Baba, Electrophoresis 30 (2009) 3250.

Acknowledgements: The authors acknowledge the Spanish Ministry of Science and Innovation (grant CTQ2009-0939) and Spanish Ministry of Education, Culture and Sports (003/EPB10/12). M.M. Barrios-Romero and A.G.Crevillén acknowledge CSIC for JAE-Pre and JAE-Doc contracts, respectively. Both contracts are co-financed by the European Union under the European Social Fund (ESF).

2º Premio ex-aequo a la mejor Comunicación Oral (300 euros): comunicación OP-38

EVALUATION OF DIFFERENT POLAR COATINGS FOR STIR BAR SORPTIVE EXTRACTION OF EMERGING POLLUTANTS FROM ENVIRONMENTAL WATER SAMPLES

N. Gilart, N. Miralles, P.A.G. Cormack, R. M. Marcé, F. Borrull, N. Fontanals
Department of Analytical Chemistry and Organic Chemistry, Faculty of Chemistry, University Rovira i Virgili, Marcel•lí Domingo, s/n, 43007, Tarragona, Spain, nuria.gilart@urv.cat

Stir bar sorptive extraction (SBSE) is a sorptive technique that overcomes the limited capacity of solid-phase microextraction (SPME) fibers. Till very recently, the only commercially available phase for SBSE has been polydimethylsiloxane (PDMS), which, due to its non-polar nature, is ideally designed to extract non-polar compounds [1]. In recent years, efforts have been made to develop new materials for the SBSE of polar compounds. Currently, due to the increasing demand for suitable materials for extracting polar compounds, Gerstel has commercialised new stir bars with more polar phases, such as polyethylene glycol (PEG) Silicone, commercialised as EG Silicone Twister, and another that compromises polyacrylate with a proportion of PEG, currently at pilot stage as Acrylate Twister. With respect to the in-house prepared stir bar different approaches have been employed, that include sol-gel technology and monolithic materials, that improve the degree of polarity in the coating and so, enhance their retentions towards polar compounds [2,3].

New monolithic materials in stir bar form have been synthesised using different hydrophilic precursor monomers such as 2-hydroxyethyl methacrylate and pentaerythritol triacrylate using thermal-initiated free radical polymerisation. These new polar coatings were then applied to SBSE followed by liquid chromatography coupled to a triple quadrupole mass spectrometry (LC-MS-MS) for the determination of a group of emerging pollutants that covers different polarities from environmental water matrices. The main parameters affecting the efficiency during both the extraction (sample pH, ionic strength, matrix characteristics, agitation speed and extraction time) and the desorption (type of solvent, desorption mode and time) of the presented methodology were optimised.

The performance of these in-house coatings was also compared to the commercial available coatings: PDMS Twister, EG Silicone Twister and Acrylate Twister. As expected, under the conditions tested, the more polar the coating the higher affinity presented to polar analytes.

Moreover, the SBSE developed method was applied for the determination of these target analytes in different complex environmental samples, including river, effluent and influent waste water from treatment plant samples and showed good results of most of the analytes studied.

[1] R. Lourdes, J. Chromatogr. A 1221 (2012) 84.
[2] F.M. Lancas, M.E. Costa, P. Grossi, I.R.B. Olivares, J. Sep. Sci. 32 (2009) 813.
[3] A. Prieto, O. Basauri, R. Rodil, A. Usobiaga, L.A. Fernandez, N. Etxebarria, O. Zuloaga, J. Chromatogr. A 1217 (2010) 2642.

1er Premio al mejor Póster (400 euros): comunicación NDE-05

ANALYSIS OF ANABOLIC STEROIDS IN URINE BY GC-APGC-MS/MS (QqQ AND QTOF). POTENTIAL USE FOR DOPING CONTROL

M. Raro[1], T. Portolés[1], J.V. Sancho[1], E. Pitarch[1], F. Hernández[1], J. Marcos[2], R. Ventura[2], O. J. Pozo[2], J. Segura[2]

[1]Research Institute for Pesticides and Water, University Jaume I, E-12071, Castellón, Spain, e-mail: mraro@uji.es

[2]Bioanalysis Research Group. IMIM, Hospital del Mar, Dr. Aiguader 88, 08003 Barcelona, Spain

Exogenous androgenic anabolic steroids (AAS) are synthetic derivatives of testosterone with a common structure which contains four rings. The use of AAS can stimulate the formation of muscle cells, increasing the muscle growth. For this reason, they are widely used for athletic performance. Since their first prohibition in 1976 [1], they remain as the most frequently detected group of substances in doping control analyses [2]. Therefore, doping control laboratories have to develop adequate analytical approaches for the detection of AAS misuse. Most of AAS are quickly metabolized after human administration. Thus, AAS metabolites are the most suitable biomarkers for the screening of AAS.

Due to the fact that their use by athletes is prohibited at any time, the mere presence of one of their metabolites in urine is enough to declare an adverse analytical finding. Consequently, any improvement in the detection of AAS is important for the doping control field. Analytical methodologies using chromatographic techniques coupled to tandem mass spectrometry with triple quadrupole (QqQ) are the most adequate approaches for the determination of AAS or their metabolites in urine samples due to their excellent sensitivity and selectivity. At the moment, doping control laboratories are using two strategies for the detection of AAS: methods based on LC-MS using atmospheric pressure interface (API) and GC-MS methods using electron ionization (EI). LC-API-MS methods allow for the reduction of sample treatment and the possibility of detecting thermolabile compounds. However, only those compounds with an ionisable centre can be detected and important AAS biomarkers such as totally reduced metabolites cannot be detected by this technique. On the other hand, besides the drawback of the compulsory derivatization step, GC-EI-MS methodologies have the limitation of the high fragmentation of the compounds in the source which can hamper the selection of an adequate precursor ion in MS/MS strategies.

In this work, a new atmospheric pressure interface with softer ionization, developed for using in gas chromatography (APGC) [3], is investigated for detection of target AAS with GC-APGC-QqQ and GC-APGC-QTOFMS. Firstly, derivatized [4] and underivatized AAS were tested, in order to evaluate the need to apply this time-consuming sample preparation step and to check the extra structural information which can be extracted from this step. Next, the fragmentation behaviour of representative AAS was investigated by QqQ and QTOFMS, in order to be extended to other steroidal structure compounds.

This interface promotes ionization with very little fragmentation for underivatized analytes, with the result of $[M+H]^+$ or $M^{\cdot+}$ ions (depending on the presence or not of water in the interface) as the base peak of the spectra, similar to those obtained by LC-MS. The reduced fragmentation observed by using this new source can have a significant impact on target analysis at trace levels. In the case of trimethylsilyl (TMS) derivatives, a slightly higher fragmentation was observed but also related with OTMS losses.

In both approaches, with and without derivatization, the reduced fragmentation in the full scan spectrum given by the APGC source facilitates the selection of abundant and/or more specific precursor ions in tandem MS experiments, allowing for the development of more efficient tandem MS methods, which would increase the selectivity and the sensitivity of the method.

[1] World Anti-Doping Agency (WADA) http://list.wada-ama.org/ (*last accessed* 8/6/12).

[2] WADA accredited laboratories statistics. http://www.wada-ama.org/Documents/Resources/Statistics/Laboratory_Statistics/WADA_2010_Laboratory_Statistics_Report.pdf.
[3] T. Portolés, J. V. Sancho, F. Hernández, A. Newton, P. Hancock, J. Mass Spectr. 45 (2010) 926.
[4] J. Segura, R. Ventura, C. Jurado, J. Chromatogr. B. 713 (1998) 61.

2º Premio al mejor Póster (300 euros): comunicación ENV-42

DETERMINATION OF ILLICIT DRUGS IN WATER SAMPLES BY COUPLING IN-LINE SOLID-PHASE EXTRACTION AND CAPILLARY ELECTROPHORESIS

T. Baciu, F. Borrull, M. Calull, C, Aguilar
Departament of Analytical Chemistry and Organic Chemistry, Faculty of Chemistry, Rovira i Virgili University, Marcel.lí Domingo s/n, 43007, Tarragona, Spain, tatiana.baciu@urv.cat

The abuse of illicit drugs has become a serious problem around the world. The residues of these substances and their metabolites that are excreted by humans flow into and through wastewater treatment plants. The fraction that is not removed remains in the environment, representing the main source of pollution in surface waters [1, 2] and even in drinking water [2, 3]. The study of the levels of these drugs in water samples can provide information about their consumption.

Capillary electrophoresis (CE) has been found to be a useful approach for the determination of these kinds of drugs in different matrices [4, 5]. One of the main drawbacks of CE is its poor sensitivity when is applied to the analysis of environmental samples. Therefore, in order that CE can be suitable for determining illicit drugs in water samples, where these drugs are usually present at low concentrations, it is necessary to develop strategies to reduce the LODs. Several approaches have been reported to solve this important issue in CE. One of them is the application of a preconcentration technique based on solid-phase extraction (SPE) [6-8]. Among the different strategies to combine SPE and CE, we have chosen the in-line coupling between both techniques to preconcentrate and separate cocaine (COC) and it major metabolite, benzoylecgonine (BE), in environmental water samples.

The SPE-CE device consisted of a short length of a capillary of 2 mm packed with Oasis MCX near to the inlet end of the separation capillary. Using this sorbent, higher retention of these kinds of analytes can be achieved because it can performance both hydrophobic and ionic interactions. A detailed study of different parameters affecting the in-line SPE performance, such as sample pH, volume of the elution plug and sample injection time have been studied. This approach has resulted efficient for the determination of the illicit drugs in environmental waters samples. Using this strategy is possible to obtain LODs at sub-ng/mL levels by the injection of much larger amount of sample than conventional CE analysis.

[1] M. Pedrouzo, F. Borrull, E. Pocurull, R.M. Marcé, J. Sep. Sci. 34 (2011) 1091.
[2] I. Botello, F. Borrull, C. Aguilar, M. Calull, Electrophoresis 33 (2012) 528.
[3] M. Huerta-Fontela, M.T. Galceran, F. Ventura, Environ. Sci. Technol. 42 (2008) 6809.
[4] C. Cruces-Blanco, A.M. García-Campaña, Trends Anal. Chem 31 (2012) 85.
[5] M. Janicka, A. Kot-Wasik, J. Namiesnik, Trends Anal. Chem 29 (2010) 209.
[6] P. Puig, F. Borrull, M. Calull, C. Aguilar, Trends Anal. Chem. 26 (2007) 664.
[7] R. Ramautar, G.W. Somsen, G.J de Jong, Electrophoresis 31 (2010) 44.
[8] P. Puig, F. Borrull, M. Calull, C. Aguilar, Anal. Chim. Acta 616 (2008) 1.