14as JORNADAS DE ANÁLISIS INSTRUMENTAL

RECINTO FIRA GRAN VÍA. BARCELONA, 1-3 OCTUBRE 2014

14th INSTRUMENTAL ANALYSIS CONFERENCE

GRAN VIA VENUE. BARCELONA, OCTOBER 1st - 3rd 2014

LIBRO DE ABSTRACTS

SECYTA Sociedad Española de Cromatografía y Técnicas Afines

SEQA Sociedad Española de Química Analítica

EXPOQUIMIA Salón Internacional de la Química

JAI

Fira Barcelona

MIÉRCOLES, 1 DE OCTUBRE		
HORA	**SALA 4.1**	**SALA 4.2**
8.30 - 9.00	**Recogida de documentación**	
9.00 - 9.30	**Ceremonia de inauguración**	
9.30 - 10.30	**Conferencia Plenaria** Dr. Marcos N. Eberlin (Universidad de Campinas, Brasil)	
10.30 - 11.00	Café y colocación de todos los pósters (Pabellón 2)	
11.00 - 11.30	**Conferencia Invitada** Dr. Arben Merkoçi (ICREA, ICN2)	
11.30 - 13.00	**Comunicaciones Orales 1:** Análisis de alimentos	**Comunicaciones Orales 2:** Técnicas -ómicas
13.00 - 14.00	Almuerzo de trabajo (Anexo Hall 4/6)	
14.00 - 15.00	**PÓSTERS.SESIÓN 1** (Pabellón 2) Sesiones: Análisis de alimentos; Técnicas -ómicas; Análisis clínico; Automatización y miniaturización en análisis químico; Análisis de procesos y productos industriales; Especiación química; Sensores químicos y biosensores; Nanotecnología	
15.00 - 16.00	**Conferencia Plenaria.** Dr. Jeroen Kool (Universidad de Amsterdam)	
16.00 - 16.30	Café	
16.30 - 17.00	**Conferencia Invitada** Dra. Mª Teresa Galcerán (Universidad de Barcelona)	
17.00 - 18.00	**Asamblea del Grupo de especiación de la SEQA**	**Comunicaciones jóvenes investigadores SECyTA** **Premios José Antonio García Domínguez**
18.00 - 19.30	**Asamblea de la SEQA**	

JUEVES 2 DE OCTUBRE		
HORA	**SALA 4.1**	**SALA 4.2**
9.00 - 10.00	**Conferencia Plenaria** Dr. Salvatore Fanali (CNR, Roma)	
10.00 - 10.30	Café	
10.30 - 11.00	**Conferencia Invitada** Dr. Romá Tauler (IDAEA-CSIC)	
11.30 - 13.00	**Comunicaciones Orales 3:** Análisis medioambiental	**Comunicaciones Orales 4:** Desarrollos en instrumentación analítica; Nanotecnología; Otros campos de la química analítica y del análisis instrumental
13.00 - 14.00	Almuerzo de trabajo (Anexo Hall 4/6)	
14.00 - 15.00	**PÓSTERS. SESIÓN 2** (Pabellón 2) Sesiones: Análisis medioambiental; Desarrollos en instrumentación analítica; Otros campos de la química analítica y el análisis instrumental; Nuevos desarrollos en preparación de muestras; Contribuciones teóricas y Quimiometría	
15.00 - 16.00	**Conferencia Plenaria** Dr. Eugeny Katz (Clarkson University, USA)	
16.00 - 16:30	Café	
16.30 - 17.30	**Comunicaciones jóvenes investigadores SECyTA** **Premios José Antonio García Domínguez**	**Discusión Posters SEQA**
17.30 - 19.00	**Asamblea de la SECyTA**	**El Arte de Presentar**
21.00 - 24.00	**Cena en Hotel Avenida Palace** (Barcelona)	

VIERNES, 3 DE OCTUBRE		
HORA	**SALA 4.1**	**SALA 4.2**
9.30 - 10.30	**Comunicaciones Orales 5:** Contribuciones teóricas y Quimiometría; Nuevos desarrollos en preparación de muestra; Análisis Clínico	**Comunicaciones Orales 6:** Especiación Química
10.30 - 11.30	**Conferencia Plenaria** Dr. Peter Schoenmakers (Universidad de Amsterdam)	
11.30 - 12.00	Café	
12.00 - 12.30	**Conferencia Invitada** Dra. María del Mar Puyol (Universidad de Barcelona)	
12.30 - 13.00	Recogida de Pósters (Pabellón 2)	
13.00 - 14.00	Almuerzo de trabajo (Anexo Hall 4/6)	
14.00 - 14.30	**Conferencia Invitada** Dra. Pilar Bermejo (Universidad de Santiago de Compostela)	
14.30 - 15.30	**Comunicaciones Orales 7:** Automatización y miniaturización en análisis químico; Análisis de procesos y productos industriales	
15.30 - 16.00	Café	
16.00 - 17.00	**Clausura y entrega de premios**	

CARTA DE BIENVENIDA

En nombre del comité organizador de las 14as JORNADAS DE ANÁLISIS INSTRUMENTAL (JAI) tengo el placer de daros la más calurosa bienvenida a todos los asistentes a este evento. Esta edición, organizada por la Sociedad Española de Cromatografía y Técnicas Afines (SECyTA) en colaboración con la Sociedad Española de Química Analítica (SEQA), y con el apoyo de la Sociedad de Espectroscopia Aplicada (SEA), la Sociedad Española de Espectrometría de Masas (SEEM) y la Sociedad Española de Proteómica (SEProt), ofrece una oportunidad única para conocer los avances, retos y fronteras de las últimas investigaciones en el campo de la Química Analítica y el Análisis Instrumental, tanto desde el punto de vista de la investigación fundamental como aplicada a la resolución de los problemas que la sociedad demanda.

En esta edición vamos a contar con diez conferenciantes invitados, todos ellos procedentes de centros de investigación de reconocido prestigio internacional, que nos presentarán los aspectos más novedosos de las técnicas y el análisis instrumental en diferentes campos de aplicación. El programa ofrece un número importante de comunicaciones científicas, tanto orales como pósters que configuran un programa científico atractivo, competitivo y sugerente, que hacen de las JAI, una edición más, un punto de encuentro imprescindible para todos los profesionales implicados en este sector.

Durante el desarrollo de las jornadas se presentarán los últimos avances en miniaturización, automatización, acoplamientos on-line, tratamiento de muestra, etc. y sus aplicaciones a diversas áreas de conocimiento, como medio ambiente, alimentos, fármacos y sistemas biológicos. El hecho de que las JAI tengan lugar en el marco de Expoquimia permitirá crear un foro de discusión entre todos los profesionales del sector, tanto industrial como académico, que revertirá en beneficio de todos.

La organización de un evento de estas características es siempre complicada, por ello quiero agradecer al resto de las Sociedades implicadas en la organización su inestimable contribución y apoyo en todo momento, especialmente a la SEQA. También quiero agradecer a Expoquimia y a la secretaría técnica de las jornadas su asistencia y disponibilidad en todo momento.

Finalmente, quiero desearos a todos los que asistís en Barcelona a estas jornadas una estancia agradable y científicamente provechosa.

María José GONZÁLEZ
Presidenta del comité organizador de las JAI 2014

COMITÉS

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CONFERENCIAS PLENARIAS

CP-01

AMBIENT MASS SPECTROMETRY: THE WHOLE WORLD IN YOUR HANDS

Marcos N. Eberlin
University of Campinas – UNICAMP, Brazil

Mass spectrometry is generally viewed as a highly complex and demanding technique, full of troubles and worries; hence, ease or simplicity are hardly found in use as attributes of MS. People sometimes also think that samples should be pure and volatile, and demanding sample preparation protocols may be required to acquire a useful mass spectrum. But this is no longer the best scenario for MS since a series of contemporary revolutions have moved MS out from “the hell of complexity” to “the heavens of simplicity”, making MS easier and simplier than ever. The ultimate goal of MS – to bring MS to the “real world” open atmosphere environment – allowing everyone to perform fast, selective and highly sensitive chemical and biochemical analyzes with great ease and simplicity avoiding pre-separation and sample work-up for samples at their natural environment and primary location – at wherever “easy MS” is needed and by whoever needs it – is therefore now fully feasible. Without compromising its unique combination of high speed, selectivity, sensibility and separation competences, simplicity has become a new attribute - the 5th S of MS! In this lecture the main actors and acts of this revolution will be presented, and examples from many different applications, focused EASI-MS, will demonstrate that indeed, MS can currently put the whole world in your hands for fast, precise, accurate, and simple analysis at the molecular level.

CP-02

ANALYTICS FASTER THAN A SNAKE'S ATTACK

Jeroen Kool
VU University, Section of BioAnalytical Chemistry, Group of BioMolecular Analysis, Amsterdam, The Netherlands

For profiling of complex bioactive mixtures, different integrated bioaffinity screening approaches are pursued. This presentation focuses on on-line screening technologies and high resolution nanofractionation approaches.

On-line systems combine separation sciences, mass spectrometry and biochemical methodologies in single integrated platforms. The basic idea is the post-column infusion of eluting compounds to an on-line bioassay with a short incubation time. The on-line bioassay is operated by continuous infusion of target enzyme or receptor, substrate or tracer ligand, and eluting compounds from LC, into a continuous flow reaction chamber. Detection usually takes place with a fluorescence detector and hence most assay formats are fluorescence based. Via a post-column split, MS data is collected. This enables parallel bioaffinity data and MS data to be collected for accurate bioactivity to identity peak shape correlation.

Cone snail and snake venom proteomes are a rich source of peptides with high affinity for several voltage– and ligand-gated ion channels, including the nicotinic acetylcholine receptors (nAChRs). As these receptors comprise drug targets for Alzheimer, Parkinson and pain syndromes, peptide toxins have therapeutic potential for biopharmaceutical purposes. Natural samples are traditionally screened for ligands ‘off-line’ by collecting liquid chromatographic (LC) fractions in a well-plate, followed by a bioassay. This is a very elaborate, time consuming and costly process. Instead of fractionating the separated compounds, on-line screening provides a good alternative for some types of assay formats. As many venom samples are only available in low amounts, such as those from cone snails, spiders and scorpions, we developed a microfluidics on-line bio-analysis methodology that uses only minute sample amounts. The methodology was able to directly pinpoint bioactive compounds in venom proteomes, even when these toxin proteins were poorly separated. Again, simultaneous identity analysis of the bioactives was obtained by parallel MS. Our screening campaign towards bioactives in venom proteomes, especially neurotoxic venoms, will be elaborated on towards full identification of bioactive toxin peptides from cone snails and snakes.

In many cases, when on-line analysis is less suitable, nanofractionation strategies are a good alternative. This methodology is based on chromatographic separation of mixtures coupled to high-resolution fractionation onto (multiple) microtiter well plates (96 to 1536 well plates) for post-column assaying. The nanofractionation strategy allows assaying of any micro plate based assay of choice. We demonstrated the concept for several enzymatic assays as well as (functional) cell-based and membrane receptor binding assays. Snake venoms also comprise potential biopharmaceutical candidates for cardiovascular diseases (mainly from heamotoxic snakes such as vipers and rattlesnakes). Angiotensin converting enzyme, Factor 10a and Thrombin are important drug targets in cardiovascular drug discovery. We screened over 50 snakes for inhibitors of these three drug targets. At the moment we are finishing this screening campaign from which we identified several venom toxins targeting either thrombin, Factor 10a or the angiotensin converting enzyme. Currently, we are elucidating the structures of these toxins, that might be interesting biopharmaceutical candidates. After this analytical work flow, a molecular biologist will be able to take the DNA coding for a bioactive protein, place it in an expression system of choice, and then over-express this protein for further biological studies.

CP-03

NANO-LIQUID CHROMATOGRAPHY APPLIED TO FOOD ANALYSIS

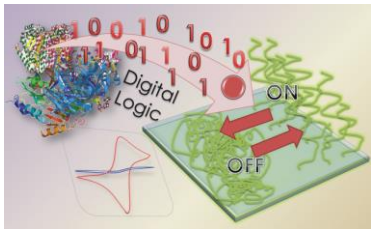
Salvatore Fanali
Institute of Chemical Methodologies, Italian National Council of Research,
Rome, Italy

Nano-liquid chromatography (nano-LC) is a recent developed miniaturized technique with great potentiality, especially for analytical purposes. It is currently used in various application fields. Agrochemical, biomedical, pharmaceutical, environmental, proteomic and food, are the most important. Analytes separation is performed into capillary columns of small I.D. (<100 □m) containing the stationary phase (SP). The SP can be formed by either packed particles or polymers (monolithic) or wall coated material. The limited capillary I.D. offers higher efficiency and higher sensitivity than HPLC mainly due to the decreased chromatographic dilution. This is a great advantage of nano-LC because also the mobile phase flow is reduced to nL/min offering better performances in coupling the separation system with a mass spectrometer (MS). On the other hand, such low flow rate presents some drawbacks, e.g., requires dedicated instrumentation and high skills of operators. The instrumentation must be carefully controlled taking in mind the reduction of band broadening and void volumes. Therefore connecting tubes, pump type, injection, detector etc. have to be properly selected. Concerning the sensitivity, it is true that this is higher than the one observed in conventional LC, however, considering the low injected sample volumes (few nL) often the analysis of complex matrices is difficult. As a result sample treatment or pre-concentration steps must be considered (e.g., on-column focusing, two dimensional separation, trap columns can be useful). Aim of this communication is the presentation of the features of nano-LC and its potentiality in the field of separation science. Instrumentation used, preparation of capillary columns packed with silica-based particles (porous and non-porous), selection of mobile phases will also be illustrated. Finally several examples documenting the applicability of this technique to the analysis of compounds of great interest in food chemistry (wine analysis, phytosterols in olive oil, amino-acid enantiomers in juices etc.) will be discussed.

CP – 04

BIOELECTRONICS: FROM NOVEL CONCEPTS TO PRACTICAL APPLICATIONS -TOWARDS SMART BIOSENSORS AND IMPLANTABLE DEVICES

Evgeny Katz
Department of Chemistry and Biomolecular Science, Clarkson University, Potsdam NY USA



The talk will outline the conceptual foundations of the novel approach to biosensing and bioactuating based on multi-step processing of biochemical signals through biocatalytic/biorecognition processes, adapting ideas recently developed in the field of bioelectronics and biocomputing (biomolecular logic).

Biomolecular computing is an emerging field of unconventional computing that attempts to process information with biomolecules and biological objects using digital logic. Enzymatic systems which involve biocatalytic reactions utilized for information processing will be exemplified. Extensive ongoing research in biocomputing, mimicking Boolean logic gates has been motivated by potential applications in biotechnology and medicine. Furthermore, novel sensor concepts have been contemplated with multiple inputs processed biochemically before the final output is coupled to transducing “smart-material” electrodes and other systems. These applications have warranted recent emphasis on *networking* of biocomputing gates. First few-gate networks have been experimentally realized, including coupling, for instance, to signal-responsive electrodes for signal readout. In order to achieve scalable, stable network design and functioning, considerations of noise propagation and control have been initiated as a new research direction. Optimization of single enzyme-based gates for avoiding analog noise amplification has been explored, as were certain network-optimization concepts. We review and exemplify these developments, as well as offer an outlook for possible future research foci. The latter include design and uses of non-Boolean network elements, e.g., filters, as well as other developments motivated by potential novel sensor and biotechnology applications.

Recent advances in biomedical applications of enzyme-based logic systems, particularly for the analysis of pathophysiological conditions associated with various injuries will be briefly reviewed. Novel biosensors digitally processing multiple biomarker signals produce a final output in the form of YES/NO response through Boolean logic networks composed of biomolecular systems. The Biocomputing approach applied to biosensors leads to a high-fidelity biosensing compared to traditional single-analyte sensing devices. By processing complex patterns of multiple physiological biomarkers, such multi-signal digital biosensors should have a profound impact on the rapid diagnosis and treatment of diseases, and particularly can provide timely detection and alert of medical emergencies (along with immediate therapeutic intervention). The novel

biosensing concept has been exemplified with the systems for logic analysis of various injuries, including soft tissue injury, traumatic brain injury, liver injury, abdominal trauma, hemorrhagic shock and oxidative stress.

Other developments in the general area of bioelectronics include novel biofuel cells operating *in vivo*. The first fully implanted biofuel cell continuously operating in a snail and producing electrical power over long period of time using physiologically produced glucose as a fuel will be discussed. The “electrified” snail, being a biotechnological living “device” was able to regenerate glucose consumed by biocatalytic electrodes, upon appropriate feeding and relaxing, and then produce a new “portion” of electrical energy. The snail with the implanted biofuel cell will be able to operate in a natural environment producing sustainable electrical micropower for activating various implantable bioelectronic devices.

Overall, integration of bioelectronics, biocomputing, materials science, and bionanotechnology resulted in the novel “smart” bioelectronic systems for medical, environmental and homeland security applications. The recent advances in this rapidly developing research area will be discussed.

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CP - 05

DEVELOPING AND APPLYING SUCCESSFUL COMPREHENSIVE TWO-DIMENSIONAL LIQUID CHROMATOGRAPHY (LC×LC) METHODS

Peter Schoenmakers, Petra Aarnoutse, Anna Baglai, Michelle Camenzuli, Henrik Cornelisson van de Ven, Andrea Gargano, Bob Pirok and Gabriel Vivó Truyols
University of Amsterdam, Faculty of Science, Amsterdam, The Netherlands

Introduction to LC×LC

Comprehensive two-dimensional gas chromatography (GC×GC) is a highly successful and largely mature analytical technique that has secured an undisputed position in several application fields. Comprehensive two-dimensional liquid chromatography (LC×LC) is still used rather sporadically and the technique may be considered relatively immature. In this presentation a case will be made for the proliferation of LC×LC and concepts and strategies will be provided to help analytical scientists with the successful implementation.

LC×LC is arguably much more useful than its GC counterpart. Only a small fraction of all known chemicals are sufficiently volatile and stable to render them compatible with GC. LC is more suitable for very polar molecules (*e.g.* carbohydrates, peptides), as well as for large molecules (*e.g.* polymers, proteins). Many complex non-volatile samples are encountered in, for example, life science, food analysis and the chemical industry. One-dimensional LC analysis are less efficient than one-dimensional GC analysis, which suggests a greater need for LC×LC. Finally, detection is always an issue in LC. In LC×LC sample may be diluted more during the separation than in one-dimensional LC, unless focussing can be achieved between the two separation stages (*e.g.* at the inlet of the second-dimension column). LC-MS is not as easy and robust as GC-MS. Again, in significant role can be envisaged for LC×LC.

Performing LC×LC in practice is only slightly more difficult than performing one-dimensional LC separations. Two mobile-phase delivery systems are needed instead of one, two columns are needed and some interface between the two dimensions. The latter usually consists of one or two switching valves, for example a 2-position, 10-port valve as illustrated in Fig.1. In the first position (left) Loop 1 is being loaded with a fraction of the effluent of the first column, while the fraction contained in Loop 2 is separated on the second-dimension column and subsequently detected. By switching the valve (right) this situation is reversed. Provided that the two loops are significantly larger than the volume of the fractions of the first-dimension effluent that need to be collected, all of the sample can be fractionated and analysed in two dimensions. Controlling the system is relatively straightforward, even if gradient elution is allowed in both dimensions. Collecting and analysing the data is somewhat more complicated, but it is not more difficult than in GC×GC. Fully controlled and reliable LC×LC are now becoming commercially available. Thus, there appear to be few obstacles to the rapid proliferation of LC×LC.

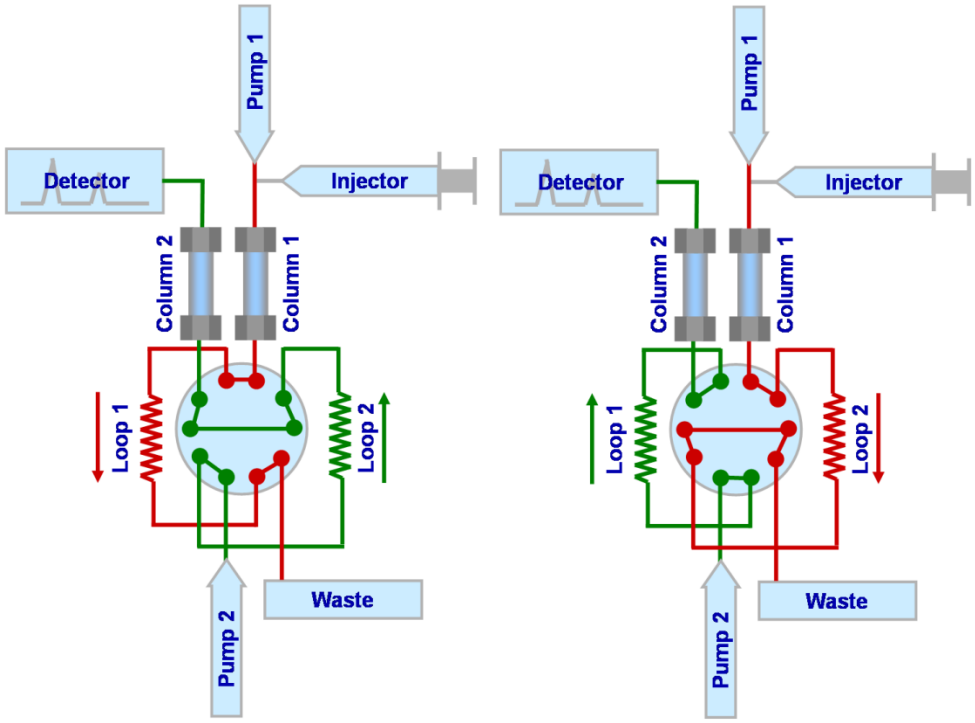

Figure 1: LC×LC system with two mobile-phase delivery systems (Pump 1 and Pump 2), two columns and a 2-position 10-port valve, shown in both positions [i].

Developing LC×LC methods

The one really demanding aspect of LC×LC is the development of successful methods. If this is not done correctly LC×LC may result in a "comprehensive waste of time" rather than in a comprehensive characterization of complex samples.

To develop LC×LC systems the analyst needs to be able to select and understand not one, but two good one-dimensional LC methods from his or her repertoire. Ideally, these methods should exhibit completely different ("orthogonal") selectivities for the (relevant analytes in the) sample. If the main structural parameters of the sample ("sample dimensions") [ii] can be matched with the chromatographic selectivities structural chromatogram may be obtained that allow rigorous interpretation and quantitation.

The physical parameters of the two separation stages need to be carefully optimized [iii,iv]. These include the column dimensions (lengths and diameters), particle sizes and flow rates. Also the modulation time (second-dimension analysis time) and first-dimension analysis time must be optimized in this process. The optimization needs to be performed such that losses in resolution (peak capacity) due to first-dimension "undersampling", second-dimension band broadening and incompatibility of the first-dimension effluent with the second-dimension system are minimized.
Finally, the chromatographic conditions in both dimensions should be optimized as a function of time. Gradient elution is often used in both dimensions and the gradient program (initial and final compositions, duration of the gradient) may be chosen differently for each second-dimension run. While the optimization of the physical parameters can be performed independently of the sample to be analysed, the selection of the separation dimensions and the optimization of the gradient programs is highly sample dependent. Thus, a new optimization will need to be performed for each new type of sample.

Because method development is the most-difficult aspect of LC×LC we are developing efficient, user friendly strategies and software to help analysts implement the technique successfully.

Applications of LC×LC
In Amsterdam we have been specifically successful in applying LC×LC for the separation and characterization of polymers [i]. Samples of synthetic polymers have a relatively low sample dimensionality, allowing structured chromatograms to be obtained. In addition, LC-MS techniques are often of limited use, emphasizing the need for LC×LC. Selected applications from this and other fields will be used to illustrate the presentation.

i P.J. Schoenmakers and P.J. Aarnoutse, *Anal.Chem.* **86** (2014) 6172-6179.
ii J.C. Giddings, *J.Chromatogr.A* **703** (1995) 3-15.
iii P. . Schoenmakers, . iv -Truyols and W.M.C. Decrop, *J.Chromatogr.A* **1120** (2006) 282-290.
iv G. Vivó-Truyols, Sj. van der Wal and P.J. Schoenmakers, *Anal.Chem.* **82** (20) (2010) 8525-8536.

CONFERENCIAS INVITADAS

CI-01

NANOMATERIALS IN DIAGNOSTICS AND SENSOREMOVAL APPLICATIONS

Arben Merkoçi
ICREA & Catalan Institute of Nanoscience and Nanotechnology (ICN2), Bellaterra (Barcelona), Catalonia, Spain

Nanomaterials (NM) with electrical and optical properties are playing a key role in the design of cutting edge biosensing technologies. Electrocatalytic, plasmonic and quantic properties of NMs such as gold nanoparticles, quantum dots or graphene while operating in simple plastic or paper matrix in diagnostic and safety/security applications will be shown. The effect of the platform architecture and other chemical and physical parameters upon biosensing and actuation including nano/micromotors pick-up or mixing operations will be discussed. The developed smart nanobiosystems are with interest for integration of diagnostic with therapies (nanotheranostics) or sensing and destruction/removal (sensoremoval) for health and environment industries. Examples related to protein (ex. neurodegenerative disease biomarkers), DNA (pathogen related) or cells (cancer cells) with interest for point of care applications will be shown. The developed devices and strategies are intended to be of low cost while offering high analytical performance in screening scenarios beside other applications.

References:

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2. Adaris M. Lopez_Marzo, Josefina Pons, Diane A. Blake, Arben Merkoçi, “All-Integrated and Highly Sensitive Paper Based Device with Sample Treatment Platform for Cd2+ Immunodetection in Drinking/Tap Waters”, Anal. Chem., 2013, 85 (7), pp 3532–3538
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7. Eden Morales-Narváez, Maria Guix, Mariana Medina-Sánchez, Carmen C. Mayorga-Martinez, Arben Merkoçi, “Micromotor Enhanced Microarray Technology for Protein Detection”, Small 2014, In print.

CI-02

ANALYTICAL CHALLENGES AND NEW TRENDS IN LC-MS

María Teresa Galceran.
Department of Analytical Chemistry, University of Barcelona

When atmospheric pressure ionization (API) mass spectrometry coupled to liquid chromatography (LC-MS) was first introduced in the 1980's, it solved a great deal of analytical problems in industrial, academic and governmental laboratories. LC-MS showed high capabilities to analyse compounds that were not amenable by gas chromatography-mass spectrometry due to their high mass or high polarity. The technique was considered to require minimal sample treatment, to provide high sensitivity and selectivity, to increase identification guaranties and to enable high throughput analysis. All these considerations explain the rapid introduction of LC-MS instruments in analytical laboratories all around the world. Moreover, the significant progress made in mass spectrometry in ionisation sources, mass analysers and in ion-optics design that resulted in much improved analyte detectability and in robust, user friendly and fast instruments, have led LC-MS to be considered as the gold standard in numerous fields, such as biological, pharmaceutical, environmental and food analysis.

However, in recent years LC-MS users have realized that some traditional challenges still exist. Poor ionization, difficulties in selecting ion transitions and in analyte confirmation when using tandem MS in multiple reaction monitoring (MRM), false negative/positive findings and incorrect quantification are examples of frequent problems. Moreover, LC-MS is susceptible of interferences from the matrix that may affect the analysis mainly when trace analytes are measured in complex matrices such as environmental or food. To solve these problems several strategies related to MS ionization sources and analysers can be employed. In this presentation some examples of using ionization sources different from electrospray (ESI) and the advantages of high resolution analysers are going to be discussed. In addition, some new trends will be commented.

Among the ionization sources, ESI is that most commonly used in LC-MS because of its wide range of applicability and easy of ionisation. However, for some compounds ESI does not provide enough ionization, moreover this technique is prone to ion suppression produced by ionic species or highly polar compounds present in the sample or in the mobile phase. Examples related of these problems found in the analysis of different compounds such as veterinary drugs, pharmaceuticals and emerging contaminants will be shown and the advantage of utilising other ionization sources, such as Atmospheric Pressure Chemical Ionization (APCI) or Atmospheric Pressure Photoionization (APPI) will be discussed.

In LC-MS analysis, parameters affecting the mass spectra such as the resolving power and mass accuracy of the MS analyser and also the type of mass spectrometry experiments performed, are important as regards the results obtained. In this context, the advantage of using multiple stage mass spectrometry (MS^n) in an ion trap for the establishment of fragmentation pathways will be commented. Moreover, the advantage of using accurate mass measurements will be illustrated by the determination of elemental compositions and characterization of fragments obtained in MS/MS experiments. Examples of the correct assignment of product ions obtained in the fragmentation of several compounds will be commented.

An additional problem that will be addressed in this presentation is the formation of adducts in MS/MS. Gas phase reactions can occur between charged and neutral species inside the mass analyser yielding product ions with mass-to-charge ratios (*m/z*) difficult to explain by logical losses, which complicated MS/MS spectra interpretation. Possible causes for these adducts might be the interaction of the product ions generated by collision-induced-dissociation (CID) with neutral molecules arising from the mobile phase (water, methanol or acetonitrile), and/or from the atmospheric water adsorbed on some parts of the instrument. Examples showing the influence of instrument configuration, mobile phase composition and purity of CID gas will be presented.

It is worth to mention that instruments allowing working at high mass resolution improved both selectivity and sensitivity. The benefit of increasing resolving power will be illustrated with examples on the elucidation of the structure of unknown compounds. For instance, both Full MS scan at high resolution (70,000 full width half maximum (FWHM) at m/z 200) and data-dependent scan operating in All Ion Fragmentation (AIF) has been used for the identification of some pentaclorophenol (PCP) degradation products produced during fungal cultivation in soils contaminated by PCP.

Recent developments of ionization techniques termed “direct ionization” or “ambient ionization” have burst into the LC-MS world simplifying and increasing the speed of MS analysis, thanks to the possibility of performing the analysis in an open atmosphere directly on samples avoiding or highly reducing sample preparation steps (solid-phase or liquid-liquid extraction, preconcentration, off-line derivatization) and eliminating LC separation. Among the myriad of ambient MS techniques the two more frequently used are desorption electrospray ionization (DESI), based on the ionization of the compounds desorbed from the surface by a jet of charged liquid droplets, and direct analysis in real time (DART) that used a plasma as source of reactive species to induce ionization. However, due to the complexity of the samples and limitations of the instrumentation available, direct analysis remains a challenging task. Advantages of using high resolution MS with these ionization techniques to reduce matrix interferences will be discussed and some examples of application to the analysis of a wide range of compounds and samples will be shown.

Acknowledgments:
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CI-03

DESARROLLO Y APLICACIÓN DE MÉTODOS QUIMIOMÉTRICOS PARA EL ANÁLISIS DE DATOS ÓMICOS AMBIENTALES

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Se propone el desarrollo de nuevos métodos quimiométricos para el análisis de datos obtenidos con técnicas analíticas ómicas con la finalidad de poder evaluar los efectos del cambio global (en el medio ambiente y en el clima) sobre sistemas biológicos elegidos como representativos de los ecosistemas acuáticos Se presenta la combinación de la aplicación de los métodos quimiométricos con las metodologías analíticas de alto rendimiento y con las pruebas toxicológicas que permitan examinar los efectos de posibles contaminantes ambientales y de los efectos de parámetros físicos como la temperatura sobre los perfiles genómicos y metabonómicos de sistemas biológicos específicos. La magnitud y enorme complejidad de los datos experimentales producidos por las técnicas analíticas ómicas de alto rendimiento, como son las micromatrices de DNA, la espectrometría de masas acoplada con la cromatografía de gases o líquida o la espectroscopia de resonancia magnética mono- y multidimensional, requieren herramientas de análisis de datos potentes que permitan extraer, resumir, integrar e interpretar la gran cantidad de información contenida en estos conjuntos de datos megavariates y extraer conocimiento sobre los efectos estudiados . Hay una necesidad urgente de mejora, difusión y automatización de cada paso en el análisis de los datos generados en los estudios de genómica y de metabonomica utilizando las nuevas herramientas quimiométricas. En la presentación se mostraran algunos resultados obtenidos en el análisis quimiométrico de datos genómicos con micromatrices de DNA y de datos metabonómicos con LC-MS, CG-MS o RMN sobre diferentes tipos de muestras y organismos biológicos.

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CI - 04

MINIATURIZED ANALYTICAL SYSTEMS: SIMPLIFICATION AND IMPROVEMENT OF CONVENTIONAL ANALYTICAL INSTRUMENTATION

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Scientists working on analytical chemistry face an important challenge of developing and validating new analytical methods trying to operate at the extreme edges of analysis to obtain meaningful real time and in-situ information from smaller or more complex samples, and of species present at lower concentrations. Besides, there is a current trend towards employing more user friendly instrumentation in some research fields as the development of drugs, biotechnology, medicine and environmental monitoring, because their evolution depends on the obtained information from the chemical analysis. In this context, a significant part of analytical chemists focus their research on trying to avoid the use of large laboratories (centralized and remote) and sophisticated and expensive instruments to conversely develop systems closer to user. This clearly implies the simplification of the analytical procedure, reducing sample and reagents consumption and minimizing manual intervention.

Our research group has a wide experience on developing Total Analysis Systems, aimed to make more efficient the environmental management with the goal of protecting natural resources. These systems grant optimized results but are not portable, what encouraged us to focus on instrumentation miniaturization and the development of the so called Micrototal Analysis Systems or Lab-on-a-chip. They are miniaturized systems designed to perform all the steps of the analytical procedure (sampling, sample transport, sample pre-treatment, separation, detection and data analysis) in order to automatically obtain chemical information. Miniaturization obviously offers some advantages as portability, autonomy, costs saving, greener chemistry, improvement of the process operation, access to new effects due to scaling down and the possibility of performing in-situ measurements or 'point-of-care' diagnostics. However, more difficulties are expected from the ideal concept of a μTAS to their implementation. This begins with more technological aspects like difficulties to standardize designs and processes, problems with the integration of different operations in one device, which is neither obvious nor an easy task and difficulties to connect devices to the real macro word. On the other hand, one run into more fundamental issues as phenomena or negligible effects on the macroscopic level become important to micrometer scale and *vice versa* and also, and as the reduction in size takes the conventional analytical techniques to the limit and also reduces the practical operability of the microsystems in the real world.

The present talk is addressed to show some of the approaches developed in our research group regarding the design, fabrication and application of μTAS in different fields such as quality control processing in industry, environmental monitoring and manned space flights.

14as JORNADAS DE ANÁLISIS INSTRUMENTAL
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SECYTA SEQA Sociedad Española de Química Analítica
JAI

CI - 05

METAL-PROTEIN COMPLEXES SPECIATION IN THE MARINE ENVIRONMENT

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The importance of marine dissolved organic matter (DOM) and particulate organic matter (POM) derives from their essential participation in the global carbon cycle. Nevertheless it is also important because the bioavailable fraction of DOM/POM, due to its chelation properties, influences the marine microbial loop as well as controls metal toxicity and metal bioavailability. Improvements in analytical instruments have allowed the characterization of marine DOM/POM and have shown important differences in surface and deep seawater. DOM found in surface seawater consists of biochemically active substances released by zooplankton and phytoplankton grazing, microbial exudation and cellular lysis. So that, it comprises a very labile DOM fraction with a high turnover rate. These reactive substances, mainly proteins, are the key factors in the direct effect of DOM in the global carbon cycle, and they provide the clues for a long-term preservation ocean's carbon and nitrogen. POM encompasses marine zooplankton and phytoplankton, which are seawater's source of dissolved proteins, and which also play other several roles in the marine ecosystem such as the atmospheric CO_2 fixation in the surface ocean to produce organic carbon via photosynthesis.

DOM and POM in deep and surface seawater occur at very low concentrations while inorganic salts are present at very high levels. To solve these problems, analytical techniques able to detect and quantify many different compounds in difficult matrices are necessary. Most of the current analytical techniques to assess/characterize DOM/POM require the absence of the matrix concomitants so pre–concentration/separation methods are needed. Several methods based on tangential flow ultrafiltration usage and centrifugal ultrafiltration techniques have been developed for pre-concentrating dissolved large molecules. They have been proposed for isolating protein and also deoxyribonucleic acid (DNA) from seawater and interstitial water (pore water). Similarly, different sample pre-treatments have been optimised for isolating proteins and DNA from marine plankton.

Proteins, (dissolved proteins from seawater and pore water, and also from plankton samples), have been first fractionated by offgel electrophoresis (proteins separation according with the isoelectric point, pI) and lab-on-chip (LOC) electrophoresis (second dimension) for achieving protein sizing. Several offgel electrophoretic conditions (denaturing and non-denaturing) were tested to prove the integrity of the isolated metal-protein complexes. Atomic spectrometric techniques such as electrothermal atomic absorption spectrometry (ETAAS), inductively coupled plasma – optical emission spectrometry (ICP-OES) and inductively coupled plasma – mass spectrometry (ICP-MS) have been used for assessing trace metals bound to dissolved/particulate proteins. In addition, isolated DNA (dissolved DNA and particulate DNA) has also been sized by LOC electrophoresis.

Methods based on conventional 2DE (SDS-PAGE) for protein fractionation have been also developed for comparative purposes (pI and molecular weight assessment of proteins), and for the assessment of metal-protein complexes using Laser Ablation (LA)-ICP-MS. On the other hand, to perform the protein identification, a conventional 2DE(SDS-PAGE) and Matrix-Assisted Laser Desorption/Ionization (MALDI) time-of-flight (TOF) mass spectrometry (MS) has been used for dissolved proteins and plankton proteins.

COMUNICACIONES ORALES

AAL

Análisis de alimentos

AAL-OC01

EVALUATION OF AVOCADO COMPOSITION CHANGES OVER THE DEVELOPMENT AND MATURATION BY OMICS TOOLS: A LONGITUDINAL STUDY

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To determine the specific and adequate avocado picking time is a very difficult task, since physiological maturation is not reflected on changes in external appearance. Moreover, there are growing evidences nowadays about the positive effect that some avocado metabolites have on human health; thus, being aware about how the ripening process affects their concentration, could help to assure the optimum time to harvest the fruits maximizing the benefits.

Herewith, a very complete longitudinal study where the metabolic evolution of 4 avocado varieties ('Hass', 'Reed', 'Bacon' and 'Fuerte') collected at different periods over their harvest season is presented (a total of 172 samples were studied, having approx. 40 of each variety belonging to 8-10 time points over the season). Longitudinal studies considering multiple sampling over time are very interesting, since can overcome possible negative effects of the intrinsic variability of the metabolome of any biological system on the data interpretation. The current study is quite unique, not only for the sampling design, but also for the kinds of analytical and statistical tools used.

The avocado extracts were analyzedby a powerful reverse phase-HPLC-DAD/FL/ESI-IT MS method (Zorbax C_{18} analytical column (4.4x150mm, 1.8 µm particle size)) able to detect around 200 compounds within a single run (30 min). The raw chromatograms were pre-processed (baseline correction, normalization, peak alignment, etc.) and analyzed by using different statistical tools; this kind of data treatment could allow achieving a very complete picture of the fundamental biochemistry of the avocado fruit, facilitating the understanding of the pathways responsible for the biosynthesis of nutritionally relevant metabolites. Apart from this exploratory analysis, a targeted approach was also used for studying the chromatograms, carrying out the quantification of 4 relevant metabolites (*p*-coumaric, pantothenic and abscisic acids, and epicatechin) in terms of their own commercially available pure standards. The concentration of these metabolites was, in general, decreasing over the season, except for *p*-coumaric acid, which showed the opposite trend.

AAL-OC02

TETRODOTOXINS IN MEDITERRANEAN PUFFERFISHES BY HYDROPHILIC INTERACTION LIQUID CHROMATOGRAPHY−MASS SPECTROMETRY

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A high-performance liquid chromatography (LC) coupled with tandem mass spectrometric detection (-MS/MS) via an electrospray ion source has been developed for the determination of tetrodotoxins (TTXs) in puffer fish samples (family Tetrodontidae). Separation was based upon hydrophilic interaction chromatography (HILIC) on an XBridge Amide column (2.1mm × 100 mm, 3,5 µm particle size) and mobile phases consisted in 30 mM ammonium acetate at pH 5.8 and acetonitrile/30 mM ammonium acetate (90:10), for mobile phases A and B, respectively. The gradient elution was optimized to improve chromatographic resolution among different TTX-analogs, by using positive control samples from the puffer fish species *Lagocephalus sceleratus* from Greece. As a result, a gradient elution from 100% B to 50% A was programmed, in a total run time cycle of 12 min including post-run equilibration.

Compound-dependent detection parameters were optimized by direct infusion of TTX standard to the mass spectrometer, among others, a declustering potential of 50 V and a collision energy of 29 and 53 V for the transitions precursor ion > product ion of *m/z* 320 > 302 and 320 > 162 quantification and confirmation, respectively. The electrospray ion source temperature was adjusted to 600ºC after LC coupling to maximize the ionization yield. The triple-quadrupole multi reaction monitoring (MRM) method allowed determination of 10 different tetrodotoxins in different tissue samples of puffer fish (skin, muscle, gonad, intestinal track, liver) including sub-samples obtained from a fish individual of the species *Sphoeroides pachygaster* caught at Palamós, in the coast of Catalonia, Spain (NW Mediterranean Sea). Preliminary results on method validation were obtained, showing good linearity in the range 25-1250 µg TTX/kg ($r^2 \geq 0.99$) and a very low limit of detection of 1 µg TTX/Kg. A preliminary assessment of the puffer fish found in Catalonia revealed a much lower toxicity compared to that found in the highly toxic *L. sceleratus*, the former showing TTX > 25 µg /Kg only the skin and at relatively low level of ca. 300 µg TTX/Kg. The set up and optimization of this method will contribute in the next future to perform the risk assessment of the invasion of these lessepsian migrants through the Mediterranean Sea.

Acknowledgements
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AAL-OC03

TUNING THE SELECTIVITY OF MOLECULARLY IMPRINTED POLYMERS FOR THE ANALYSIS OF ANTIMICROBIAL RESIDUES BY SPE-HPLC

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The evolution of food production systems from small farming units to large scale intensive production systems has been accompanied by an increasing administration of antimicrobials to food producing animals, to prevent and control the spread of infections in the farm. Fluoroquolone and beta-lactam antibiotics, especially penicillins and cephalosporins (CPs) are among the most used antimicrobials in veterinary practice and their analysis in such complex matrices is usually carried out by liquid chromatography after a solid phase extraction step (SPE) to achieve the required sensitivities. This work describes the preparation of novel molecularly imprinted polymers for their application as solid phase extraction sorbents (MISPE) for multi-residue analysis of beta-lactam and fluoroquinolone antimicrobials in food samples. The use of antimicrobial surrogate molecules has been evaluated for polymer synthesis to avoid target bleeding during MISPE. The polymers were prepared by a non-covalent imprinting approach in the form of monoliths, or as spherical micropaticles using sacrificial silica beads (40-75 µm) to further improve the packing efficiency of SPE cartridges. A combinatorial screening approach has been applied to select the optimal functional monomer and cross-linker formulation for the selected antimicrobial families. The rebinding capactity of the MIP/NIP libraries has been evaluated in batch mode assays by high-performance liquid chromatography (HPLC) with fluorescence (FLD) or diode array (DAD) detection. MISPE conditions (namely, loading, washing and elution solvents and flow rates) have been optimized in each case to allow multi-residue analysis of cephalosphorins, pencilinins or fluoroquinolone [1] antimicrobials in different food matrices. The methods have been validated according to European Union Decision 2002/657/EC in terms of linearity, accuracy, precision, selectivity, decision limit (CCa) and detection capability (CCb) by HPLC-FLD/DAD and HPLC-MS/MS.

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AAL-OC04

GC-MS/MS ALLOWS ONE STEP ANALYSIS OF GLYCOSYL-FLAVONOIDS AND FLAVONOIDS IN FRUIT SAMPLES BY IN-PORT DERIVATIZATION

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Flavonoids, as a class of diet-derived antioxidants, have recieved significant public attention due to their prevention against cancer, cardiovascular and age-related diseases [1]. The analysis of these compounds has usually been carried out with HPLC. However, there are several studies reporting GC analysis of flavonoid aglycones using sylilation to convert the analytes into volatiles, which overcome the main drawback of gas chromatography analysis[2].

In this work, the analysis of flavonoids has been extended to glycosyl-flavonoids, including anthocyanins, using a high temperature HT-1 (15 m x 0.32 mm; 0.10 µm) capillary column. Extraction of lyophilized fruit samples was carried out with methanolic mixtures assisted with ultrasounds. Then, samples were dried using a SpeedVac and the carbonyl groups of the analytes were protected with methoxilamine in pyridine. Afterwards, samples were analyzed by GC-MS/MS using a in-port drivatization procedure.

In-port derivatization presents some avantages versus convencional off-line derivatization. Indeed, in-port process increases speed and efficiency of the analysis performed [3]. This second derivatization step was optimized in terms of optimal MSTFA/sample ratio, injection port temperature and derivatization time. In that sense, the best derivatization efficiency was found to be at 2/1 ratio, 100 ºC and 1 min reaction, respectively. Furthermore, fragmentations of 11 commercial standards of flavonoids and glycosyl-flavonoids were investigated in order to carry out the quantitation of the analytes in real fruit samples of apple (*Malus domestica)* and peach *(Prunus persica)* by using MRM and liniar calibration curve.

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AAL-OC05

METABOLIMICS BY CE-MS. POTENCIAL OF A NEW POLYMER-COATED CAPILLARY

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Metabolomics is a valuable tool within the context of Systems Biology for investigating cellular responses and exploring the underlying mechanisms of external actions on metabolomic pathways. Currently MS-based approaches yield a higher sensitivity than NMR when analyzing minimal amounts of complex mixtures. The MS-based approaches most widely used in metabolomics are coupled to separation techniques due to the high complexity of biological matrices. In that context, capillary electrophoresis-mass spectrometry (CE-MS) has demonstrated to be a powerful technique for the analysis of polar and ionic metabolites in a variety of samples. High efficiencies, fast analysis times, low sample and reagent consumption are some advantages of CE over liquid- and gas chromatography. Up to date, the number of CE-MS applications involving the analysis of cationic metabolites using a low-pH BGE and detection in ESI-MS positive mode far exceeds the number of works related to the analysis of anionic metabolites. This is due to the fact that for the CE-MS analysis of anionic metabolites it is necessary to reverse CE polarity, and this is associated with current instability and long analysis times (more than 40 min.). In this work we propose a new polymer coating of the inner wall of the capillary to reverse the electroosmotic flow (EOF) and thereby avoiding CE instability problems and reducing analysis time. This coating is based on physical adsorption of the copolymer poly(TEDETAMA-co-dimethylacrylamide), where TEDETAMA is a methacrylic unit with a dendronic side chain derived of ligand TEDETA (N,N,N',N'-tetraethyldiethylenetriamine). The poly(TEDETAMA -co-dimethylacrylamide) interacts with the ionized silanol groups, giving rise to a cationic inner capillary surface with a reversed EOF. After CE-MS method optimization very good selectivity of a mixture of 17 standard anionic metabolites in less than 15 min was obtained. Good intra-day and inter-day repeatability for migration times: lower than 0.6% and 0.8% RSD, respectively, and for peak areas: lower than 13% and 14% RSD, respectively, were obtained. This method was successfully applied for anionic metabolite profiling of food matrices (wine and juice) and complex biological samples, such as plasma, urine, cell culture, feces fluid, mouse liver andcerebrospinal fluid.

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AAL-OC06

ULTRA-SENSITIVE DETECTION OF NON DIOXIN-LIKE PCBs AND PAHs IN BIVALVE MOLLUSCS

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A GC-MS/MS method has been developed for the analysis of PCBs and PAHs (including 16 EPA priority PAHs) in seafood samples on the Bruker SCION TM TQ triple quadrupole gas chromatography mass spectrometer. The outstanding sensitivity allows the detection of sub-ppb amounts with high confidence by injecting 1µL of sample. A wide linear calibration range was obtained from 0.5 to 100 ppb. Really good linearity was also achieved with r^2>0.99 and RSD of the response factor below 15%. Repeatability studies reported values around 4% for all compounds under study. This method fulfills all the sensitivity, selectivity and specificity requirements demanded in the European Union Regulations[1,2,3,4].

(1) Commission regulation EU No 252/2012. Laying down methods of sampling and analysis for the official control of levels of dioxins, dioxin like PCBs and non-dioxin-like PCBs in certain foodstuffs and repealing Regulation (EC) No 1883/2006.
(2) Commission regulation EU No 1259/2011 amending regulation (EC) No 1881/2006 as regards maximum levels for dioxins, dioxin-like PCBs and non dioxin-like PCBs in foodstuffs.
(3) Commission regulation (EU) No 835/2011 amending regulation (EC) No 1881/2006 as regards maximum levels for polycyclic aromatic hydrocarbons in foodstuffs.
(4) Commission regulation (EU) No 836/2011 amending regulation (EC) No 333/2007 laying down the methods of sampling and analysis for the official control of the level of lead, cadmium, mercury, inorganic tin, 3-MCPD and benzo(a)pyrene in foodstuffs.

AAL-OC07

COMPREHENSIVE TWO-DIMENSIONAL LIQUID CHROMATOGRAPHY TO CHARACTERIZE POLYPHENOLS FROM *SARGASSUM MUTICUM* BROWN ALGAE

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*Sargassum muticum*is a brown algae widely distributed along the European Atlantic coast. This species is well-known for possessing a special class of polyphenols that are typical from brown algae, phlorotannins. These compounds are complex polymers of phloroglucinol units that can be attached through different linkages and to a variety of degrees of polymerization, which brings about a greatly complex natural mixture. Moreover, they have been described to possess several important bioactivities including, most-notably, antioxidant activity. Due to the great similarity among components as well as to the high number of closely related different structures that can be naturally found, the analysis of these components is quite difficult. We have already developed an analytical strategy based on the use of comprehensive two-dimensional liquid chromatography (LC × LC) to separate and identify these complex components in algae [1]. In the present contribution, that method is further optimized and applied to the analysis of phlorotannins from different *Sargassum muticum* samples harvested at five different geographical locations from Portugal to Norway. An experimental design was applied to select the best extraction conditions (including extraction temperature and extraction solvent mixture) to obtain these components using pressurized liquid extraction. The attained extracts were characterized in terms of total phenols content, total phlorotannins amount and antioxidant activity. The obtained results show that environmental growing conditions significantly affect the chemical composition of the extracts obtained. Besides, LC × LC is demonstrated as a useful technique to obtain chemical patterns to compare among different samples.

[1] L. Montero, M. Herrero, E. Ibáñez, A. Cifuentes, *Electrophoresis* 2014 DOI: 10.1002/elps.201400133.

AAL-OC08

QUANTIFICATION OF AROMA COMPOUNDS IN FOOD MATRICES BY HS-SPME AND GC-O: COMPARISON OF TWO DIFFERENT AEDA APPROACHES

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One of the most important properties for consumers' acceptance or rejection of any foodstuff is its aroma which is caused by hundreds of different odorants. The only technique that allows identifying these aromatic compounds among the entire volatile fraction is the gas chromatography-olfactometry (GC-O), where the chromatographic response given by a traditional detector is combined with the human nose detection.

In this study, the *headspace solid-phase microextraction* (HS-SPME) has been the selected technique to obtain a representative aroma extract to be chromatographically analysed because of its easy and fast handling. However, when characterizing food aroma, identifying the odour-active compounds is not enough and it is necessary to determine their relative contribution to the whole aroma. *Aroma extract dilution analysis* (AEDA) is one of the techniques that allow this hierarchical classification by stepwise dilutions of the aroma extract. Nevertheless, since no physical extract is obtained when working with SPME, the aim of this study is to compare two different approaches to the AEDA: stepwise dilutions of the samples themselves before extraction (*a*) and successive shortening of the fibre length exposed to the undiluted samples (*b*).

Thus, 24 aromatic standards (alcohols, ketones, acids, esters, aldehydes, phenols, terpenes and lactones) at different concentration levels were added to three different matrices similar to the most common food ones: water, deodorized oil and a 14% (v/v) hydroalcoholic solution. The study showed that the aroma characterization results are very similar whatever the approach used and the matrix analyzed, although the oil one always presented higher response variability.
Regarding the repeatability and the reproducibility values, both are better when dealing with the (*b*) AEDA approach. However, it has to be noted that it can only provide a first hierarchical classification of the odorants as the stepwise shortening of the fibre length exposed is limited. When fully characterizing a food aroma, the (*a*) AEDA approach should be used.

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COMUNICACIONES ORALES

TOM

Técnicas -ómicas

TOM-OC01

SIMULTANEOUS CUANTIFICATION OF ACTIVE AND INACTIVE THIOREDOXIN REDUCTASE IN HUMAN SERUM BY HPLC-IDA-ICP-MS

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Thioredoxin Reductase 1 (TrxR1) is a cytosolic enzyme containing a selenenylsulfide/selenolthiol redox active site which catalyzes the reduction of disulfide containing substrates. Therefore, the enzyme plays a critical role in regulating cellular redox homeostasis and also signalling pathways which are involved in cell survival and proliferation. In fact, TrxR1 overexpression have been associated with enhanced tumour proliferation, decreased apoptosis, increased angiogenesis, increased resistance to chemotherapeutic drugs, and reduced survival [1]. Hence, accurate and sensitive measurement of the thioredoxin level in biological fluids, cells and tissues is of paramount importance in the field of anticancer research studies.

Most analytical methods for TrxR1 determination are based on immunoassays using polyclonal antibodies or relative activity measurements using spectrophotometric assays, which are not specific for TrxR1 [2]. Here we propose the absolute quantification of this protein through the measurement of the Se present in their structure using isotope dilution-ICP-MS after anion exchange HPLC separation. Moreover, the determination of the active form of the enzyme was also conducted by using auranofin as an activity-based probe. This compound reacts with the selenolthiol group of the active enzyme. Once optimized this reaction, the derivatized active form of the enzyme was quantified by HPLC with ICP-MS detection of both Au and Se.

This method was applied to the determination of the enzyme in human serum samples after a first chromatographic step using affinity columns to remove the interferences due to other selenocompounds present in the sample [3].

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TOM-OC02

QUANTITATIVE PROTEOMICS FOR EVALUATING THE POTENTIAL TOXICITY OF CdSe/ZnS QUANTUM DOTS

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Due to their particular optical properties, quantum dots (QDs) are currently used in biological, biochemical and biomedical applications for labeling cellular structures, drug delivery and even in magnetic resonance imaging (MRI) and positron emission tomography (PET). Although the benefits of QDs are clear, their increasing commercialization and massive used could make these nanoparticles a potential emergent contaminants in a near future. Many *in-vitro* and *in-vivo* studies have been made to evaluate the potential toxicity of QDs, nevertheless there is still some controversy.

In the present work, we have used human hepatocarcinoma cells (HepG2) to evaluate the potential toxic effects of CdSe/ZnS QDs. We have measured cell viability by the MTT assay and cellular internalization by transmission electron microscopy (TEM) and fluorescence microscopy. We have also evaluated the induction of apoptosis and the arrest of the cell cycle in HepG2 cells exposed to QDs using flow cytometry.

In addition, we have used a state-of-the-art quantitative proteomic approach called SILAC (Stable Isotopic Labeling by Amino acids in Cell culture) in combination with biological mass spectrometry for identifying differentially expressed proteins after QDs exposure. These altered proteins helped us to elucidate the biomolecular mechanisms involved in the QDs-induced toxicity.

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TOM-OC03

HUMAN FAECAL METABOLOME AFTER MODERATE CONSUMPTION OF RED WINE

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Faecal metabolome contains information of the metabolites formed in the intestine and therefore, of the metabolic function of the gut microbiota. Changes in the metabolomic profile of faeces reflect, among others, changes in the composition and activity of the intestinal microorganisms. In an effort to improve our understandingon the biological effects that phenolic compounds (including red wine polyphenols) exert at the gut level, in this study we have undertaken a metabolome characterization of human faeces after moderate consumption of red wine by healthy subjects for 4 weeks. The experimental work included LC-TOF MS-based metabolite profiling of 82 human faecal samples. After statistical analysis, MS response was found significantly different before and after the wine intake period for 37 metabolites, being 20 out of them tentatively or completely identified. Metabolites whose content changed after moderate wine consumption corresponded to: I) compounds present in wine (exogenous metabolites), II) microbial-derived metabolites of wine polyphenols, and III) endogenous metabolites and/or others derived from other nutrient pathways. After wine consumption, faecal metabolome was fortified in flavan-3-ols metabolites such as phenolic acids, and in derivatives of phenyl-γ-valerolactone and 4-hydroxy-5-hydroxyphenyl valeric acid. Also, of relevance was the down regulation of xanthine and bilirubin-derived metabolites such urobilinogen and stercobilin after moderate wine consumption. As far as we know, this is the first study about the faecal metabolome after wine intake.

Acknowledgements
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TOM-OC04

FOODOMICS EVALUATION OF SIX ALGAE BASED ON ANTIOXIDANT CAPACITIES, CYTOTOXIC ACTIVITY AND METABOLOMICS APPROACHES

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In the present work, a comprehensive methodology was initially carried out for the screening of bioactive compound of algae commonly commercialized in Spain (Arame, Dulse, Hijiki, Nori, Wakame and Kombu), based on in vitro and LC-HRMS metabolomics approaches. Different algae species were studied in order to identify bioactive compounds, which could be used in the industry as functional ingredients, as well as for the authentication of these algae.

To carry out the screening for bioactive compounds, first hydroalcoholic extracts (70%) obtained from algae were directly measured by UHPLC-HRMS and evaporated and redissolved in PBS for in-vitro studies. These extracts were used to determine antioxidant capacity (2,2'-azino-bis-3-ethylbenzothiazoline-6-sulphonic acid (ABTS) assay) and to evaluate cell cytotoxicity (3-[4,5-dimethythiazol-2-yl]-2,5-diphenyltetrazolium bromide (MTT) assay) in the human cancer cellline, TD47, after 24 h or 48 h, and at different doses (from 25 up to 250 µg/well).

The *in-vitro*assays revealed that the processing method and extraction condition affected the antioxidant capacity of algae and cell cytotoxicity. Antioxidant activities of Dulse and Wakame ethanolic extracts were higher than those from aqueous extracts. However, it remained similar for Arame, Hijiki, Nori and Kombu. It was found a wide range of antioxidant activity (from 0.65 to 5.07 µmol/g of dry solid) being Arame the algae with the highest antioxidant capacity. Preliminary results indicate that in most of the cases the growth of TD47 was inhibited in a time- and dose-independent manner. Arame and Nori were the most cytotoxic algae causing 40% growth inhibition (IC50) of TD47 cells at 250 µg/well over 48 h in the MTT assay.

In order to interpret changes in the metabolome, intracellular and extracellular metabolites were evaluated using liquid chromatography coupled to high resolution tandem mass spectrometry and multivariate data analysis, PCA and OPLS-DA. The identification of critical metabolites, markers, highlighted different cell responses to different algae treatments.

TOM-OC05

COMBINED METALLOMIC AND METABOLOMIC APPROACH TO STUDY THE EFFECTS OF SELENIUM RICH DIET IN *MUS MUSCULUS* METABOLISM

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Selenium (Se) is an essential trace element for both human and animals, and it has important nutritional and biological roles in living systems. An adequate intake of Se has many potential health benefits, including protective actions against cardiovascular disease, enhancement of immune responses, improvement of thyroid health, and reduction of cancer risk [1].

The need for food supplemented with essential elements has becoming an important issue. Because of the high content of proteins and other nutritional elements in *Chlorella sorokiniana*, this microalgae has been widely cultivated for the production of health food products [2].

In this study, *C. sorokiniana* has been exposed to Se in the form of selenate which is rapidly absorbed at the cell surfaces where is irreversibly fixed in the form of selenomethionine [3]. To study the biochemical effects of Se enriched alga in mammals a combined metallomic and metabolomic approach has been developed, complemented with the measurement of biochemical parameters in blood. Size-exclusion chromatography (SEC) was combined with affinity chromatography (AF) and ICP-MS detection using species unspecific isotopic dilution analysis (SUID) to characterize the biological effects of diet rich Se on selenium containing proteins in the bloodstream of feed mice. On the other hand, direct infusion mass sprectrometry (DIMS) provided information about changes in metabolites caused by this diet. The results indicate that selenium supplementation lead to increase in tissue Se concentration producing changes in metabolites of liver and blood caused by the diet of Se.

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TOM-OC06

GC-APCI-TOF MS AND GC-EI-Q MS METHODOLOGIES TOGETHER WITH CHEMOMETRICS FOR THE IDENTIFICATION OF MARKERS IN AVOCADO

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The main objective of this work was to evaluate the influence that the ripening process has on the metabolic profile of different avocado varieties. To achieve this purpose, avocado extracts were analyzed, following an untargeted approach, by GC-APCI-TOF MS and GC-EI-Q MS.

13 avocado varieties -grown under identical pedoclimatic conditions- at 2 different ripening degrees were selected. Sample preparation (solid-liquid extraction by adding methanol), derivatization reaction (silylation by using BSTFA) and chromatographic conditions were carefully optimized and were the same for both analytical platforms. However, the ionization and detection conditions were specifically optimized for each coupling considering the ionization source and the MS analyzer used.

Both platforms showed an enormous potential to characterize the avocado metabolome, allowing the identification of an important number of metabolites belonging to different chemical classes (80 by GC-EI-MS and 100 by GC-APCI-MS). Moreover, pattern recognition techniques (supervised and unsupervised), were used to identify possible varietal or ripening markers among all the detected compounds in the analyzed avocado extracts. Both PCA and PLS-DA were applied; in a first stage, the use of PCA allowed obtaining a global view of the data structure, and afterwards, a classification model was built by using PLS-DA. In the case of GC-APCI-MS, data treatment consisted on the alignment of the chromatograms by using a software developed at the Leiden University Medical Center, followed by peak picking (XCMS package) and multivariate analysis (SIMCA software). For GC-EI-Q MS data, the package Mass Profiler Professional was used after data deconvolution by using AMDIS. The results achieved after the statistical treatment for both couplings were very similar, being the most influential metabolites on the avocado samples classification mannoheptulose, aspartic acid, mannitol and linoleic acid, among others, for GC-APCI-TOF MS; and abscisic acid, mannoheptulose, linoleic and aspartic acids for GC-EI-Q MS.

The similarity of the conclusions accomplished by using different GC-MS platforms and diverse statistical data treatments is, from our point of view, very interesting and the metabolites identified as possible markers (varietal and/or ripening) could help to establish the optimum moment for harvesting the avocado fruit over the whole season, representing an alternative strategy to the ones currently used, such as oil content.

TOM-OC07

FOODOMICS STUDY OF THE CHOLESTEROL-MODULATING ACTIVITY OF ROSEMARY ON COLON CANCER CELLS USING GC-MS AND MICROARRAY

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Colorectal cancer is the third most common malignant neoplasm worldwide. In last years, in order to prevent this disease, efforts have been made to identify naturally dietary compounds to use them as chemopreventive agents against cancer. Rosemary (*Rosmarinus officinalis*) extracts have shown a strong antioxidant activity mainly associated to the presence of phenolic diterpenes as carnosol and carnosic acid. In addition, rosemary extracts have demonstrated antiproliferative activity on colon cancer and leukemia cell models [1, 2]. Previous studies performed in our laboratory suggest that treatment of HT-29 colon cancer cells with rosemary extracts induces gene expression changes in a relevant number involved in lipid and cholesterol metabolism [3]. The objective of the present work was to corroborate potential changes in cholesterol metabolism and fatty acids induced by rosemary extracts in HT-29 cells. To achieve this goal, we adopted a Foodomics approach that combines targeted metabolomic analysis with transcriptome-wide analysis to investigate the cholesterol- and fatty acid-modulating activity of rosemary extracts in HT-29 cells. GC-MS was used for the quantification of intracellular free fatty acids, cholesterol and other cholesterol metabolites. Lipid fraction from untreated (control) and treated cells with rosemary extracts and carnosic acids were obtained at different time points and then subjected to sample treatment prior GC-MS analysis. Under optimum GC-MS conditions, analysis of cell extracts revealed a significant ($p<0.05$) intracellular cholesterol accumulation upon rosemary extract treatment starting at 12 hours (9% increase over untreated cells), and increasing through 72 h (31% increase over untreated cells), while free fatty acids levels remained unchanged compared to control. To support metabolite data and to gain new insights into the molecular mechanisms associated with the modulating activity of rosemary on the cholesterol metabolism, a transcriptome-wide study was carried out using Affymetrix Human Gene 2.0 ST microarrays. Microarray data were examined with functional enrichment analysis tools for a reliable interpretation of the results. The Foodomics approach presented in this work provides new evidences, and also opens new questions on the activity of rosemary compounds against colon cancer cells at molecular level.

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TOM-OC08

HIGH RESOLUTION TANDEM MASS SPECTROMETRY AS A CHALLENGING TOOL IN BIOLOGICALLY ACTIVE COMPONENTS: BIOPROSPECTING

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During the last decade, consumers´ interest to support their health through the use dietary supplements or nutraceuticals continues to increase. In this context, searching for new sources of biologically active substances with positive health effects realizes a great challenge. For example, the deep waters surrounding the coastline of the sea represent an exciting biotope for marine exploration. Dark and cold Arctic water generates a hostile environment where the ability to adapt is crucial to survival. These waters are nonetheless bountiful and a diverse plethora of marine organisms thrive in these extreme conditions, many with the help of specialized chemical compounds. This presentation will demonstrate a comprehensive analytical strategy we have already used in investigation of bio-matrixes for which the composition is completely unknown. The following steps were taken and critically evaluated: (i) various ways of mechanical treatment of algae biomass to disintegrate the cell walls and increase the extraction efficiency, (ii) extraction-fractionation steps enabling isolation of polar, medium-polar, and non-polar compounds, and selection of the optimal approach (iii) evaluation for non-target screening of fingerprinting followed by assessment of different forms of identified compounds employing ultra-performance liquid chromatography coupled with high resolution tandem mass (HRMS/MS). For example, fish skins, which are commonly waste material, were evaluated and potential bioactives components were found, such as Gadusol, its ability to reduce radicals is comparable to that of ascorbic acid.

Subsequently, mammalian cell may be used to carry out a broad metabolomics studies. UHPLC-HRMS could obtain a global metabolomic examination of the effect of a food extract (fraction) or bioactive component in different mammalian cells, in this case human breast cancer and prostate cancer cells were evaluated for algae extracts and sesquiterpene lactones (trilobolide extracts), respectively. In this way, changes in the metabolome, intracellular and extracellular metabolites, were explored using liquid chromatography coupled to high resolution tandem mass spectrometry (UHPLC-Triple TOF 5600 (AB Sciex)). Consecutively, data analysis was carried out using various chemometric tools, such as Marker View (AB Sciex) and SIMCA (Umetrics). The identification of markers showed different cell responses, metabolite pathways, to different treatments.

COMUNICACIONES ORALES

AME

Análisis medioambiental

AME-OC01

PREDICTING ENVIRONMENTAL CONCENTRATIONS OF CYTOSTATIC DRUGS IN SEWAGE EFFLUENTS AND SURFACE WATERS OF CATALONIA

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In the last years, the incidence of cancer in Catalonia has increased considerably, with 33715 cases registered in 2007. Cytostatic drugs are excreted unchanged from the body or modified as metabolites via different routes [1]and released to wastewaters. Recent works have demonstrated that elimination of many drugs in wastewater treatment plants (WWTPs) is often incomplete [2]. Thus, traces of pharmaceuticals ranging from ng L^{-1} to µg L^{-1} have been detected in surface waters and groundwater [3].The level of these compounds in the natural environment depends on many factors: their consumption patterns, the excretion fraction and the effectiveness of the processes used for wastewater treatment.

The objectives of this study are to provide data on the occurrence and risk quotient values of anticancer drugs in the aquatic environment by calculating predicted environmental concentrations (PECs), based on the consumption of 132 cytostatic compounds in Catalonia in the period of 2010-2012. PECs were estimated using publicly available consumption data, published or calculated excretion values and wastewater elimination rates for the target compounds. This allows predicting the range of concentrations in effluent wastewaters and surface waters.

PEC indicates that cytostatics can be discharged by WWTP and become surface water contaminants. Five out of the 132 cytostatics have PEC values higher than 10 ng L^{-1}. Hydroxycarbamide is the compound with the highest PEC (84 ng L^{-1}), followed by megestrol acetate and prednisone (both with 30 ng L^{-1}). Mycophenolic acid is the most consumed drug used to prevent rejection in organ transplantation, which represents 40% of cytostatics consumed. However, PEC value of mycophenolic is 3 ng L^{-1} due to the low excretion of the unchanged drug. Considering PEC values, a risk assessment was conducted to determine the potential adverse effects of cytostatics in the environment.

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AME-OC02

EVALUATION OF DIFFERENT EXTRACTION PROCEDURES FOR PESTICIDE ANALYSIS IN FISH

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Pesticideresidue determination in biota deals with samples that have low analyte concentrations and large number of interfering compounds [1]. Aiming the delineation of an ideal preparation procedure for fish analysis, the commonly used extraction methods such as solvent extraction (QuEChERS and ethyl acetate), pressurized liquid extraction (PLE) and matrix solid phase dispersion (MSPD) were evaluated in the present study.

The methods were optimized and compared by the extraction efficiency. In order to make the methods more comparable the ratio sample/solvent in the extract was 0.2 and always that possible acetonitrile was used as extraction solvent. The extraction by MSPD, briefly, involved to take 0.2 g of the fish sample and blend it with 0.4 g of the C_{18}. The mixture was then transferred to the top of 0.5 g packed silica (as clean-up phase) syringe and the pesticides were eluted with 10 mL of acetonitrile. PLE was carried out in a similar way as MSPD, 0.240 g of fish sample was dispersed with 0.5 g of $C_{18}$and 2 g of silica, put the mix in a 6 mL cell and, once the cell was place in the ASE200 system, was extracted with acetonitrile at 75 ºC using 2 cycles. The QuEChERS is a very well known platform that involved an extraction with acetonitrile by salting out and cleaned up of the supernatant by dispersive solid phase microextraction. The ethyl acetate is also very simple, 2 g of samples were homogeneized with ethy acetate and anhidrous sodium sulfate. Then, filtered, evaporated and the solvent changed to acetonitrile.

The PLE and the ethyl acetate extraction methods showed lower extraction efficiencies (71-80 % for most of the analytes). The use of MSPD showed good efficiency (81-100%), but with high consumption of time. Among the evaluated extraction techniques the use of QuEChERS showed the best results. All the methods were validated for analysis of pesticide residues in salmon and hake muscle regarding selectivity, linearity, precision and limits of detection and quantification. All methods could adequate for the investigation of the analytes at residue levels in river fish.

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AME-OC03

A SYSTEMATIC APPROACH TO ODOR SOURCE IDENTIFICATION IN THE INDOOR ENVIRONMENT

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During the last two decades, there have been many attempts to understand complaints related to poor indoor air quality as well as their impact on occupant health, comfort and performance. Odor nuisances from unknown origin have significantly increased in residential dwellings, schools and offices. Fast and reliable identification of indoor odor sources remains a challenge due to the measurement and analytical costs required to track individualcompound-by-compound effects rather than a total volatile organic compound (VOC) indicator. A systematic approach will increase the chances of identifying the odorants and their sources.

We describe a sensitive and reliable method for the determination of odorants in indoor air by dynamic Solid-Phase MicroExtraction (SPME) combined with Gas Chromatography - Mass Spectrometry (GC-MS). Compounds are quantitatively collected onto SPME fibers at a flow-rate of 0.1-0.2 L/min for 2-8 h. Calibration is performed with representative compoundsbelonging to 16 chemical families.

Individual and group concentration profiles are automatically calculated and chemical fingerprints collated into a database of real case studies gathered over the last 10 years, for comparison against known samples. Additional odor threshold and air quality criteria databases gathered over the same time period are used to compare odor and air quality fingerprints between new and existing samples by a process of elimination, i.e. confirming or rejecting the suspected odor source. Several examples of point/multiple sources of odorants and associated human health effects are described for residential dwellings, offices and schools.

The absence of regulation in this field has increased the need of such a systematic and reliable approach for litigation purposes.

AME-OC04

BIOCONCENTRATION OF PHARMACEUTICALS USING ALTERNATIVE METHOD WITH ZEBRAFISH LARVAE AS MODEL ORGANISM

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Increasing human and animal consumption of drugs in the last decades have raised these products as potential emergent contaminants. Furthermore, pharmaceuticals and their residues at low concentrations levels have been reported to be present in surface waters. This fact has led to a public, regulatory and scientific concern about their environmental impacts. European Legislation (REACH) requires evaluation of the ecotoxicity assessing information on bioaccumulation factors (BCF) or persistence. OECD Guideline 305 describes methods to determine bioconcentration factors using adult fishes. However, the methodology proposed is complex and highly costs (more than one hundred animals are required) [1]. Here, we report the use of zebra fish larvae as model organism to replace adult fish for bioconcentration studies.

Three groups of pharmaceutical products belonging to the family of lipid regulators as clofibric acid, non-steroidal anti-inflammatories as ibuprofen, naproxen and diclofenac and antidepressant SSRIs drugs as fluoxetine, norfluoxetine, sertraline, norsertraline, citalopram, desmethylcitalopram and paroxetine have been selected for the present study.

Zebra fish larvae were exposed to the selected analytes at two concentration levels following the OECD 305 guideline (1% and 0,1% of the LC_{50}). Larvae were exposed for 48 h and then remained other 24 h in clean media to simulate accumulation and depuration process. About 20 larvae were taken from the tanks at different times and the analytes were extracted with an organic solvent. Different extractants were tested and the extracts clean up, by solid phase extraction, optimized [2]. An analytical method to determine the selected compounds in the exposure media, using a liquid-liquid extraction, was developed. Gas chromatography coupled to mass spectrometer (GC-MS) was used as detector.

The bioaccumulation assays in larvae exposed to clofibric acid, ibuprofen, naproxen and diclofenac at 5 and 30 µg/L showed a quite low bioaccumulation factor of all the analytes tested, establishing values below 5.

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AME-OC05

OCCURRENCE AND FATE OF BISPHENOL A IN THE BESOS RIVER: PHOTODEGRADABILITY AND RISK

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Bisphenol A (BPA) has been used for a long period of time in the production of polycarbonate plastics and it is considered as an emerging pollutant as a result of its extensive use. After release from host products, BPA enters the aquatic environment via Wastewater Treatment Plant effluents, direct discharges or run-off. BPA has an important interest due to its endocrine disrupting properties [1].

The objectives of this study were to evaluate the presence of BPA along Besòs river waters (Catalonia, Spain) from source to month (17 sampling points), study its seasonal variability, determine its risk and evaluate its fate by studying the photodegradation. Sampling points included pristine areas close to the source, with little anthropogenic impact, and very impacted areas with high urban density and industrial activity. For the analysis of BPA, solid phase extraction and ultra-high performance liquid chromatography-tandem mass spectrometry (UHPLC-MS/MS) operating in multiple reaction monitoring mode was used.

BPA was detected in all sampling points and increasing concentrations were observed from source to mouth, ranging from 32.2 ng L^{-1} to 954 ng L^{-1}, with some seasonal variability. Considering these concentrations and *Daphnia magna* EC_{50} values, the risk quotient (RQ) was not found significant. The highest concentration site had a RQ of 0.955, near to unit value, which indicates a small potential for adverse effects.

To determine the fate of BPA in river water, the kinetics of the BPA photodegradation under UV-light was studied in both milli-Q water and river water and the photoproducts were identified by high resolution mass spectrometry (HRMS). The half life ($t_{1/2}$) was of 7.2 min for milli-Q water and 30.3 min for river water, obtaining similar values to other studies [2]. It was observed that the presence of organic matter in water decreased the degradation constant. Five photoproducts were identified and the following molecular formulas were proposed with the aid of experimental mass: $C_{15}H_{16}O_3$, $C_{15}H_{16}O_4$, $C_{15}H_{14}O_3$, $C_{15}H_{20}O_4$ and $C_9H_{12}O_3$.

This study demonstrates that ng L^{-1} concentrations of BPA in an impacted river do not have any significant toxicity risk and that BPA is rapidly degraded by photolysis. However, other risk can be associated to continuous inputs.

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AME-OC06

SUPRAMOLECULAR SOLVENT-BASED MICROEXTRACTION FOR THE DETERMINATION OF DRUG ENANTIOMERS IN SEWAGE AND FISH SAMPLES

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The growing consumption of pharmaceuticals in the developed world has resulted in a noticeable increase in environment pollution by pharmacologically active compounds (PhACs), effluents from wastewater treatment plants (WWTPs) being the major sources of PhAC contamination. Chiral drugs, that represent a half of market pharmaceuticals, are enantioselectively degraded in WWTPs and in the environment, and drug enantiomers can have quite different ecotoxicity. Therefore, enantiomeric ratio (ER) of PhACs can be a useful marker of drug biotransformation during wastewater treatment and an important factor for environmental risk assessment. However, information on enantiomeric distribution of PhACs in wastewater and environmental samples is scarce, primarily because measuring drug enantiomers at low concentration levels in such complex samples is difficult. In fact, only a few methods for the enantioselective determination of PhACs in natural and wastewater samples have been described and no methods to analyze other environmental samples such as biota are available.

This work deals with the development of simple, rapid and reliable methods for the determination of ibuprofen, naproxen and ketoprofen enantiomers in wastewater and fish samples using chiral liquid chromatography coupled to tandem mass spectrometry after supramolecular solvent-based microextraction. Supramolecular solvents (SUPRAS) are water-immiscible liquids consisting of surfactant aggregates with the capacity to extract analytes of different nature through a variety of interaction mechanisms. The SUPRAS used in this research that consisted of decanoicacid (DeA) aggregates, solubilised profens through hydrogen bonds between the carboxyl/carbonil/ether groups of the analytes and the carboxyl groups of DeA, and dispersion interactions between the apolar moieties of the drugs and the DeA hydrocarbon chain. Extractions of both wastewater and fish samples were performed in a single step in a short time (c.a. 20 min.), and the extracts were directly injected in the chromatograph where the drug enantiomers were separated on a (R)-1-naphthylglycine/3,5-dinitrobenzoic acid stationary phase and quantified in a mass spectrometer equipped with an electrospray ionization source and a triple quadrupole mass analyser. The high extraction efficiency provided by the SUPRAS permitted to obtain elevated concentration factors for wastewater samples (i.e. 456-715) and quantitative recoveries for fish ones using a low SUPRAS volume/sample amount ratio (i.e. 1.7 µL/mg). The quantitation limits for the determination of profen enantiomers in wastewater and fish samples were in the intervals 1-4 ng L^{-1} and 2-7 ng g^{-1}, respectively.

AME-OC07

CHROMATOGRAPHIC ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN BREATH OF TOBACCO AND ELECTRONIC CIGARETTE SMOKERS

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The changes in smoking habits of human population require new methods for assessment of the exposure to chemical compounds absorbed into the respiratory system as consequence of these activities. A simplified method for the characterization of these compounds is presented here. The method affords a direct comparison of the composition of the smoke from the smoking items and exhaled breath.

Both types of air samples were collected with a Bio-Voc from which they were subsequently transferred to a Tenax cartridge. The volatile organic compounds (VOCs) retained in these cartridges were desorbed into an Agilent J&W DB5-ms column (length 60 m, internal diameter 320 µm, phase thickness 1 µm). The VOCs were analyzed in a gas chromatograph coupled to a mass spectrum equipped with an automatic thermal desorption device. This method allowed to identifying a large range of volatile compounds, encompassing between 2-butene (molecular weight, MW: 56) and dimethylaminocinnamonitrile (MW 172). The VOC present in tobacco and electronic cigarette smoke and in breath after smoking were analyzed with this method and the equivalent smoke-breath compositions were compared

Exhaled breath during tobacco smoking showed VOC mixtures predominated by isoprene and C5 hydrocarbons (trans-2-pentene, cis-2-pentene, isopentene, 1,3-pentadiene, 1,3-cyclopentadiene), benzene, toluene, m-cymene, d-limonene and nicotine. These compounds were also present in tobacco smoke.

Breath of electronic cigarette smoking was predominated by acetone, isoprene and cyclosiloxanes (hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane). In the vapors emitted to the atmosphere these cigarettes emit propylene glycol, glycerin and nicotine. Use of these electronic devices therefore involves ingestion of these last three compounds which are the reported constituents of the nicotine solutions introduced into these systems.

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AME-OC08

POLYCHLORINATED DIBENZO- DIOXINS, FURANS AND BIPHENYLS IN AIR AND PLANKTON FROM THE GLOBAL OCEANS

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The open oceans are one of the most pristine environments in the world, away from anthropogenic persistent organic pollutants (POP) sources, but not exempt of them because of the long range atmospheric transport (LRAT). Several families of POPs have been regulated by the Stockholm convention on POPs aiming at reducing or eliminating the production and use of these harmful substances. Polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF) and dioxin like polychlorinated byphenils (dl-PCB), are among the most toxic POPs listed in the Stockholm Convention. The lipophilic nature and stability of POPs allow efficient assimilation and accumulation in the fat tissue of organisms leading to their biomagnification trough the food chain. The trophic transfer of PCDD/F and dl-PCB has been studied previously as well as bioaccumulation in the food chain. In marine food webs, plankton is the lower trophic level, and the first step for the pollutant incorporation in the food chain. Additionally, plankton uptake of POPs and the subsequent settling fluxes of organic matter bound POPs play an important role in the oceanic biogeochemical processes and as controlling factors of the oceanic occurrence of POPs. Previous studies have reported the occurrence of POPs, such as PCBs, in plankton from the Mediterranean and black sea [1], Southern Oceanand Strait of Georgia. Despite PCDD/F have been studied in other marine organisms, no data on PCDD/F and dl-PCB are available in marine plankton except for some results from PCDD/F bioaccumulation studies. There are only two previous studies on the dioxin atmospheric occurrence and fate in Atlantic Ocean north-south transects, but no in the global oceans.

The aim of this study is to provide for the first time the global oceanic air and plankton occurrence of PCDD/F and dl-PCB in the Pacific, Indian and Atlantic Oceans, and assess the influence of atmospheric deposition and water column biogeochemical processes as drivers of their occurrence in the oceanic plankton. Sampling was carried out within the framework of the Malaspina Expedition 2010, which consisted on an oceanographic circumnavigation campaign sampling all oceans between 40ºN and 35ºS.

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AME-OC09

DEVELOPMENT OF AN ANALYTICAL METHOD FOR DECHLORANE PLUS AND RELATED COMPOUNDS IN FISH SAMPLES

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Dechlorane Plus (DP) is a flame retardant additive used in polymeric systems such as electrical hard plastic connectors in televisions and computer monitors, wire coatings and furniture. This product, currently classified as a high production volume chemical by the U.S. EPA, was created by OxyChem in the 70s when Mirex, another flame retardant from the same company, was banned. The existence of DP in the environment was first detected in samples from the Great Lakes in 2006. Since then, studies have been performed in order to determine the environmental behavior and presence of this compound and its main relatives: Dechlorane 602, 603 and 604. These compounds have been mainly studied in environmental matrices, such as water, air, soil and biota with monitoring purposes, but the dietary exposure to these chemicals has been hardly investigated. Thus, there is a need for the development of analytical methods for de determination of these compounds on food and feed matrices. In this work, we focus on fish samples.

The main steps of the methodology are the following: (1) addition of ^{13}C-labelled internal standards, (2) extraction, (3) clean-up, (4) concentration (5) instrumental determination by HRGC-HRMS and (6) quantitation.

Extraction was performed in Soxhlet apparatus. Several solvents (hexane, hexane:acetone 41:59 and hexane:dichloromethane 50:50) and different extraction time (3 h, 6 h, 12 h and 24 h) were tested.

Clean up was based on the purification on a multilayer silica column. However, an additional purification in a pyrenyl HPLC column was tested. Results showed that dechlorane compounds eluted between 3.5 min and 10 min, using hexane as mobile phase at 1 ml/min. Residual interferences from the matrix were discarded in the first fraction (0 to 3.5 min).

Instrumental determination was performed with an Agilent 6890N gas chromatograph coupled to an Autospec Ultima high resolution mass spectrometer, operating in the SIR mode at 35 eV (EI) and 10,000 resolving power. Two fragments for each compound were monitored in time windows. Quantification was carried out by the isotopic dilution method, based on the use of ^{13}C-anti DP. Accuracy, precision, linearity, limit of detection and limit of quantification of the method were evaluated in real samples.

AME-OC10

UPLC-HRMS FOR ANALYSIS OF PHARMACEUTICALS AND THEIR METABOLITES IN FISH

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In the last decade, the occurrence of pharmaceuticals in the rivers has caused concerns about potential adverse effects on exposed wildlife. Although some studies have been reported the occurrence of pharmaceuticals in different fish tissues, still very little is known about mechanisms of drugs in fish. This study focusses on the identification of metabolites of most commonly detected drugs first on fishes placed in tanks at laboratory conditions and then the determination of drugs and their identified metabolites in different wild fishes. To this end, a group of fishes received a single intraperitoneal dose of drugs (ibuprofen and carbamazepine). The carrier, sunflower oil was administered to other group which served as control group. Bile samples were analyzed by ultra-high performance liquid chromatography - high-resolution mass spectrometry (UPLC-HRMS). The HRMS identification of the fish metabolites was carried out on the Q Exactive (Orbitrap) system with MS/MS capability which was revealed to be of great value in establishing the fragmentation pathways. The examination and comparison of the chromatograms from treated and control animals allowed detection of several metabolites of the test compounds in the bile samples. The accurate mass measurements provided the chemical formulae of the metabolites and the comparison of MS/MS spectra of metabolites and the parent compounds allowed proposing plausible structures for metabolites in fish bile. Phase I metabolites corresponding to the different hydroxylation of drugs and phase II metabolites such as glucuronide and taurine conjugations were identified. Different marine and freshwater species were selected and a total of 150 fishes were collected. Two types of fish samples were analyzed: Bile and muscle, which require very different analytic approach. Bile samples were analyzed directly after a dilution step by UPLC-HRMS. Muscle samples were extracted by pressurized liquid extraction (PLE) and analyzed using on-line turbulent flow liquid chromatography coupled to HRMS. In order to extent our knowledge on metabolism of pharmaceuticals in fish further work will be performed using suspect screening with Thermo-Scientific software.

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AME-OC11

ANALYSIS OF PERFLUOROALKYL SUBSTANCES IN SOIL AND SEDIMENT. COMPARISON OF FOUR EXTRACTION PROCEDURES

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A number of recent studies have reported the presence of perfluoroalkyl substances (PFASs) in water and food [1, 2]. Consequently, general concern has increased because of the persistence and bio-accumulative characteristics of these compounds. The choice of a suitable sample-preparation technique is essential for the accurate and reliable characterization of PFASs in trace concentrations.

In the case of sediment and soil analyses, there are certain difficulties in their extraction and clean-up steps: background contamination problems, selection of the analyte-isolation and pre-concentration technique, optimization of the operational parameters (time consuming steps), and matrix effects, which make practically impossible the quantitative analysis of some compounds. Extraction procedures include ion pair extraction [3] or methanol extraction and alkaline digestion or liquid extraction using methanol and acetic acid [2]. Additionally, a clean-up step is used in general by solid phase extraction. Thus, the main objectives of this study were: (I) to compare cited extraction schemes for the analysis of 23 PFASs (carboxylates, sulfonates, sulfonamides and telomere acid) in soil and sediment samples to fulfil requirements for routine analysis.

The best results were obtained using acidic extraction, improving detection limits down to 0.013-2.667 ng g^{-1} dry weight (dw) and allowed effective quantitation down to 0.04-8 ng g^{-1} dw. Procedure also showed good recoveries ranging between 65% and 102% for all target compounds. The applicability of this extraction method was tested in 22 soil and 22 sediment samples of the Turia River basin. The results showed that of the 23 target compounds, 7 were identified, with concentrations ranging from 0.71 to 868 ng g^{-1} dw (PFOA). These results suggest that the optimized methodology used in this research proved to be the most feasible and efficient way for systematic PFASs determination in sediment and soil samples.

Acknowledgements
We acknowledge the Spanish Ministry of Economy and Competitiveness through the Projects CSD-665-2009, http://www.scarceconsolider.es/publica/P000Main.php,and CGL2011-29703-C02-02; http://mefturia.es/.

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AME-OC12

PART-PER-QUADRILLION DETERMINATION OF FULLERENES IN SURFACE WATERS, SOILS, AND SEDIMENTS

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Fullerenes are carbon based nanomaterials in a hollow-spherical shape which, during the recent years, have been extensively studied from an environmental point of view. While some relevant aspects of their behaviour, fate and their ecotoxicity effects start to be well understood, their quantification in real environmental samples is still an analytical challenge, mostly because of their extremely low concentration levels of these nanomaterials. In comparison with other emerging contaminants, very few works have reported the occurrence of fullerenes in the environment. Nevertheless, characterizing their concentrations in several environmental compartments is an important task for properly assessing the real environmental risks of fullerenes.

In this work, several types of environmental matrices (river water, wastewater, soils and sediments) have been analyzed by liquid chromatography (LC), with buckyprep columns, coupled with an atmospheric photoionization source (APPI) to a high resolution mass spectrometer (HRMS) with a hybrid quadrupole-orbitrap analyzer. This instrumentation offers unique sensitivity and selectivity and the method performance allows the detection of fullerenes in the low pg/L order in water samples. The performance of the method will be comprehensively compared with other previous methods based in electrospray ionization (ESI) and C18 based LC.

Surface water and sediments samples from two rivers from Barcelona (Spain), under high anthropogenic pressure, have been analyzed, showing concentrations of fullerenes in the pg/L order. Results about their occurrence of fullerenes, their aggregation, heteroaggregation and partition to the sediments will be exposed. In addition, the analysis of soils from Sul Catarinense (Brazil) will be presented. Fullerenes C_{60} and C_{70} were detected at pg/g concentrations in those samples which were located close to the largest fossil combustion power station in Latin America. Urban samples also exhibited significant levels of fullerenes while rural soils levels were under the limit of detection in about 50% of the samples.

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AME-OC13

OCCURRENCE AND TOXICITY OF IODO, BROMO AND CHLORO CONTAINING ACETALDEHYDES IN DRINKING WATERS

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Chlorinated and brominated acetaldehydes are considered the 3rd largest class of DBPs by weight. Moreover, iodinated disinfection byproducts (DBPs) are among the most genotoxic of all DBPs identified. In this context, the objectives of this study were to investigate the occurrence of iodoacetaldehyde for the first time in source and disinfected waters, to compare its levels with those measured for chloro- and bromoacetaldehydes, and to evaluate the *in vitro* genotoxicity and cytotoxicity of the entire class of haloacetaldehydes (HALs) in mammalian cells.

Two analytical methodologies based on gas chromatography coupled to mass spectrometry were validated to investigate the occurrence of HALs in water. Mono-HALs and di-HALs were derivatized with pentafluorobenzylhydroxylamine (PFBHA), and subsequently liquid-liquid extracted. Tri-HALs were preconcentrated by means of solid-phase extraction. Application of these methods to the analysis of water samples revealed: (1) the presence of all target HALs in drinking waters; (2) the absence of HALs in source waters, except in one case where trace levels of dibromoacetaldehyde, tribromoacetaldehyde, dibromochloroacetaldehyde and iodoacetaldehyde were detected; (3) the formation of iodoacetaldehyde exclusively after water chloramination; and (4) the occurrence of iodoacetaldehyde at levels between 0.6 ppb and 4.6 ppb. Overall, iodoacetaldehyde concentrations were similar to those observed for tri-HALs and dibromoacetaldehyde, and slightly higher than those measured for dichloroacetaldehyde, chloroacetaldehyde, and bromoacetaldehyde.

Toxicity results showed that: 1) the cytotoxicity and genotoxicity of HALs were not statistically correlated with chemical structure; 2) no toxicity trends were observed in terms of the type of halogen or the number of halogens attached; 3) iodo-, dibromo-, tribromo-, bromochloro-, and dibromochloroacetaldehyde were more cytotoxic (based on LC_{50} values) than regulated trihalomethanes (THMs) and haloacetic acids; and 4) chloro-, dibromo-, and dibromochloroacetaldehyde were more genotoxic than most regulated DBPs.

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COMUNICACIONES ORALES

DIA Desarrollos en instrumentación analítica
NAN Nanotecnología
OQA Otros campos de la química analítica y del análisis instrumental

DIA-OC01

FLEXIBLE HF RFID LABEL FOR MULTIPLE GAS DETERMINATION

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In a previous work the authors presented a screen printed RFID for the monitoring of oxygen in modified atmosphere packaging (MAP) [1]. There, a resolution of few ppm was achieved in the determination of oxygen inside a package thanks to the use of a digital color detector of high resolution. This measurement provided information about a possible failure in the sealing of the packaging that could affect to the quality of the content. Here, a novel design is proposed to be applied in intelligent packaging not only monitoring the concentration of O2 but also determining the concentration of other gases such as CO2, NH3, H2O or SH4 that supply useful data about the state of the packaged food or beverage. The system includes four sensing units consisting of the combination of a specific gas-sensitive membrane together with a new digital color detector for reading the optical response.
A flexible RFID tag has been developed using screen printing techniques and silver ink. A RFID chip model IDS-SL13A is included in the design as interface between the radio link and the microcontroller. In addition, this chip integrates a temperature sensor that allows a compensation of the temperature drifts of the sensors response. A coil of 5.5 µH is printed as the antenna for the radio communication. Four sensing modules are placed surrounding a white LED that acts as common light source. The optical responses of the sensors are registered using the digital color detector S11059 from Hamamatsu, that provides a reading of the incident light in form of 16-bits words for the red, green and blue components. This is a very high resolution and low consumption device that allow to reach low values of gas detection, in the order of ppb. Optical response of the membranes have been quantified through the values of the red (R) and blue (B) components of the RGB space provided by the color detectors.

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DIA-OC02

SIZE AND COMPOSITION ANALYSIS OF VOLATILE COMPOUNDS THROUGH DIFFERENTIAL MOBILITY ANALYSIS AND MASS SPECTROMETRY

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The direct (non-chromatographic) size characterization of volatile compounds can be accomplished using ion mobility spectrometry. Furthermore, a Differential Mobility Analyzer (DMA) coupled with an atmospheric pressure interface (API) mass spectrometer is capable of providing both size and composition information. These attributes are useful in applications such as the study of biological compounds. In other highly demanding applications such atmospheric studies or explosive trace detection, an additional mobility filtering dimension can be used to improve sensitivity.

The instrument described here relies on a high-performance planar differential mobility analyzer that includes a secondary electrospray ionizer (SESI), used to charge the incoming particles sampled at atmospheric pressure. Once ionized, compounds are size-sorted based on their electrical mobility (U) and then are guided to the mass spectrometer where a second sorting based on their mass-to-charge ratio (m/z) is performed. Mass spectra corresponding to specific mobility values, yielding specific fragments in the mass spectrum, or 3D plots corresponding to the different mass spectrum at different mobility values may be obtained. Different sampling modes including the direct sucking of an air stream, or the on-site sample collection in adsorbent filters followed by thermal desorption are possible.

The communication presented will detail some aspects of the technology used in the instrument as well as highlight some examples of applications such as security, biological analysis or environmental analysis that will help to illustrate the possibilities of the technique.

DIA-OC03

PYROLYSIS COMPOUND SPECIFIC ISOTOPE ANALYSIS (Py-CSIA). APPLICATIONS IN NATURAL AND SYNTHETIC MATRICES

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Nowadays the study of isotopic signature of light elements through isotope ratio mass spectrometry (IRMS) is being extensively used to enlighten relevant scientific questions and important aspects for the geochemistry, environment and the industry i.e. global element cycles, past climatic conditions, paleodiets, trace food sources/webs, polymer signatures /traceability, etc. Thus, isotopic analysis has become a key tool for scientists in many disciplines and the practical applications of the technique are continuously growing.

Compound-specific isotope analysis (CSIA) using gas chromatography-combustion/pyrolysis isotope ratio mass spectrometry (GC-EA/TC-IRMS), usually require intermediate preparative procedures prior to chromatographic analysis to isolate analytes from bulk samples i.e. soils, sediments, or other biological or synthetic materials. Non-volatile compounds must be made amenable to GC by derivatization or treated by different methods in order to be amenable to the chromatographic separation. Analytical pyrolysis is a long established technique ideally suited for one-stage combination with GC. The sample is heated up in an inert atmosphere to decompose into smaller units which are carried by a gas to the next instrument for separation and characterization. The pyrolyzer is usually linked to a GC which can further be connected to detectors such as MS or FTIR.

In this communication the results obtained by effectively hyphenating analytical pyrolysis (Py-GC) with IRMS of light elements (C, H, N) stable isotopes are described. These include a variety of matrices of increasing complexity such as synthetic polymers, biopolymers from C3 and C4 photosystem plants, recent sediments, fossil materials, etc.

First a bulk isotopic characterization of light elements (δ15N, δ13C, δ18O and δD) was performed for each material using a Flash 2000 HT elemental analyzer coupled to a Delta V Advantage IRMS (Thermo Scientific) (EA/TC-IRMS).

Chemical structural information of pyrolysates released by the different matrices was first acquired by conventional analytical pyrolysis (Py-GC/MS). The direct study of specific compounds isotopic signature of light elements (δ13C, δ15N and δD) was done by coupling a pyrolysis unit (double-shot pyrolyzer “Frontier Laboratories, model EGA/Py-3030D”) – to a gas chromatograph fitted with a flame ionization detector (GC/FID) and coupled to the Delta V Advantage IRMS (Thermo Scientific GC-Isolink System) (Py-GC-(FID)-EA\TC-IRMS).

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DIA-OC04

GC-MS/MS WITH ATMOSPHERIC PRESSURE CHEMICAL IONIZATION FOR PERFLUORINATED ALKYL SUBSTANCES DETERMINATION

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Perfluorinated carboxylic acids as perfluorooctanoic acid (PFOA) and perfluorinated sulfonates as perfluoroctane sulfonate (PFOS) have been used for over 50 years in the production of consumer products. Their ubiquity in the general population, long half-lives, and increasing evidence of adverse health effects, is of great concern. Due to their non-volatile and lower water-soluble properties, two different theories exist concerning their transportations pathways. Either the moderately water-soluble compounds including shorter-chain PFCAs could be transported directly by sea currents or by means of sea-spray. Alternatively, a suite of volatile, neutral precursors as fluorotelomer alcohols (FTOHs), N-alkylated fluorooctane sulfonamides and sulfonamidoethanols (FOSAs/FOSEs) could undergo long-range atmospheric transport and be degraded in situ to form persistent PFOA and PFOS.

Analytical methods for FTOHs and FOSAs/FOSEs in environmental samples include mainly gas chromatography coupled to mass spectrometry with chemical ionization (GC(CI)-MS) in positive mode. In the case of FOSAs, confirmation must be performed in negative mode (NCI). Electron ionization (EI) is not normally used because of the low intensity of the molecular ions and the lack of specific fragments. In LC-MS methods the co-analysis of nonionic and ionic PFAs is impeded by ionization suppression of FTOHs caused by the buffered mobile phases needed to separate ionic PFAs.

In the present work the potential of atmospheric pressure chemical ionization (APCI) combined with GC-MS/MS with triple quadrupole analyzer has been investigated for the sensitive determination of FTOHs and FOSAs/FOSEs in surface water. Their ionization behavior by APCI has been studied. $[M+H]^+$was the base peak of the spectrum in all cases giving the possibility of selecting it as a precursor ion for MS/MS experiments. The CID fragmentation showed common product ions for all FOSAs/FOSEs (C_4F_7 and C_3F_5). Nevertheless, the different functionality gave characteristic pattern fragmentations. For instance, FTOHs mainly loss (H_2O+HF), FOSAs showed the loss of SO_2 and HF, FOSEs showed the losses of H_2O and SO_2.

Linearity, repeatability and LODs have been studied obtaining instrumental LODs between 1-20 fg. Concentrations found in real samples were in the range of 0.02-2 µg/L showing the improvements in detection capabilities of this new technique in comparison with the traditionally used methodologies.

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NAN-OC01

SELENIUM NANOPARTICLES: SYNTHESIS, CHARACTERIZATION AND APPLICATION AS POTENTIAL CHEMOTHERAPEUTIC AGENTS

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Nanotechnology is a relatively new scientific discipline, which is drawing high attention because of the novel and promising possibilities it offers within the biomedical field [1]. On the other hand, selenium is a dietary component recognized as an essential trace element. Various selenospecies have shown chemopreventive activity being able to suppress tumor cell growth *in vivo* and *in vitro*. However, the mechanism of this anti-cancer action is not yet fully understood and it seems that the chemical form and the concentration in which Se is administered, is crucial [2].

Based on these premises and in order to evaluate the potential chemotherapeutic properties of selenium nanoparticles (SeNPs), we have synthesized SeNPs using different stabilizing agents such as chitosan, gelatin, bovine serum albumin and transferrin. We have used transmission electron microscopy (TEM), z-potential and dynamic light scattering (DLS) for the characterization of these materials.

We have also evaluated the effect of these SeNPs as compared to other selenospecies in terms of cell viability, proliferation, induction of apoptosis and ability to arrest the cell cycle of cancer cells using colorimetric assays, fluorescence microscopy and flow cytometry. Additionally, we have determined the differential cellular internalization rates as a function of the stabilizers used, their potential interaction with cell receptors and the type of cell lines. We have used inductively coupled plasma mass spectrometry (ICP-MS) for measuring total Se in exposed cells and TEM for cellular localization of the SeNPs.

Our results show the potential of stabilized-SeNPs for targeting cancer cells and for inducing their mitotic arrest through the inhibition of a protein complex involved in the protein synthesis machinery and the alteration of key regulators of the cell cycle progression.

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OQA-OC01

THE ROLE OF HIGH RESOLUTION MASS SPECTROMETRY IN DIRECT ANALYSIS

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Who would not want to achieve direct analysis of any sample avoiding laborious sample treatment and long analysis time? In the last decade, a new group of mass spectrometric techniques has been introduced to achieve this goal. They were classified as “ambient ionization sources”: Direct Analysis in Real Time(DART) and Desorption Electrospray Ionization(DESI). These techniques can desorb molecules from samples by exposing their surfaces to some ionizing gas or aerosol. DART uses a “dry” heated gas stream carrying ionizing atoms previously formed in a plasma discharge and analyte ions are immediately formed upon interaction of the electronically excited atoms with sample surface. DESI uses an electrically charged aerosol generated by electrospray. The charged aerosol is directed toward the sample surface and analyte is extracted/ionized into the electrically-charged secondary droplets that are ejected from the surface into the mass spectrometer. The possibility of using different solvents offers the possibility to improve selectivity and sensitivity making DESI suitable for direct, rapid, real-time, and high-throughput analysis in many applications. Over time the term “ambient ionization” has been applied to ionization techniques that enable examination of untreated samples in the open environment while maintaining sample integrity performing “Direct Analysis”. However, “Direct Analysis” can have a broader meaning. Could a sample, introduced into an electrospray source (ESI) by infusion or by flow injection analysis (FIA), be considered “Direct Analysis”?

Direct analysis of samples with low matrix complexity can be affordable using low mass resolution instruments. The selectivity and the sensitivity of the mass spectrometer operating in full scan and in tandem mass spectrometry is enough for target and non-target analysis, providing information about molecular weight, elemental composition and isotope patterns. Nevertheless, direct analysis of complex samples such as those of environmental and food origin, demands much more from mass spectrometry. Very sensitive high resolution mass spectrometers (HRMS) for unequivocal identification and to prevent isobaric interferences, accurate mass measurements, isotope pattern analysis, tandem mass spectrometry with accurate mass fragment measurements, and mass spectrometric databases, etc. must be considered. In this communication all these topics supporting the importance of HRMS for direct analysis of complex samples will be discussed. DESI-HRMS and FIA-HRMS examples in the fields of environment, food and drug abuse, will illustrate the discussion.

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OQA-OC02

COMPREHENSIVE ANALYTICAL APPROACH TO INVESTIGATE THE COMPOSITION AND EFFECTS OF WEATHERED MARINE OIL SPILLS

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Oil spills in the marine environment are an issue of growing concern. Oil exploration and extraction is moving from the continental shelf to deeper waters where the risk of an oil spill is potentially greater. Moreover, oil spills from shipping activities are expected to increase due to the higher volume of maritime transport. Therefore, it is essential to develop analytical approaches which are able to comprehensively assess all the important aspects of marine oil spills. In particular, there is a need to evaluate how the weathering processes, such as photooxidation, affect to the oil molecular markers o biomarkers (compounds used for the identification of spill sources, i.e. fingerprinting. On the other hand, the compounds in fresh and weathered oils responsible for specific biological responses and chronic effects must be unambiguously identified.

In this work, a complementary set of methodologies was combined to assess the composition and effects of artificially and naturally weathered oils, such as the samples from the *Prestige* tanker spill and the *Deepwater Horizon* platform incident. This included conventional and comprehensive two-dimensional gas chromatography (GC×GC), thin-layer chromatography, infrared spectroscopy, and chemometrics-assisted effect-directed analysis (CAEDA). The selected strategy was able to determine the compounds affected by photooxidation in short- and medium-term, and to evaluate the implications of the observed compositional changes for the typically used fingerprinting methodology. Chemometric N-way partial least squares (N-PLS) model was able to successfully predict the aryl-hydrocarbon receptor (AhR) mediated activity of the investigated oil fractions and to facilitate the identification of the responsible compounds by relating the GC×GC dataset and the bioassay results.

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OQA-OC03

MAKING YOUR OWN ELECTROCHROMATOGRAPHY CAPILLARY FOR THE ANALYSES OF 5-NITROIMIDAZOLE RESIDUES IN MILK SAMPLES

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Capillary electrochromatography (CEC) is a hybrid separation technique which combines the high efficiency of capillary electrophoresis (CE) with the selectivity of liquid chromatography (LC) [1]. Open tubular, monolithic and packed capillaries are used as stationary phases where liquid mobile phases are propelled due to an electric field instead of a hydraulic pressure. Differences between analyte electrophoretic velocities and analyte-stationary phase interactions involve their final separation. CEC requires low sample volumes while solvent consumption is lower compared to traditional LC methods. Therefore CEC results an attractive separation technique that should be further studied in the residue analyses field.

A simple, quick and cheap methodology for producing C18 packed capillaries is proposed in this work. Capillaries are packed with C18 particles (5 µm, non-encapped) disposed as a suspension in a compact steel unit (SP-400 Nanobaume^{TM}) designed for packing capillary columns. Packing unit is coupled to a high pressure pump which propels the transporting particles solvent (acetone) towards the capillary at 42 MPa. Capillary frits are made by heating the packed capillary just in the area where frits are desired to be located. A metallic strip (80%Ni-20%Cr, 28cm×2mm×0.2mm, electric resistance 1.3 Ω) connected to a 7 AC power supply is used for capillary heating. Packed capillaries of different internal diameters and lengths were successfully made. For each capillary, the application of the proposed methodology took less than five hours considering all fabrication steps.

Determination of 5-nitroimidazole drugs in milk has been carried out in order to check the suitability of homemade packed capillaries. Separation was performed in a C18 packed capillary (40 cm effective lenght and 50 µm internal diameter) using a mixture 60:40 acetonitrile:buffer (ammonium acetate, pH 5, 1 mM) as mobile phase. Separation took place at 30°C under an applied voltage of 27 kV in less than 11 min. Milk samples pretreated by solid phase extraction were hydrodynamically injected for 150 s at 11.5 bars. Method characterization resulted satisfactory in terms of linearity (R^2≥0.992), repeatability (RSD≤12.2%) and reproducibility (RSD≤14.5%), obtaining detection limits lower than 28.8 µ/L for all studied analytes.

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OQA-OC04

TIME-RESOLVED LASER-INDUCED PHASE CHANGE MICROSCOPY: UNDERSTANDING LASER-MATTER EFFECTS AT THE FEMTOSECOND SCALE

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The particular coupling of energy and high peak power enabled by ultrashort laser pulses facilitates energy coupling inside materials by multi-photon or tunneling ionization mechanisms. Thus, ultrashort laser pulses have proven to be a powerful tool for the solids spectroscopy, surface micro- and nano-structuring as well as for the production of subsurface photonic and micro-fluidic devices. From the analytical point of view, ultrashort laser ablation opens new possibilities due to the significantly different properties when compared with their nanosecond counterpart. The most relevant is due to the lack of interaction between the incoming laser beam and the expanding plasma what allows the visualization of the different phenomena occurring until mass transfer occurs.

The present communication details the design, construction and evaluation of a microscope with time-resolved imaging capabilities. With such instrument, femtosecond-resolved micrographies of the surface of samples exposed to ultrashort laser pulses are obtained, allowing the dynamic observation of the phase-change during the laser-matter interaction. The results obtained are in the basis of the physics governing the ablation process and are in close contact with analytical techniques as LIBS, LIMS, MALDI or LA-ICP.

The results presented demonstrates the appearance of dynamic Newton rings at the surface of the sample that corresponds to the formation of a thin laser-induced surface layer resulting in constructive and destructive interference of the light reflected from the surface with the light reflected from the layer interface. The phenomenon is highly dependent of the material used as will be shown in the comparison of the micrographies obtained with the same sample (Si) in different crystalline forms. The effect of the laser energy per pulse and the time-scale of the different dynamic events occurring will be discussed.

COMUNICACIONES ORALES

CTQ Contribuciones teóricas y Quimiometría
NDP Nuevos desarrollos en preparación de muestra
ACL Análisis clínico

CTQ-OC01

AD-HOC BLOCKED EXPERIMENTAL DESIGN TO STUDY THE ROBUSTNESS TO EIGHTEEN FACTORS OF A PTV-GS-MS PROCEDURE

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An important step in the validation of an analytical procedure is the study of its robustness, which is approached in this work for the simultaneous determination of the herbicide dichlobenil (DIC) and its main metabolite (BAM) in onions by PTV-GC-MS.

Eighteen factors were considered [1]: seven related with the extraction and clean up step, eight with the PTV injection step and three factors related with the derivatization step.

The robustness of the experimental response to these factors is usually checked by slightly varying them above and below their 'nominal' values. With eighteen factors, that means a high number of experiments that, in general, cannot be performed in a single experimental session and/or under homogeneous experimental conditions.

In this work, we assumed that at much fifteen experiments can be performed under homogeneous conditions of the chromatography equipment (same session, same liner,...). Taking into account the need of measuring matrix-matched standards, experiments for estimation of the variance and the ones to study robustness, three sessions were necessary. Accordingly, to study the possible effect of the different sessions the design must be blocked, so we had eighteen factors at two levels and the block at three levels.

To handle the problem, for the first time, a method to compute ad-hoc experimental designs was developed. The resulting design simultaneously minimizes the joint variance of the coefficient estimates and the correlation between the block and the factors. In this way, the effect of the factors is not aliased with the block avoiding misinterpretations.

The computed design is coupled to PARAFAC2 [2,3], which allowed solving the specific problems of the chromatographic determination such as co-elution of interferents (silylation artifacts) and small shifts in the retention time and, besides, the unequivocal identification of target compounds according to document SANCO/12571/2013.

Extraction vortex mixing time, clean-up centrifugation time, initial PTV temperature and vent flow were the critical factors found.

Acknowledgments
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NDP-OC01

POROUS MEMBRANE PROTECTED MIP FOR Δ^9-TETRAHYDROCANNABINOL AND METABOLITES EXTRACTION FROM HUMAN BLOOD BY HPLC-MS/MS

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Synthesized molecularly imprinted polymers (MIPs) for selective tetrahydrocannabinol (THC) recognition were packed inside a polypropylene membrane, and the protected MIP was then used for pre-concentrating THC and metabolites (11-hidroxy-Δ^9-tetrahydrocannabinol, 11-Nor-9-carboxy-Δ^9-tetrahydrocannabinol, cannabidiol and cannabinol) from human blood before high performance liquid chromatography – tandem mass spectrometry (HPLC-MS/MS) determination. MIP synthesis was performed by the precipitation method (N_2 atmosphere, constant stirring at 40 rpm, 60 °C for 24 hours) using 11-Nor-9-carboxy-Δ^9-tetrahydrocannabinol as a template, ethylene dimethacrylate (EDMA) as a monomer, divynilbenzene (DVB) as a cross-linker, and 2-2'-azoisobutyronitrile (AIBN) as an initiator. Variables affecting the MIP-MIMSPE (batch mode, 50 mg MIP, 5 mL blood) process were fully studied. Optimum loading (retention) conditions were: pH of 6.5 (sodium dihydrogen phosphate/sodium hydroxide buffer for pH adjustment), and mechanical stirring at 150 rpm, 30 °C for 15 minutes. Target elution was performed with 5 mL of a methanol/acetic acid 90:10 mixture under ultrasounds irradiation for 8 minutes. The eluates were further N_2 evaporated to dryness, and the residue re-dissolved in 100 µL of mobile phase (acetonitrile). A pre-concentration factor of 50 was achieved.

HPLC-MS/MS targets separation/detection was performed under a gradient elution which involves two mobile phases: aqueous 0.1 % formic acid, pH 6.5 (A) and 0.1 % formic acid in acetonitrile (B). The flow rate (Zorbax Eclipse XDB-C8 column) was set at 0.40 mL min^{-1}, and the gradient program consisted of 0 % A for 0.1 minutes, followed by a 2 minutes ramp until 100 % A, holding this value for 2 minutes and next a 1 minute ramp until 0 % A, and 1 minute hold at 0% A. The developed method was fully validated and applied to several blood samples.

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NDP-OC02

FABRIC PHASE SORPTIVE EXTRACTION: A NEW DIRECTION IN ENRICHING POLAR EMERGING POLLUTANTS FROM ENVIRONMENTAL SAMPLES

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A new sorptive extraction technique, fabric phase sorptive extraction (FPSE) [1], which incorporates the advantages of solid-phase microextraction (equilibrium based extraction), exploits the benefits of sol-gel coating technology for microextraction sorbents, enhances the ability to fine tune selectivity parameter by using hydrophobic or hydrophilic fabric substrate, augments the primary contact surface area for fast analyte-sorbent interaction, is presented. FPSE constists of 25 x 20 mm fabric pieces coated with different sorbent chemistries using sol-gel technology. Due to the high primary contact surface area (1000 mm^2) of FPSE medium, inherently porous sol-gel sorbent coating, high volume of sorbent loading as thin porous film, and strong chemical bonding between the substrate and the sorbent, FPSE medium demonstrates remarkably fast extraction kinetic, exceptionally high extraction sensitivity, as well as high solvent and chemical stability.

In this study three of these sorbents, sol-gel polytetrahydrofuran (PTHF), sol-gel polyethylenglycol (PEG) and sol-gel polydimethyldiphenylsiloxane (PDMDPS) were evaluated in FSPE to extract a group of pharmaceuticals and personal care products (PPCPs) from aqueous samples. Firstly, different parameters affecting FPSE were optimized for each sorbent. Under optimum conditions, FSPE using sol-gel PEG provided the highest recoveries for the most polar analytes. Nevertheless, all three sorbents offered better recovery results compared to the commercially available coatings for stir-bar sorptive extraction based on polydimethylsiloxane (PDMS Twister), polyacrylate (Acrylate Twister) and polyethylelglycol silicone (EG SiliconeTwister) [2].

Finally, the new FPSE method using sol-gel PEG coated media and liquid chromatography–electrospray ionization tandem mass spectrometry (LC-ESI-MS/MS) was validated with the extraction of environmental samples. The extraction recoveries, linearity range, detection limits, repeatability and reproducibility were found to be satisfactory.

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NDP-OC03

DEVELOPMENT OF A POROUS METAL-ORGANIC POLYMER HYBRID SUPPORT FOR THE PURIFICATION OF PHOSPHOPEPTIDES

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We have developed a simple room temperature solution-based method for the preparation of highly porous iron(III) benzenetricarboxylate coordination polymer [1] films on the internal surface of a macroporous polystyrene-divinylbenzene-methacrylic acid polymer monolith [2]. The resulting metal-organic polymer hybrid (MOPH) maintains a high specific micropore surface area of 389 m^2/g and thermal stability above 250 °C in air. The MOPH preparation is readily adapted to a capillary column, yielding a flow-through separation device with excellent flow permeability and modest back-pressure. We demonstrate the excellent separation capability of the MOPH column by enriching phosphopeptides from mixtures of digested proteins. This approach to MOPH synthesis is easily implemented and likely adaptable to a wide range of coordination polymers and metal-organic frameworks.

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NDP-OC04

DETERMINATION OF FRAGRANCES AND PRESERVATIVES IN BABY WIPES BY PRESSURIZED LIQUID EXTRACTION AND GC-MS

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The use of personal care products, and in consequence, general population exposure to personal care product ingredients (PCPs) is growing. The number of products devoted to babies and children is also increasing.

Babies and young children are exposed to PCPs through the use of an important number of cosmetic products in their daily life. Some products of very frequent use are the baby wipes (up to 16 units per day) and wet toilet paper which are mainly applied in the diaper area comprising the genital area. As well, the skin of this sector of population is more vulnerable to the income of contaminants.

Fragrances and preservatives are common ingredients in all kind of personal care products including baby wipes. Fragrances provide nice and attractive scents and preservatives are used to prevent microbial growth because the wet tissue liquids are aqueous, and the hard surface wipe (commonly cellulose) is an optimal medium for microbial growth. European legislation [1] requires the monitoring of 26 fragrances considered as suspected allergens (PAS). Parabens and phenoxyethanol are the most frequently preservatives used and they are restricted according regulations. Some of them have been classify as suspected endocrine disruptors. Isopropyl-, isobutyl-, phenyl-, pentyl- and benzylparaben will be banned from October 2014.

PLE-GC-MS is proposed for the rapid simultaneous determination of forty PCPs including fragrance allergens, galaxolide and preservatives commonly used in cosmetic formulations. Multivariate optimization was carried out by means of experimental design to select working conditions. Under the optimal conditions, the method was extensively validated and it was applied to a broad range of baby wipes and wet toilet paper, in which 26 of the 40 target analytes were found. Phenoxyethanol was present in all analyzed samples at high concentration levels. The fragrance allergens limonene and benzyl alcohol were found in 60% of samples, whereas the other target compounds, including the near future banned isopropyl- and isobutylparabens were found in 5-45% of the samples.

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ACL-OC01

DISTINCTION BETWEEN SYSTEMIC AND NON-SYSTEMIC ADMINISTRATIONS OF BETAMETHASONE IN SPORTS

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Betamethasone (BET) is a glucocorticosteroid prohibited in sport competitions when administered by conventional systemic routes (oral or intramuscular, IM), and it is allowed by other routes (topical, TOP or intraarticular, IA). Therefore, distinction between administration ways needs to be performed. The aim of the work was to detect and characterize BET metabolites in urine and to study their excretion profiles after administration of BET using different routes in order to look for strategies to distinguish between legal and illegal administrations of the drug.

Urine samples collected after BET administration were hydrolysed with β-glucuronidase enzymes, subjected to extraction with ethyl acetate in alkaline conditions, and analysed by LC-MS/MS using open methods (precursor ion and neutral loss scan methods characteristic to detect fluorine corticosteroids) to detect BET metabolites. BET and nineteen metabolites were detected and the structure of most of them was proposed based on mass spectrometric data. A selected reaction monitoring method was validated to quantify BET and 6β-hydroxy-BET and to qualitatively determine the remaining identified metabolites. The method was applied to urines collected in studies where BET was administered to volunteers by different routes: a single oral dose (0.5 mg, n=2 volunteers), single IA dose (12 mg, n=13), and TOP doses (10 mg) for five consecutive days followed by a single oral dose (0.5 mg) and, then, a single IM dose (6 mg) to 6 volunteers.

The excretion profiles of all metabolites after the different administrations were evaluated. Concentrations of BET and metabolites after TOP administration were very low, and those of BET were well below the current reporting level of 30 ng/mL. After oral, IM and IA administrations, concentrations were greater and related to the dose administered. In the first hours after oral, IM and IA administrations, concentrations of BET were in the range 10-90, 40-490 and 60-1300 ng/mL, respectively. No differences on the excretion profiles of the metabolites were observed after IM and IA administrations. These results suggest that IA administration has the same systemic effects than IM use and, therefore, the status of IA administration in sports drug testing needs to be re-evaluated. The reporting level of 30 ng/mL of BET is adequate to distinguish TOP administration from oral, IM or IA uses, however the detection of systemic administrations may be limited when low doses are used.

COMUNICACIONES ORALES

ESP

Especiación química

ESP-OC01

QUANTITATIVE SELENIUM SPECIATION IN HUMAN VITREOUS AND AQUEOUS HUMOR BY HPLC-ICP-MS POST COLUMN IDA

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Selenium is an essential micronutrient for man and animals. The nutritional and biological role of selenium has been attributed largely to its presence in selenoproteins where the element is incorporated as the aminoacid selenocysteine (Secys),considered essential for redox catalytic activity. Overall, glutathioneperoxidases, thioredoxin reductases, and iodothyronine deiodinases are the three best characterized selenoprotein families involved in biological redox reactions.

Glutathione peroxidases (GPxs) are the general name of an enzyme family of multiple isozymes which constitute major components of human antioxidant defense.

This enzyme, together with catalase, superoxide dismutase and vitamin E are involved in defense mechanisms of cellular and extracellular matrix against free radical attack caused by reactive oxygen species (ROS). Oxidative stress reflects excess formation and/or impaired removal of ROS. Therefore, adequate levels of the antioxidant enzymes responsible for scavenging free radicals are essential for redox homeostasis. Nowadays, it has been accepted that oxidative stress is involved in many ocular diseases including age-related disorders, including age-related macular degeneration, retinopathy of prematurity, retinal light damage, and cataract. Ocular tissues and fluids contain antioxidants that play a key role in protecting them against ROS oxidative damage [1].

In particular selenium [2] is considered one of such ROS protective agents and then identification and quantification of selenium species (Se speciation) constitutes a new tool to investigate the role of selenoproteins in healthy eye and eye related diseases, particularly in relation to the enzymatic redox activities of GPx species.

Thus, the aim of this work was twofold: first, the development of a new methodology for quantitative selenium speciation (Se enzymes) in human vitreous and aqueous humor samples using HPLC-ICP-MS and post-column isotopic dilution analysis (IDA); second, to investigate the relationship between selenoprotein GPx levels, GPx n-mers and enzyme activity in humor samples and possible connection of such parameters with ocular diseases.

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ESP-OC02

ARSENIC SOURCE APPOINTMENT IN ATMOSPHERIC PM IN RELATION TO ITS EXTRACTION AND SPECIATION BY HPLC-HG-AFS

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Arsenic is a toxic element that affects human health. Its toxicity depends on the chemical form, oxidation state and rate of absorption and elimination into cells. Arsenic is considered a carcinogenic element and is also related respiratory and cardiovascular adverse effects. The presence of arsenic in atmospheric particulate matter (PM) can be due anthropogenic sources (e.g. copper smelters or mining exploitations).

A speciation analysis of arsenic has been performed in PM_{10} samples collected during one year (2012-2013) from the copper mining exploitation "Cobre las Cruces" (province of Seville, SW Spain) and the nearby town of Gerena, ca. 2 km away, in order to evaluate the possible influence of the mine on the air quality of Gerena.

PM_{10} samples were extracted using a $NH_2OH{\cdot}HCl$ solution, as it has been employed for other areas with high arsenic concentration due to the presence of a copper smelter [1]. The extract was analyzed for arsenic speciation by Liquid Chromatography coupled to Hydride Generation and Atomic Fluorescence Spectrometry (HPLC-HG-AFS). Total arsenic content was also determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).

The results indicated that mean arsenic values in Gerena were 2 ng/m^3, in comparison to ca. 20 ng/m^3 at "Cobre las Cruces". Extraction efficiency of 90% was found the samples in Gerena, whereas only a 30% extraction was obtained for "Cobre las Cruces". As arsenic is associated to the sulphur content of the samples, this indicates a different origin for the arsenic found in Gerena. Sulphur was present mainly as soluble SO_4^{2-} in the samples of Gerena, whereas in "Cobre las Cruces" sulphur is mainly as insoluble S^{-2}(related to pyritic material), thus indicating a different source.

This results support the different source appointment of arsenic in both places, indicating a minimal atmospheric transport of the mining exploitation to the nearby population.

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ESP-OC03

TOTAL DETERMINATION AND QUANTITATIVE SPECIATION OF ZN IN HUMAN AND COMMERCIAL FORMULA MILK USING ICP-MS

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Zinc is a metal with great nutritional importance, essential for cellular replication and the development of the immune response, playing an important role for normal fetal growth and development during the first years of life. On the other hand, Zinc has a recognized action on more than 400 enzymes by participating in their structure or in their catalytic and regulatory actions. In fact, today Zinc deficiency is a serious nutritional problem[1].

During the first months of life, milk constitutes the only source of nutrients for the newborn, providing all the macronutrients (proteins, lipids, carbohydrates) and micronutrients (vitamins, enzymes and minerals) needed to ensure the correct development of the newborn. In addition, the composition of maternal milk changes along the postpartum time, from colostrum (days 1-3) to mature milk (28 days), according to the requirements of the newborn.

On the other hand, Zinc bioavailability from human milk is higher than that from formula milk [2]. This difference can be attributed to the existence of a citrate rich fraction, the presence of lactoferrin, and the lower casein or phosphorous content of breast milk. In general due to the fact that metal speciation is different depending on the milk type [2].

Thus, the aim of this work is develop a speciation tool for the quantitative speciation of Zn in milk whey by HPLC-ICP-MS and post-column Isotope Dilution Analysis (IDA). Milk whey of premature and full term mothers, at four different stages of lactation (colostrum, 7^{th},14^{th},28^{th} day after delivery), have been investigated on Zinc distribution and content among different milk proteins. Colostrum, which is rich in proteins and Zn, is gradually replaced by mature milk and the Zn speciation profiles changed during lactation period. Also, there is a gradual increase in maternal milk production and a substantial drop in total Zn concentrations. The elemental Zn distributions in human milk whey was compared with those obtained for infant formulas commonly used to feed low-weight premature and normal full-term children. Quantitative IDA-ICP-MS results confirm important differences in quantitative Zn speciation exist between such formulas and breast human milks.

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COMUNICACIONES ORALES

AMA Automatización y miniaturización en análisis químico

API Análisis de procesos y productos industriales

AMA-OC01

TRACE DETERMINATION BY MEANS OF A COMBINED USE OF FLOW TECHNIQUES WITH CHROMATOGRAPHIES

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Non separative flow techniques present the advantages of cheap cost, a great simplicity, a high versatility and a high sample throughput. Their main drawback is their low resolution. On the other hand, chromatographic techniques present a high resolution, but low versatility.

In this contribution we would like to underline the great advantages which may be obtained by means of the hyphenation of both techniques, providing the non separative flow techniques their facilities in the sample handling, both before and after chromatographic separation

In this paper, a revision will be presented on the combined use of non–separative flow techniques with the chromatographies: MSFIA–LOV–HPLC, Sequential injection chromatography (SIC), Multisyringe chromatography (MSC), Multisyringe capillary electrophoresis (MSCE). The current and future developments of our group will be considered as well.

AMA-OC02

FACTORS AFFECTING ON-CAPILLARY LABELING OF PROSTATE-SPECIFIC ANTIGEN (PSA) FOR CE-LIF ANALYSIS OF ITS ISOFORMS

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The biomarker for prostate cancer (PCa) used currently in clinics is concentration of the glycoprotein prostate-specific antigen (PSA) in serum; however this test leads to a high number of false positives. To find more selective biomarkers of PCa, the alterations in the structure of the glycans of PSA are being studied. Our group developed a capillary electrophoresis (CE) method that allows the separation of different isoforms of intact PSA [1]. However, the low level of PSA (around 10^{-10} M) in some biological fluids requires using more sensitive detection techniques such as laser induced fluorescence detection (LIF). Protein derivatization with fluorogenic substances is challenging because the formation of multiple derivatives hinders the resolution of the isoforms and because the kinetics are very slow due to the low concentration of proteins. Recently, we developed an on-column derivatization method of PSA, through the amino groups, using the pyrylium dye Chromeo™ P503. This method allows the analysis by CE-LIF of several isoforms of PSA derivatized at a concentration of 1.5 10^{-5} M [2].

In the present study, to improve the sensitivity with LIF detection, different factors that control the on-column derivatization reaction between PSA and Chromeo™ P503 were investigated, namely dye-to-protein ratio, dye solvent nature, injection time for the dye plug, mixing voltage and time, and reaction time and temperature were tested.

The most critical factor among those studied is the dye-to-protein ratio; the sensitivity increases up to a ratio of 100:1 (mol/mol). Although some loss in isoforms resolution occurs at high ratios, it still allows the separation of different isoforms. The use of higher ratios than those does not improve sensitivity or resolution. Good reaction yields are obtained when Chromeo is solved in water or mixtures of water with 5 or 10% of methanol. It is not necessary to include steps for mixing and reaction because a satisfactory labeling takes place during the loading and separation steps. Reaction temperature does not have a significant effect on the reaction yield.

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Acknowledgments
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API-OC01

PROCESS SPECTRUM STRATEGY FOR NIR CALIBRATION SET PREPARATION: AN INNOVATIVE TOOL FOR PHARMACEUTICAL ANALYSIS-PAT

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Accomplish high quality in the pharmaceutical industry is a constant challenge that require strict control and supervision not only from final products but also from all manufacturing steps according to process analytic technologies (PAT) initiative.

In recent years, the simplicity and expeditiousness of near infrared spectroscopy (NIRS) have substantially fostered its use for the determination of pharmaceutical´s physical and chemical properties.

During the manufacturing process the physical characteristics of the samples changed due to different steps such as: granulation, compaction, coating. The NIR spectrum is strongly influenced by these changes; therefore, developing appropriate NIRS calibration models requires careful selection of calibration sets containing all potential sources of variability in the production samples to be analysed.

In this work firstly, we assessed three strategies to calculate calibration models capable of quantifying API (in a low concentration ~10 $mg.g^{-1}$) in granulated pharmaceutical formulation. These strategies were compared using samples of variable origin including laboratory-made powder mixtures and industrial samples, and variability in production samples was incorporated via a mathematical algorithm (calculation and addition of process spectrum *SP*). Although all the strategies are suitable for the purpose, the strategy involving calculation and addition of *SP* has some advantages over the other two including robustness, easiness, a good predictive ability (*RMSEP = 0.225* mg^{-1}) and the need for no reference method.

Secondly, the utility of the proposed method was evaluated in the development of NIR calibration models for determining API in tablet´s pharmaceutical formulation throughout its manufacturing steps. The sample´s physical changes due to the industrial process as compaction and coating were successfully incorporate into the calibration set using the SP strategy and subsequently the calibration models were calculated. Three models with good predictive ability were obtained for the different steps: Powder (mix of components), cores and coated cores, showing low prediction errors *RMSEP*(%w/w) = 0.071, *RMSE*P(%w/w) = 0.211, *RMSEP*(%w/w) = 0.254 respectively.

The obtained results in both studies confirm the suitability of the methodology for pharmaceutical formulations analysis in different physical forms (granulates, cores and coated cores) contributing to pharmaceuticals quality control from both end products or into the production chain.

All the proposed method were validated in accordance with the International Conference on Harmonization (ICH) and The European Agency for the Evaluation of Medicinal Products (EMEA) guidelines.

API-OC03

FULLY AUTOMATED ON-LINE SPE-HPLC-QQLIT-MS/MS TRACE ANALYSIS OF MULTICLASS ANTIBIOTICS AND METABOLITES IN WATER

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Recent research pointed out that some pharmaceuticals can produce adverse ecological and human health effects even at the low concentrations observed in the environment. Reports have shown that many pharmaceuticals and their metabolites do not degrade during municipal conventional wastewater treatment being, therefore, discharged to environmental waters [1]. As a consequence, pharmaceutical residues are being constantly released in environmental waters.

Antibiotics are one of the pharmaceutical classes with higher usage worldwide. They are used in human and veterinary (farming and aquaculture) medicine, mainly for treating or preventing bacterial infections.

One of the most significant negative effects attributed to the occurrence of antibiotics in the environment is the development of bacterial antibiotic resistance. Antibiotic-resistant bacteria are found in the natural environment, but significantly higher numbers of these bacteria are present in wastewater or even in treated wastewater [2]. In addition to continental waters, marine ecosystems are also impacted by antibiotic residues, mainly as a consequence of the waste discharges into the sea and through aquaculture, where antibiotics are extensively used.

The present work describes the development, validation and application of a fully automated analytical method for the determination of more than 50 antibiotics (including new-generation ones, like moxifloxacin), covering various therapeutic groups i.e. penicillins, tetracyclines, aminoglucosides, nitrofuranes, sulfonamides, macrolides, quinolones, and cephalosporins in water. The method was based on on-line solid-phase extraction (SPE) followed by high-performance liquid chromatography coupled to quadrupole-linear ion trap-tandem mass spectrometry (HPLC-QqLIT-MS/MS). Comparing with the off-line methodologies used, the presented method provides several advantages including a shorter extraction time, lower solvent and sample volumes and minimum manipulation.

To assess the applicability of the developed method, we analysed several river, ground, sewage and sea water samples. The performance of the method and the prevalence of the selected antibiotics observed in the analysed samples will be presented and discussed.

Acknowledgements
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SESIÓN DE PÓSTERS 1

AAL Análisis de alimentos
TOM Técnicas -ómicas
ACL Análisis clínico
AMA Automatización y miniaturización en análisis químico
API Análisis de procesos y productos industriales
ESP Especiación química
SQB Sensores químicos y biosensores
NAN Nanotecnología

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AAL-P01

DETERMINATION OF SYNTHETIC PHENOLIC ANTIOXIDANTS IN BEVERAGES BY STIR BAR SORPTIVE EXTRACTION COUPLED TO GC-MS

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Synthetic phenolic antioxidants are a group of chemicals usually added to foods to prevent degradation. The safety of these compounds is of a great concern, since they may cause allergen reactions in sensitive subjects, so their levels in food have been restricted [1]. A method for the determination of three of these compounds (butylated hydroxyanisole (BHA, E320), butylated hydroxytoluene (BHT, E321) and *tert*-butyl hydroquinone (TBHQ, E319)) using stir bar sorptive extraction for preconcentration purposes, coupled to thermal desorption, gas chromatography and mass spectrometry (SBSE-TD-GC-MS) has been developed.

Both the analysis of the underivatized analytes, as well as two different derivatization reactions, *in situ* acetylation, and *in tube* silylation, have been considered. Several parameters affecting the derivatization step, as well as the SBSE extraction and thermal desorption stages, were carefully optimized for each procedure. When the responses of the analytes in their acetylated, silylated and underivatized forms were compared, best results were obtained when the *in situ* derivatization procedure with acetic anhydride was employed.

The proposed method was applied to analyze canned soft drinks. In order to minimize any possible matrix effect, samples were diluted in a 1:5 ratio and an internal standard (carvacrol) was added to the samples for quantification purposes. Calibration graphs were found to be linear in the 0.5 – 20 ng mL^{-1} range. Quantification limits between 0.11 and 0.15 ng mL^{-1}, depending on the compound, were obtained, with good repeatability, RSD values ranging 6.5-7.4%.

The optimized procedure was applied for the analysis of ten soft drink samples. Even though the presence of these compounds in this kind of sample is forbidden [2], some of the analytes were found in five of the samples, probably as result of their addition as antioxidants to the essential oils used as flavouring additives. Recovery assays for samples spiked at two concentration levels, 1 and 5 ng mL^{-1}, provided recoveries in the 81-117% range.

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AAL-P02

ANALYSIS OF EMERGING CONTAMINANTS IN HERBAL TEAS AND WATER BY IN-SITU DERIVATIZATION WITH UA-DLLME AND GC-MS/MS

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In recent years, increasing attention has been directed to the presence and potential effects of pharmaceuticals and personal care products, known as emerging contaminants, in the environment.Although the concentrations of these compounds found in water are relatively low it has been suggested that a long-term exposure via drinking watermay produce health effects. On the other hand, these compounds may be present in herbal infusions by means of the water used to brew them, or in addition, by their occurrence in the plant itself.

A simple and rapid method has been proposed for the determination of fourteen emerging contaminants in water and different herbal infusions (tea, chamomile, linden-blossom and pennyroyal). This procedure is based on the derivatization of the target analytes with ethyl chloroformate and the derivatives are extracted applying ultrasound-assisted dispersive liquid-liquid microextraction (UA-DLLME) followed by gas chromatography-tandem mass spectrometry (GC-MS/MS).

Optimization of DLLME parameters includes the volume of sample, the dispersing solvent and the time of sonication. Under the optimized conditions, chloroform (100 µL) was injected into 4 mL of water or herbal infusion samples and sonicated for 10 min. The parameters of the in situ derivatization as the effect of solvent and volume of pyridine and ethyl chloroformate were also optimized. The use of alkyl chloroformate as derivatization reagent for phenols, alcohols, amines and carboxylic acids enables the reaction to be carried out directly in the aqueous phase at room temperature within seconds to minutes. After centrifugation, the chloroform phase was evaporated and analyzed after byGC-MS/MS.

Under the optimum experimental conditions, the limits of detection of the target compounds in water and the different herbal infusions were in the range 5 to 22 ng L^{-1}. The method was found to be linear over the range 50-25000 ng L^{-1} with correlation coefficients > 0.991. The developed method was applied to water samples from different sources (tap, well, river and dam) and six of the target compounds were detected at levels below 1 ng mL^{-1}. It was also applied to different herbal infusions and one hormone was detected.

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AAL-P03

STUDY OF ABSORBED FATTY ACID DEGRADATION ON EXPERIMENTAL AND PREHISTORIC VESSELS

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Lipid analysis is suitable for the study of vessels contents because they are present in human food and have a relatively high stability with increased temperature compared to carbohydrates and proteins. Residues can be characterized on the basis of fatty acid composition [1,2].

Previous analysis of prehistoric vessels and pots (2450 cal BC) by gas chromatography with flame detection (GC-FID) showed the presence of fatty acids to different degrees of degradation and high content of saturated fatty acids, especially C16 and C18, with traces of omega-3 and other long chain fatty acids, indicating the presence of fat fish in the extracted fat.

To study the degradation of the fatty acid from fish, trout has been selected, which according to the evidence found was consumed by our ancestors. Fat was extracted with chloroform-methanol 2:1, and the fatty acids were derivatized to the corresponding esters for analysis by gas chromatography. As experimental ceramic a handmade vessel has been selected and cooked over an open fire. The result is a relatively permeable material which absorbs the fat.

The next step is to impregnate the ceramic fragments with the extracted fat and to subject them to different degradation processes for a time (heat, burial, sunlight ...). After this period, fat was extracted from the ceramic and subjected to the same treatment and analysis that fat non absorbed on the ceramic (free fat).

From the obtained results we can deduce that effectively the fat deterioration pathway varies depending on the storage conditions, and allows us to compare the fatty acid profile of prehistoric ceramic samples with experimental ceramics subjected to different degradation processes.

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AAL-P04

AROMATIC PROFILE OF APPLE JUICES OBTAINED FROM NEW VARIETIES CIDER APPLE BY SPME AND HIGH SPEED GAS CHROMATOGRAPHY

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A method of Headspace Solid-Phase Microextraction (SPME) coupled to High-Speed Gas Chromatography with Flame Ionization Detector (HS-GC-FID) has been developed and applied to study the volatile compounds in apple juices. These juices have been obtained from new apple varieties showing special features like improved strength (resistance to fireblight, fungus *Venturia inaequalis* and *Dysaphis Plantaginea*), production regularity and obtaining bitter and late ripening varieties. The new varieties were obtained by crossing Asturian native varieties with others with suitable biological characteristics.

The identification of volatile compounds in genitors was carried out by Headspace SPME-GC-MS, seventeen of these compounds were selected for analysis due to their abundance and biological relevance.

Analyses were performed in a high-speed gas chromatograph equipped with a polyethileneglicol acidified capillary column and a flame ionization detector (FID). Chromatographic conditions were optimized to afford the separation of the compounds studied in less than twelve minutes. Different commercial fibers were evaluated by comparing the different normalized extraction efficiencies. The best extraction efficiency was obtained using fibers of 65 µm PDMS/DVB. In order to establish the optimal conditions for SPME extraction and obtain the maximum sensitivity, a 2^3 two levels full factorial design (FFD) was performed to investigate the effects of temperature, equilibration time and extraction time. NaCl amount stirring effect and sample volume were fixed according to univariate analysis results.

The feasibility of the SPME method was investigated. The regression coefficients for calibration curves of all compounds were in the range of 0,972 to 0,998. The accuracy was evaluated by calculating the percentage of recovery at three levels of concentration not being evidenced matrix effects. The proposed method shows good results in terms of reproducibility and repeatability consistent with the inherent uncertainty of the SPME techniques.

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AAL-P05

ANALYSIS OF POLYPHENOLIC COMPOUND BY LC-MS/MS FOR THE CHARACTERIZATION OF NATURAL EXTRACTS

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American cranberries (*Vaccinium macrocarpon*) and derived products possess a high content in different types of polyphenols (flavonols, flavan-3-ols, oligomeric and polymeric tannins (proanthocyanidins, PAC), anthocyanins and phenolic acids) which are responsible for a variety of potential health benefits such as preventive effects on urinary tract infections. This is due to the presence of A-type PAC oligomers that have the ability to inhibit the adhesion of pathogenic bacteria to tissue cells of the urinary tract [1]. Therefore, dietary supplements containing PACs at concentrations equivalent to the daily dose recommended to effectively combat these infections are being marketed. Recently, it has been suspected that some of the products sold as cranberry derivatives actually contain other fruits like grapes or blueberries, which do not have the adequate polyphenols to combat these infections. Hence, to protect consumers from possible fraud, analytical methods allowing an efficient authentication of natural extracts are needed.

An LC-ESI-MS/MS method was developed for the analysis of several polyphenolic compounds in different types of fruits products, such as fruit, juices and powder capsules, using a triple quadrupole analyzer with an electrospray ionization source (ESI). The chromatographic separation was achieved with a C_{18} column under gradient elution using 0.1% formic acid aqueous solution and methanol as mobile phase [2]. Data acquisition was performed in selected reaction monitoring (SRM) mode for quantification of polyphenolic compounds in food samples after applying a simple and fast sample extraction procedure. Principal component analysis (PCA) was used in order to explore the connection between polyphenolic profiles of marketed products and fruits of origin, thus achieving discrimination and characterization of these products to prevent misuses.Quality parameters, such as the limits of detection (12-116 µg/L) and quantification, linearity, accuracy, and run-to-run and day-to-day precisions at three concentration levels (RSD values < 13%) were calculated, obtaining satisfactory results. Finally, samples were characterized by their polyphenolic content and classified according to the fruit of origin, allowing the identification of a fraud from a natural extract labeled as cranberry-based.

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AAL-P06

DESORPTION ELECTROSPRAY IONIZATION/QUADRUPOLE-ORBITRAP FOR THE SCREENING OF VETERINARY DRUGS IN FEED SAMPLES

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Ambient mass spectrometry techniques (DESI: desorption electrospray ionization; DART: direct analysis in real time) have been incorporated to the ionization sources in mass spectrometry (MS). These techniques are designed for the direct analysis of compounds from sample surfaces recording mass spectra from bulk samples in their native environment and without sample treatment or chromatographic separation. The analysis is performed in few seconds, which is a significant advantage when compared to conventional analysis methods [1]. In DESI, charged droplets and ions produced from the electrospray are directed as a high-velocity gas jet into the surface dissolving analytes into the electrically-charged secondary droplets that are ejected from the surface into the MS instrument. The possibility of using different solvents to improve selectivity and sensitivity make DESI a suitable technique for rapid, selective and in situ analysis of samples in many application fields.

Veterinary drugs are widely used across developed countries to treat animals and protect their health. Despite the requirements set for feed business operators (Regulation EC No 183/2005), it is generally acknowledged that during the production of mixed feeds, a certain percentage of a feed batch remains in the production circuit and these residual amounts can contaminate the subsequent feed batches. This cross-contamination may result in the drug exposure to non-target animal species. For the analysis of these cross-contaminated feedstuffs extensive sample treatment and confirmatory methods, mainly based on LC-MS/MS, are required.

In this work the applicability of DESI/HRMS (q-Orbitrap) for the screening of veterinary drugs in cross-contaminated feed samples is explored. DESI-HRMS and DESI-MS/HRMS working conditions (geometrical parameters, electrospray solvent, mass spectrometry parameters) are optimized in order to achieve the best sensitivity and selectivity. The behavior of veterinary drugs with DESI is studied using spiked blank feed samples to assess matrix effects. The use of a database with mass spectral information of veterinary drugs for the identification of unknown cross-contaminants is evaluated. DESI-HRMS results are compared with those obtained by well-established LC-MS/MS methods [2] and advantages and limitations of DESI-HRMS for routine analysis of veterinary drugs cross-contamination in feedstuffs are discussed.

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AAL-P07

FEEDING RAPESEED OILCAKE TO SHEEP IMPROVES NUTRITIONAL QUALITY OF IDIAZABAL CHEESE

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Taking into account oilseeds fat composition and studies reported in the scientific literature, the objective of this study was to improve the nutritional quality of Idiazabal cheese by increasing the concentration of compounds with positive effects in human health. Simultaneously, the use of byproducts from locally-produced agricultural crops for sheep feeding could reduce production costs.

Two homogeneous groups of 36 sheep each were used for the study. Animals of group 1 (control) received commercial concentrate and animals of group 2 received 20% rapeseed oilcake concentrate. The experiment was carried out for a total of 22 days, allowing the first 7 days as adaptation time for the sheep. In addition, *Festuca* hay was offered to all animals.

During the experiment, animal production parameters (daily milk yield, live weight and body condition score) were determined. Cheeses (1 kg) were made with tank milk from both groups and ripened during 90 days. Gross composition, the composition of total fatty acids (FA), tocopherols and retinoids, cholesterol concentration and sensory analysis were evaluated.

FA composition was analyzed by gas-liquid chromatography with a FID detector as described (1, 2). NP-HPLC with fluorescence detection was used for tocopherols and retinoids composition and cholesterol analysis (3, 4). Accredited method (ENAC: 472/L1020) was used for sensory analysis (5).

Animal production parameters were identical for the two groups. Cheeses of group 2 had significantly higher amounts of unsaturated FA and lower amounts of saturated FA with chain lengths between 10 and 16 carbon atoms. The concentration of total tocopherols increased 24% and cholesterol decreased around 10% with respect to those of the control group. Sensory parameters of both types of cheeses were similar, with the exception of paste eyes, for which cheeses of group 2 had better scores.

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AAL-P08

SEPARATION OF TRIACYLGLYCEROLS IN HUMAN MILK SAMPLES BY HPLC-ELSD-APCI-MS WITH A SMALL-SCALE SAMPLE PREPARATION

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Human milk is considered the optimal way of providing to young infants the nutrients for a healthy growth and development. With regard to human milk composition, the lipid fraction is crucial, contributing in 40-55% to the total energy intake; and particularly, triacylglycerols (TAGs) represent 98% of this total lipid fraction.

In this work, a highly efficient separation method of TAGs present in human milk fat by RP-HPLC with UV and evaporative light-scattering detectors (ELSD) is proposed. TAGs separation was optimized in terms of mobile phase composition, column temperature and flow rate. An excellent resolution between more than 50 peaks in analysis time of 65 min was achieved. A total of 40 TAGs were identified by mass spectrometry (MS) detection with an atmospheric pressure chemical ionization (APCI) source. TAGs were recognized according to the protonated TAG molecule, their fragmentations into the respective diacylglycerols and its relative order of partition number.

Additionally, a small-scale method for fat extraction in human milk using minimal amounts of sample and reagents, in accord with green chemistry, has been developed. The proposed protocol and the traditional method for fat extraction were compared, giving similar results, with respect to total fat content and relative content of each TAG for more than 85% of identified TAGs.

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AAL-P09

METABOLIC PROFILE MODIFICATIONS IN BROILER CHICKEN TISSUES AFTER ENROFLOXACIN ADMINISTRATION

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In modern agricultural practice, antibiotics are extensively used and administered as feed additives or via the drinking water as therapeutic, prophylactic and growth promoting agents, but the inappropriate and abusive use of these substances can leave residues in food products from animals. The concern about their residues in foodstuff and the misuse in humans has increased as a result of the transfer of antibiotic-resistant bacteria to man, toxicity and allergy problems and their illegal use as growth promoters.

Up to this time, a large number of published articles have been focused on the development and validation of analytical methods to determine target substances and their main metabolites in several matrices, but there are few studies focused on the influence of antibiotics on the endogenous metabolism to evaluate changes in metabolite levels in animals. Accordingly, metabolic alterations caused by the use of antibiotics in veterinary and human medicine might be of great interest in the research of new potentially toxic or healthy compounds and to determine possible markers of the pharmaceutical treatments.

In this work, we studied the differences in the metabolome of chicken liver, kidney and muscle tissues from non-medicated, medicated and post-treatment samplesafter applying a pharmacological treatment with the widely used antibiotic Enrofloxacin.

Data analyses, combining high-resolution mass spectrometry with powerful pattern recognition techniques (PCA and PLS-DA), showed the clearly segregation of non-medicated, medicated and post-treatment samples of chicken tissues according to their metabolite profile, which demonstrate the existence of differences in the metabolome of the animal tissues due to the therapeutic treatment with the antibiotic. This fact reveals that levels of endogenous metabolites altered as a consequence of the drug administrationdid not returned to their original levels after the applied withdrawal period indicated in the product specifications (4 days), which could lead to unknown toxicological effects on consumers. In addition, 22 markers as the most contributing features for the separation between non-medicated, medicated and post-treatment samples were tentatively identified.

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AAL-P10

ANALYSIS OF IMINOSUGARS AND OTHER LOW MOLECULAR WEIGHT CARBOHYDRATES IN *AGLAONEMA TREUBII* EXTRACTS BY HILIC-QTOF MS

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Aglaonema is a genus of around 20 perennial species of plants of the Araceae family, native from tropical areas of Asia. Leaf extracts from *Aglaonema treubii* have been found to strongly inhibit α-glucosidases and could be potentially useful as antidiabetics, antiviral or immunomodulatory agents [1] and be used as food ingredients. These properties are attributed to its iminosugar (polyhydroxylated pyrrolidine and piperidine alkaloids) composition, including α-homonojirimycin, β-homonojirimycin, α-homomannojirimycin and 7-*O*-β-*D*-glucopyranosyl-α-HNJ, among others [1]. Different methods based on GC or LC have been proposed for the analysis of iminosugars present in mulberry extracts [2, 3]. However, little attention has been paid to other plant extracts such as those from *A. treubii* with a more complex iminosugar composition.

In the present work we have assayed different chromatographic conditions such as eluting solvents and mobile phase additives for the analysis of iminosugars and other low molecular weight carbohydrates (LMWC) of *A. treubii* leaf and root extracts by hydrophilic interaction liquid chromatography coupled to a hybrid quadrupole-time of flight mass spectrometer (HILIC-QTOF MS). Chromatographic retention mechanism of these compounds has also been evaluated.

Binary gradients of acetonitrile:water with different additives showed better resolution than those with methanol:water. Two eluting zones were clearly distinguished using acetic acid as additive: (i) sugars and inositol (13.0-16.6 min) and (ii) iminosugars (31.5-33.5 min). The same elution pattern was observed when formic acid and ammonium acetate were used as additives, although retention times for iminosugars were shorter (between 15 and 26 min). Lower resolution between iminosugars and interfering LMWC using 0.1% ammonium hydroxide as additive was obtained. In general, more narrow peaks with better symmetry were obtained using 5 mM ammonium acetate.

Plots of log *k* of target carbohydrates *versus* the linear and the logarithmic function of the water content of the eluent indicated a better correlation with surface adsorption mechanisms rather than with partitioning mechanisms.

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AAL-P11

IDENTIFICATION OF OLIVE OIL SENSORY DEFECTS BY MULTIVARIATE ANALYSIS OF MID INFRARED SPECTRA

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Virgin olive oil (VOO) has well-known nutritional and sensory qualities. In order to assure product quality and to protect consumers from frauds, it is important to authenticate the product. The only homologated methodology to evaluate sensory quality of olive oil is based on an expert panel test which recognizes and evaluates sensory attributes represented by several descriptors.

In this study a methodology using Mid Infrared (MIR) Spectroscopy in combination with chemometric methods has been developed to identify olive oil sensory defects. Spectra were obtained in the wavelength range from 4000 to 600 cm^{-1} and different specific regions were correlated to the four main sensorial defects in olive oils: *musty, winey, fusty* and *rancid*, previously evaluated by an expert sensory panel.

Classification models were developed using partial least squares discriminant analysis (PLS-DA) using different spectra preprocessing. PLS-DA multivariate models were able to discriminate between defective and non-defective oils with predictive abilities between 80-90% for the *musty* defect and between 70-80% for *winey, fusty* and*rancid* defects. A further analysis of the results (PLS-DA loadings) revealed the most important variables responsible for the discrimination.

The method proposed is fast, affordable and could complement the results obtain by the panel test and help to distinguish between extra-virgin olive oils (non-defect presence) and lower quality oils.

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AAL-P12

DIRECT DETERMINATION OF MINERALS IN HUMAN DIETS BY INFRARED SPECTROSCOPY AND X-RAY FLUORESCENCE

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The use of near and mid infrared spectroscopy (NIR and MIR) and X-ray fluorescence (XRF) to determine the concentration of mineral elements in Spanish human diets was investigated. Thirty-five commercial baby foods, six children fast food menus and thirteen university canteen menu samples were analysed by infrared and XRF spectroscopy and spectra evaluated by PLS regression using reference data obtained by inductively coupled plasma optical emission spectroscopy (ICP-OES). Models for calcium, potassium, iron, magnesium, sodium and zinc determination were built and validated. Spectra were pre-treated by using different pre-processing algorithms (multiplicative scatter correction, standard normal variation, first derivate, orthogonal signal correction, smoothing and mean centre) prior to developing calibration models using partial least squares and were evaluated by cross-validation and external validation. The highest coefficients of determination in validation (R^2_{val}) and the lowest relative root-mean-square error of prediction (RRMSEP) were obtained for potassium determination by MIR (0.86 and 11%, respectively) and NIR (0.9 and 11%); and for zinc determination by XRF (0.9 and 10%). Results founded through this study indicate that XRF, MIR and NIR spectroscopy, combined with chemometrics could be applied as a rapid and green method for the determination of the main minerals in human diets.

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AAL-P13

DIRECT DETERMINATION OF MAJOR COMPONENTS IN HUMAN DIETS AND BABY FOODS BY NEAR AND MID INFRARED SPECTROSCOPY

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A fast method has been developed for the direct determination of fat, proteins, carbohydrates and energy value of mixed foods using near-infrared (NIR) and mid-infrared (MIR) spectroscopy measurements in association with chemometric tools. Reference standard methods were employed to build and validate the infrared methods in order to provide screening tools for the evaluation of the human diet. The correlation coefficients obtained between predicted values and reference ones for fat, proteins, carbohydrates and energy value were 96.7, 98.1, 98.9 and 96.5 for NIR and, 91.0, 93.0, 92.0 and 84.1 for MIR, respectively, with relative root mean square error of prediction (RRMSEP) below or equal to 9% for NIR and 16% for MIR.

PLS models built provide predictive abilities of the major components in mixed foods in a quick and environment friendly way, being verified that models built are suitable to be used for the analysis of total fat, proteins, carbohydrates and energy values in only few minutes without using any chemicals nor heating steps.

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AAL-P14

TIME TREND AND INFLUENCE OF FOODS ENRICHED WITH OMEGA-3 ON PCDD/F AND PCB LEVELS IN EGGS AND COW'S MILK FROM SPAIN

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For the general population, dietary intake is the major route of dioxins (PCDD/Fs) and dioxin-like PCB (DL-PCBs) exposure, contributing with more than 90% to the daily exposure. Recent reports have led to a reevaluation of the toxic equivalency factors (TEFs) for PCDD/Fs and DL-PCBs and a new regulation with maximum permitted levels of dioxins in foods[1,2]. Nowadays, the use of supplements in industry to obtain functional foods such as food enriched with omega-3 has increased. This enrichment occurs generally through the addition of fish oils to the food product since they are rich in long chain fatty acids omega-3. Although the levels of PCDD/Fs and DL-PCBs in food have decreased throughout the years, fatty fish with high omega-3 content, have been reported to have high concentrations of pollutants like PCDD/Fs and DL-PCBs. This could add to the dioxin levels in those functional foods. In this study we present the concentrations of PCDD/Fs and non-ortho PCBs in Spanish commercially available cow's milk and eggs enriched with omega-3 fatty acids, collected in 2012. Also, their influence on temporal trend of their concentrations in the same type of non enriched foods randomly acquired from supermarkets during the first surveillance programme carried out in Spain since 1993.

The extraction and clean-up methodology have been described elsewhere[3]. Purified extracts were analysed by GC-HRMS/EI(+)-SIM[4] and GC-QqQ-MS/MS[5]. Blanks, recoveries, and parallel analyses were complied with analytical standards as recommended by the EU Commission. WHO-TEQ values have been calculated in the lower bound determination level.

PCDD/F and non-ortho PCB levels in eggs and cow's milk enriched with omega-3 fatty acids were higher than those expected according to the decreasing trend with years. A significant decrease of PCDD/F and non-ortho PCB concentrations in the studied foodstuffs was found over the years, in particular for PCDD/Fs. That decrease suggests that the efforts to control dioxin emissions and to reduce human exposure through foodstuffs are succeeding.

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AAL-P15

ANALYSIS OF PRIMARY AROMATIC AMINES IN FOOD CONTACT MATERIALS BY UHPLC-MS/MS

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Food contact materials (FCM) are those materials and articles intended to come into contact with foodstuffs, including packaging materials, cookware, processing machines and containers. Most of cookware are made of polyurethane (PUR), which is formed by the polymerization of polyols and diisocyanate monomers. In case of incomplete curing, the remaining unpolymerized aromatic isocyanates can be hydrolyzed and converted into primary aromatic amines (PAA) when come into contact with aqueous-acid based foodstuffs. European Union (EU), according to the regulation for food contact materials [1], has established a specific migration limit (SML) 0.01 mg of total PAAs that can migrate from the plastics material into 1 kg of food or food simulant.

The aimof this work is to develop an ultra-high performance liquid-chromatography (UHPLC) method with a pentafluorophenylpropyl (PFPP) column coupled to tandem mass spectrometry (MS/MS) using electrospray ionization (ESI) and a triple quadrupole mass analyser. The chromatographic behaviour of these compounds showed the U-shape performance on the PFPP column allowing an elution gradient with a high content of acetonitrile. Regarding mass spectrometry, the electrospray ionization provided the $[M+H]^+$ for all the compounds. Tandem mass spectrometry fragmentation has been studied to identify the most intense and characteristic product ions. In general, second generation product ions have been selected for quantitation, while ions of third generation were chosen for confirmation purposes. The UHPLC-MS/MS method showed a high sensitivity and selectivity providing limits of detection in the range of 0.56-9.98 µg eq ANL kg^{-1}. Correlation coefficients for the linearity were better than 0.998, and RSD% values below 10.5% were obtained. Different cookware has been analysed and aniline was found in most samples at concentration levels between 100 and 150 µg eq ANL kg^{-1}.

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AAL-P16

INTRA-ORAL HS-SPME-GCMS IS A USEFUL TOOL TO MONITOR AROMA RELEASE FROM ORAL MUCOSA AFTER WINE INTAKE

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Aroma is one of the main attributes of wine quality and an outstanding aspect related to food preferences and choices. In recent years, there is a growing interest in knowing what happens with the aroma compounds during food consumption and how these compounds might interact with the individual physiology. During wine consumption different oro- physiological factors (saliva, mucosa, air flows, etc) might modify (quantitatively and qualitatively) the original aroma composition of wine, therefore, changing the aroma profile that will interact with the olfactory receptors and ultimately, wine aroma perception.

Among the physiological factors, oral mucosa might have an outstanding role in the interaction and release of wine aroma after wine intake. This phenomenon can be related to the aroma persistence (or after-odour) which is defined as a long lasting aroma perception of wine odorants after swallowing. In spite of the large impact of this phenomenon for wine quality, the chemistry and mechanisms behind it are almost unknown.

To monitor aroma release from oral mucosa a sensitive, simple, non-invasive technique which allows aroma monitoring in *in vivo* conditions is required. In this sense, the use of SPME might represent important advantages over other analytical technologies usually employed for *in vivo* aroma release studies (PTR-MS, API-MS). Some of these advantages can be its higher selectivity and sensitivity, simplicity, low cost and the possibility to implement it in any lab.

Therefore, the objective of this study was to develop an intra-oral HS-SPME-GCMS methodology to allow monitoring the aroma release from oral mucosa after wine intake and its application to different types of wines, in order to assess the effect of wine matrix composition on the ability of oral mucosa to release wine odorants. Results of this study showed a good adequacy of this technique for monitoring aroma release exhibiting a good inter-individual repeatability for the majority of aroma compounds, which was dependent of the physicochemical properties of the aroma compounds. The study of the regressions lines of the different compounds after oral monitoring showed important differences in linearity depending on the wine matrices. In addition, it was proven that the consumption of red and white wines produces important differences in the total amount of aroma release showing that wine matrix composition could be an outstanding factor to explain wine aroma persistence.

AAL-P17

INFLUENCE OF COOKING IN DIOXIN AND PCB CONCENTRATION IN MEAT

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Polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are persistent organic pollutants originated as by-products in industrial processes (especially, thermal processes). Due to their lipophilic characteristics, these compounds can bioaccumulate in animal lipid tissue and biomagnify through the food chain. Dioxin-like polychlorinated biphenyls (dl-PCB) are also persistent organic pollutants and elicit similar toxic effects as PCDD/F. Maximum level of PCDD/Fs in meat of bovine animals is 2.5 pg WHO-TEQ/g lipid and 4 pg WHO-TEQ/g lipid for the sum of PCDD/F and dl-PCB (Regulation EU 1259/2011). These levels are established to control raw meat when it is bought or sold. However, since dioxins are by-products originated in thermal processes, the cooking process could have some influence on the concentration of these compounds in cooked meat.

To evaluate this influence, several samples were analysed: (a) raw meat, (b) grilled meat, (c) grilled meat, previously spiked with PCDD/F and dl-PCB, (d) boiled meat, and the liquid obtained in the boiling process (e) boiled meat, previously spiked with PCDD/F and dl-PCB, and the liquid obtained in the process. In addition, the olive oil used for cooking was also analysed.

Determination of PCDD/F and dl-PCB were performed following a validated analytical method based on international norms (USEPA 1613) and related European Directives. The main steps of the method were the following: (1) Addition of extraction internal standards of $^{13}C_{12}$-labelledPCDD/Fs and dl-PCBs to the sample, (2) Soxhlet extraction with hexane/dichloromethane, (3) clean-up in multilayer silica column, (4) separation of PCDD/Fs and PCBs by fractionation in SPE prepacked carbon tubes, (5) separation of dl-PCBs from the bulk of PCBs by fractionation in HPLC equipped with a pyrenil column, (7) concentration and addition of syringe standards, (8) instrumental determination of dl-PCBs and PCDD/Fs by high resolution gas chromatography coupled to high resolution mass spectrometry and quantitation by the isotopic dilution method.

According to the results obtained, the studied cooking processes do not increase the concentration of PCDD/F or dl-PCB in food.

AAL-P18

SUITABILITY OF VOLATILE COMPOUNDS AS MARKERS IN GEOGRAPHICAL DISCRIMINATION OF NORTH MOROCCAN VIRGIN OLIVE OILS

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Besides its nutritional value and healthy properties, the characteristic sensory attributes, flavors and aromas of virgin olive oil play a crucial role in the consumer acceptance of this foodstuff and have been widely used as geographical and botanical markers.

The volatile compounds of monovarietal virgin olive oil produced in the north of Morocco were investigated to check their suitability as markers of geographical origin. A total of 92 olives samples of *"Picholine marocaine" cv.*, grown in 7 different regions in the north of Morocco (Chefchaouane, Fès, Meknès, Ouazzane, Sefrou, Taounate and Taza), were collected over the period November-December 2012. Ripening index of the fruits was determined and olive oils were extracted using Oliomio system. Physicochemical quality parameters were determined for all the samples under study. Volatile compounds were analyzed by using headspace solid-phase microextraction and gas chromatography coupled to flame ionizationand mass spectrometry detectors (HS-SPME-GC-FID/MS). About 40 volatile compounds have been completely characterized (identified and quantified); the determined compounds belong to alcohols, esters, aldehydes, ketones and hydrocarbons chemical classes and represent from 97.4 to 99.9% of the total area in the chromatogram. Results showed no qualitative differences in the volatile fractions among the virgin olive oils from the 7 geographical regions evaluated; however, significant quantitative differences could be established.

Furthermore, multivariate data analysis was performed through the application of stepwise linear discriminant analysisand, the results revealed a satisfactory discrimination of the studied olive oil samples according to their area of origin. Taking into account the achieved results, it can be concluded that the volatile compounds determined by HS-SPME-GC-FID/MS together with an adequate chemometric treatment can be considered as an appropriate tool for the geographical discrimination of virgin olive oils from the North Moroccan.

AAL-P19

INFLUENCE OF STONE REMOVAL AND DEHYDRATION PROCESSES ON THE PHENOLIC COMPOSITION OF THE PRODUCED OILS

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The olive oil industry has been traditionally based on the olives crushing and centrifugation or pressing, to obtain olive oil, which involves a simultaneous waste production, mainly of'alperujo' (a mixture of pieces of stones, seeds, skin, pulp and water). Over the last years the interest in the recovery, recycling and upgrading of residues from olive oil industry has drastically increased.

An alternative for obtaining olive oil avoiding the production of 'alperujo' consists on performing a stone removal treatment from clean olives, followed by a dehydration process, a cold press and, afterwards, an oil filtration. The obtained olive oil -with potential use in food, pharmaceutical and cosmetics industries- has quite different physicochemical and organoleptic characteristics if compared with an olive oil produced by conventional procedures. Moreover, the dehydrated and defatted olive pulp (high fiber and bioactive compounds content) could be used as an ingredient in functional foods.

Herewith, we show the most relevant results of a study where the phenolic composition of 'conventional' olive oils and oils obtained with the method described above, from six different olive varieties, were compared. First, a reverse phase LC-ESI-TOF MS method (Zorbax C18 column (4.6x150mm, 1.8 µm)) was used for the comprehensive characterization of the phenolic fraction of the oils under study. After that, the samples were re-analyzed under identical chromatographic conditions and three different detectors working in parallel (DAD/Fluorescence/ESI-IT MS^n). A total of 12 extracts were analyzed, and it was possible to identify and quantify compounds belonging to different categories (simple phenols, secoiridoids, flavonoids, lignans, and phenolic acids). Compounds such as hydroxytyrosol, tyrosol, hydroxytyrosol acetate, elenolic acid, ligstroside aglycone, oleuropein aglycone, and pinoresinol, among others, were found both in conventional oils and those from pitted and dehydrated olives. From our point of view, the quantitative comparison was particularly interesting, showing that compounds such as hydroxytyrosol acetate (described as an excellent antioxidant) are present at much higher concentrations in the oils produced using the novel process.

Even though the results discussed here show the potential of the new method, a further physicochemical and organoleptic characterization of the produced oils is required. In any case, the new system has some obvious advantages: enhancement of oil content in terms of certain metabolites, possibility of full utilization of defatted pulp, and prevention of the generation of 'alperujo'.

AAL-P20

CARBOHYDRATE COMPOSITION OF PREBIOTIC SUPLEMENTED INFANT FORMULA

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Oligosaccharides, one of the main components of human milk, promote the growth of probiotic bacteria such as lactobacilli and bifidobacteria, in the colon, a microflora with beneficial effects on infant health. Since cow's milk, the source of most infant formula contains oligosaccharides in a very low concentration, in recent years, to mimic the beneficial effects of human milk an increasing number of infant formulas are supplemented with prebiotic carbohydrates [1]. Despite the importance of these compounds in the diet during the first months of infant's life, no data are available on the detailed composition of the carbohydrate fraction of supplemented prebiotic infant formula. The purpose of this study was to determine the composition of the oligosaccharide fraction present in twenty eight commercial infant formula using GC-FID and HPLC–RID.

After precipitation of fat and protein by Carrez reagents, analysis of supernatant solutions was performed by HPLC-RID in isocratic mode using acetonitrile:water (55:45, v:v) as mobile phase on a Kromasil NH_2column [2]; and by GC-FID using a HT5 aluminium-clad column [3]. To avoid interference in the GC analysis of galactooligosaccharides (GOS), samples containing maltodextrins were previously treated with α-amilase.

The results showed that the simultaneous use of both analytical techniques provided a complementary information on the oligosaccharide composition.. The analyses by HPLC-RID allowed the detection and quantification of oligosaccharides with a degree of polymerization up to 21; while GC-FID analyses permitted the quantification of the minor monosaccharides, disaccharides and prebiotic oligosaccharides such as GOS and fructooligosaccharides (FOS). Of the 17 samples with added prebiotics 7 have GOS in a content of 2.9 to 7.2 g/100 g dry matter (DM), 6 contained a mixture GOS/FOS (4.0 to 7.2 g/100 g DM) and 4 have FOS (0.1 to 2.5 g/100 g DM).

Although the oligosaccharide composition is not disclosed in the label of products, the total prebiotics content found was similar to the values declared, with exception of samples containing only FOS as prebiotic source, probably due to presence of inulin with higher DP difficult to quantify.

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AAL-P21

DEVELOPMENT OF A HILIC-MS METHOD FOR THE ANALYSIS OF GOAT COLOSTRUM OLIGOSACCHARIDES

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Currently, there is a high interest in the study of human milk oligosaccharides considering their beneficial activities such as anti-inflammatory properties or modulation of the immune system. Goat milk contains higher amount of oligosaccharides (GMO) than cow or sheep milk and it is known to be composed by fucosylated and sialylated oligosaccharides, which makes it similar in composition to human milk [1, 2].

Due to their complexity and structural diversity, GMO characterization presents a challenging analytical task and appropriate chromatographic and spectrometric methods should be developed. Scarce studies have been conducted for the characterization of GMO structures [1,2] and even less regarding those from goat colostrum. Considering that concentration of these biologically active oligosaccharides is supposed to be higher in colostrum, the objective of this work was to develop a new methodology using hydrophilic interaction liquid chromatography coupled to mass spectrometry (HILIC-MS) which allows the separation and characterization of goat colostrum oligosaccharides.

GMO were extracted from colostrum by precipitation of fat and proteins using the methodology described by Martinez-Ferez *et al.* [2]. Mono- and disaccharides were removed by size-exclusion chromatography using a Bio-Gel P2 (Bio-Rad). GMO analysis was performed on an Agilent 1200 series HPLC system coupled to an ESI quadrupole HP-110 mass detector. Two HILIC stationary phases were tested: a sulfoalkylbetaine zwitterionic (ZIC®-HILIC column) and an ethylene bridge hybrid with trifunctionally-bonded amide phase (BEH X-Bridge column). Influence of chemical additives (formic acid, acetic acid, ammonium acetate and ammonium hydroxide), organic modifiers (acetonitrile and methanol) and gradients of the mobile phases in the separation of GMO was studied. Due to the complexity of the sample, nine molecular ion adducts $[M+H]^+$ corresponding to acidic and neutral GMO were recorded in the selected ion monitoring (SIM) mode for the optimization of the method. The best separation was achieved with the BEH column using acetonitrile:water with 0.1% ammonium hydroxide (85:15, v/v) as mobile phase and 0.4 mL min^{-1} as flow rate. The methodology here developed will be applied for further characterization of GMO from several colostra using LC-QTOF MS.

Acknowledgments: This work was funded by Junta de Andalucía (project P11-AGR-7626) and CSIC (project i-link0827).

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AAL-P22

MIGRATION OF ADDITIVES, IMPURITIES AND OTHER NON-INTENTATIONALLY ADDED SUBSTANCES FROM COMMERCIAL POLYPROPYLENE FOOD CONTAINERS

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Polypropylene (PP) is one of the most commonly used packaging materials in food market. The synthesis of PP is a low cost process that involves the use of different types of additives and stabilizers in order to improve the properties and durability of the final packaging material. However, the presence of other components such as antioxidants, non-intentionally added substances or decomposition, reaction and intermediate products which can migrate from the food containers into foodstuffs have also been reported [1].

In this work, the migration of different components from PP food containers into four food simulants accepted by current legislation [2]: simulant A (distilled water), simulant B (acetic acid 3%, w/v), simulant C (ethanol 10%, v/v) and simulant D (ethanol 95%, v/v) has been investigated. Migration was evaluated at 30 ºC for 10 days to simulate long term use. The collected extracts were concentrated to incipient dryness and analyzed without additional treatment by comprehensive two-dimensional gas chromatography coupled to time of flight mass spectrometry detector (GC × GC-ToF MS) [3]. Analyses were done in duplicate.

This study provides a general overview of the most relevant compounds migrating from PP-based containers into food simulants. Different types of additives (including benzothiazole and derivatives or benzamide), specific flame retardants, plasticizers, and antioxidants (such as Irgafos 168 and its degradation product) have been identified in the extracts. The nature of other volatiles and semivolatiles substances detected in the extracts was elucidated and the presence of several polycyclic aromatic compounds, phthalates, biphenyles and furanes confirmed.

Acknowledgments:

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AAL-P23

CHARACTERIZATION OF TRIACYLGLYCEROLS PROFILE FROM DIFFERENT MAMMALIAN SPECIES BY HPLC-ELSD

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Human milk has a unique composition to provide young infants with the nutrients they need for a healthy growth and development. Infant formulas, which are used when breastfeeding is not possible, attempt to reproduce that composition as much accurately as possible. In formulas, milk from other mammalian species is normally used as human milk substitutes. However, their composition differs in terms of both lipid and protein content with respect to human milk. Since triacylglycerols (TAGs) represent 98% of the total lipid fraction of human milk, to precisely establish the lipid composition of the surrogates is of much interest.

In this work, a method of determination of TAGs in human milk, previously developed by our research group, has been now applied to the study of the composition of milk of different mammalian species. Firstly, fat was extracted following a multi-step procedure. Then, HPLC with evaporative light scattering detection (ELSD) was used to establish the TAG profiles. Separation was carried out with a Kinetex™ C18 column by stepwise elution. All samples gave chromatograms with more than 50 peaks; then, a reduced number of them, which were common to milks from the different sources (human, cow, goat and sheep), were selected to construct linear discriminant analysis (LDA) models for mammalian species prediction. Ratios of areas of selected peaks by pairs were also used as predictors. A study of the reliability of classifying milks according to their mammalian specie using TAG profiles by HPLC-ELSD followed by LDA of the chromatographic data was accomplished.

AAL-P24

PRESSURIZED LIQUID EXTRACTION OF IMINOSUGARS FROM *AGLAONEMA* SP. STABILITY, TOXICITY AND BIOACTIVITY OF THE EXTRACTS

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Diabetes and obesity are chronic diseases of high prevalence in our current society. Among different drugs, glycosidase inhibitors such as iminosugars are used for treating these metabolic disorders. They are found in several plants such as *Morus* sp., *Hyacinthus orientalis*, *Aglaonema* sp., and their extraction from natural sources is attracting great interest from the food industry with the intention of incorporating them as bioactive food ingredients. Pressurized liquid extraction (PLE) is a fast and efficient technique which has gained a great acceptance for the extraction of metabolites with low solvent consumption. Previously we have developed a PLE method for the extraction of 1-deoxynojirimycin and fagomine from mulberry leaves [1]. In the present study, a new PLE method has been optimized to obtain the highest yields of iminosugars from *Aglaonema* sp. leaves and roots. Bioactivity, stability and toxicity of *Aglaonema* extracts have also been evaluated.

Eighty mg of *Aglaonema* sample, 100ºC and 2 minutes of extraction time were selected as optimal conditions. Similar amounts of total iminosugars were obtained by both PLE and conventional extraction. However, PLE solvent volumes (0.8 mL) were lower than those used in the conventional procedure (10 mL). To remove the relatively high concentration of other interfering low molecular weight carbohydrates present in these extracts, a yeast (*Saccharomyces cerevisiae*) treatment was optimized. Thus, 5 hours at 37ºC were enough to remove mono- and di-saccharides from the extracts, while preserving the initial content of iminosugars.

In addition, α-glucosidase inhibitory activity of iminosugars extracted from *Aglaonema* sp. was confirmed. IC_{50} for *Aglaonema* extracts were 0.03 mg mL^{-1} using concentrations of 0.25 U mL^{-1} of *α*-glucosidase and 1 mM of 1-O-(4-nitrophenyl)-*α*-*D*-glucopyranoside as substrate.

In vitro studies with Caco-2 cells, showed no potential toxicity for *Aglaonema* sp. leaf and root extracts at concentrations lower than 125 and 25 µg mL^{-1}, respectively. Stability of *Aglaonema* iminosugars was also confirmed for 1 and 2 months of storage at 50°C and 25°C, respectively.

The results from this comprehensive study show the potential of PLE for the extraction of *Aglaonema* bioactives with a view to their further industrial exploitation.

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AAL-P25

IRON-BINDING PROPERTIES OF CASEINOPHOSPHOPEPTIDES DERIVED FROM A CASEIN BY-PRODUCT

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The phosphorylated regions of caseins or caseinophosphopeptides (CPPs) are known to bind metal ions avoiding their precipitation at alkaline pH in the distal small intestine [1]. This property of CPPs has been associated to their ability to improve the bioavailability of minerals such as iron, calcium, zinc and selenium. In our study, the CPPs present in a casein-derived by-product released during the manufacture of an antihypertensive ingredient have been identified. Initially, an enzymatic hydrolysis process with trypsin during 30, 60, and 120 min followed by selective precipitation of CPPs with calcium chloride and ethanol at pH 4.0, 6.0 and 8.0 was carried out. The released peptides were identified using tandem mass spectrometry and compared with those liberated after gastrointestinal digestion of casein by-product simulating physiological conditions [2]. The results showed a high homology between the identified sequences by both hydrolysis procedures (73%). These results demonstrate that the by-product could be used as a source of CPPs liberated after its passage through the gastrointestinal tract without the need to perform a previous hydrolysis process. A second set of experiments was conducted in order to evaluate the iron-binding capacity of the CPPs-enriched by-product. Three different ferrous salts were used to prepare formulations with the by-product at different protein:iron ratio. A colorimetric method [3] to measure the iron binding capacity was optimized for these formulations. It was observed that the type of iron salt affected the amount of iron bound to the by-product. With one of the salts, the bound iron was higher than 90% at protein:iron of 50:1 (p/p). The complexes prepared with this salt may serve as basis on new CPPs-based formulations with capacity to improve the iron bioavailability.

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AAL-P26

CHROMATOGRAPHIC DETERMINATION OF SOLUBLE FRACTION OF CARBOHYDRATES IN LEGUMES FROM ALGERIA

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Legumes are an essential source of energy and nutrients for humans and their cultivation has facilitated the settlement of people in different regions of the world. In countries from the north of Africa, such as Algeria, these foods can be consumed as cooked seed or as flour in the preparation of some foodstuffs. According to FAO (2012) the consumption of legumes in Algeria is 17 g/person/day.

Considering the water soluble fraction, α-galactosides, galactosyl derivatives from sucrose are one of the most important compounds. These carbohydrates act as antinutritional factors or beneficial compounds (prebiotics, immunomodulators, antihipertensives…), depending on the dose at which they are consumed. Thus, it has been found that 3 g/day is the effective daily dose of α-galactosides to obtain health benefits, whereas higher intake can cause negative effects. It is also known that the processing can exert a certain protection against these components. Therefore it is of paramount importance the knowledge of the occurrence of these compounds in legumes in order to select the most adequate processing to preserve their quality and bioactivity. In this work, chromatographic determination of soluble fraction of carbohydrates in five samples of legumes (chick peas, lentils, beans, peas, faba) from Algelia has been carried out. Two different methods HPLC-RID and GC-FID were used for their characterization. In the former, the extraction of carbohydrates was carried out with water at 60°C and glucose, sucrose, raffinose, stachyose and verbascose were detected in all samples. The highest recovery was obtained for the carbohydrates with the highest polymerization degree (DP), with values close to 99% in the case of verbascose. For GC analysis, apart from those carbohydrates previously detected, ajugose and different cyclitols, as *myo*-inositol, were found. In these analyses, Carrez solution was used for sample preparation and the highest recovery values (≥83%) were obtained for compounds with DP ≥2, verbascose presenting a value close to 98%. In general, the most abundant carbohydrates were stachyose and verbascose and the quantified levels were variable depending on the analysed specie and within the range showed for legumes from other countries. Similar total amounts of α-galactosides were obtained by both chromatographic methods, although GC allowed the detection of higher number of compounds, including galactosyl cyclitols.

AAL-P27

ANALYSIS OF SULFONYLUREAS IN WATER AND JUICES BY SALTING-OUT ASSISTED LIQUID–LIQUID EXTRACTION AND CAPILLARY-HPLC

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Sulfonylurea herbicides (SUHs) are one of the most important pesticides used worldwide for the control of many grasses and most broad-leafed weed species in a variety of crops and vegetables [1]. SUH products are now the second most common kind of herbicides after the glyphosates and more than 30 products have been commercialized.In this work a sensitive capillary HPLC-UV method has been developed for the quantification of nine SUHs in environmental water and banana juice samples. The separation was achieved in 24 min, using a Luna C18 column (150 mm×0.3 mm I.D., 5 µm particle size)at 25 °C, with a mobile phase of water and acetonitrile, both of them with 0.01% acetic acid.

Moreover, salting-out assisted liquid–liquid extraction (SALLE) has been optimized for the satisfactory extraction of SUHs.This technique is based on liquid–liquid extraction, in which the addition of an appropriate amount of salt to a mixture of aqueous sample and water–miscible organic solvent causes the separation of the solvent from the mixture and thus the formation of a two-phase system and simultaneously the target analytes are separated into the organic phase [2]. Several parameters affecting the extraction process such as the type and volume of the organic solvent, sample volume, type and amount of salt, pH of the sample and vortex time were optimized. Under optimum conditions, matrix-matched calibration curves were established using river water and banana juice samples. Good linearity as well as low limits of detection, LODs (0.4–1.3 and 3–13 µg/L) and quantification, LOQs (1.3–4.3 and 10–43 µg/L) were obtained in water and banana juice samples, respectively. The precision (intra- and inter-day) of the peak areas, expressed as relative standard deviations (%, RSD), at two concentration levels were below 10 % in both matrices. Recoveries obtained from spiked environmental waters (river water and groundwater) and banana juice samples, at two concentration levels, ranged from 72 to 115%. The results of the analysis revealed that the proposed SALLE-capillary HPLC method is simple, rapid, cheap and environmentally friendly, being successfully applicable for the determination of SUHs in these matrixes.

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AAL-P28

LC-MS APPLIED TO DETECT AND QUANTIFY A BIOACTIVE FOOD-DERIVED PEPTIDE AND ITS METABOLITES IN PLASMA

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The detection and quantification of food-derived peptides in biological samples represents a challenging issue. The complexity of matrices, such as plasma or urine makes the detection of compounds very difficult for bioavailability studies. Moreover, the concentration of food-derived peptides present in these kind of samples is usually in the range of picograms due to the low absolute absorption rate into blood circulation after ingestion (0.1% of ingested compound). This fact implies the development of very sensitive analytical methods such as LC-MS, which must be optimised to achieve the best conditions for a targeted analysis. Likely, it is important to assess the metabolism of peptides by the action of plasma peptidases. In this regard, MS-based techniques have become indisputable tools to detect derived fragments generated in plasma. In addition, the previous clean-up of the sample is a very important step when performing analysis of plasma by MS-based techniques. Proteins or phospholipids may impair the identification of peptides by MS, since in the latter case they interfere with ionization. Little information is available on the absorption of food-derived peptides into blood circulation. However, the information provided by these kind of studies is essential in order to attribute a certain biological activity to a given peptide. This is important to assess the efficacy of functional foods. In this work, a sensitive MS-based method was developed in order to detect a milk-derived antihypertensive penta-peptide (β-casein f134-138, HLPLP) in plasma samples by the use of Ultrahigh Performance Liquid Chromatography (UPLC) coupled *on line* to a Q-TOF instrument. A pseudo-selected reaction monitoring (SRM) method was optimised, in which the parent ion corresponding to the target peptide was selected for fragmentation. Previous cleaning step based on protein removal by addition of acidic solution and heating at 99ºC was followed by sample solid-phase purification. Mixed mode cation exchange cartridges were selected for maximal recovery (94.7% - 99.9%). The limits of detection quantification were 0.02 ng/mL and 0.10 ng/mL, respectively. This method was applied to plasma samples collected after intravenous and oral administration of the antihypertensive penta-peptide to rats and it was successfully detected and quantified. In addition, several derived fragments probably generated through the action of plasma peptidases could also be detected and therefore permitted to follow the fate of the administered peptide and its metabolites.

AAL-P29

STUDY OF ROSEMARY POLYPHENOLS STABILITY AND BIOACTIVITY IN CELL CULTURE USING UHPLC-QTOF-MS AND FLOW CYTOMETRY

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In recent years, the anti-inflammatory, antioxidant and antiproliferative activities of rosemary polyphenols have been demonstrated *in vitro* using different cell lines. However, the stability of rosemary compounds under culture conditions is unclear. In addition to this, in most of the experiments *in vitro*, measurements were usually made a day or few days after the addition of rosemary polyphenols to the culture media, complicating the identification of the primary targets of action of these compounds, as well as their molecular mechanisms. In this work, a study of the stability of the main rosemary polyphenols in cell culture systems was carried out to understand the action and fate of these compounds using *in vitro* conditions. Also, a study of the early effects of rosemary polyphenols on the intracellular redox status and cell cycle progression was performed with HT-29 human colon adenocarcinoma cells using flow cytometry. The analysis of rosemary polyphenols in culture media at different time points was carried out using UHPLC-qTOF MS. Chromatographic data indicated that carnosic acid, a major polyphenol in the rosemary extracts, was not stable with a half-life lower than 24 h. Flow cytometry data revealed that rosemary extracts stimulated the production of intracellular ROS in a concentration-dependent manner, increasing up to 2.7-fold in HT-29 cells incubated with 45 µg/mL rosemary extract compared to untreated cells. The study of cell cycle progression using flow cytometry demonstrated a differential effect of rosemary extracts on cell cycle depending on the extract concentration. Thus, incubation of HT-29 cells with rosemary extracts at 30 µg/mL resulted in a substantial inhibition of cell cycle progression from 12 to 24 h, manifested by the accumulation of cells in the G1 phase, whereas incubations with 45 µg/mL rosemary extract exerted the inhibition of cell cycle progression by the blockade of G2/M phase. Further experiments based on the co-treatment of cells with rosemary extracts and different antioxidant agents (catalase and superoxide dismutase) suggested an association between G2/M arrest and the observed early exacerbated ROS generation in HT-29 cells upon treatment with 45 µg/mL rosemary extract.

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AAL-P30

SIMPLE AND EFFICIENT METHODOLOGY TO DETERMINE MYCOTOXINS IN CEREAL SYRUPS

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Cereal syrups are obtained by isolation of starch after wet milling of grains, hydrolysis and purification, being widely applied in foods and pharmaceuticals. Mycotoxins are highly toxic natural secondary metabolites produced by filamentous fungi belonging mainly to the genera of *Aspergillus*, *Penicillium*, and *Fusarium*that grow in a wide range of agricultural products before, during and after harvest. They may be found in syrups resulting from the use of contaminated raw material or invading microorganisms in the final manufactured product.

Liquid extraction followed by clean-up with immunoaffinity columns (IAC) is the most popular sample treatment for routine analysis of mycotoxins. However, IAC is an expensive and complex purification system which suffers from low recoveries for some mycotoxins, due to matrix complexity and their use in multi-residue analysis is limited. As an alternative, QuEChERS is an effective simple method, which has been recently applied for extracting mycotoxins from different cereals [[1],[2]], among other food commodities.

In this work, a simple method for the determination of ten mycotoxins (ochratoxin A, fumonisin B_1, fumonisin B_2, deoxynivalenol, fusarenon-X, T-2 and HT-2 toxin, citrinin, sterigmatocystin and zearalenone) in cereal syrups (rice, wheat and barley) has been developed using UHPLC-MS/MS. The sample treatment consists on a QuEChERS-based extraction, but no further clean-up of extracts was required. Extraction was performed with phosphate buffer and 10 mL of 5% formic acid in acetonitrile (extractant) and subsequent addition of Agilent SampliQ EN QuEChERS extraction kit (4 g $MgSO_4$, 1 g NaCl, 1 g sodium citrate and 0.5 g disodium hydrogen citrate sesquihydrate). Matrix-matched calibration curves were established and limits of quantification were below the limits usually established by current legislation in different foodstuff. The RSD was lower than 12% in all cases, with recoveries from 70.2 to 100.6 %.

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AAL-P31

EXTRACTION AND IDENTIFICATION BY HILIC- AND RP-HPLC-ESI-Q-TOF-MS/MS OF BIOACTIVE PEPTIDES IN PLUM SEEDS

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Fruit industry produces a great amount of waste which is mainly discarded [1]. Seeds of stone fruits such as plums are part of these residues. Plum (*Prunus domestica L.*) seeds are rich in proteins, with a protein content close to 20 % [2]. These proteins could be a source of high valuable compounds like bioactive peptides. Therefore, it is interesting to recover these underused and undervalued waste material and to find new opportunities for its utilization.

The aim of this work has been to develop a method for the extraction of plum seed proteins, to obtain peptides from these proteins using different enzymes, to study the antihypertensive and antioxidant activities of obtained peptides, and to comprehensively identify bioactive peptides using HILIC- and RP-HPLC-ESI-Q-TOF-MS/MS.

For that purpose, buffers at different pHs and compositions and high intensity focused ultrasounds were employed for the extraction of plum seeds proteins. Four enzymes (alcalase, thermolysin, flavourzyme, and protease P) and different digestion conditions were tried to obtain a high content of peptides from extracted proteins. Antioxidant and antihypertensive capacities of peptide extracts were evaluated and those extracts showing the highest capabilities were selected and fractionated by ultrafiltration. Reversed-phase (RP)-HPLC coupled to electrospray-mass spectrometry (ESI-Q-TOF-MS/MS) was firstly employed for the separation and identification of bioactive peptides. It was possible the identification of 16 and 7 peptides in the antioxidant and the antihypertensive fractions, respectively. Since digestion was performed using non specific enzymes, obtained peptides presented short chains and, many of them, were poorly retained by RP-HPLC. Hydrophilic interaction liquid chromatography (HILIC) is suitable for the separation of polar compounds, like this kind of peptides, and is highly compatible with ESI-MS. The analysis of fractions by HILIC-ESI-MS/MS enabled the identification of 5 additional peptides in the case of the antioxidant extract and 4 in the case of the antihypertensive fraction.

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AAL-P32

PEPTIDE CHARACTERIZATION OF POTENTIALLY IMMUNOMODULATING OVALBUMIN HYDROLYSATES

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Background: In Europe, food allergy is continuously growing with an incidence today of 6-8% in young children. Peptides released from enzymatic hydrolysis of certain proteins could exert stimulatory activities on immune system disorders such as egg allergy. Ovalbumin (OVA) is the major protein of egg white and several of its hydrolysates have been described as a source of bioactive peptides, some of which may present immumodulatory activity. Cell cultures derived from mouse models of food allergy have proven useful in the evaluation of the modulatory activities of hydrolysates, but identification of the immunomodulatory peptides and reactive epitopes in protein hydrolysates is still scarce and mass spectrometry has become a necessary tool in food allergy. The aim of this study was the peptidic characterization of OVA hydrolysates and their evaluation as allergenic modulators by using splenocyte cultures of OVA-sensitized mice.

Methods: Endotoxin free-OVA was hydrolyzed with commercial enzymes (Pepsin, Alcalase and Neutrase). The hydrolysates were characterized by SDS-PAGE, and RP-HPLC. The sequence of the peptides present in the hydrolysates was deciphered byRP-HPLC-MS/MS and UPLC-Q-TOF. OVA-sensitized mice splenocytes were isolated and cultured in presence of the hydrolysates. The immunomodulatory effect of the hydrolysates was based on the cytokine profile, as determined by direct ELISA.

Results: The two mass spectrometry methods were optimized to perform the analyses of all the peptides present in the hydrolysates. In the case of the ion trap, the target mass was set at a *mass-to-charge* (*m/z*) of 750, in order to identify short sequences. However, in the case of the Q-TOF was optimized to achieve the identification of larger peptides (mass ranges of 200-1500 and 1000-4000 *m/*z) increasing the ionization by adding formic acid (0.1%) to the hydrophobic phase. A marked down-regulation of Th2-biased cytokines (IL-4, IL-5 and IL-13) was observed in splenocyte cultures incubated in presence of the hydrolysates being higher in those obtained with Pepsin and Alcalase. The levels of Th1-biased cytokines (IFN-γ and TNF-α) were significantly increased in the presence of the hydrolysate with Pepsin.

Conclusion: The hydrolysate of OVA with Pepsin exhibited an immunomodulatory effect on the cytokine profile of OVA-sensitized mice splenocytes. We are currently investigating the structure-activity relationship of the identified peptides.

AAL-P33

EFFECT OF POLYMERIZATION WITH TRANSGLUTAMINASE IN THE ALLERGENICITY OF OVALBUMIN

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Egg allergy is an abnormal immunological response to HEW compounds which is IgE-mediated and affects around 1-2% of young children. Among the major allergenic HEW proteins, ovalbumin (OVA) is the most abundant. OVA is a globular protein very resistant to physiological digestion which results in non-fragmentation of some epitopes that can cross the intestinal barrier. Among the strategies to decrease food protein allergenicity, enzymatic cross-linking with transglutaminase (TG) has been widely used and OVA has been previously described as an adequate substrate to TG after its denaturalization. The aim of this study was to characterize the OVA cross-linked products before and after their*in vitro* digestion and identify those with reduced allergenic potential.OVA used for polymerization was previously denatured by either heat treatment or high hydrostatic pressurization (HHP). Then treated OVA at different concentrations was cross-linked with TG. OVA was also cross-linked under HHP without a previous denaturalization. Polymerized products were digested under simulated physiological conditions. Samples were analyzed by SDS-PAGE, RP-HPLC and size-exclusion chromatography (FPLC). Allergenicity of cross-linked OVA and their digestion products were evaluated by inhibition ELISA using sera from egg allergic childen. Allergenic effect of polymerized OVA was also evaluated in splenocytes from HEW sensitized mice and its cytokine profile was analyzed by direct ELISA. The degree of cross-linking was higher when pre-heated OVA was used as substrate as shown by SDS-PAGE. Pressurized OVA cross-linked products showed a strong concentration dependence, looking at FPLC separations, where the peak of OVA appeared higher at increasing concentrations. RP-HPLC was used to evaluate the peptide profile of the samples after digetion and it was observed that pre-heated OVA cross-linked products were more easily digested than those cross-linked after or under HHP. Percentage of IgE binding increased in pressurized samples, decreased in those pre-heated, and it was drastically decreased after gastric and duodenal digestion in all samples. When samples were assayed in splenocytes culture, it was observed an important reduction of IL-5 and IL-13 in all cross-linked samples in relation to OVA control, pointing to a reduction in allergenicity of polymerized samples.

AAL-P34

PEACH KERNELS AS AN UNDERVALUED AND UNDERUSED SOURCE OF FUNCTIONAL PEPTIDES

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Peach (*Prunus persica (*L.*) Batsch*) is a seasonal fruit originally from China. Countries from the Mediterranean basin, specially Spain and Italy, are the main producers of peach worldwide. Peach contains a kernel with a seed inside. This kernel is considered a by-product or waste despite the protein content of the seed is around 43% (in dried and defatted seeds).These seedsare, so,a cheap sourceof proteins thatareunderusedandundervalued. The aim of this work was to evaluate the possibility to obtain bioactive peptides from this waste material and to identify them by HPLC-MS/MS.

Peach seed proteins were extracted by a previously developed method using a Tris-HCl buffer at pH 7.5 and employing high intensity focused ultrasounds to accelerate the extraction. Extracted proteins were digested under optimal conditions using four different enzymes. Peptide extracts were analyzed for their antioxidant and antihypertensive capacity using different *in vitro* assays. The highest antioxidant and antihypertensive capacities were observed in the thermolysin whole extract. Peptides were next fractionated by ultrafiltration obtaining fractions with molecular weights above 5 kDa, from 3 to 5 kDa, and below 3 kDa. *In vitro* assays revealed that the thermolysin whole extract showed the highest antioxidant capacity while antihypertensive peptides were mostly focused in fraction below 3 kDa. Simulated gastrointestinal digestion (GID) using pepsin and pancreatin enzymes enabled to evaluate the effect of gastrointestinal enzymes on peptides bioactivity. Antioxidant capacity of the thermolysin whole extract showed a 12% decrease after GID while antihypertensive capacity of fraction below 3 kDa did not yield a significant decrease. Peptides were identified by HPLC-ESI-Q-ToF using PEAKS software. Comparison of peptides identified in fractions before and after GID enabled to select most advantageous peptides for the enrichment of foods.

AAL-P35

DETERMINATION OF PAHS IN EDIBLE OIL SAMPLES USING HPLC-FLUORESCENCE

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Polycyclic aromatic hydrocarbons (PAHs) are a group of compounds, which derive from incomplete burning of carbon-containing materials, so a few of them are in considerable amounts in the environment and food. PAHs comprise the largest group of chemical compounds known to be carcinogenic and mutagenic.

Concerning to the maximum levels for PAHs in foodstuffs, the Commission Regulation (EU) 835/ 2011 of 19 August 2011[1]. establishes that maximum levels for the sum of four substances (PAH4) (benzo(a)pyrene [BaP], benz(a)anthracene [BaA], benzo(b)fluoranthene [BbF] and chrysene [Cry]) should be controlled, whilst maintaining a separate maximum level for benzo(a)pyrene [BaP]. When talking about edible oils and fats the maximum levels are PAH4: 10 mg/ kg and BaP: 2 mg/ kg.

Although there are some methods for this analysis, they imply long term periods with several steps of extraction and purification[2]. So, we have developed and validated an analytical method for the analysis of these PAHs in edible oil samples.

Firstly, sample preparation procedure is based on an extraction using special Sep-Packs: "SupelMip TM SPE PAHs" Supelco®, which consist of highly cross-linked polymers that are engineered to extract a class of structurally related analytes[3]; followed by concentration and reconstitution with acetonitrile. Samples are analysed then by HPLC with fluorescence detector, using different wavelengths (excitation/ emission) for each compound in order to minimize possible interferences caused by the lipophilic nature of matrix.

Method has been validated focusing on selectivity and getting good accuracy and precision values. Considering these results, the uncertainty associated value was also estimated.

Given the importance of these compounds and the need for their analysis, we have achieved an alternative for an optimal, fast and versatile analysis.

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AAL-P36

CHOROPHYLL-DERIVED COMPOUNDS ANALYSIS IN FRUIT AND VEGETABLE PRODUCTS BY UPLC-PDA-MS

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Chlorophyll and its derivatives, which are not considered dietary antioxidants, have exhibited important health promoting functions such as antimutagenic and anticarcinogenic activities [1,2]. Thus, the presence of chlorophylls and their transformations products contribute to added value to the fruit products. There are numerous studies of the effect of temperature on the stability of chlorophylls in different matrices, and also about grind and storage stability.During food processing in acidic conditions the chlorophylls are affected mainly by the pheophytinization reaction, which yields pheophytins and pyropheophytins. The processing conditions can also promote the activity of hydrolytic endogenous enzymes such as chlorophyllase, which promote the formation of dephytylated chlorophyll derivatives, mainly pheophorbides [3]. In this context, we have focused on the development of an analytical methodology that allows the characterization of chlorophyll derivative profiles of different fruit and vegetable products.

To optimize the extraction step, several solvent combinations were tested in various matrices to assess the performance of each extracting system, paying attention to the allomerization of compounds in alcoholic solutions. To date, RP-HPLC has mainly been employed to separate the chlorophyll and derivatives. We used an UPLC method which provided us a rapid and suitable chromatographic separation for the chlorophyll–derived compounds present in the samples, such as pheophytins, pyropheophytins and pheophorbides. The identification of chlorophyll-derived compounds was based on UV/Vis spectra, mass spectrometry operating in mass scan mode and published data of the main chlorophyll derivatives found in the similar studied matrices.

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AAL-P37

UHPLC-MS/MS METHOD FOR THE CONTROL IN FISH OF RESIDUES OF AN ALLIUM DERIVATIVE USED AS ADDITIVE IN FEED

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Farming fish, shellfish and aquatic plants is one of the world's fastest growing food sectors. Since the ban of antibiotics as growth promoters in 2006 [[1]], the search of new alternatives in fish nutrition has been increased. Garlic (*Allium Sativum*) and onion (*Allium Cepa*) are members of *Liliaceae* family, being traditionally used as medicinal plants, vegetables and spices. They have antibiotic, antiseptic and antiinfectious properties, which are attributed to the organosulfur compounds, including alkyl thiosulfonates. The use of *Allium*extracts as additives in fish feeding stimulates the appetite, increases the nutritional value and controls the health through direct effects as a coccidiostats.

Domca S.A. located in Alhendin (Granada, Spain) has developed under the trademark AQUAgarlic® a new antiparasitic additive for fish feeding whose main ingredient is based on the allium derivative propyl propane thiosulfonate (PTSO) whose healthy effects were already proved in poultry, swine and rumen, being now studied in fish. In order to assess the amount of residue transferred to the edible part of fish, its possible interaction with proteins and their influence on the organoleptic and nutritional characteristics, analytical methods to control PTSO are needed. In this work, a rapid method for its determination in fish has been developed using UHPLC-MS/MS and a sample treatment consisted in a simple extraction with methanol.

Similarly to other allium derivative (diallylthiosulfinate) [[2]], we observed that PTSO reacts instantaneously with cysteine and glutathione, giving s-propyl mercaptocysteine (CSSR) and s-propyl mercaptogluathione (GSSR). From this fact, in the proposed method PTSO was quantified as sum of CSSR and GSSR. Matrix-matched calibration curves were established for different kind of fish (trout, salmon and gilt-head bream) and limits of quantification were between 17 and 29 ng ml^{-1}. The precision was evaluated in terms of repeatability and intermediate precision and RSDs were lower than 10% in all cases.

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AAL-P38

IDENTIFICATION OF PHENOLIC COMPOUNDS FROM CHILEAN PROPOLIS EXTRACT BY HPLC-UV-ESI-MS/MS

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The current trend in the developed world as far as food is concerned, indicates a clear increase by consumers for foods that are nutritionally balanced and safe. This change in the tastes, preferences and the demands of modern consumers creates a new area of development and challenges in food and nutritional science. Within this context, the food industry needs to meet such demands by, for example, incorporating additional ingredients in the manufacture and development of new products. One alternative that has great potential within the food industry is the use of natural product, such as propolis.

The total phenols of propolis extract (PE) from six different areas of the central valley of Chile, were quantified by a spectrophotometric method and thirty phenolic compounds were identified by HPLC-MS/MS analysis. Pinobanksin is the only phenol present in the six samples of propolis so it may be a good candidate for the standardization of propolis ethanolic extracts in the central valley of Chile.

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AAL-P39

ADSORPTION OF PHENOLIC COMPOUNDS ONTO THREE POLYMERS TO THE POTENTIAL OPTIMIZATION OF FOLIN-CIOCALTEU ASSAY

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In this study we quantified by HPLC-DAD the adsorption of a matrix of phenolic compounds (PCs) such as gallic acid, 4-methylcatechol, resveratrol, hesperetin, catechin, genistein, epigallocatechin gallate, quercetin and butylated hydroxyanisole, in the presence of ascorbic acid onto three polymers named Polyvinylpolypyrrolidone, poly(acrylamide-co-ethylene glycol dimethacrylate) (PAEGDMA) and the copolymer of N-vinyl-2-pyrrolidinone with ethylene glycol dimethacrylate and triallyl isocyanurate (PVPDT). Moreover, the isotherms based on Langmuir and Freundlich models were obtained and its parameters were related to the contribution of the total phenolic content measured by Folin-Ciocalteu (FC) assay. These results implicate potential uses of the proposed polymers to determinate the PCs contribution by the FC assay in complex matrices as antioxidant-containing food products.

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AAL-P40

RAPID AND SIMPLE DETERMINATION OF DIFLOXACIN IN MILK BY TERBIUM-SENSITIZED CHEMILUMINESCENCE

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Quinolone antibacterials are veterinary drugs authorized for use in food animal production. The analysis of residual amounts of drugs in food from animal origin is important for quality control of products for consumers. For this purpose, Maximum Residue Limits have been set up by a European Union Council Regulation on Veterinary Drug residues (No. 90/2377/EEC and subsequent). In the specific case of Difloxacin (DF), metabolite Sarafloxacin, EU regulation clearly establishes that it can not be used in animals from which milk is produced for human consumption.

Quinolones in milk are typically determined by capillary electrophoresis and chromatography. These methods usually include deproteination of the milk, and subsequent clean-up and preconcentration by solid-phase extraction. This step is usually performed off-line before separation, which can reduce the effective sample throughput.

It is necessary to develop rapid, selective and sensitive analytical methods for the determination of these antibacterial agents.

The analytical method applying chemiluminescence (CL) coupled with flow-injection analysis (FIA) shows the advantages of simplicity and rapidity, and has been used for the analysis of pharmaceutical compounds that after a few chemical reactions result in significant CL. A new CL flow system for difloxacin combined with FIA is presented. It is based on the energy transference from difloxacin to terbium (III). The weak CL produced by potassium permanganate-sulfurous acid-difloxacin system can be enhanced when Tb (III) is added to the system.

A modified simplex method was used for optimization of the chemical and instrumental variables. The effects of interaction of permanganate, Tb(III), sodium sulphite and sulphuric acid concentration, flow rate and sample injection volume were thoroughly investigated. The response factor for the CL emission intensity was chosen to measure the system performance and the optimum conditions for the variables chosen at the maximum response value. Under optimal experimental conditions, the CL response was proportional to the concentration of difloxacin over a wide range with a determination coefficient of 0.999 and a detection limit of 9.0 ng/ml according Clayton criterion. The relative standard deviation for ten repeated determinations of 60 ng/ml difloxacin was 2.7 %.

This method was successfully applied to some real samples by using the standard addition methodology, obtaining excellent recoveries in all cases, with a not difficult prior steps, it is only necessary the precipitation the protein fraction of milk.

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AAL-P41

DETERMINATION OF CARBARYL IN MILK BY FLUORESCENCE IN ANGULAR PROJECTION AND TOTAL TRAJECTORIES

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En este trabajo se aborda la determinación fluorimétrica directa de un compuesto intensamente fluorescente, como es el carbaril, en una matriz que también presenta una elevada fluorescencia como es la leche. Para realizar la determinación se ha desarrollado una nueva metodología denominada Fluorescencia en Proyección Angular con Trayectorias Totales.

El carbaril (1-naftol-N-metilcarbamato) es un plaguicida extensamente utilizado perteneciente al grupo de los carbamatos. Se usa tanto en el medio agrícola como directamente sobre algunos animales como aves de corral y ganado.

Puede incorporarse a la cadena alimentaria humana a través de la leche del ganado bovino, por lo que muy interesante el contar con metodologías rápidas que permitan una determinación directa de este plaguicida en suero láctico.

Se realizó la optimización de diferentes variables experimentales (intervalo de pH, concentración de disolución reguladora, influencia del % de etanol, influencia de la concentración de analito e influencia de la temperatura) y se seleccionaron las condiciones más adecuadas para la determinación.

Se estudiaron posteriormente cómo influían las los diferentes centros de las trayectorias cerradas y las proyecciones a que daban lugar. Se seleccionó como óptima aquella trayectoria con centro en 288 nm de longitud de onda de excitación y 335 nm de emisión. Debido al intenso solapamiento espectral del analito con la matriz, hubo que recurrir a la derivación utilizando la técnica de medida de pico a pico. El máximo del espectro elipsoidal se sitúa en un ángulo de 24.9 grados sexagesimales y el mínimo a 341.1 grados.

Se realizó la calibración utilizando tres tipos de suero lácteo y se concluyó, tras el estudio quimiométrico, que no existían diferencias estadísticamente significativas entre los calibrados, presentaban homogeneidad de varianzas, no presentado puntos discrepantes ni puntos leva.
Se aplicó el método propuesto a leche entera, semidesnatada y desnatada, obteniéndose porcentajes de recuperación próximos al 100 %.

Como conclusión, se propone una nueva metodología fluorimétrica, Fluorescencia en Proyección Angular con Trayectorias Totales, que completa a la descrita anteriormente por Murillo y col. [1] para la determinación de compuestos fluorescentes en matrices que también lo son. Pueden incluso mejorarse los resultados utilizando técnicas de derivación.

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AAL-P42

DETERMINATION OF ANTIOXIDANT ACTIVITY OF ROOIBOS INFUSIONS USING A SYSTEM BASED ON THE ATTENUATION OF LUMINOL CHEMILUMINISCENCE

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The evaluation of natural products with potential antioxidant effects is an important field of research in the human nutrition that requires of reliable, simple, fast and inexpensive analytical methods.
This study describes a flow injection methodology for the estimation of the radical scavenging activity of rooibos, which is based on the inhibition of the chemiluminiscent emission during the luminol oxidation in simultaneous presence of perborate and the Co(II)/EDTA complex. The mechanism of the attenuation is due to the reaction of rooibos polyphenols with the radical formed from perborate catalyzed decomposition [1]. At the following optimum operational conditions, pH = 10.5; EDTA concentration of mg L^{-1}, luminol concentration of 2.4 mM, 0.72 Co(II) concentration of 0.24 mg L^{-1} and reagents flow rate = 12.8 mL min^{-1}. Stable and reproducible signals were obtained in the presence of the natural antioxidants.

The antioxidant activities were measured in terms of % Inh_{50} that represented the mass of rooibos that reduced in a 50 % the CL intensity in the absence of the antioxidant substances. Rooibos infusions were prepared by brewed rooibos bags in 100 mL of water at 95 º C for 5 minutes. Several aliquots were diluted in Milli Q water and injected directly to the FIA system. The percentage of inhibition (% Inh) was determined as the quotient between the final (I_{min}) and the initial (I_{max}) chemiluminiscence signals. % Inh was plotted against the *napierian logarithm* of sample mass in each dilution to obtain the straight lines used to calculate the by interpolation the % Inh_{50}.The highest antioxidant activity was found for rooibos (0.53 mg L^{-1}).

These results that correlated well with the total polyphenols content determined by the Folin-Coicalteu method were explained on the basis of catechins content in rooibos. It was concluded that the proposed method is adequate to evaluate the antioxidant activity with run times less than five minutes for each sample and requiring low amount of reagent being an environmental friendly analytical tool.

In order to compare the antioxidant capacity of the rooibos infusion with a reference infusion sample, three samples of different teas were studied and the antioxidant capacity of tea is, at least, three times higher.

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AAL-P43

SUMULTANEOUS DETERMINATION OF QUINOLONES BY FLUORESCENCE IN ANGULAR PROJECTION AND TOTAL TRAJECTORIES

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Las quinolonas se utilizan como antibióticos para tratar infecciones en animales y humanos. El análisis de los posibles residuos de éstos en alimentos de origen animal tiene gran importancia en el control de calidad de los productos que llegan a los consumidores. Entre estos antibióticos se encuentran cinoxacina y difloxacina.

Existen métodos que necesitan separaciones previas, utilizando SPE o métodos cromatográficos, y en cuanto a determinaciones directas hay descrito un método fluorimétrico que requiere tiempos de análisis prolongados por el uso de reacciones de derivatización previas.

En primer lugar se aborda el análisis de cinoxacina y difloxacina mediante fluorescencia sincrónica por isopotenciales de la matriz, FSIM [1], y posteriormente para superar sus restricciones, se propone una nueva metodología fluorimétrica, que puede utilizarse con cualquier trayectoria de fluorescencia y que alcanza su mayor potencial cuando se usan proyecciones angulares.El método propuesto, permite la determinación directa de compuestos fluorescentes en matrices que también lo son sin necesidad de técnicas de derivatización ni procedimientos de extracción previa: fluorescencia en proyección angular con trayectorias totales.

Se realizó la optimización de diferentes variables experimentales (intervalo de pH, concentración de disolución reguladora, influencia del % de etanol, influencia de la concentración de analito e influencia de la temperatura) y se seleccionaron las condiciones más adecuadas para la determinación.

Se seleccionaron trayectorias isopotenciales de ambos analitos para la determinación mediante FSIM, y posteriormente se seleccionó y optimizó una trayectoria total y un centro de proyección para la determinación simultánea mediante fluorescencia en proyección angular. Se pasa de dos trayectorias utilizadas en FSIM a una única trayectoria total, combinación de las dos anteriores, la cual viene definida por un centro de proyección que permite alcanzar la selectividad y sensibilidad óptimas para la determinación.

De manera novedosa, se cambió la forma de representar y tratar matemáticamente los espectros, representándolos de forma elipsoidal en diferentes ángulos de giro, lo que permite realizar su estudio más completo.

Se realizó el calibrado de los analitos, y un estudio quimiométrico completo para demostrar la validez del método, cuyos resultados fueron satisfactorios.

Como conclusión, se propone una nueva metodología fluorimétrica, Fluorescencia en Proyección Angular con Trayectorias Totales, que completa a la descrita anteriormente por Murillo y col. [1].

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AAL-P44

VOLATILE THIOLS BY DERIVATIZATION AND HPLC-ESI-HRMS. APPLICATION TO COFFEE POWDER AND COFFEE BREW

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A fast derivatization/extraction method followed by LC-ESI-HRMS was optimized for the determination of volatile thiols in roasted coffee powder and brew, using ebselen as the derivatization agent. The analytical conditions were optimized on real coffee matrix, which was spiked with representative volatile thiols. The method sensitivity, precision, accuracy and selectivity were evaluated by using representative standard thiols. Estimated LOQs were between 0.02 and 14.8 ng/kg in coffee powder and between 0.1 and 0.01 ng/L in coffee brew. Recoveries and intra-day and inter-day RSD values obtained in coffee matrix were in general around 40% and between 11 and 30%, respectively. The optimized and validated method was applied to real coffee samples. According to the established identification criteria, seven target thiols were identified and quantified in coffee powder samples. Among them, 4-mercapto-1-butanol and 2-methyl-3-tetrahydrofuranthiol were identified and quantified for the first time in roasted or brewed coffee. Moreover, an approach based on the formation of a diagnostic product ion was applied to detect non-target thiols, allowing the detection of nineteen and twelve thiols derivatives in coffee powder and brew, respectively. Several of them were tentatively identified on the basis of their molecular formula. Thiols such as methanethiol and 3-mercapto-3-methylbutyl acetate were known to be present in coffee volatile fraction, while the rest were not previously described in this product.

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AAL-P45

VOLTAMMETRIC ANALYISIS OF HYDROXYMETHYLFURFURALDEHYDE IN HONEY

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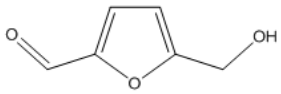
The freshness of honey is determined, in addition to the content diastase, for the content of 5-hydroxymethyl-2-furfuraldehyde (HMF). The maximum content of this compound in honey is regulated by EC normative, in Spain BOE 1049/2003 a maximum content 40mgHMF/Kg honey bees is allows. On the other hand, some papers indicate that the presence of high amounts of HMF has a correlation with carcinogenic effects.



HMF

In this communication the electroanalytical study of HMF, and also of the honey alone, has been carried out by using different electroanalytical techniques, such as differential pulse polarography (DDP) and square wave voltammetry (SWV). A single signal is obtained with a reduction potential nearly to -1.2 V. The influence of pH indicates that the protons are involved in the electrodic process, and the Ip maximum is achieved at pH values close to 6. The influence of other instrumental parameters has been optimized.

The study of the influence of the concentration of HMF on I_p (DPP and SWV) allows establishing the figures of merits: Ip (nA) = 18.97 [HMF] +0.17 (DPP) and Ip (nA) = 48.2 [HMF] +0.6 (SWV). The detection limits were: 0.012 ppm (DPP) and 0.021 ppm (SWV) by Winefordner-Long method´s, and 0.036 ppm (DPP) and 0.066 ppm (SWV) by Clayton method´s.

The electroanalytical method developed has been applied to the determination of HMF in four honeys purchased at the supermarket, using the standard addition method in different media: phosphate (pH 6.5) borate (pH 5.6) and borax (pH 6.4) by DPP and SWV respectively.

In order to validate the electroanalytical proposed methods, honeys have been also analyzed by spectrophotometric Winkler´s method. The comparison of both methods, conclude that the results are in good agreement, but the method of Winkler gives higher values due to the spectrophotometric methods includes other aldehydes present.

The honeys analyzed gives lower content than 40 mg HMF/kg honey. This indicates the freshness of honey. The advantages of the electroanalytical methods proposed are: direct analysis on honey without pretreatment, nor use the toxic reagent derivatization, fast and low cost.

Acknowledgements: Authors are grateful with FEDER, Gobierno de Extremadura (PCJ100501) and GR10033 (FQM003-FEDER) for financial support.

AAL-P46

FRONT-FACE FLUORESCENCE SPECTROSCOPY IN COMBINATION WITH LC DATA AND CHEMOMETRICS FOR THE POLYPHENOLS ANALYSIS IN WINE SAMPLES

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The possibility of using front-face fluorescence spectroscopy to analyze polyphenols in red wines was investigated, and a tentative quantification of their main polyphenols was attempted. Their fluorescence excitation-emission matrices (EEMs) were registered directly on 3-mL aliquots of untreated samples. The assayed excitation and emission ranges were 245-340 and 300-500 nm, respectively.

Red wines EEMs, present two zones of high fluorescence and the emission region between 340-400 nm,when the sample is excited at wavelengths between 260-300 nm,correspond with the polyphenols present in the samples and is the objective of this study.

The red wines have been previously analyzed by a LC developed method using a short column and fluorescence detection at different excitation/emission wavelengths. An appropriate gradient program was optimized with the objective of getting a good separation. In these conditions ten polyphenols were quantified.

In first place The quantification of the polyphenols in EEMs was carried out by PARAFAC and the concentrations used for the calibration set and for the validation set were the previously calculated by LC. The number of components was selected applying the so-called core consistency analysis and three components were estimated.The excitation and emission profiles of the first and third components have been associated with gallic acid and epicatechin, respectively.
With the purpose of testing the applicability of the method, a set of five wine samples were analyzedand gallic acid and epicatechin have been adequately determined

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TOM-P01

LC-HRMS IN THE IDENTIFICATION OF METABOLITES AND TRANSFORMATION PRODUCTS FROM β-LACTAM ANTIBIOTICS IN MILK

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Antibiotics such as β-lactam derivatives (penicillins and cephalosporins) are frequently used in veterinary medicine. The presence of these antibiotics together with their metabolites and/or products produced in subsequent treatments at which milk is submitted (sterilization, pasteurization), may be responsible for bacterial resistance, allergy and/or toxicity on sensitive individuals.

The development and validation of analytical methods to determine these antibiotics and their metabolites is well established. However, few studies focused on the identification of transformation products (TPs) from the administered drugs. These TPs may be produced during sample treatment, prior to the analysis of residues of antibiotics, or during treatments at which milk is submitted to eliminate pathogenic entities.

In this study, liquid chromatography coupled with high resolution mass spectrometry (LC-HRMS) is used to identify TPs from four β-lactam antibiotics (amoxicillin (AMOX), cephapirin (PIR), ceftiofur (TIO) and penicillin G (PENG)) in thermally treated cow milk. In addition, metabolites of PENG have been studied in milk from animals that have been medicated with this drug.

The identified TPs, some of them not previously described, come mainly from hydrolysis and decarboxylation reactions of the main drug. The more degraded products (those of lower molecular weight) were observed preferable after treating milk at higher temperatures.

Products identified in milk samples from cows medicated with PENG have been classified as TPs, products coming from chemical/thermal degradation, and products resulting from the biological metabolism of the drug. While TPs are formed by hydrolysis and decarboxylation processes, the metabolites result from the enzymatic conjugation with amino acids.

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TOM-P02

BOTTOM-UP ANALYSIS FOR GLYCOPROTEIN CHARACTERIZATION

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Glycosylation is the most common posttranslational modification in proteins. *O*- and *N*-glycan structures have been found altered in many diseases such as congenital disorders of glycosylation (CDG) or cancer [1]. Moreover, certain glycan structures elicit immunogenic responses in humans, being necessary an exhaustive quality control of the recombinant glycoproteins marketed as biopharmaceuticals[1]. High performance separation techniques coupled to mass spectrometry have become indispensable in glycoproteomics. Bottom-up strategies consisting in the analysis of specific glycosylation markers of low molecular mass originated after glycoprotein digestion is a spreading alternative to the top-down approach, where the lower MS sensitivity for intact glycoproteins hinders detailed characterization [2].

The aim of this work is to describe different bottom-up methodologies for the accurate characterization of the oligosaccharide structures present in glycoproteins. In this regard, glycosylation may be analysed through the glycans released from the protein or the glycopeptides. In the first case, glycans released from the glycoprotein with PNGase-F are derivatized by reductive amination, and separated and identified by zwitterionic-hydrophilic interaction liquid chromatography coupled to mass spectrometry (ZIC-HILIC-MS). This method provides information about the structure and composition of the oligossacharides, but not about the glycosylation sites or their degree of occupancy [3]. In the second case, glycopeptides are obtained from the native glycoprotein by tryptic digestion and analysed using capillary electrophoresis and capillary liquid chromatography coupled to mass spectrometry (CE-MS and µLC-MS). While CE allows for a simple and rapid separation of glycopeptide glycoforms according to their charge-to-mass ratios (M/q^{α}), µLC offers the possibility of using different stationary phases such as C-18, ZIC-HILIC or porous graphitic carbon (PGC) to separate glycopeptides from more hydrophobic non-glycosylated peptides, or even separate isomeric glycoforms.

Both bottom-up strategies are applied to different glycoproteins (e.g. erythropoietin, apolipoprotein C-III, transferrin and alpha-acid glycoprotein), resulting in an excellent glycoprotein characterization thanks to the valuable complementary information. While more glycan diversity is found with the first approach, the second one provides more information about the glycosylation sites.

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TOM-P03

DEVELOPMENTS ON MALDI-TOF-MS FOR IDENTIFYING DISSOLVED AND PARTICULATE PROTEINS IN SEAWATER AFTER 2D-SDS-PAGE

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Two-dimensional sodium dodecyl sulfate–polyacrylamide gel electrophoresis (2D-SDS–PAGE) was applied to separate protein molecules in dissolved organic matter (DOM) and in particulate organic matter (POM) from seawater. Dissolved proteins were concentrated and purified using tangential flow ultrafiltration (UF), centrifugal ultrafiltration, and protein precipitation by chloroform/water/methanol techniques. Twelve proteins spots were observed in Sypro Ruby stained 2D-gel. Separated proteins exhibited isoelectric points (pIs) ranging from 3.5 to 6.0; whereas, the molecular weights (MWs) were within the 10-50 kDa range.

Regarding particulate proteins, marine plankton were concentrated by centrifugation, and proteins were isolated by grounding the biomass under liquid nitrogen before several washing stages [10 % trichloroacetic acid (TCA) in acetone followed by 0.1 M ammonium acetate in 80/20 methanol/water] and extraction with a phenol – SDS (30 %(m/v) sucrose, 2 %(m/v) SDS, 0.1 M Tris-HCl, pH 8.0, 5 %(v/v) β-mercaptoethanol and protease inhibitor cocktail) mixture. Plankton proteins were precipitated from the phenol phase with 0.1 M ammonium acetate in methanol at -20 ºC for a time of at least 2 hours, and finally the protein pellets were subjected to a purification step by washings with methanol and with 80/20 acetone/water. 2D-SDS-PAGE showed the presence of approximately 150 – 180 different protein spots in the Sypro Ruby stained 2D-gels. In general, plankton proteins exhibited MWs ranging from 12 to 150 kDa with pIs between 3 and 10.

Separated dissolved (twelve protein spots) and plankton (twenty-four protein spots) proteins were further enzymatically in-gel digested (trypsin) and analyzed by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS). Dissolved proteins in eight of the twelve resolved spots were identified by mass mapping, and eleven different proteins were successfully assigned: penicillinase repressor, flagelar hook-associated protein FliD, glucose/sorbosone dehydrogenase, carbamoyl-phosphate synthase small subunit, TRAP-T family transporter, L-aspartate oxidase, translation elongation factor Tu, malate synthase A, ATP-dependent DNA helicase RecQ, Glycogen/starch/alpha-glucan phosphorylase, and LysA proteins. However, only seven of the twenty-four resolved plankton protein spots were identified by mass mapping, and four different proteins were successfully assigned: Ribulose bisphosphate carboxylase small chain, Cytochrome C-550, Photosystem I reaction center subunit II, and Photosystem II (12 kDa extrinsic protein).

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TOM-P04

UNTARGETED LC-MS FOR STUDYING METABONOMICS OF RICE ROOTS AND LEAVES EXPOSED TO CADMIUM AND COPPER STRESS

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During the last centuries, the level of heavy metals on soil and surface water has increased radically. These pollutants are introduced into environment by many anthropogenic activities, such as mining, agriculture and industry [1]. Among heavy metals, cadmium and copper have been listed in the priority list of hazardous materials by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) in 2013. These two pollutants are easily absorbed by roots and rapidly translocated to the aerial parts of plants [2]. Since diet is the main source of heavy metals exposure to general population, studying the effects that these two pollutants cause on edible plants, such as rice, is important [3]. Metabonomics is a powerful tool to study molecular mechanisms and understand complex biological systems, and therefore is a good approach to perform the studies mentioned above.

This work aims at studying and comparing the changes in metabolite concentrations on rice roots and leaves under cadmium and copper exposure. For this purpose, Japanese rice (Oryza sativa japonica) was cultivated at optimal conditions during 10 days. After this period, rice cultures were exposed to different concentrations of cadmium and copper (from 10 to 1000 μM) for 10 days more. After harvesting, roots and leaves were separated and analyzed independently.

An untargeted HPLC-MS approach has been applied. The chromatographic separation was carried out using an HILIC TSK gel Amide-80 column (Tosoh Bioscience 5μm, 250mm, 2.0 mm i.d.), and a waters LCT Premier XE TOF mass spectrometer was used for metabolite detection.

Chromatographic peaks modified under cadmium and copper exposure were resolved, and their corresponding high resolution mass spectra were used for metabolite identification. Different multivariate data analysis tools, such as Principal Component Analysis and Partial Least Squares, were applied for this purpose.

The research leading to these results has received funding from the European Research Council under the European Union's Seventh Framework Programme (FP/2007-2013) / ERC Grant Agreement n. 32073

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TOM-P05

IMMOBILIZED METAL AFFINITY CHROMATOGRAPHY SORBENTS FOR THE ANALYSIS OF β-AMYLOID PEPTIDES BY SPE-CE-MS

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Immobilized metal affinity chromatography (IMAC) is based on the affinity for metal ions of certain exposed electron-donating groups in the target compounds, in general, peptides, proteins and nucleotides [1]. In on-line immobilized metal affinity solid phase extraction capillary electrophoresis (IMA-SPE-CE), the affinity for immobilized chelated metal ions is exploited for preconcentration, clean-up and separation of such peptides and proteins [2-3]. In this work,several commercial IMAC sorbents have been evaluated for the analysis of two small peptide fragments of the amyloid β-protein (Aβ) (Aβ(1-15) and Aβ(10-20) peptides) by IMA-SPE-CE. Aggregation of Aβ into plaques in the brain is associated with the development of Alzheimer's disease. The performance of a nickel metal ion (Ni(II)) sorbent based on nitrilotriacetic acid (NTA) as a chelating agent was significantly better than with copper metal ion (Cu(II)) sorbents based on iminodiacetic acid (IDA). A background electrolyte (BGE) of 25 mM phosphate (pH 7.4) and an eluent of 50 mM of imidazole (in BGE) allowed a 25-fold and 5-fold decrease of the limits of detetection (LODs) for Aβ(1-15) and Aβ(10-20) peptides with regard to CE-UV. Later, the method was adapted to on-line MS detection, basically changing to an eluent of 0.5% acetic acid (v/v). Under optimum preconcentration and detection conditions reproducibilities of peak areas and migration times were acceptable (23.2% and 12.0% of %RSD, respectively). The method was more sensitive for Aβ(10-20) peptide, which could be detected until 0.25 $\mu g \cdot mL^{-1}$. Linearity for Aβ(10-20) peptide was good in a narrow concentration range (0.25-2.5 $\mu g \cdot mL^{-1}$, R^2=0,93). Finally, the potential of the optimized Ni(II)-IMA-SPE-CE-MS method for the analysis of amyloid peptides in biological fluids was evaluated analyzing spiked plasma and serum samples.

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TOM-P06

METABOLOMIC TECHNIQUES FOR EXTRA VIRGIN OLIVE OIL ORIGIN DISCRIMINATION BY UHPLC-QTOF MS

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Extra Virgin Olive Oil (EVOO) is a traditional Mediterranean food product with highly appreciated organoleptic attributes provided by its minor components as phenolic compounds, polyphenols/tocopherols (vitamin E) or sterols. This composition determines its quality, which depends, amongst others, on its origin [1]. Since the quality is one of the most important characteristics for customers, it determines the prize [2]. Analytical methodologies may help to reliably distinguish different origins and to detect fraud [3]. Metabolomic firgerprinting in the food science is a very useful tool to solve this kind of problems and can provide essential information to the industry and customers about the real origin and quality of the products [4].

For this purpose, 91 Spanish EVOOs, from different Protected Designations of Origin (PDO) are included in an untargeted metabolomic study in order to find biomarkers which could discriminate between different origins. Samples were treated with methanol-water and n-butanol to analyze both saponifiable and unsaponifiable matter, respectively. Afterwards, extracts were analyzed by ultra high-performance liquid chromatography coupled to hybrid quadrupole time-of-flight mass spectrometry (UHPLC-ESI-QTOFMS).

Reliable peaks were extracted with XCMS, a freeware R-package and later, data were standardized. Principal Component Analysis (PCA) was used to obtain a general idea about the separation of the groups while Partial Least Square - Discriminant Analysis (PLS-DA) was applied to confirm the information provided by the PCA and to build a statistical model based on origin classification. Finally, significant biomarkers were highlighted using an orthogonal PLS-DA (OPLS-DA) to differentiate between different PDOs.

With the information obtained applying this multivariate analysis, a prediction model was built involving 13 different compounds, which give us information about the origin of a Spanish extra virgin olive oil. These compounds have tentatively been elucidated by MS^E and/or MSMS experiments and the validation of the model will be carried out with new olive oil samples.

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TOM-P07

QUANTIFICATION OF GENE COPY NUMBER BY COMBINATION OF PCR AMPLIFICATION AND GEL ELECTROPHORESIS-ICP-MS

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Changes in copy number of genes contribute to the pathogenesis of various genetic disorders and cancer[1]. Copy number variations (CNVs) are imbalances that alter the diploid status of a locus so that copy numbers increase (duplications) or decrease (deletions). The screening of genome-wide CNVs in single cells is of special importance for a variety of applications in basic research and clinical diagnosis of diseases like Alzheimer's disease, autism, schizophrenia, breast cancer or obesity[2].

The quantitative aspects of end-point polymerase chain reaction (PCR) have been fully exploited here in combination with on-column agarose gel electrophoresis as separation and inductively coupled plasma mass spectrometry (ICP-MS) for detection. The calibration of the separation system with a DNA ladder permits the direct estimation of the size of the amplified gene after PCR. With this knowledge and considering the compound independent quantification capabilities exhibited by ICP-MS for P (only dependent on the number of P atoms per molecule), the correlation of the P-peak area of the amplified gene in respect to the gene copy numbers (in the starting DNA) will be established. Such correlation will permit the determination of copy number variations (CNVs) in genomic DNA using ICP-MS measurements. The suitability of the proposed strategy will be used to address CNVs due to cells exposure to a chemotherapeutic treatment with cisplatin.

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TOM-P08

A QUANTITATIVE PROTEOMIC APROACH FOR UNCOVERING THE SELENIUM-MERCURY ANTAGONISM

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Methylmercury (MeHg) is a persistent environmental toxic agent, which represents a risk to human health, particularly causing brain and neural damage. In contrasts to the potential harm from mercury, selenium is an essential trace element for the normal functioning of many biological processes.

The interaction between mercury and selenium in organisms has been thoroughly studied due to the protective effect of selenium against mercury-induced toxicity. However, the specific antagonic mechanism between both species is still unknown.

In this study, we have tested different selenospecies and their protective effect against MeHg on neuroblastoma cells (Neuro-2a) by measuring cell viability. We have also evaluated morphological changes of cells exposed to MeHg and the combination MeHg/Se(IV) using fluorescence microscopy. For all the experiments, we have selected a 1:1 molar ratio of MeHg/Se (IV). In addition, we have used inductively coupled plasma mass spectrometry (ICP-MS) and cold-vapor atomic fluorescence spectroscopy (CV-AFS) for the determination of the total selenium and mercury uptaked by the cells.

Furthermore, we carried out two large-scale SILAC experiments for the identification of a set of de-regulated proteins upon MeHg/Se (IV). This set of proteins helped us to identify the molecular pathways involved in the protective effect of Se(IV) against MeHg induced toxicity.

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TOM-P09

CHALLENGES IN IDENTIFICATION OF MS DATA IN -OMICS: PROFILE/CENTROID ACQUISITION AND THE BENEFIT OF CHEMOMETRICS

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Increased MS resolution from TOF-MS and FT-MS allows reliable identification of unknown ions. Their high mass accuracy, relevant to the monoisotope peak, provides a first filter for the number of formula candidates. Recent studies have proved that other isotope clusters contain more information than monoisotopic assignations and provide a second filter for candidates [1], related with spectral accuracy. However, in complex matrices, identification can become a difficult challenge even with the information of both mass and spectral accuracy. This occurs in -omic studies such as lipidomics, due to the high amount of data and multiple chromatographic coelutions. In those cases, enhanced resolution achieved with chemometric methods represents a step forward [2].

In this study, UHPLC-TOF-MS lipidomic data were analyzed using multivariate curve resolution (MCR-ALS) methods, which allowed the resolution of 86 pure components, solving chromatographic coelutions and permitting the determination of minor compounds. Information of concentration and spectra profiles of all the pure MCR-ALS resolved components was used in the first step of their identification process, following four distinct pathways. Within these strategies, different parameters were evaluated concerning: a) acquisition in **profile versus centroid mode**, b) formula search based on **mass accuracy or isotope information**, c) use of **Micromass MassLynx** or **MassWorks** softwares as formula search tools and d) use of information of accurate mass derived from the **MCR-ALS analysis**. Overall, this study proposes distinct strategies for identification of MS data valid for general –omic sciences such as lipidomics.

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TOM-P10

UNTARGETED METABOLOMIC ANALYSIS FOR THE ASSESSMENT OF BISPHENOL-A EFFECTS ON ZEBRAFISH EMBRYOS

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Zebrafish (*Danio rerio*) is a model vertebrate organism for biological, behavioural and biomedical research. In particular, zebrafish embryos are a well-recognized model for environmental risk assessment of chemicals due to their rapid development into larvae (within 48 hours) and their high sensitivity to chemical treatment. In addition, their small size, wide distribution and easy growth conditions offer the possibility to perform small-scale and high-throughput analyses for -omics studies, including metabolic profiling [1,2].

In this work, the effects of bisphenol A (BPA) on metabolic profiles of five-day old zebrafish embryos were evaluated using hydrophilic interaction liquid chromatography-mass spectrometry (HILIC-HPLC-MS). BPA is a chemical produced at large-scale for use in the production of plastics and epoxy resins. Furthermore, BPA is an endocrine-disruptor that interferes in the endocrine system of aquatic biota at concentrations often found on certain ecosystems.

For this purpose, an untargeted metabolomic approach by HILIC-HPLC-MS was used to evaluate the metabolic changes induced by BPA exposure in the zebrafish embryos. HPLC-MS data were analyzed by a combination of different chemometric tools such as principal component analysis (PCA), partial least squares discriminant analysis (PLS-DA) and multivariate curve resolution (MCR) [3]. Results show discrimination between control and BPA exposed samples considering the extracted ion chromatograms and allowed the identification of metabolites potentially affected by BPA exposure on the basis of their resolved characteristic mass spectra.

This research has been funded by the European Research Council under the European Union's Seventh Framework Programme (FP/2007-2013) / ERC Grant Agreement n. 32073

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TOM-P11

METALLOMICS AND METABOLOMICS IN ENVIRONMENTAL METAL TOXICITY ASSESSMENT

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Metals play an important role in biological systems. Therefore, the study of metal-induced changes in cellular metabolic pathways is crucial for understanding the biological response under environmental issues. In this matter, the application of -omics techniques, such as metallomics[1] and metabolomics[2], represents a powerful alternative. In addition, experiments exposure of model organisms to enriched stable isotopes allow the evaluation of element metabolism under experimental conditions. In these approaches the use of inorganic and organic mass-spectrometry[3] is fundamental. The aim of the present work is to evaluate the response of bioindicators such as the laboratory mouse *Mus musculus* or the crab *Procambarus clarkii*[4] under exposure to toxic (As, Cd and Hg) and non-toxic (Se and Zn) metals and the changes induced in both metallome and metabolome. For this purpose a metallomic approach based on size exclusion chromatography (SEC) in combination with multidimensional orthogonal separation techniques and heteroelements monitoring by ICP-MS has been performed, in combination to identification of metallobiomolecules by organic mass spectrometry. In addition, the simultaneous changes of metabolic expression in mice caused by metals exposure (metabolome) was considered, using direct infusion mass spectrometry (DI-ESI-QqQ-TOF-MS) to extracts from liver, plasma and kidney of exposed animals. Subsequently, altered metabolites were identified using MS/MS experiments. Conclusions on effects of these metals and their interactions on toxicity have been drawn.

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TOM-P12

A METABOLOMIC APPROACH BASED ON LC-MS FOR THE DISCOVERY OF NOVEL MARKERS IN SAFFRON ADULTERATION

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Saffron, obtained from dried stigmas of *Crocus sativus L*., is renowned as one of the most expensive spice in the food and flavoring sector. Along with its traditional value as food additive for tasting, flavoring and coloring, saffron is also highly appreciated for its biological and medicinal properties. Due to its high price in the market, saffron has been frequently adulterated with the most diverse materials. Water-soluble food dyes, oil-soluble azo dyes or plant stuff with similar color and morphology have been dishonestly added in saffron. Saffron authenticity is, therefore, of great importance from the viewpoint of consumer protection, quality assurance, active properties and economic impact. Undoubtedly the search for markers of adulteration in saffron is a complex task in which the implementation of metabolomic strategies provides the tools needed to face this challenge.

In this work, a non-targeted LC-MS metabolomic approach was developed to discover novel markers for detecting saffron adulteration. For this purpose, metabolic fingerprinting of authentic and suspicious saffron (styles and ground samples) from different geographical origin was analyzed. To do that, different extracting protocols and chromatographic columns were evaluated to obtain the most adequate extracting and separation conditions. Using an ethanol/water mixture at pH 9.0 and a C18 column it was possible to obtain the highest number of significant differences between authentic and adulterated saffron, being the chromatographic profile of the different authentic samples very similar. By using multivariate statistical analysis, a predictive classification model was obtained. Furthermore, a identification based on the obtained accurate mass of each metabolite, several metabolites database, and analysis of standards was carried out to propose markers of saffron adulteration.

ACL-P01

IN VIVO HUMAN METABOLISM ON MDPV BY UHPLC-QTOF MS

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Since the late 1990s, there has been a huge increase in “designer drugs” sold in Internet. Among them, methylenedioxypyrovalerone (MDPV), a stimulant drug chemically related to methylenedioxymethamphetamine (MDMA), is one of the most consumed. Although the metabolism of MDPV has been studied in rats or *in vitro* using human liver microsomes, to the best of our knowledge, no dedicated study with human volunteers has been performed. The aim of this work was to investigate *in vivo* metabolism of MDPV. The resulting metabolites (both Phase I and Phase II) were detected and identified by accurate-mass full-spectrum measurements using UHPLC-QTOF MS.

In metabolism studies carried out under controlled conditions, both control samples and samples collected after drug intake are commonly available, facilitating the comparison of their full-spectrum mass data using commercial spectral/chromatographic comparative software. However, in this work no control sample was available, as the urine was collected from a consumer of MDPV. Therefore, an alternative strategy based on common fragmentation pathway was applied. Assuming that most metabolites share the same fragmentation pathway with the parent drug, specific narrow-mass window extracted ion chromatograms (nw-XICs) at the expected m/z of MDPV fragments were obtained from full spectrum TOF MS acquisitions. The presence of chromatographic peaks at different retention times (Rt) than the parent would alert the researcher on the presence of potential drug metabolites.

An extension of this approach has been applied, based not only on the fragmentation pathway of the parent compound but also on those metabolites identified in urine samples. The use of MS^E experiments was helpful to this aim as it allowed the fragmentation of compounds in the collision cell without a previous precursor ion selection. MS^E involves the simultaneous acquisition of accurate mass data at low (LE) and high collision (HE) energy. In the LE function,fragmentation is minimized and the information obtained corresponds normally to the parent molecule (adducts in some cases). However, at HE, fragmentation of the molecule is favoured. So, both (de)protonated molecule and fragment ion data are obtained in a single acquisition without the need of selecting the precursor ion. Following this strategy, more than 20 metabolites were detected and tentative structures were proposed.

ACL-P02

DEVELOPMENT OF AN SPE PROCEDURE FOR THE DETERMINATION OF URINARY NUCLEOSIDES DERIVED FROM DNA AND RNA BY LC-MS/MS

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The present paper describes the development, validation and application of a quantitative method for the simultaneous determination of endogenous nucleosides derived from DNA and RNA in urine by LC-MS/MS.

Modified nucleosides excreted in human urine are related to RNA turnover and to oxidative DNA damage by reactive oxygen speciesproduced during normal metabolic processes inside the cell. Their urinary levels during active disease will show a significant increase over normal levels. Their clinical interest has expanded considerably in recent decades, being studied as possible biomarkers for cancer and other metabolic disorders or age-related diseases.

Different analytical techniques have been reported for the determination of nucleosides, reverse phase liquid chromatography (LC) being one of the most widely employed.In most reported methods nucleosides were isolated from urine by SPE in affinity mode, using an immobilized phenylboronic acid group, which specifically binds cis-diols. However, this is not applicable to non-cis-diol compounds, which prevent the simultaneous extraction of RNA- and DNA-derived nucleosides such as 2´-deoxyribose and ribose-based nucleosides.

In the present work we report the development of a solid-phase extraction step for the isolation/preconcentration of urinary nucleosides derived from DNA/RNA damage simultaneously. The SPE procedure is based on the use of a sorbent prepared by mixing three polymeric materials, which facilitates the simultaneous retention of nucleosides, regardless of whether they have cis-diol groups or not. The target compounds were, 8-hydroxy-2'-deoxyguanosinederived from DNA and its analogue 8-hydroxyguanosinederived from RNA, together with adenosine, 1-methyladenosine,7-methylguanosine, 5.methyluridine and inosine.

Different SPE sorbents (reversed-phase, cationic and anionic exchange and phenylboronic type) were assayed individually for the retention of the target nucleosides. In light of the results, it was decided to prepare a sorbent by mixing three polymeric materials. This mixed-sorbent afforded satisfactory retention for all nucleosides assayed in a single extraction step. Recoveries higher than 80% were found.

Further LC-MS/MS analysiswas accomplished in reversed-phase mode with a superficially porous particle column and a triple quadrupole-mass spectrometer. The SPE-LC-MS/MS method was validated in terms of calibration curves, precision, accuracy, selectivity and the verification of matrix-effects.

The application to human urine from smokers and non-smoker volunteers is also reported. Our results showed no evidence that cigarette smoking is related to increased levels of these urinary nucleosides.

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ACL-P03

A NEW ANALYTICAL METHODOLOGY FOR THE DETERMINATION OF KETAMINE AND ITS MAIN METABOLITE IN HUMAN URINE

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Ketamine (KT) is catalogued as a synthetic anesthetic in human and veterinary surgery, which induces sedation, immobility and amnesia. It can be injected, consumed in drinks or added to joints or cigarettes as a recreational drug [1]. KT was placed on the list of controlled substances in the US in 1999.

KT and its main metabolite norketamine (NK) have been traditionally analyzed in biological samples by high performance liquid chromatography (HPLC) coupled to different detection systems such as UV or mass spectrometry while the use of capillary electrophoresis (CE) has been poorly explored.

In this communication we present anovel capillary zone electrophoresis (CZE) method with UV detection at 205 nm for the analysis of KT and NK in human urine, employing a background electrolyte consisting on a 75 mM NaH_2PO_4/Na_2HPO_4 buffer (pH 7.0) for the separation of both substances. Separation temperature and voltage were studied, being the optimum values 20 ºC and 25 kV, respectively. The separation was achieved in less than 6 min in a 56-cm effective length capillary with 50 µm i.d. Field amplified sample injection (FASI) has been employed for on-line sample preconcentration in order to improve the sensitivity of the method. Injection voltage and time were optimized using response surface experimental design methodology, achieving the best results at 8.6 kV and 23 s, respectively.

The method was applied to urine samples, employing dispersive liquid–liquid microextraction (DLLME) as sample treatment.The on-line and off-line preconcentration obtained by combination of CZE-FASI with DLLME allowed the determination of the analytes of interest at their typical levels in urine, even using UV detection.

Linear ranges were established in urine matrix, between 25.0 and 100 ng/mL for both substances. LODs of 1.70 and 1.65 ng/mLfor KT and NK, respectively, were obtained according to Long and Winefordner criteria [2]. The method has been successfully applied to the analysis of the drug and its metabolite, with mean recoveries of 92 and 88%, respectively. The proposed methodology could be satisfactorily applied in routine for the monitoring of these compounds in biological samples.

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ACL-P04

DETERMINATION OF SELECTED ENDOCRINE DISRUPTING CHEMICALS IN HUMAN URINE BYDLLME PRIOR TO GC–MS/MS ANALYSIS

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In the last century, as a consequence of the huge industrial development, wildlife and humans are exposed to a large amount of synthetic chemicals that can interfere with the normal functioning of the endocrine system. These compounds, commonly called endocrine disrupting chemicals (EDCs), are present in many types of products, such as personal care products (PCPs), pharmaceuticals, sunscreens, foodstuffs, beverage cans, etc. The exposure to EDCs has influenced an increase in diseases and syndromes that are markedly frequent nowadays [1-3]. Therefore, it is necessary to develop new analytical procedures to evaluate the exposure with the ultimate objective of establishing, in an accurate way, relationships between EDCs and harmful health effects.

In the present work, a new method based on a sample treatment by dispersive liquid-liquid microextraction (DLLME) for the extraction of six parabens (methyl-, ethyl-, isopropyl-, propyl-, isobutyl- and butylparaben), six benzophenones (benzophenone-1, benzophenone-2, benzophenone-3, benzophenone-6, benzophenone-8 and 4-hydroxybenzophenone) and two bisphenols (bisphenol A and bisphenol S) in human urine samples, followed by gas chromatography-tandem mass spectrometry (GC–MS/MS) analysis is proposed. An enzymatic treatment allows determining the total content of the target EDCs. The extraction parameters were accurately optimized using multivariate optimization strategies. Ethylparaben ring-$^{13}C_6$ and bisphenol A-d_{16} were used as surrogates. Found limits of quantification ranged from 0.2 to 0.5 ng mL^{-1} and inter-day variability (evaluated as relative standard deviation) ranged from 2.0% to 14.9%. The method was validated using matrix-matched standard calibration followed by a recovery assay with spiked samples. Recovery rates ranged from 94% to 105%. A good linearity, for concentrations up to 300 ng mL^{-1} for parabens and 40 ng mL^{-1} for benzophenones and bisphenols, respectively, was obtained. After validation, the proposed method was satisfactorily applied for the determination of target compounds in human urine samples from 20 randomly selected individuals.

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ACL-P05

A FAST METHOD FOR THE DETERMINATION OF DRUGS OF ABUSE IN HAIR BY IN-LINE SPE-CE

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Drugs of abuse are a major concern that is increasingly affecting every sector of society. Consequently, there is a need for the continuous development of methods for the efficient determination of these substances and their metabolites in biological samples. Hair offers several advantages over more traditional biological matrices, such as blood and urine, which have already been discussed elsewhere [1].

Among the analytical techniques currently used, capillary electrophoresis (CE) represents an attractive alternative to chromatographic approaches because only few nanoliters of sample are needed to be injected. However, it is well known that this advantage leads to a relatively poor concentration limit of detection (LOD) by the fact that many analytes are present at very low concentrations.

To overcome the detection sensitivity limitations, solid-phase extraction (SPE) coupled in-line to CE proved to be highly useful [2,3]. Unfortunately, in order to reach low LODs, large sample injection times are usually required, and this can be considered as a drawback, since it clearly lengthens the analysis time. In this respect, further research is needed and should be focused on the development of faster in-line SPE strategies without sacrificing the sensitivity of the method.

With this in mind, the benefits of applying a higher (external) pressure than the common one (930 mbar) during sample injection in the determination of cocaine and its major metabolite, benzoylecgonine, in hair samples were evaluated. Furthermore, different geometries of in-line SPE-CE device were also investigated in order to improve the results, since increasing the quantity of the SPE sorbent introduced in the micro-cartridge, greater the load capacity of sample and, consequently, lower LODs.

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ACL-P06

NEW SCREENING OF METHYLTESTOSTERONE IN SPORTS: DIRECT DETECTION OF PHASE I AND PHASE II METABOLITES BY LC-MS/MS

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Methyltestosterone, a synthetic anabolic androgenic steroid (AAS), is one of the most frequently detected AAS in doping analysis. AAS are extensively metabolized in humans and mainly excreted in urine as phase II metabolites. Current screening methods, based on the enzimatic hydrolysis of steroid glucuronides and analysis of the released phase I metabolites, are not able to detect some of the recently reported long-term phase II metabolites, such as sulphates. Liquid chromatography-tandem mass spectrometry (LC-MS/MS) technology allows for the direct detection of phase II (glucuronides and sulphates) and unconjugated metabolites excreted in urine. The objective of this study was to evaluate the detection capabilities of methyltestosterone misuse using direct and simultaneous detection by LC-MS/MS of unconjugated metabolites as well as glucuronic and sulphate conjugates present in urine.

The method consisted of a solid-phase extraction of 2 mL of urine using a C18 cartridge, followed by LC-MS/MS analysis using a triple quadrupole instrument and electrospray ionization in positive and negative mode. Chromatographic separation was carried out using an Acquity UPLC®BEH C18 column (2.1 mm x 100 mm i.d., 1.7 µm particle size). Mobile phases contained water and acetonitrile with ammonium formate (1mM) and formic acid (0.01 %). Elution was done in gradient mode. A selected reaction monitoring method was used to monitor at least two specific transitions for each metabolite. Because the studied metabolites are not available as standards, ionization and collision induced dissociation were studied in-depth through excretion urine samples and, some of them, by the corresponding synthesis.

The following metabolites were studied: glucuronides of M1 and M2 (17α-methyl-5α-androstan-3α,17β-diol and 17α-methyl-5β-androstan-3α,17β-diol, respectively; these are the metabolites monitored in the current methods), unconjugated metabolite M3 (17α-hydroxy-17β-methylandrost-4,6-dien-3-one), and recently described sulphates S1 (17α-methyl-5β-androstan-3α,17β-diol 3α-sulphate), S2 (17β-methyl-5α-androstan-3α,17α-diol 3α-sulphate) and S3 (17β-methyl-5β-androstan-3α,17α-diol 3α-sulphate). All metabolites were detected simultaneously in urine samples collected after oral administration of methyltestosterone (1-10 mg) to four male volunteers. The detection times of each metabolite were evaluated and compared with those obtained using conventional methods.

For the first time, combined detection of unconjugated, glucuronide and sulphate conjugated metabolites of methyltestosterone is described. Short analysis time, simple sample preparation and the possibility to detect simultaneously different markers of methyltestosterone abuse, make this method very useful for doping control purposes.

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ACL-P07

SERUM IS NOT AN APPROPRIATE FLUID TO ANALYZE PROSTATE-SPECIFIC ANTIGEN (PSA) ISOFORMS BY CE-UV

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Prostate-specific antigen (PSA) is a glycoprotein present in serum as a complex mixture of several species. The most abundant form is a covalent complex of PSA with alpha-1-antichymotrypsin (ACT), while free PSA (PSAf) accounts only for 5–30% of the total PSA (PSAt). Concentration of PSAt in serum is the biomarker currently employed in clinical for prostate cancer (PCa) diagnosis. However, the limited specificity of this test makes necessary to find better PCa biomarkers.

PSA glycosylation is modified in prostatic pathologies, so distinguishing glycoforms of PSA could be a useful approach to differentiate patients with non-malignant prostatic diseases from those with PCa, as shown by the study performed by two-dimensional gel electrophoresis (2-DE) [1]. Capillary electrophoresis (CE) allows separating up to eight peaks (isoforms) of free PSA [2] and it has higher speed of analysis, improved quantitation, and easier automation than conventional gel electrophoresis.

However, to analyze isoforms of PSAf from serum by CE, one must isolate PSA from the serum sample and dissociate the PSA-ACT complex prior CE analysis. In this way a larger concentration of PSAf will be available.

The aim of this work is to study the feasibility of analyzing isoforms of PSAf from serum, taking into account the combined effect of purification by immunoaffinity chromatography (IAC) [3] and of the dissociation of PSA-ACT complex over the PSA profile in CE.

The PSA-ACT dissociation was achieved using ethanolamine pH 10.3 during 24 hours [4]. Dissociation of PSA-ACT complex before and after IAC was tested.

Changes experienced by PSA in each step of the sample treatment were studied by CE, 2-DE and circular dichroism.

The changes in resolution and peak size experienced in the CE profile of PSAf due to the sample treatment necessary to isolate the free glycoprotein from serum indicate that this fluid is not appropriate to study by CE changes in PSAf glycosylation as PCa biomarker.

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ACL-P08

CHIRAL DETERMINATION OF THE CONSTITUENTS INVOLVED IN THE PHENYLALANINE-TYROSINE METABOLIC PATHWAY BY CE-ESI-MS^2

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Neurotransmitters, the chemical messengers of the nervous system, play an essential role in neuroscience research. One of the most important metabolic pathways where neurotransmitters are released is the phenylalanine-tyrosine pathway. The constituents of this metabolic pathway are phenylalanine, tyrosine, DOPA, dopamine, norepinephrine, and epinephrine which are subsequently originated. The plasmatic concentration of these constituents can be altered in drug dependence processes. Since all these compounds, except dopamine, possess an asymmetric carbon, analytical methodologies are needed to obtain a better understanding of their enantioselectivity in a biological system. To the best of our knowledge, the unambiguous enantiomeric simultaneous separation of all these compounds has never been described in the literature.

In this work, a chiral CE-ESI-MS^2 methodology was developed based on the use of a dual cyclodextrin (CD) system consisting of methyl-β-CD and 2-hydroxypropyl -β-CD. This methodology enabled to avoid difficult derivatization steps and allowed the enantioresolution of all the constituents involved in this important pathway. The obtained LODs were close to 100 nM which are below the expected plasma levels which make it a very promising method.

Since research on the combined effect of cocaine and alcohol is scarce, their synergic effect was studied in adult rats by means of the developed chiral method. Cocaine is the psychostimulant drug most frequently used in Europe and the neurological damages caused by its consumption are frightening. The consequence of the combination of cocaine and alcohol produces the powerful cardiotoxic drug cocaethylene, which not only reinforces the cocaine effects but also increases its plasmatic concentration.

AMA-P01

IN-SYRINGE DISPERSIVE LIQUID-LIQUID MICROEXTRACTION AND SILYLATION OF UV FILTERS IN WATER SAMPLES COUPLED TO GC/MS

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A fully automated method for the determination of seven ultraviolet (UV) filters, commonly included in the formulation of sunscreen products, in aqueous samples is presented. The proposed method is based on the use of the in syringe dispersive liquid–liquid microextraction (DLLME) technique, coupled as front end to gas chromatography - mass spectrometry(GC–MS). This method enabled the integration of the extraction steps, derivatization and sample injection in an instrumental setup easy to operate. Derivatization with *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) was used to increase the volatility of hydroxylated analytes and to improve sensitivity. Although BSTFA is prone to hydrolysis in presence of water and is therefore unstable in aqueous solutions, it was compatible with the DLLME process due to the kinetics of the derivatization and given that extraction of the hydroxylated UV filters is faster than the decomposition of BSTFA.

Dispersion was achieved by aspiration of the organic (extractant and disperser) and the aqueous phase into the syringe very rapidly. The denser-than-water organic droplets released in the extraction step, were accumulated at the head of the syringe, where the sedimented fraction was transferred to a loop where the ultrasonication and derivatization take place. After silylation the sedimented phase was transported to a micro-volume injection valve where finally was introduced via an air stream into the injector of the GC, through a stainless steel tubing used as interface. Factors affecting the microextraction efficiency were optimized using multivariate optimization.

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AMA-P02

MAGNETIC STIRRING ASSISTED DISPERSIVE LIQUID-LIQUID MICROEXTRACTION COUPLED TO HPLC FOR DETERMINATION OF UV FILTERS

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Nowadays UV filters are widely used, being not only present in cosmetics products to protect the skin from solar radiation but also in textiles and plastics. This excessive use of them has lead to increase their presence in the environment, especially in the aquatic media highlighting their potential toxicity. Coastal waters present a challenging matrix owing to the expected variety of parameters. In fact, these waters are often highly stressed due to recreational activities, so it is important to evaluate marine contamination in order not only to assess global effects but also to ensure the quality of bathwaters. Therefore, it is justified the necessity of developing an efficient analytic method for UV filters determination.

The aim of this research was to develop a fully automated method, based on on-line in-syringe magnetic stirring assisted dispersive liquid-liquid microextraction (MSA-DLLME) of a group of UV filters from coastal samples coupled to high performance liquid chromatography (HPLC) with ultraviolet detection. In this scenario, a greener alternative was proposed using ionic liquids instead of using organic solvents due to their lower toxicity. The analytical system used an automatic burette as propulsion unit, and where the overall MSA-DLLME steps were automatically performed. The extraction was enabled within the syringe containing a magnetic stirrer for homogenization of the sample and the required reagents. In-syringe stirring was made possible using a specially designed driving device placed around the syringe barrel to achieve a rotating magnetic field in the syringe, forcing the stirrer to spin. Afterwards, the enriched droplets of the ionic liquid accumulated at the bottom of the syringe were transferred to a loop coupled to HPLC. The separation of UV filters was achieved using a C18 column and 85:15 (v/v) ACN/H_2O as mobile phase in isocratic mode. The flow rate was 0.8 mL/min and quantification was carried out at 307 nm.

Acknowledgements
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AMA-P03

FULLY AUTOMATED LQUID-LIQUID MICROEXTRACTION FLOW SYSTEM FOR URANIUM DETERMINATION IN ENVIRONMENTAL SAMPLES

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Uranium is a naturally occurring radioactive element, which is widespread in nature at trace levels. All natural uranium isotopes emit alpha particles. Uranium has both chemical and radiological toxic effects. During the last decades large amounts of this element have been released into the environment from anthropogenic sources such as nuclear industry and fertilizer products. Thus, uranium determination is needed in order to establish an environmental control. Therefore, an on-line liquid-liquid microextraction (LLME) method linked to a liquid waveguide capillary cell (LWCC) has been developed for the determination of low levels of uranium in environmental samples. This miniaturized and automatic SIA-MSFIA system (Fig. 1) allows uranium isolation and preconcentration from sodium salicylate media using Cyanex 272 in dodecane as extractant solution. The extracted uranium is stripped from the organic phase with hydrochloric acid and determined after reaction with arsenazo (III) at 655 nm. To achieve maximum efficiency in the retention and detection of uranium, the concentrations of reagents and their volumes were subjected to screening (fractional factorial experimental design 2^{k-2}), and to a response surface design. Seven factors were tested in the range of values indicated below:

Cyanex 272 concentration (0.00025-0.0005 M); extractant volume (0.5-1.5 mL); HCl concentration (0.5-2.5 M); HCl volume (0.5-1.5 mL); arsenazo (III) concentration (0.0001-0.001%); arsenazo (III) volume (0.25-1 mL)

AMA-P04

COMPARISON BETWEEN INTITIAL RATE AND FIXED TIME DETERMINATION METHOD FOR V(V) AUTOMATED CATALYTIC ANALYSIS

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A highly sensitive and fully automated kinetic-catalytic spectrophotometric method for vanadium determination is presented. This method is based onthe oxidation of Gallic acid with bromate catalyzed by V (V). The reaction was followed by measuring absorbance change using the fixed-time and the initial rate methods at 384 nm. For its automation, a multisyringe flow injection system was coupled to a monolithic flow conduit, called chip (CHIP-MSFIA). All reagents and sample were simultaneously propelled into the CHIP to achieve complete mixing, heating, and measuring inside the CHIP. This was possible due to the incorporation of the detection cell inside the thermostatic zone of the CHIP. Both methods were used to quantify the V (V) concentration in the samples being these results critically compared. Under optimal conditions, the determination of V (V) was performed in the range 0.2-75µg L^{-1} achieving limits of detection of 0.14 and 0.08 µg L^{-1} for fixed-time and initial rate methods,respectively. Relative standard deviations were between 1- 4%. Good recoveries were obtained varying from 94% to 102%.The accuracy of the method was validated comparing our results with those obtained by ICP-AES and satisfactorily analyzing a certified reference sample.

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AMA-P05

SENSITIVE KINETIC-CATALYTIC SPECTROPHOTOMETRIC METHOD FOR COBALT DETERMINATION USING A FULLY AUTOMATED CHIP-MSFIA

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The development of an automatic kinetic-catalytic spectrophotometric method for Co determination is presented. The method is based on the catalytic effect of Co in the oxidation of hydroxybenzoic acid by H_2O_2 in basic media. The method was automated using a multisyringe flow injection system coupled to a monolithic flow conduit called chip (CHIP-MSFIA). All reagents and sample were simultaneously propelled into the CHIP to achieve complete mixing and detection at 482 nm.The reaction occurred very fast at room temperature, thus the fixed-time method was exploited to quantify the Co concentration in samples. Variables such as reagents concentration, pH, flow rate and reaction time were optimized to improve the selectivity and sensitivity of the proposed system. Under optimal conditions, the determination of Co was performed in the range 0.02-10 µg L^{-1} achieving a limit of detection of 0.021 µg L^{-1}. Relative standard deviations were below 3%. The method was satisfactorily applied to water samples and a pharmaceutical formulation. Good recoveries were obtained varying from 91% to 99%. The accuracy of the method was validated comparing our results with those obtained by ICP-AES and the reported values of the pharmaceutical formulation.

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AMA-P06

AUTOMATED CATALYTIC SPECTROPHOTOMETRIC METHOD FOR MANGANESE ANALYSIS BY USING A CHIP-MULTISYRINGE FLOW INJECTION SYSTEM (CHIP-MSFIA)

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In this work, we present an automated catalytic spectrophotometric method fordetermination of Mn(II) by using a multisyringe burette coupled to a chip microfluidic-conductor (Chip-MSFIA). The reaction is based on the catalytic effect of Mn(II) in the auto-oxidation reaction of succinimidedioxime (SIDO). Reagents and sample were simultaneously dispensed to the chip for their complete mixing, heating, and measurement. The absorbance of the reaction product was measured at 700 nm. The product concentration could be determined by the fixed-time and the initial rate method under optimum conditions (temperature 35 ºC, 4.70 mmol L^{-1} SIDO, and 0.60 mol L^{-1} NaOH). For this work, the fixed-time method was selected for Mn(II) samples in the working range of 1-20 µg L^{-1} of Mn(II). The estimated precision was 0.67 % (5 µg L^{-1}, n=15) and the limit of detection of 0.33 µg L^{-1} of Mn(II). The proposed method is highly sensitive, selective, and simple for trace Mn(II) determination without extraction and separation steps. The system was successfully applied to water samples with a sample throughput of 22 injections h^{-1}.

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AMA-P07

EARLY WARNING DEVICE FOR DETECTION OF POLLULANTS IN WATER

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Due to a growing need to protect water resources from contamination, there is a requirement for the deveopment of more reliable and cost effective devices for water quality monitoring [1,2]. The aim of the AQUAWARN project is to develop and deploy a fully autonomous water quality monitoring device that can measure nitrite, nitrate, phosphate and pH colorimetrically in freah water and wastewater, and communicate the information to skateholders in real time.

The initial focus of the project is the assesment and optimisation of appropiate colorimetric chemistries for phosphate and pH. The chemistry for each analyte has been tested using bench-top instrumentation and once optimised, it was then integrated within microfluidic chips. Table 1 shows the methods used for each analyte and the ranges achieved.

Table 1. List of analytes, method of detection and range studied

Analyte	Method	Range	Detection Limit
Phosphte	Vanadomolybdate method	0.1-100 µM	0.1 µM
pH	Mixture of dyes (PR, CPR, BPB)	4 - 10 pH units	n/a
Nitrite	Griess method	0.25 - 350 µM	0.02 µM
Nitrate	Cd reduction followed by Griess method	0.25 - 350 µM	0.025 µM

The use of microfluidic chips allows for minute amounts of reagent per sample measurement allowing for an increase in the operational lifetime of the device. Moreover, the integration of light emitting diodes (LEDs) and photodiodes as light sources and detectors, coupled with syringe pumps, enable the development of a low-cost, portable and autonomous device.

Acknowledgements
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AMA-P08

AUTOMATED EXTRACTION METHOD FOR SOLUBLE ARSENIC DETERMINATION IN SOIL

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High arsenic levels in the environment constituted an important public health problem. The intake of water and agricultural products contaminated with arsenic are considered the principal pathway arsenic exposure for human and can be affected mainly by the amount of phytoavailable arsenic rather than the total arsenic content in soil. The soluble/total arsenic ratio in soil can vary from one place to another due to variability of chemical soil proprieties. Due to high toxicity of arsenic at low concentrations and its high transference through the trophic chain is imperative to develop fast, efficient and sensitive methodologies to properly determine phytoavailable arsenic fraction in soil. Three-step BCR sequential extraction method is a batch-wise protocol proposed by European Community Bureau of Reference (1993) in order to harmonize the fractionation of heavy metals in soil samples according to the chemical process involved: 1) Acid soluble fraction or interchangeable, 2) reducible fraction, and 3) the oxidizable fraction. The acid soluble and reducible fractions are considered available for plants in soil. However, conventional BCR sequential extraction method is inadequate to determine kinetics of the leaching extraction process of trace elements under the action of the corresponding extractant solutions, and experimental results in each step might be biased by arsenic readsorption process. In this work, an automated online sequential extraction method is proposed for phytoavailable arsenic determination in soil. The total arsenic in each fraction determined by hydride generation atomic fluorescence spectrometry (HG-AFS) was coupled to the automated extraction system using photo-oxidation step for the degradation of the organic arsenic species.The optimal conditions of HG-AFS for each extractant agent were found using central composite design 2^3 (STATISTICA v. 7). The LODs under optimal conditions were 5 and 14 µg L^{-1} for soluble acid and reducible fractions, respectively. The linear working range for both extractant agents was from 0 to 600 µg L^{-1}. No significant difference in HG-AFS for dimethylarsenic (DMA) after degradation during photo-oxidation step, was achieved obtaining the same instrumental response than those for As(V) (p=0.5). The proposed automated online system for the sequential extraction of arsenic in soil samples is a versatile, sensitive, low cost and rapid method compared to batch-wise BCR method.

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AMA-P09

MOLECULARLY IMPRINTED POLYMER AS IN-LINE CONCENTRATOR IN CE-MS FOR THE DETERMINATION OF QUINOLONES IN MILK

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Quinolones (Qns) are antibiotics widely used in veterinary practice to treat bacterial infections of animals in livestock farming and bovine milk production, causing residues in foodstuffs that produce adverse effects, as allergic reactions or antibiotic resistance. Therefore, to ensure food safety, European Union has set maximum residue limits (MRLs) of antibiotics in foodstuffs of animal origin by means of Commission Regulation N.37/2010. Eight Qns have been included in this regulation, named danofloxacin, sarafloxacin and its metabolite difloxacin, enrofloxacin and its metabolite ciprofloxacin, flumequine, marbofloxacin and oxolinic acid.

Capillary electrophoresis (CE) could be the method of choice to determine antibiotics in foods but an improvement in sensitivity is required. An interesting option [1]], consists of in-line solid phase extraction (SPE) which is carried out using the so-called analyte concentrators (ACs) or preconcentrators. In these devices, a small amount of sorbent is located at the capillary inlet allowing the retention of the analytes. Molecularly imprinted polymers (MIPs) could be used as sorbent materials due to their interesting properties. They are able to selectively recognize a molecule in the presence of closely related interfering species, as they contain specific recognition sites with a shape and geometry of functional groups complementary to those present in the template molecule. Thus, the strong retention between the MIP and its target molecules makes it ideal for the selective extraction of compounds at trace levels, being of special interest for complex samples.

In this communication, MIPs were evaluated as sorbents for the construction of an in-line AC in CE coupled with mass spectrometry. The method was used for determination of the regulated Qns in bovine milk samples. Different parameters affecting the AC performance, such as sample pH, volume and composition of the elution plug and injection time were studied. Recoveries ranging from 70.0 to 102.3 % and RSD below 12.0 % were obtained. The method is simple for the monitoring of these residues in milk, allowing the direct injection of the samples with minimum pretreatment, achieving LODs between 3.8 and 4.7 μg kg^{-1}.To the best of our knowledge, this is the first application of MIPs as AC for CE with MS detection.

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AMA-P10

COMPARISON OF SORBENTS IN ON-LINE SPE COUPLED TO UHPLC-MS/MS FOR THE DETERMINATION OF HORMONES IN WATER SAMPLES

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Endocrine disrupting compounds (EDCs) are a wide group of compounds that can affect the endocrine system of organisms, producing different problems. Since last decades, several authors it has been established the potential toxic effects of EDCs over different marine and aquatic organisms like changes in fertility or feminization [1]. These changes are linked with the effluent discharges of wastewater treatment plants, because these are the principal way of EDCs into the environment. Among the EDCs, steroid hormones are an important group because their effects in biota can be appreciated even at low concentrations. Steroid hormones have been measured in environmental waters at very low concentrations, so it is necessary to develop extraction and preconcentration methodologies to achieve that concentrations. Solid phase extraction (SPE) has been used widely in recent years to separate and preconcentrate hormones from environmental water samples [2] and the use of on-line SPE present many advantages like less samples handling or shorter time analysis.

In this study, an on-line SPE coupled with ultra-high performance liquid chromatography following by mass spectrometry detection (on line SPE-UHPLC-MS/MS) method has been developed to determine several natural and synthetic hormones (estrogens, androgens, progestogens and corticosteroids). Two different sorbents and all the parameters involved into the extraction procedure and the separation and detection processes have been optimized. This method has been used for the determination of target hormones in different environmental water samples of Gran Canaria (Spain).

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API-P01

USED OF MIXED MICELLAR BRIJ-35/SDS SYSTEMS IN THE ANALYSIS OF BASIC DRUGS

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Micellar liquid chromatography (MLC) is a reversed-phase chromatographic mode that uses solutions containing a surfactant at a concentration above the critical micelle concentration (CMC). Surfactant monomers adsorb on the alkyl-bonded stationary phase through hydrophobic interactions, creating a neutral or charged double layer, depending on the nature of the adsorbed surfactant. In the mobile phase, surfactant monomers aggregate to form micelles. MLC offers interesting results in terms of retention and selectivity, being the surfactant monomers adsorbed on the stationary phase the main responsible for the changes observed in the chromatographic performance.

Micellar mobile phases usually consist of aqueous solutions of a unique surfactant, in the absence or presence of an organic solvent. The organic solvent is added to improve the poor elution strength and efficiency shown by pure micellar solutions. The addition of a second surfactant to the micellar solution is an alternative to the use of organic solvents that can also lead to satisfactory results. However, mixed micellar systems have been scarcely explored in MLC.

Mixtures composed by the anionic surfactant sodium dodecyl sulphate (SDS) and the non-ionic polyoxyethylene(23)lauryl ether (known as Brij-35) are the most common mixed micellar mobile phases. In the literature, it is accepted that these mixed micellar solutions have an influence on the retention and separation of analytes of different nature, and are able to improve the results given by micellar systems that make use of a single surfactant. However, it is difficult to find information about the retention mechanism that takes place inside the column, or about parameters related to the peak profile.

In this work, mixed mobile phases of Brij-35 and SDS were used to elute a group of basic cationic solutes of pharmaceutical interest. The results were analysed in terms of retention, selectivity, peak profile and resolution. The association constants solute-stationary phase and solute-micelle were calculated in order to elucidate the retention mechanism that takes place in the mixed micellar system. The results show that mixed Brij-35/SDS mobile phases are able to improve the separation of basic drugs with respect to conventional RPLC or other micellar systems, without requiring the addition of organic solvent.

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API-P03

DETERMINATION OF HYDROXYTYROSOL AND TYROSOL FOR THE QUALITY CONTROL OF COSMETIC PRODUCTS BASED ON OLIVE EXTRACTS

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An analytical method for the simultaneous determination of hydroxytyrosol and tyrosol in different types of olive extract raw materials and cosmetic cream samples has been developed.

The determination was performed by liquid chromatography with UV spectrophotometric detection. Different chromatographic parameters, such as mobile phase pH and composition, oven temperature and different sample preparation variables were studied. The best chromatographic separation was obtained under the following conditions: C18 column set at 35 ºC and isocratic elution of a mixture ethanol:1% acetic acid solution at pH 5 (5:95, v/v) as mobile phase pumped at 1 mL min^{-1}. The detection wavelength was set at 280 nm and the total run time required for the chromatographic analysis was 10 min, except for cosmetic cream samples where 20 min runtime was required (including a cleaning step).

The method was satisfactorily applied to 16 samples including solid, water-soluble and fat-soluble olive extracts and cosmetic cream samples containing hydroxytyrosol and tyrosol. Good recoveries (95-107%) and repeatability (1.1-3.6%) were obtained, besides of limits of detection values below the µg mL^{-1} level. These good analytical features, as well as its environmentally-friendly characteristics, make the presented method suitable to carry out both the control of the whole manufacture process of raw materials containing the target analytes and the quality control of the finished cosmetic products.

API-P04

DETERMINATION OF ATRANOL AND CHLOROATRANOL IN PERFUMES BY SIMULTANEOUS DERIVATIZATION-DLLME FOLLOWED BY GC-MS

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A new analytical method based on simultaneous derivatization and dispersive liquid-liquid microextraction (DLLME) followed by gas chromatography-mass spectrometry (GC-MS), for the determination of the allergenic compounds atranol and chloroatranol in perfumes, is presented. Derivatization of the target analytes by means of acetylation with anhydride acetic in carbonate buffer was carried out. Thereby volatility and detectability were increased for improved GC-MS sensitivity. In addition,extractability by DLLME was also enhanced due to a less polar character of the solutes. A liquid-liquid extraction was performed before DLLME to clean up the sample and to obtain an aqueous sample solution, free of the low polar matrix from the essential oils, as donor phase.

Different parameters, such as the nature and volume of both the extraction and disperser solvents, the ionic strength of the aqueous donor phase or the effect of the derivatization reagent volume, were optimized. Under the selected conditions (injection of a mixture of 750 µL of acetone as disperser solvent, 100 µL of chloroform as extraction solvent and 100 µL of anhydride acetic as derivatization reagent) the figures of merit of the proposed method were evaluated. Limits of detection in the low ng mL^{-1} range were obtained. Matrix effect was observed in real perfume samples and thus, standard addition calibration is recommended.

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API-P05

METALLIC IMPURITIES ANALYSIS BY ICP-MS AND AAS-FLAME IN DRUGS ACCORDING TO NEW PHARMACOPOEIAS

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Despite the vast technological development that has occurred during the last century, the analysis of heavy metals in drugs has not evolved. For the last 100 years the official method of analysis has been the precipitation of the heavy metal sulphides and a colorimetric analysis [1].This method has two disadvantages. The first is that not all heavy metals are capable of forming sulphides, and the second is the lack of selectivity of this method. Due to these factors, the application of this method makes the correct quantification of the total metallic impurities impossible and it does not allow the determination of the toxicity of the product because not all the heavy metals are equally toxic.

In order to take care of those issues, by the end of 2015 it will be necessary that all the drugs available give more detailed information about their heavy metal content according to changes in Pharmacopoeias [2,3].

The current standard for the European Union compared with the United States takes into account neither the same elements nor their respective concentrations. While the USP finds it necessary to evaluate all the toxic heavy metals that could potentially harm the consumer, the EP only takes into consideration those metals that could be present in the pharmaceutical products through the catalysts and the raw materials used during their production.

The ICH, whose role is to provide guidelines to harmonize the standards, has published as July 2013 a draft that collects the heavy metals and their concentration limits in drugs [4]. The requirements in this draft could presumably end up being the ones applied by 2015.

In this paper a method optimization is performed to analyse these metals by using AAS-Flame and ICP-MS techniques. The developed method is suitable for determining metallic impurities content in pharmaceutical products according to new specifications.

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[2]2.4.20; 5.20 Metal Catalyst or Metal Reagent Residues. Eur. Pharmacopoeia 8.0
[3] <232>; <233> United States Pharmacopoeia USP 37-NF 32
[4] ICH Q3D Step 2b

API-P06

A PORTABLE AND LOW-COST NEAR-INFRARED SPECTROSCOPY SPECTROMETER SAFEGUARDS THE SOLID PHARMACEUTICAL INDUSTRY

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1. Objective

The aim of this research is to investigate a method which is suitable for application of Near-infrared spectroscopy (NIR) in solid pharmaceutical industry. In order to reduce the cost for changes in production line and simplify the modeling process for different active pharmaceutical ingredients (API), the portable, low-cost and miniaturized spectrometer needs to be adopted to reach this goal.

2. Materials and methods

2.1 Instrument and software

Near infrared spectrums were recorded by the portable Micro-NIR (JDSU NO.38, USA). Dimensions is (diameter x height) 45 x 42mm, weight<60g. Spectral region is from 1158.800nm to 2153.100nm. The multivariate models were built up with Unscrambler 9.8 (Trondheim, Norway).

2.2 Production samples

Granulate samples of nimesulide and powder samples of cetirizine from several production batches were offered by laboratory Menarini S.A (Spain).

2.3 Laboratory samples

Laboratory samples consisting of accurately weighed amounts of the powdered ingredients spanning a concentration range ±20% around the nominal API content were prepared according to the ICH guidelines. The sample set was established by using a D-optimal design in order to minimize correlation between concentrations.

2.4 Calibration

For every sample, 3 spectrums were selected to be averaged. These average spectrums were divided into calibration set and validation set. The principal component analysis (PCA) was computed to select calibration samples in order to cover the maximum of variability. The calibration model of nimesulide was built by the PLS with 7 factors. The pretreatment was Median filter smoothing (segment size 3) + Standard normal variate (SNV) + Gap-segment Derivatives (order 1, gap size 5, segment size 2). And the spectral region was 1558.150nm-1851.55nm. The calibration model of cetirizine was built by using the PLS model with 7 factors. The pretreatment was Median filter smoothing (segment size 7) + Norris 1st derivate (gap size 7). And the spectral region was 1158.800 nm-2153.100 nm.

3. Results and discussion

According to the ICH guidelines, the linearity, range, accuracy, robustness, repeatability, and intermediate precision of the models have been validated. These items were assessed by relative standard deviation (RSD) of the residual, paired t-test at the 95% confidence level, and analysis of variance (ANOVA). The results show that there is no significant difference and large residual among the validation set.

Acknowledgments

Thank you for the cooperation from the laboratory Menarini S.A (Spain).

API-P07

SEPARATION OF ARGININE ENANTIOMERS BY HPCE-UV

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Arginine with an isoelectric point of 10.76 is a basic amino acid. Arginine includes in its structure an asymmetric carbon, therefore, has two enantiomers:D-arginine and L-arginine. L-arginine is the most abundant structure in the nature and this is the enantiomer employed for pharmaceuticals synthesis.It is therefore important the separation of the enantiomers of the arginine.

There are different analytical techniques, which enable the enantiomeric separation of amino acids such as liquid chromatography, gas chromatography and capillary electrophoresis [1, 2, 3].

We have developed a method for the separation of arginine enantiomers by capillary electrophoresis using a UV detector (HPCE-UV). It has studied the influence of pH, buffer concentration and the use of cyclodextrins (type and concentration) in the enantiomeric separation. Moreover, the derivatization process has been optimized in order to improve sensibility.

This method is suitable to determine the concentration of D-enantiomer relative to L-enantiomer from 1% (w / w) to 5% (w / w).

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API-P08

ON-LINE PRECONCENTRATION IN CAPILLARY ELECTROPHORESIS FOR ANALGESICS DRUGS IN URINE AND PHARMACEUTICAL PREPARATIONS

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Commonly administered drugs used as local anesthetics (procaine, lidocaine and bupivacaine) have been analysed in urine samples and pharmaceutical preparations by a sensitive and reliable capillary zone electrophoresis method with diode-array detection (CZE-DAD). Sensitivity has been increased by the use of an on-line preconcentration methodology such as field amplified sample injection (FASI) [1].

Parameters involved in FASI preconcentration have been optimized in order to obtain the highest sensitivity. Different sample injection media such as methanol, isopropanol, acetonitrile and their corresponding binary mixtures with water were assayed. The best results, in terms of sensitivity and reproducibility, were obtained when a mixture of ultrapure water and acetonitrile (50:50) was employed. Injection time and injection voltage were optimized through an experimental design obtaining 13 s and 13 kV, respectively, as optimum values. On the other hand, different mixtures of methanol:water were tested as pre-injection plug, achieving the highest sensitivity when a plug of pure methanol (3 s, 50 mbar) prior to the electrokinetic injection was introduced.

Drug separation has been achieved in less than 7 min in a standard fused silica capillary (48.5 cm capillary length and 50 µm i.d.), using 150 mM citrate buffer (pH 2.5) as background electrolyte (BGE). Separation has been performed under a voltage of 25 kV and 25º C of capillary temperature. The possible irreproducibility associated to electrokinetic injection has been corrected by using tetracaine as internal standard.

UV determination at 212 nm enabled limits of detection between 1.5 and of 2.1 µg mL^{-1} in presence of urine matrix. Satisfactory results were obtained for intraday and interday precision (RSD <9.5 % and <10.7 %, respectively) in this biological sample. Simplicity and sensitivity make this method really useful for estimating the content of these anesthetics in different pharmaceutical preparations and urine samples.

Acknowledgement
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API-P09

A CHIRAL CE-ESI-MS^2 METHODOLOGY FOR THE DETERMINATION OF THE OPTICAL PURITY OF S-DULOXETINE IN PHARMACEUTICALS

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The antidepressant drug duloxetine possesses an asymmetric carbon and therefore it exists as a mixture of two enantiomers. Although the S-enantiomer is slightly more potent, both enantiomers are active. Since this drug is commercialized as a pure enantiomer, the development of selective and sensitive methods to guarantee its quality control is needed. CE is a well-established technique to achieve enantioseparations and MS hyphenation offers many advantages such as the unequivocal identification and sensitivity improvement.

In this work, a chiral CE-ESI-MS^2 methodology enabling the enantiomeric determination of duloxetine was developed. 2-hydroxypropyl-β-CD was employed as chiral selector and the partial filling technique was used in order to avoid sensitivity loss. A LOD of 20 ng/mL was obtained. This value is 10 times lower than that obtained by CE with UV detection, and corresponds to 0.02 % of the duloxetine enantiomeric impurity. This is the lowest LOD ever reported for the enantiomers of this drug, being possible to accomplish with the ICH guidelines requirements (content of enantiomeric impurities lower than 0.1 %).

The developed method was applied to the determination of duloxetine in pharmaceutical formulations. The content of the enantiomeric impurity of duloxetine was below the LOD and the amount of S-duloxetine was in agreement with the labeled content.

ESP-P01

CHROMIUM SPECIATION BY CLOUD POINT EXTRACTION USING SILVER NANOPARTICLES AND ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

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Low concentrations of chromium are present in the environment and particularly in waters. Trivalent chromium is considered essential for human nutrition [1]. On the contrary, hexavalent chromium has been shown to be a human carcinogen by inhalation [2]. Not only toxicity but also mobility and bioavailability of the element mainly depend on its chemical form. The Cr (VI) compounds are generally soluble, their mobility and bioavailability being greater than those of the less soluble Cr(III). It is clear that a detailed knowledge of each species, rather than the total level of Cr is necessary to adequately assess the physiological and toxicological effects of this metal. The task is difficult due to the very low concentrations involved but can be achieved taking benefit of a preconcentration stage before the final measurement.

In this communication, the determination of chromium by its interaction with non-functionalized silver nanoparticles (AgNPs) and subsequent collection in the micellar phase generated by Triton X-114 using a typical cloud point extraction (CPE) treatment is studied. Under these conditions, both chromium species are adsorbed onto AgNPs and thus transferred to the surfactant-rich phase. The measurement of the chromium content in this phase by means of electrothermal atomic absorption spectrometry (ETAAS) allows the total content of the metal to be obtained. Despite the very low concentrations, speciation is possible by means of a second CPE experiment in which EDTA is incorporated in the sample solution. In this way the Cr(III) present in the solution is not extracted, and the measurement in the surfactant-rich phase permits the Cr(VI) concentration to be obtained. Trivalent chromium is then calculated by difference. The reliability of the procedure is verified by analyzing three standard reference water samples with certified content of the element.

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ESP-P02

SPECIATION OF SILVER NANOPARTICLES AND SILVER IONS USING ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY AND CLOUD POINT EXTRACTION

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Silver has been known since antiquity for its properties useful to humans, and claims of medicinal applications were made many years ago. Thus, silver has long been recognized as a disinfectant and widely used for topical application due to their particular properties, such as the wound healing by silver nanoparticles, AgNPs[1]. Nanosilver is being spun into thread, incorporated into plastics, impregnated into filters and painted onto product surfaces. Nowadays, AgNPs can be found in personal-grooming kits, female-hygiene products, beauty soaps, cleansers and fabric softeners, among a large variety of commonly used products. Consequently, this increasing use has resulted in very low amounts of AgNPs and silver ions appearing in natural waters, and the U.S. Environmental Protection Agency includes the element as a priority pollutant in waters due to its persistence in the environment [3].

On the other hand, coacervates made of supramolecular assemblies are being increasingly used for the liquid–liquid extraction of organic pollutants [4] and also provide an interesting way for the separation of inorganic species.

In this work, a procedure for the determination of silver ions andsilver nanoparticles at very low concentrations is proposed by means of a cloud point microextraction and subsequent measurement of the metal in the microvolume micellar phase by electrothermal atomic absorption spectrometry. No mineralization of the sample is required. Speciation is carried out using two extractions, one of them in the presence of thiocyanate. The optimized procedure has been successfully applied to the determination of AgNPs and Ag^{+}in water and aqueous lixiviates of dressings and cleaning textiles.

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ESP-P03

DETERMINATION OF TOTAL AND INORGANIC ARSENIC AND CHROMIUM SPECIES IN SEAWATER SAMPLES

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Methods for total and inorganic species determination of As and Cr in seawater samples have been developed. Total As and Cr determination has been performed using the SeaFAST2 (Perkin Elmer, Norwalk, EEUU) coupled to ICP-MS. Inorganic species of As and Cr were separated and quantified by HPLC-ICP-MS.

Regarding total As and Cr determination, the use of the SeaFAST2 system allow the on-line sample dilution (10 times) before its introduction into the ICP-MS. Because of the influence of the sample matrix, calibration using standard addition method has been used for the determination of both elements and the introduction of several internal standards (Y, Rh) did not improve the results or the linearity of the calibration graphs. The limits of detection obtained were 0.28 and 0.03 μg L^{-1} for As and Cr respectively. The method showed a good precision with relative standard deviations lower than 5% (n=10) and accuracy.

Inorganic species of As and Cr were separated and quantified by HPLC-ICP-MS. The separation was performed using the column Phenomenex, kinetex C18, working with a mobile phase (pH 7.2) containing 1.0 mM tetrabutylammonium hydroxide (TBAH), 0.7 mM ethylenediaminetetraacetic acid disodium salt (EDTA) and 5% methanol. Working in these conditions, its is possible the separation of the As and Cr inorganic species in less than 5 minutes.

The developed method was applied to the determination in real samples from the Galician coast.

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ESP-P04

OCCURRENCE OF INORGANIC ARSENIC IN EDIBLE SHIITAKE (*LENTINULA EDODES*) PRODUCTS

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The consumption of wild edible mushrooms has increased worldwide during recent years. *Lentinula edodes* (also known by its Japanese name of Shiitake) is one of the five most cultivated edible mushrooms in the world, being particularly popular in China, Japan and other Asian countries.

Due to the increasing focus on inorganic arsenic in food and given that mushroom consumption had increased considerably in recent years due to their nutritional properties, the present study reports arsenic speciation analysis in edible Shiitake products. The study focused on the extraction, and accurate quantification of inorganic arsenic (iAs), the most toxic form of arsenic, which was selectively separated and determined using anion exchange HPLC-ICPMS. A wide variety of edible Shiitake products (fresh mushrooms, food supplements, canned and dehydrated) were purchased and analysed. In addition, a preliminary study of Shiitake cultivation was performed in a small-scale mushroom facility in order to estimate the possible health risks of home-cultivated Shiitake grown on a commercial substrate. Arsenic speciation revealed that iAs was the major As compound up to 1.38 mg As kg^{-1} dm (with a mean percentage of 84% of the total arsenic) and other organoarsenicals were found as minor species. The extraction method showed satisfactory extraction efficiencies (>90%) and column recoveries (>85%) for all samples. Shiitake products had high proportions of iAs and therefore should not be ignored as potential contributors to dietary iAs exposure in populations with a high intake of Shiitake products [1].

The analytical method used may contribute to increase the availability of reliable results on inorganic arsenic in edible mushrooms. Furthermore, the present results may be useful in ongoing discussions in the European Commission and the CODEX Alimentarius for establishing and implementing future maximum levels of inorganic arsenic in food commodities.

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ESP-P05

DETERMINATION OF ARSENIC SPECIES IN MARINE REFERENCE MATERIALS AND BRAZILIAN AND SPANISH SEAFOOD BY HPLC-ICPMS

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Recently, the EFSA published in 2014 a scientific report about the dietary exposure to inorganic arsenic in the European population providing information on the levels of arsenic (total arsenic and inorganic arsenic) found in a range of foods on the European market. It is pointed out that more analytical data on inorganic arsenic (iAs) would be needed, in particular in fish and seafood, and in food groups that provide a significant contribution to the dietary exposure to iAs (e.g. rice and wheat-based products) to reduce the uncertainty of the exposure assessments to iAs.

Therefore, an analytical method for determination of arsenic species (inorganic arsenic (iAs), methylarsonic acid (MA), dimethylarsinic acid (DMA), arsenobetaine (AB), trimethylarsine oxide (TMAO) and arsenocholine(AC)) in Brazilian and Spanish seafood samples is reported. This study was focused on extraction and quantification of inorganic arsenic (iAs), the most toxic form. Arsenic speciation was carried out via HPLC with both anionic and cationic exchange with ICPMS detection (HPLC-ICPMS). The detection limits (LODs), quantification limits (LOQs), precision and accuracy for each arsenic species were established. The proposed method was evaluated using eight reference materials (RMs). Arsenobetaine was the main species found in all samples. The total and iAs concentration in 22 seafood samples and RMs ranged between 0.27–35.2 and 0.02–0.71 mg As kg^{-1}, respectively. Recoveries of between 100% and 106% for iAs, based on spikes, were achieved.

The present results provide reliable iAs data for future risk assessment analysis in seafood that could be used in further Directives on iAs in food commodities.

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ESP-P06

SYNTHESIS OF 57FE ENRICHED FERRITIN: FORMATION AND CHARACTERIZATION OF ISOTOPICALLY ENRICHED FE NANOPARTICLES

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Serum ferritin is the most valuable parameter in the diagnosis and follow-up of iron deficiency and iron-overload diseases. However, in patients with substantial iron overload, the correlation between serum ferritin and the individual iron stores is poor. In addition, secondary factors such as infection, inflammation, or the presence of a tumour can also increase serum ferritin values. The measurement of Fe in ferritin or Fe:ferritin ratios has been reported to be superior to that of serum ferritin. It was hypothesized that these ratios could be an alternative biomarker for iron metabolism which is not confounded by inflammation [1]. Nowadays, there are not methods for measuring Fe:Ferritin ratios. We propose the use of labelled ferritin with ^{57}Fe for this purpose. We have achieved the synthesis of labelled ferritin from apo-ferritin and $(NH4)_2$ $^{57}Fe(II)(SO4)_2$. During the synthesis of ^{57}Ferritin the protein was monitorized by size exclusion chromatography with UV-VIS detection (380 nm). This shows that during the synthesis process the formation of aggregates of the protein can be observed. Therefore, different strategies were evaluated to minimize these aggregates and obtain a stable isotopically labelled standard. A process involving incubation with guanidine hydrochloride (pH=3.5) and subsequent washing with water provided the ideal conditions for maintaining the structure, without formed aggregates and which remaining stable at -20 ºC for at least two weeks. Abundances and concentration of Fe were evaluated in the labelled ^{57}Ferritin. As average, 57Fe-ferritin contains 2200 atoms of Fe/mol. Furthermore, evaluation of the Fe core after incubation by transmission electron microscopy (TEM) revealed that ^{57}Fe nanoparticles inside the protein cage were formed with diameter similar to those existing in commercial ferritin. This confirms that uptake, oxidation and mineralization occur within the cavity of the protein. To prove the spike stability, different methods for purification of ferritin were tested (precipitation of proteins with methanol, heat precipitation, ultracentrifugation with membrane filters and heat precipitation with subsequent filtration).

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ESP-P07

SPECIATION OF LEAD USING REVERSED PHASE HPLC-ICPMS

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A method has been developed for the speciation of inorganic lead Pb(II), trimethyllead chloride (TML) and triethyllead chloride (TEL) using reversed phase high performance liquid chromatography (RP-HPLC) and inductively coupled plasma-mass spectrometry (ICPMS) as detector. The separation was performed using a µBondapak C18 column (125 Å, 10 µm, 3.9 mm x 300 mm), and an injection volume of 50 µL. The composition of the mobile phase (concentration of ethylenediaminetetraacetic acid (EDTA) and the ratio methanol:buffer), and the influence of flow rate were studied to obtain a separation in less than 7 minutes. The optimised mobile phase consisted of 80% buffer (0.1M acetic acid-0.1 M ammonium acetate buffer at pH 4.7), 20% methanol and 50 mg/L of EDTA, and the separation was carried out at a flow rate of 1.0 mL/min.

The method was evaluated for the separation of lead in different matrixes such as seawater and extracts of marine products, and the analytical performance was studied. The limits of detection for seawater taking into account the dilution (10-fold) were 0.21 µg/L (Pb(II)), 0.12 µg/L (TML) and 0.62 µg/L (TEL). The calibration graphs showed good regression coefficients (r > 0.995) and the analytical recoveries ranged from 91.2 to 101.0 %. The precision was estimated by calculating the relative standard deviations (n=11) that were lower than 2.2%.

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ESP-P08

MERCURY DETERMINATION IN BIOLOGICAL SAMPLES BY DISPERSIVE LIQUID-LIQUID MICROEXTRACTION AND SCREEN-PRINTED ELECTRODES

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Mercury is one of the most well-known toxic elements and presents a high bioaccumulation factor. Determination of mercury in biological samples gives information about the cumulative exposure from the diet or a contaminated environment and allows to prevent severe health effects.

In this work, a novel approach is presented, whereby in-situ ionic liquid formation dispersive liquid-liquid microextraction (in-situ IL-DLLME) [1] is combined with gold nanostructured screen-printed carbon electrode (SPCnAuE) as electrochemical transducer for the determination of mercury in biological samples. Mercury complexes with ammonium pyrrolidinedithiocarbamate are extracted from digested samples into a water-immiscible IL formed in-situ. Then, an ultrasound-assisted procedure is employed to back-extract mercury into 10 µL of an acidic aqueous solution, which is finally analyzed using SPCnAuEs.

Screen-printed electrodes (SPELs) [2] are miniaturized, inexpensive, mass-produced, disposable devices and very suitable for analyzing low volume extracts obtained after microextraction techniques. SPELs are nanostructured with gold nanoparticles, and mercury is determined by anodic stripping voltammetry, by using the under potential deposition process.Gold nanoparticles synergistically combine the properties of gold as high affinity material, which improves the sensitivity and selectivity of the method, with the advantages of including nanomaterials to increase the electrode surface area.

The proposed methodology exploits the benefits of including a miniaturized sample preparation technique (*e.g.,* low sample and reagents consumption, reduction of wastes, ease of handling) with the quickness, low cost, high sensitivity and specificity that offers the electrochemical determination of mercury using SPCnAuEs.

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ESP-P10

BIOACCESIBILIDAD DEL CINC EN FÓRMULAS INFANTILES MEDIANTE ESTUDIOS *IN VITRO* Y ANÁLISIS POR SEC-ICP-MS

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El cinc es un micronutriente de crucial importancia durante el crecimiento y desarrollo infantil puesto que juega un papel muy importante en la expresión genética, en la regulación del crecimiento y diferenciación celular y en el desarrollo de la respuesta inmune. La Organización Mundial de la Salud (OMS) recomienda que la leche materna sea la única fuente de nutrición de los recién nacidos hasta los 6 meses de edad. Sin embargo, las fórmulas infantiles suponen en algunos casos un suplemento alimentario muy importante, mientras que en otros suponen la única fuente de alimento.

En base a lo expuesto anteriormente, el objetivo del presente trabajo se centra en el estudio de la bioaccesibilidad de cinc en distintos tipos de fórmulas infantiles con el fin de poder evaluar la fracción de cinc disponible por el organismo y la forma química en que se encuentra el cinc una vez ingerido. Para ello, se estudiaron distintos tipos de formulas infantiles, desde 1 día (fórmulas de soja, formulas sin lactosa, formulas con proteínas hidrolizadas) hasta leches de continuación (6 meses). A través de un ensayo de simulación gastrointestinal, y tras la acción de las enzimas pepsina y pancreatina, se comprobó que la fracción de cinc bioaccesible en las leches normales estaba alrededor de un 60- 70%, con respecto al cinc presente en la leche. Resultados similares se obtuvieron en las leches para niños con intolerancia a la lactosa o a la proteína de la leche. Sin embargo disminuye significativamente en el caso de la leche de soja, donde está por debajo de un 25%. Además se comprobó que el contenido lipídico del alimento no afectaba a la biodisponibilidad del cinc. Por último, se evaluó la incorporación de cinc a biomoléculas mediante el acoplamiento cromatografía de exclusión molecular acoplado al plasma de acoplamiento inductivo (SEC-ICPMS). Los resultados pusieron de manifiesto que el cinc se encuentra asociado a biomoléculas de peso molecular alrededor de 10KDa, tanto en las formulaciones infantiles como en los extractos derivados de los ensayos descritos.

SQB-P01

DEVELOPMENT OF AN ELECTROCHEMICAL SENSOR FOR DETERMINATION OF SELENIUM USING GOLD NANOPARTICLE MODIFIED ELECTRODE

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Traditionally, stripping voltammetric techniques were produced using two types of electrodes: mercury film (MFE) and hanging drop mercury (HMDE) which have high sensitivity and reproducibility, however, due to the high mercury toxicity begins to use restricted. For this reason, it is necessary to search electrodes formed by alternative materials friendly to the environment and which have similar characteristics to mercury electrodes, thus, appear modified electrodes with gold nanoparticles (Au-NPs) which have the advantages of increasing: the effective surface area, the mass transport and provide possible catalytic properties, in addition to exhibiting excellent conductivity thus become an important alternative to the design and improvement of sensors, particularly electrochemical sensors and biosensors.

In this work the construction of a glassy carbon electrode modified with Au - NPs for the determination of inorganic selenium in aqueous matrices by anodic stripping square wave (SWASV) is proposed. The Au - NPs will be obtained by electrodeposition of $HAuCl_4$ solution. The parameters that directly affect the signal of selenium were studied and optimized by SWASV. Optimal instrumental conditions encountered are: initial potential: -400.0 mV, final potential 1000.0 mV, 25 mV amplitude , frequency 15 Hz , -800.0 mV accumulation potential, accumulation time 120 s, pH 1.0 . Detection limit is 0.089 µg L^{-1} and quantitation is 0.299 µg L^{-1} respectively to Se (IV), with a linear range 10 to 50 µg L^{-1}. The standard deviation was 1.11 % at a concentration of Se (IV) = 10 µg L^{-1}, while the accuracy based on certified reference material has an error of 3.33 %

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SQB-P02

GLASSY CARBON ELECTRODE MODIFIED WITH AZA MACROCYCLE FOR DETERMINATION OF COPPER (II) BY ANODIC STRIPPING VOLTAMMETRY

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The mercury electrode, in its different forms, has been widely used in stripping voltammetric techniques, such as anodic (ASV), cathodic (CSV) and adsorptive (AdSV), however the limited use of this electrode as anode and its high toxicity have motivated the search for new materials. Thus, chemically modified electrodes (CME), with the selected modifying agent, provide to the electrode a higher sensitivity and selectivity. Important groups of modifying agents are macrocyclic compounds which through host - guest interaction with the analyte, allow the more selective determination.

This work describes the chemical modification of a glassy carbon electrode with 1-aza-15-crown-5 through the drop-coating technique, for a rapid, sensitive and selective detection of Cu (II) using anodic stripping voltammetry with square wave (SWASV). The optimum conditions were: pH 4,0; accumulation time 80 s; accumulation potential -0,7 V and concentration 0,31 mM, detection limit was 0,021 μg L^{-1} and linear range was 10-50 μg L^{-1}. The proposed methodology was validated and subsequently used for the determination of Cu in real samples.

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SQB-P03

ELECTROCHEMICAL IMMUNOSENSOR FOR THE DETECTION OF NEUROACTIVE TRYPTOPHAN METABOLITES IN CEREBROSPINAL FLUID

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The age-related neurodegenerative diseases are one of the leading medical and societal challenges presently faced by EU. A profile definition of neuro-active tryptophan metabolites related with the serotonin-melatonin and the kynurenine-quinolinic pathways in plasma, could offer a fast, efficient and point of care means of clinical diagnose. These compounds are tentatively related with several neurodegenerative diseases such as Alzheimer and Huntington disease and several mental (neurological) disorders such as the major depressive disorder, sleep disorders or schizophrenia.

In this context, we have developed an electrochemical immunosensor for the detection of tryptophan neuro-active metabolites based on a multiplex platform. The sensing film includes self-assembled nanostructures [1,2] that can be easily implemented and extended to other analytical targets by changing the immunoreagents and thus, enabling the development of a profile-immunosensor device. The rationale of our analytical approach relies on the completion of the affinity reaction within the assemblies using enzyme labelled immunoreagents. Detection is then achieved by the displacement of the labelled immunoreagent by the presence of the sample rendering a concomitant signal decrease. The analysis only requires the addition of a sample drop to the immunochips and incubation for 30 minutes. Amperometric responses are then obtained at + 0 mV vs. Ag/AgCl, KCl_{sat} by the addition of the substrate. The obtained results show a limit of detection (LOD) in cerebrospinal fluid of 0.8 µg L^{-1} and an effective concentration of compound causing a 50% inhibition (EC_{50}) of and 150 µg L^{-1} for kynurenic acid, and a cross reactivity of 10 %, 1,0 % and 0.2 % for quinolinic acid, melatonin and serotonin respectively. This work covers the analytical description of the immunochips as well as the preparation and characterisation of the layered nanostructures for the integration of the affinity and transduction events.

Financial support from the Spanish Ministry of Education and Science (CTQ2011-29163-C03-03) is acknowledged.

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SQB-P04

ANTIMONY FILM SCREEN-PRINTED CARBON ELECTRODE FOR STRIPPING ANALYSIS OF TRACE HEAVY METALS

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Mercury-based electrodes have been used over the past 70 years in electroanalysis. However, because of the mercury toxicity, alternatives to mercury-based electrodes have been intensively searched for during the last two decades. Approximately ten years ago the bismuth film electrode (BiFE) was introduced as a convenient replacement and environmentally friendly alternative to mercury film electrodes. Although BiFEs are widely accepted for numerous electroanalytical determinations [1], there is still interest for alternative electrode materials that exhibit advantageous electrochemical features. Recently, the antimony film electrode (SbFE) was introduced as another alternative to mercury electrodes for electrochemical stripping analysis of trace heavy metals. The substantial advantage of SbFE in comparison to the already established BiFE is the wider operational potential window and the convenient operation in relatively strong acidic medium [2].

Furthermore, the screen-printing technology is a recognized method for the fabrication of sensors and biosensors. SPEs usually include a three electrode configuration (working, counter and reference electrodes) printed on the same strip. Moreover, screen-printed devices are known for their accessible, low-cost character, miniaturized size, and the possibility of connecting them to portable instrumentation.

Combining both antimony film and screen-printing technology, this work tries to examine the possibilities of an in-situ antimony screen-printed carbon electrode (SbSPCE) for the determination of heavy metal ions in groundwater samples, as an example of its applicability for the analysis in environmental samples. Several key operational parameters influencing the electroanalytical response of SbSPCE were examined and optimized, such as deposition potential, deposition time, and composition of the measurement solution.

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SQB-P05

COMPARISON OF GLUCOSE BIOSENSORS ONTO TiO_2 NANOTUBE ARRAYS USING CHITOSAN AND NAFION AS AN IMMOBILIZATION MATRICES

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Numerous glucose detection techniques such as spectrophotometry, amperometry, HPLC, polarimetry, and capillary electrophoresis have been proposed; however, only electrochemical biosensors based on the use of glucose oxidase (GOx) have been able to combine the analytical power of electrochemical techniques with the specificity of biological recognition processes.Such biocomponent–electrode combinations are commonly employed to produce easy-to-use, compact, and inexpensive devices.

Enzymes are often immobilized on solid substrates so that they can be reused and form the required close proximity between the biomaterial and the transducer.In recent years, anodized TiO_2 nanotube arrays (NTAs) attract increasing attention for enzyme biosensors due to the superior properties such as easy preparation, large specific area, chemical inertness, and excellent biocompability.It has been demonstrated that electrodes based on combination of metal nanoparticles and TiO_2 nanomaterials exhibit highly sensitive and selective response to glucose.

However, it worth to mention that noticeable disadvantages with respect to enzyme-based sensors include the difficulty in enzyme immobilization and their limited lifetimes due to desorption and deactivation of the immobilized enzymes.In order to improve the stability and activity of the enzyme immobilized on electrode surface, a variety of methods have been tried such as adsorption, entrapment in a porous matrix, covalent binding and electrochemical copolymerization. Therefore, great interest is devoted to find immobilization matrix, which can retain its specific biological function such us Chitosan and Nafion.

In this paper, we report on an amperometric glucose biosensor based on the immobilization of GOx onto highly ordered titanium dioxide nanotube arrays (TiO_2 NTAs). The goal of the project is to compare the sensors response using Chitosan and Nafion as an immobilization matrices. The morphology and the structure of the TiO_2 NTAs was characterized by scanning electron microscope, as well as the presence of Anatasa has been demonstrated using XRD.

The GOx-Chitosan/TiO_2NTAs biosensor with optimum conditions achieves a sensitivity of 5.46μA·mM^{-1} with linear range from 0.3 to 1.5mM. However, the GOx-Nafion/TiO_2NTAs biosensor with optimum conditions achieves a sensitivity of 1.83μA·mM^{-1} with linear range from 0.3 to 1.5mM. The stability of the proposed biosensors was further examined. After 20 days, the GOx-Chitosan/TiO_2NTAs biosensor retained 86% of its initial current response, however, the GOx-Nafion/TiO_2NTAs retained only 16% of its initial current response.

SQB-P06

COMPARISON BETWEEN SERPENTINE AND INTERDIGITATED PRINTED CAPACITIVE STRUCTURES AS HUMIDITY SENSORS

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The interest in printed sensors is increasing each day because they can be easily integrated in RFID tags and add them the capability of sensing different magnitudes. One of the most used transduction mechanisms is the capacitive where the change of a particular environmental property induces a change in the capacitance of the sensor. The classical capacitive structure is the interdigitated electrodes (IDE), where the capacitance usually changes when there is a variation in the electrical permittivity of the dielectric material. In this sense, we present here a novel structure with the same principle of sensing as IDE but higher sensitivity in the same area. We have called this structure “serpentine”. Firstly, we have modelled by COMSOL Multyphiscs 4.2a this novel design. The width and the distance between fingers were fixed to 50 μm in both structures, our minimum technological size by inkjet printing to avoid short-circuit between electrodes due to printing errors. Then, we have fabricated with a DMP-2831™ Dimatixboth IDE and serpentine using ink of silver nanoparticles (U5603 SunTronic) on a polyimide substrate (Kapton® HN with 75 μm of thickness) as sensitive element without including any other deposited layer. The permittivity of this substrate is directly related to the relative humidity; therefore both structures have been characterized as humidity sensors in a climatic chamber VLC4006 with a precision Impedance Analyzer 4294A. Both printed structures fill the same area (around 11.65 mm^2) and only one layer is required to define the electrodes. The mismatch is less than 5% between simulated and measured capacitances, in both structures. Their sensitivities are 4.5 fF/%RH and 6.4 fF/%RH at 100 kHz for IDE and serpentine, respectively. Regarding the time response, the measured values are almost the same. In terms of reliability, a manufacturing yield of 90% was found for IDE whereas this ratio is 80 % for serpentine due to the higher complexity of this structure. In addition, both sensors present virtually no change as consequence of aging effect. This work shows a reliable structure to make capacitive sensors with higher sensitivity than a IDE with the same area.

SQB-P07

INKJET-PRINTED DISPOSABLE METAL COMPLEXING INDICATOR-DISPLACEMENT ASSAY FOR SULPHIDE DETERMINATION IN WATER

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Most of the assays for sulphide of this type are done in hydroorganic or aqueous media with the reagents in solution, but the integration of processes in a solid-phase spectrometric assay is a way to ease the procedure, make the analysis less expensive and facilitate the use and lifetime of the reagents. The combination presented here of piezoelectric inkjet technology to increase the reproducibility of the preparation of sulphide responsive membranes, based on PAN-Cu(II) complex (1), along with the use of membrane colour as analytical parameter, namely the H coordinate of the HSV colour space (2), obtained by a digital camera results in a simple an accurate assay for sulphide.

We have successfully designed a selective colorimetric metal complexing indicator–displacement assay for sulphide in aqueous media and physiological pH based on colorimetry on a chemosensing ensemble. The solid phase assay is prepared by inkjet printing a Cu(II) complex of the azo dye 1-(2-pyridylazo)-2-naphthol on a nylon support, resulting in an inexpensive and very stable membrane for sulphide determination based on a fast displacement reaction which takes place in minutes. The reaction of both PAN and PAN-Cu(II) membranes against Cu(II) and sulphide, respectively, was modelled calculating their equilibrium constants. In order to simplify the assay, the colour of the membrane was used as the analytical parameter, measured with the H coordinate. The colour was obtained using a digital camera, which opens the door to the use of this assay with other widely distributed imaging devices, such as smartphones. The assay presents good sensitivity for sulphide with a detection limit of 0.1 µM and an analytical range up to three orders of magnitude and a precision between 2 to 11 %.

The long-term stability of sulphide membranes was studied at 180 days after the membrane was inkjet printed and maintained in darkness at room temperature, measuring the colour periodically. There was a no significant difference between the H values during the period of time studied (maximum variability 3.5%).

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NAN-P01

IN VITRO BIOANALYTICAL EVALUATION OF FUNCTIONALIZED MESOPOROUS SILICA NANOPARTICLES FOR BIOMEDICAL APPLICATIONS

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The design of novel nanosystems for controlled and simultaneous or sequential delivery of drugs and nucleic acids in the interior of targeted cells is a promising strategy in therapy against cancer [1]. However, once nanosystems are introduced into the bloodstream, a non-specific adsorption of proteins takes place allowing for the recognition of these nanotransporters by cells of the immune system, and therefore reducing its circulation time. This process can be prevented by coating nanoparticles with hydrophilic polymer chains of polyethylene glycol (PEG), which hinders the adsorption of proteins by steric hindrance. However an excessive PEGylation can lead to a strong inhibition of the cellular internalization, reducing the nanosystem potential for the delivery of drugs and nucleic acids.

Mesoporous silica nanoparticles (MSNPs) present two main advantages: the possibility of storing molecules within the pores that constitute their structure and a silanol rich surface that can be easily functionalized with different organic structures. Moreover, in addition to their use in the controlled release of drugs [2], MSNPs have the ability to act as a nonviral vector in gene transfection [3].

In this work, we have designed a novel type of fluorescent MSNPs functionalized with polyamine dendrimers that would facilitate nucleic acid complexation and delivery in tumor cells. In addition, these MSNPs have been functionalized with different amounts of PEG to avoid protein adhesion. The attachment of both polymers to the MSNPs has been characterized by means of thermogravimetric analysis, DLS and Z-potential measurements, together with MAS NMR (Magic Angle Spinning NMR). We have evaluated the effects of these materials in terms of cell viability using the MTT assay. To assess the differential internalization rates of the synthesized materials in different cell lines, such as macrophages and cancer cells, we have performed flow cytometry and fluorescence microscopy studies. The results show differences depending on the MSNPs coating and the cell line.

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NAN-P02

STUDIES ON THE PROTEIN CORONA: INTERACTIONS OF HUMAN SERUM PROTEINS AND CITRATE-STABILISED GOLD NANOPARTICLES

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The understanding of the "biological identity" of nanoparticles is rapidly revolutionising many different areas such as nanomedicine and nanosafety, especially for their use in drug delivery, as image contrast agents and for diagnostic purposes [1-3]. The crucial role of this interaction between nanoparticles and biomolecules (e.g. proteins) results in the formation of a biological corona on the NP's surface, the so-called "protein corona" [3]. The identification of the biological identity of metal NPs is decisive for their biodistribution throughout the body and their functional impacts on diverse cell processes.

In this work, we explored the formation of the "hard corona" after incubation of human serum with citrate-stabilised gold nanoparticles (Au NPs) with different sizes (10, 30 and 60 nm). We developed a purification method based on a centrifugation with the aim of separating particle-bound from unbound plasma proteins. For protein identification, the isolated protein corona was subject to SDS-PAGE with following peptide identification by in-gel tryptic digestion and electrospray ionisation-tandem mass spectrometry (ESI-MS/MS). Based on the identified most abundant proteins, a strategy will be presented for the quantification of the protein corona.

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SESIÓN DE PÓSTERS 2

AME Análisis medioambiental
DIA Desarrollos en instrumentación analítica
OQA Otros campos de la química analítica y del análisis clínico
NDP Nuevos desarrollos en preparación de muestras
CTQ Contribuciones teóricas y Quimiometría

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AME-P01

ANALYSIS OF SHORT-CHAIN CHLORINATED PARAFFINS (SCCPS) IN ENVIRONMENTAL WATER SAMPLES BY GC-ECD

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Chlorinated Paraffins (CPs) are commercial mixtures of polychlorinated n-alkanes (PCAs) with a chlorine content from 30 to 70%, and linear carbon-chain lengths between C_{10} and C_{30}. CPs present flame retardant properties and are good PCBs and PCNs substitutes in a wide variety of industrial applications. Among them, short chain CPs (SCCPs, C_{10-13}) are of particular interest because they exhibit a high toxicity towards aquatic organisms, are persistent in the environment and tend to be accumulative through the food chain. The demonstrated presence of CPs in environmental matrices underlines the need of a more permanent monitoring. In particular, SCCPs are included in the priority hazardous substance list of the Water Framework Directive 2000/60/EC [1], and recently a concentration of 0.4 µg/L was set as environmental quality standard in waters [2]. For this reason, levels of SCCPs in environmental waters must be monitored, which require reliable analytical methods.

In this work, a method for the determination of SCCPs in surface water and waste water is proposed. For sample preconcentration, a solid-phase extraction (SPE) procedure based on the method proposed by Castells *et al.* [3] and a clean-up with Florisil to remove interferences was used. Gas Chromatography with electron capture detection (GC-ECD) was employed for quantitation of SCCPs [4]. The method was validated for natural waters and waste waters according to ISO-17025. Quality parameters for SCCPs have been established. Recoveries were generally higher than 85% and instrumental quantification limits (IQLs) and limits of quantification (LOQs) were in low ng/L range with intra-day and inter-day precisions lower than 15%.

The main objective of the paper was the monitoring of SCCPs in influents and effluents of wastewater treatment plants (WWTPs) and also in surface waters. To this end, samples from four different WWTPs around Barcelona metropolitan area (Catalonia, NE Spain) were analyzed in order to evaluate the presence of these compounds in relation to the maximum levels set out in the Directive 2008/105/EC. The results and conclusions achieved in this study are presented and discussed.

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AME-P02

VOLATILE METHYL SILOXANES CONCENTRATIONS IN AIR IN SEVERAL LOCATIONS OF THE TARRAGONA REGION

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Volatile methyl siloxanes (VMS), both linear and cyclic, have been produced commercially since 1940. Yearly, tens of thousands of tones of VMS are used as intermediates in silicon polymers production and in several industrial applications. Additionally, they are widely employed in personal care products, such as cosmetics, and skin and hair care products, as well as in household cleaning agents. This leads to high and continuous emissions of these compounds to air. Even though they have been recognized as safe as cosmetic ingredients, the concern is growing in respect to their environmental distribution, due to their volatility, persistence, possible toxic effects and propensity to bioaccumulate.

VMS were evaluated in four municipalities (two sampling points in each) of the Tarragona Region (Constantí, El Morell, Vilallonga del Camp and Perafort) during 2013 and 2014. Samplings were programmed during the maximum and minimum predicted impacts coming from the nearby industrial activities in the studied urban areas. Samples were taken with LCMA-UPC pump samplers specially designed in our laboratory, with flow ranges between 80-100 ml min^{-1}. A sorbent-based sampling method, combining different sorbents (Carbotrap (20/40 mesh, weak sorption strength, hydrophobic), Carbopack X (40/60 mesh, medium sorption strength) and Carboxen 569 (20/45 mesh, high sorption strength)), and successfully developed to collect a wide-range of VOC, including VMS, was used. The analysis was performed by automatic thermal desorption (ATD) coupled with capillary gas chromatography (GC)/mass spectrometry detector (MSD). This methodology had been used in previous studies to identify and determine a wide range of VOC that cause odour nuisance and affect outdoor air quality.

Total VMS concentrations (L2-L5, D3-D6 and trimethylsilanol) were in the ranges of 0.03-6.6 µg m^{-3}, 0.2-7.6 µg m^{-3}, 0.02-2.1 µg m^{-3}, and 0.001- 40.5 µg m^{-3}, in Constatí, El Morell, Vilallonga del Camp and Perafort, respectively. D3, D4 and D5 were the most abundant siloxanes, with average contributions to the total concentrations of 44±25%, 14±12% and 22±25%, respectively. It is important to note that at relatively low temperatures (7-14ºC), VMS concentrations correlated negatively with pressure changes during the sampling period (DhPa/h). On the other hand, at medium temperatures (12-19ºC), VMS concentrations correlated positively with temperature. Finally, at higher temperatures (23-26ºC), VMS concentrations did not correlate neither with pressure changes nor with temperature.

AME-P03

OFF-LINE SPE AND FASI-CZE FOR THE ANALYSIS OF BENZOPHENONE UV-FILTERS IN ENVIRONMENTAL WATER SAMPLES

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Nowadays it has been well established that excessive UV radiation is clearly detrimental for human health. So, to reduce these harmful effects UV-filters are commonly added to sunscreen products, as well as in shampoos, lipsticks, and make-up formulations. Benzophenones (BPs) UV-filters are widely used because of their excellent absorbing abilities for the UV-A component of the solar radiation. However, these chemicals can easily reach the aquatic environment by direct and/or indirect sources (wastewater-treatment plants, domestic washing), thus being accumulated in environmental water reservoirs [1]. Additionally, some studies have shown that they could cause hormonal disruption on the reproduction of fish and they possess endocrine activity. For these reasons, some UV-filters have been recently classified as emerging contaminants hence, sensitive and reliable methods for their analysis in environmental samples are needed.

In this work a capillary zone electrophoresis (CZE) method was developed for the separation of eight BP UV-filters in water samples. In order to improve method sensitivity, the applicability of an in-line enrichment procedure, field-amplified sample injection (FASI), was evaluated. A 9- to 25-fold sensitive enhancement was observed with FASI-CZE, obtaining limits of detection (LODs) down to 21-60 µg/L for most of BPs, with good linearity, run-to-run and day-to-day precisions (RSD lower than 17%), and accuracies (relative errors lower than 8%). Despite the improvement achieved by FASI-CZE, the method sensitivity was not enough for its application to the analysis of BPs in environmental water samples. For this reason, and in order to remove sample salinity from environmental waters which can become an important handicap for FASI efficient application, solid-phase extraction (SPE) was evaluated as off-line preconcentration and sample treatment prior to FASI-CZE analysis. Several SPE sorbents were compared, and the best results were obtained with a Strata X polymeric reversed-phase sorbent, showing good recoveries (72-90%). A 2400- to 6500-fold sensitive enhancement was obtained when combining both off-line SPE and FASI-CZE for the determination of BPs in a spiked blank river water sample, achieving LODs down to 0.06-0.6 µg/L with good precision (RSD 6.8-22.9%). The proposed off-line SPE-FASI-CZE method was validated and applied to the analysis of BPs in river water samples and in several drinking water samples.

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AME-P04

PHYTOREMEDIATION OF HEAVY METALS: ANALYSIS OF PHYTOCHELATINS IN PLANTS USING HPLC WITH ELECTROCHEMICAL DETECTION

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Phytoremediation technology is based on the use of plants to remove pollutants from the environment or to reduce their toxicity to make them harmless. Plants have different strategies to fight against heavy metal toxicity. Among them, the synthesis of thiol-rich compounds, such as phytochelatins, is the main procedure. Phytochelatins (PCs) are small, cysteine-rich peptides which are synthesised in plants in response to heavy metal stress. Phytochelatins are involved in detoxification and homeostasis of heavy metals by chelating these ions through the thiol group in the cytosol and sequestering the metal-PC complexes in vacuoles. This is the reason why the study of complexation of these molecules with heavy metals is of special interest.

Several methodologies have been developed to analyse phytochelatins and related peptides. Among all, mass spectrometry is the most widely used technique. This work aims to develop a new analytical methodology which combines HPLC with electrochemical detection on a glassy carbon electrode as a sensible and cheap technique [1, 2]. With this methodology not only several phytochelatins and related peptides are separated and detected but also their Hg complexes.

This methodology has been applied to the study of plants subjected to stress by several toxic metals. First of all, *Hordeum vulgare* plants that have been grown in the presence of Hg(II), Cd(II) or As(III), or in the simultaneous presence of Hg(II) and Cd(II), have been considered, and the phytochelatins induced by these metals have been studied [3, 4]. Finally, plants from the Almadén mining district have been considered [5]. This zone is known for the largest deposits of mercury in the world yet discovered. For this reason, this study is of special interest since it permits to deep insight into the natural mechanisms that plants have developed to fight against Hg toxicity.

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AME-P05

EVALUATION OF BIOACCESIBILITY TESTS FOR ASSESSMENT OF LEACHING KINETICS OF ORGANIC CONTAMINANTS IN SEDIMENTS

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Standard methods for predicting the contamination of solid samples of environmental interest with legacy and emerging organic contaminants based on matrix solid-phase dispersion, pressurized liquid extraction, ultrasound and microwave assisted extractions and QuEChERS tend to overestimate the potential hazardous effects, as the biota is unable to interact with all of the pollutants sorbed onto or occluded in the solid matrix. To this end, different pools need to be evaluated so as to gain knowledge of contaminant bioaccesibility, bioavailability and biodegradability, namely, the fractions that can be dissolved, pass across biological membranes or be degradated by biota, respectively. Leaching tests using butan-1-ol or an aqueous solution of 50 mM hydroxypropyl-β-cyclodextrin have been repeatedly correlated with the fraction biodegradable by *Eisenia Fetida* [1]. In this contribution, the leaching kinetic of the biodegradable fraction of 16 of EPA's priority PAHs in Majorcan coastal sediments by the two above mentioned methods is presented through stopping several leaching tests at given times and evaluating the PAHs content by HPLC with fluorimetric and fotometric detection. The resulting data was fitted to a mathematical kinetic model in order to discern multiple binding compartments for the pollutants and relate them to the sediment physicochemical characteristics.

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AME-P06

AUTOMATED-FLOW SYSTEMS FOR THE MONITORING OF HEAVY METAL BIOSORPTION PROCESSES

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Our research groups have been working in the developing of sustainable and cheap technology based on vegetable wastes as sorbents for the removal of metal ions from industrial wastewater. Specifically, grape stalk wastes, generated in the wine production, resulted to be an efficient sorbent for the removal of hexavalent chromium and divalent heavy metal ions. Conventionally, analytical methods as FAAS, ICP-OES and FIA with potentiometric detection (FIP) have been used in the monitoring of metal biosorption processes. However, the limitations of these methods when working with real samples, specifically on multiparametric or speciation analysis, have led us to consider the use of electronic tongues (ET) based on arrays of multiple sensors showing cross-selectivity, and simultaneous analysis based on bivariate analysis and spectrophotometric detection. Thus, two different approaches have been developed.

First, a new methodology for the simultaneous and automated monitoring of biosorption processes based on flow-injection potentiometry (FIP) and electronic tongue detection (ET) is presented. A fixed-bed column filled with grape stalks is used as the biosorption setup to remove the metal mixtures from the influent solution. The monitoring system consists in a computer controlled-FIP prototype with the ET based on an array of up to 9 flow-through ion-selective and generic response electrodes, plus an artificial neural network (ANN) response model. Electrodes with cross-response to Cu^{2+}, Cd^{2+}, Zn^{2+}, Pb^{2+} and Ca^{2+} are used, and a dynamic treatment of the kinetic components of the FIP transient peak signals is incorporated, in which selected coefficients obtained from the Fourier transform are used to feed the ANN model.

Real-time monitoring of single, binary and ternary mixtures is achieved satisfactorily using the reported system, obtaining the corresponding breakthrough curves. Analytical performance is verified against conventional spectroscopic techniques, with good concordance of the obtained breakthrough curves with relative error values below 7%.

The second approach is based on sequential injection analysis (SIA) and spectrophotometric detection for the monitoring of Cr(VI) and Cr(III). Thus, the analysis is performed in two steps: first, Cr(VI) is directly measured and, in a second step, Cr(III) is oxidized to Cr(VI) and total chromium is then determined. For quantification, a calibration technique by bivariate analysis based on Multiple Linear Regression (MLR) has been used, with reproducibilities higher than 95%.

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AME-P07

QUANTIFICATION AND DISTRIBUTION OF SEVERAL METALS IN ZEBRAFISH LARVAE BY LA-ICP-MS

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Zebrafish is a small fish, which have attracted much scientific attention due to their unique advantageous features over other vertebrate model systems: low husbandry cost, small size, rapid generation of a large number of transparent embryos, a genomic composition similar to humans and embryonic development.[1] Zebrafish embryos and eleutheroembryos, corresponding to the embryos from hatching until the phase of free swimming and active feeding, arenot considered *in vivo* systems from a legal point of view, therefore they can provide almost the same type of information as *in vivo* systems. Consequently, we have selected zebrafish larvae as the alternative animal model to carry out the bioconcentration studies of cadmium and the metal mixture of mercury, arsenic and silver

The aim of these work was to determinate the total metal (Cd, Hg, As, Ag) larvae content and also mapping the metal distribution[2] in the larvae after the exposure of zebrafish eleutheroembryos for 48 hours to a level of ionic metal (Cd, Hg, As and Ag) concentration in the mixture from 0.1 to 1% of the LC_{50} of each ion.

Total metal content of each analyte per exposed eleutheroembryo was carried out by ICP-MS after the samples were acid digested using an ultrasound probe.

Zebrafish eleutheroembryo were also analyzed by LA-ICPMS employing two distinct sample treatments to compare the influence of preparation protocol: a) a histologic procedure to dry and fix the eleutheroembryo by means of paraffin, b) directly frozen eleutheroembryo samples. Finally, in both procedures an additional metallization (gold and silver) step was necessary before the samples were analyzed by laser ablation.

The quantification was performed through two different approaches: 1) using gelatin based standards; 2) employing a Glass NIST 612. The gelatine is a product obtained form the partial hydrolysis of collagen, derived from natural sources such as skin, connective tissue or animal bones[3], but in our study this gelatine was spiked with the metallic elements to calibrate the instrument with standards as similar as possible to the larvae matrix.

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AME-P08

MAE-ICP-MS ANALYSIS OF METALS AND METALLOIDS IN MARINE SEDIMENTS. ASSESMENT OF POLLUTION ON TENERIFE COAST

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Metals and metalloids are usually bound in the fine-grained (< 63 μm) fraction of the marine sediments, due to its high surface area and humus content [1]. In this fraction, the metals have a greater biological availability than those in the coarser fractions [2]. In order to carry out a statistical study of the levels and superficial distribution of those elements in the sediments of the continental platform near the nine wastewater discharge points of Tenerife Island (Spain), an analytical method for the determination of metals and metalloids in marine sediments is validated. The effects of marine currents in transportation are also evaluated. Thirty-six samples collected in the points of discharge located along the entire coast were analyzed. The concentration of 47 elements was determined by microwave-assisted digestion (MAE) followed by inductively coupled Plasma Mass Spectrometry (ICP-MS) analysis.

Important levels of contamination have been found in samples, being the concentrations of Pb higher than the ecotoxicological assessment criteria (EAC) established by the OSPAR (5 mg kg^{-1}) [3] in all sampling points. Principal Component Analysis (PCA) and correlation analysis were developed and the results obtained indicated that there are two principal sources of anthropogenic pollution, with a large number of elements related to them. The amounts of 13 elements found in the sediments of the sampling point of Santa Cruz of Tenerife, principal city of the island, were higher than those found in the rest of points. Modifications in the seabed were also detected due to industrial wastes; concentrations of metals related to metallurgic activities have increased in the industrial area while the proportion of original igneous sediments decreased. The mobility of pollutants, according to the sea currents, was also evaluated. For some metals, differences between sampling points in agreement with the direction of the marine currents in the area were obtained. The large number of elements analyzed allowed developing a geochemical characterization of the three slopes of the island. Significant differences between them were observed for some of the studied elements.

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AME-P09

DEVELOPMENT OF A SIMPLE METHOD TO DETECT METHANE IN *IN VITRO* ANEROBIC FERMENTATION

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Methane (CH_4) is the second most important greenhouse gas, after CO_2, and livestock farming contributes up to 14.5% of total greenhouse gas emissions (FAO, 2013), because of the enteric fermentation and manure emissions. The most numerically important source (around 60% emissions of the livestock sector) is the enteric methane from ruminant production. Also, methane is an indicator of rumen efficiency because methane production represent a loss of energy. Rumen fermentation, then, has been studied to be manipulated for a long time in order to improve milk production and animal growth, by optimization of diet formulations and the use of feed additives that are able to enhance or inhibit specific microbial populations and decrease methane emissions.

Previous to *in vivo* studies, preliminary assays are usually made *in vitro*. Most used systems are closed batch culture or continuous/semicontinuous culture of rumen microorganisms that are more appropriate to test diverse additive concentrations or feeding strategies, generating large number of samples. An additional advantage of the in vitro systems is the feasibility to obtain representative samples of gas produced during the fermentation.

A quantitative, precise and quick method has been developed in order to quantify the methane production. A sample of fermentation gas from the headspace of the in vitro vessel is introduced in a tube with vacuum inside. A gastight syringe, with an open/close valve, is used for injection.

A gas chromatograph equipped with a FID detector is used for determinations. Different isothermal programs were tested in order to improve the obtained peak areas, using pure methane as standard and tight gas sampling bags. Splitless injections were found with poor resolution and tailing peaks, so finally the minimum split was used. All samples' injections (1mL) were made in a single chromatogram, with a gap of 20-30 seconds between them, running controls of methane every ten samples. Air rinse is made before each injection. Two calibration sets (from 20 to 100 µL) were done at the beginning and at the end of the chromatogram, so the calibration curves were then performed for each assay. Finally, chromatograms of around 60 peaks of methane were generated, corresponding to whole assays, including standards and controls. The measured methane volume is then converted into methane production of each tube using total gas produced.

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AME-P10

IMPROVED SAMPLE TREATMENT FOR THE DETERMINATION OF 17 STRONG SORBED QUINOLONE ANTIBIOTICS IN COMPOST BY UHPLC-MS/MS

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The use of compost obtained from sewage sludge for agricultural application is increasing, since composting is recognized as one of best sewage sludge recycling options, being a source of nutrients for plants but also of contamination by persistent pharmaceutical residues, as it has been evidenced by the few systematic works that have been published, concerning the degradation of antimicrobials during composting [1-3].

A multi-residue analytical method for the determination of 17 quinolone antibiotic in compost from sewage sludge samples, using multivariate optimization strategies and UHPLC-MS/MS, was developed and validated. The method was based on microwave-assisted extraction at drastic conditions in order to achieve a quantitative extraction of compounds (extraction recovery >76%), due to their recognized strong interactions with the matrix. Extracts were cleaned-up by salt-assisted liquid-liquid extraction (SALLE) at pH 1.5 and then using a dispersive sorbent. After LC separation, the MS conditions were individually optimized for each analyte to obtain maximum sensitivity. The analytes were separated in less than 7 min using cincophen as surrogate. The limits of quantification ranged from 0.5 to 3.8 ng g^{-1}, while intra- and inter-day variability was under 6%. A recovery assay with spiked samples was performed in order to check the trueness and recovery values from 95.3 to 106.2% were obtained. Clean-up procedure reduced significantly matrix effects, being eliminated in 8 of the studied antibiotics, which constitutes an important achievement, considering the important drawbacks of matrix components in quality and validation parameters.

The method was satisfactorily applied on compost samples and only 6 of the studied antibiotics were not detected in any of the samples. The antibiotics with the maximum concentrations were ciprofloxacin (836 ng g^{-1}), ofloxacin (719 ng g^{-1}) and enrofloxacin (674 ng g^{-1}), which were also the only ones found in all samples. The results demonstrated that this method could also be potentially adapted for the analysis of other strong sorbed basic pharmaceuticals in solid environmental matrices.

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AME-P11

THE USE OF KAOLIN FOR PASSIVE SAMPLING OF VOLATILE ORGANIC COMPOUNDS IN AIR

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This study focuses on the green analytical determination of VOCs in air using passive samplers. The use of Kaolin as adsorbent to fill semipermeable membrane devices (SPMDs) in order to catch volatile organic compounds (VOCs) from air has been evaluated. Kaolin structure has been characterized by X-ray diffraction and EDAX spectrometry, in order to determinate its composition. Furthermore, the new filler has been characterized by SEM to determinate its morphology and the existence of pores and channels that may support the capability of the material to trap these analytes.

Besides, in order to determine the capability of this filler, a set of indoor field studies has been performed exposing the deployed samplers to a fume hood atmosphere, where the analytes under study were processed, and to the gas phase of a waste container. The quantification was performed by head-space-gas chromatography (HS-GC-MS) providing a multi-residue analytical procedure and adequate analytical figures, including correlation coefficients between 0.99 and 0.99998 and adequate %RSD.

Regarding to field studies, both in case of a fume hood atmosphere such as the gas phase of a waste container, the results indicate the feasibility of using kaolin as filler and passive sampler use as working areas, as well as presence detection method, as well as the method of quantification of the analytes present in the environment.

For all cases, the omission of sample pre-treatment and the avoidance of deleterious solvents makes possible a fast, direct and green determination of VOCs in air with limit of detection values of the order of 39 to 56ng per sampler, allowing the use of an accessible and cheap material as sampling device.

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AME-P14

DETERMINATION OF PESTICIDES IN SEDIMENTS BY PLE AND QuEChERS

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Although pesticides play an important role in the development of the agriculture, they are labeled as hazard pollutants. Therefore, they are still a problem of primary concern due to they can reach the aquatic environment and accumulated in sediments setting up strong interactions with the organic matter.

The purpose of this study is to compare PLE and QuEChERS method for the extraction of 50 pesticides in sediments in order to identify a suitable extraction method for the multiresidue analysis of sediments from Iberian river basins. Compounds studied covered several families of pesticides, with a broad range of uses, which included 21 organophosphorus, 4 carbamates, 3 insecticides, herbicides and some fungicides and acaricides of difficult chemical classification.

Sediment samples were taken using a Van Veen grab sampler and transferred to an aluminum box. Once at laboratory, samples were frozen and dried prior to extraction.

Separation was carried out on a Luna C18 column (150 x 2.0 mm, 3 µm) using a gradient elution profile with mobile phase consisting of water-methanol, both 10 mM ammonium formate; and the determination was performed by liquid chromatography tandem mass spectrometry (LC-MS/MS) in positive ionization mode with an electrospray ionization source (ESI). The two most intense precursor ion→product ion transitions were monitored to obtain unambiguous confirmation of the compound identity.

Both extraction techniques produced acceptable recoveries for the pesticides under study. For PLE method, recoveries ranged from 75% to 95% with relative standard deviation below than 18%. This method allowed LOQ from 0.3 µg/kg to 0.05 µg/kg. Recoveries obtained with QuEChERS method ranged from 40% to 105%, with relative standard deviations below 20% at limit of quantification. These limits were 0.1-5.0 ng/g. The method was applied to determine pesticides in samples taken from several Spanish River Basins. Both methods provided proper results however, QuEChERS requires less amount of solid sorbents as well as does not need to pressurized samples. Then facilities of handling operation favor the use of QuEChERS.

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AME-P15

CHARACTERIZATION NOM BY FLUORESCENCE SPECTROMETRY IN SURFACE AND DRINKING WATERS

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NOM (natural organic matter) is a heterogeneous mixture of naturally occurring organic compounds abundantly found in waters. Recently, the characterization and removal of NOM have been of major research interest in water treatment because the NOM contributes to odor, taste, colour and acidity problems in water supply and also has been identified as one of the major precursors for potential trihalomethanes (THM) formation in the chlorination process [1]. THMs are considered as one of the major DBPs (disinfection by-products). Therefore, a better understanding of the physical and chemical properties of NOM would contribute greatly towards optimization of the design and operation of drinking water treatment processes oriented to minimize DBPs [2].

In this study, fluorescence excitation-emission matrix (F-EEM) spectroscopy was used as a technique to characterize NOM with high sensitivity and selectivity in water samples. Six regions were chosen forthe characterization ofDOM: I-Aromatic proteins I, II- Aromatic proteins II, III-Fulvic acid-like products, IV- Microbial by-products; V- Humic acid-like products and VI- Algae pigments [3,4]. The accurate study of these regions, after spectroscopic treatment of raw data, provided an estimation of the increase or decrease in relative intensities as a qualitative data.

This methodology was applied to analyse surface waters from Llobregat river intake to Drinking Water Treatment Plant (DWTP) of Sant Joan Despí (Catalonia, NE Spain), and in all the steps of the treatment, including the finished water before its distribution. The behavior and removal percentages of NOM in each step has been assessed: this will be a new tool for the prediction of THMs levels in the finished water before it is supplied, as well as for the improvement of the treatment processes.

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AME-P16

DETERMINATION OF GLYCOL ETHERS AND PYRROLIDONES AND DERIVATES IN CLEANING PRODUCTS BY GC-MS

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The ethers of glycol (EG) and pyrrolidones and derivates are chemicals added to multitude of cleaning products as surfactants. They havedifferent functions (wetting, emulsifying, dispersing and solubilizing, promoting or preventing the formation of foam), they are antistatic and lubricating agents and also give shine and affect certain rheological properties. Most methods for their analysis are based on gas chromatography (GC) and liquid chromatography (LC), using conventional techniques for EG and as well for pyrrolidones, the latter also have been preconcentrated using miniaturized extraction techniques.

In the proposed procedure, solvent extraction is applied to isolate the compounds from the sample matrices and the organic solvent is evaporated from the sample extract. The dried residue is reconstituted in methanol and injected into the GC-MS system for the determination of 2-methoxyethanol (EGME), 2-ethoxyethanol (EGEE), 2-butoxyethanol (EGBE), 2-(2-methoxyethoxy)ethanol (DEGME), 2-(2-ethoxyethoxy)ethanol (DEGE), 2-(2-butoxyethoxy)ethanol (DEGBE), N-methylpyrrolidone (N-MP), N-vinylpyrrolidone (N-VP) and 2-pyrrolidone (N-P).

Methanol was used as solvent extraction considering its high extraction efficiency for the studied compounds and its low boiling point, which permitted the solvent evaporation being easily carried out in a rotary evaporator at 40 ºC. Two microliters of the dried residue reconstituted using 100 µL of methanol were submitted to the chromatographic separation. Nitrogen was used as mobile phase with a flow-rate of 1 mL min^{-1} and cyanopropyl-phenylmethylpolysiloxane as stationary phase, a bonded phase of high polarity (VF-23ms, 30 m, 0.25 mm and 0.25 µm film thickness). The GC oven heating program started at 70 ºC, this temperature was mantained for 3.5 min, then increased to 160 ºC at a rate of 10 ºC min^{-1}, and newly increased to 220 ºC at a rate of 30 ºC min^{-1} where it was held for 2.5 min. The total time for the chromatographic run was 17 min, the analytes being eluted with times in the 3.8-14.4 min range. The injector was maintained al 300 ºC and pulsed splitless mode was applied (13.1 psi for 0.7 min) because the sensitivity increased for all compounds respect to the absence of pressure pulse. The method has been applied to the analysis of 28 different cleaning products.

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AME-P17

DISTRIBUTION AND BIOACCUMULATION OF NONYLPHENOL IN SEDIMENTS AND *CORBICULA FLUMINEA* ALONG THE MIÑO RIVER

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Nonylphenol (NP) is the degradation product of nonylphenol ethoxylate (NPEO), one of the most important nonionic surfactant. Furthermore, this compound is used as plasticizer. Because of its largely use in industrial and domestic applications and its toxicity (it was recognized as endocrine disrupter compound) NP was widely studied. However, its presence in the Miño River was scarcely researched. In this study, the occurrence and behavior of NP in this region was investigated.

To achieve this objective, eight sampling points located in the Miño river basin were selected, and sediment and Asiatic clam samples *(Corbicula fluminea)* werecollected. For the analysis of NP in these matrices, previous published analytical methodologies based on selective pressurized liquid extraction followed by a liquid chromatography mass spectrometry were respectively employed [1][2]. The main advantages of SPLE-LC-MS/MS procedure are simplicity, automaticity, no-labour and no-time consuming, free solvent and low cost.

As expected, nonylphenol was determined in all samples which showed the ubiquity of this compound. In sediments, concentrations between 170 and 2858 ng g^{-1} dw were measured. Meanwhile, levels ranged from 749 to 1641 ng g^{-1} dw were found in clams samples.

Concerning of risk assessment, the biota-sediment accumulation factor (BSAF) was estimated. A mean BSAF of 2.1 was obtained which suggest that clams possess a moderate ability for NP accumulation.

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AME-P18

MULTIRESIDUE ANALYSIS OF PERSISTENT ORGANIC POLLUTANTS IN BIOTA BY GC-MS-MS

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Control of Persistent Organic Pollutants presence in the environment is very important due to its high toxicity. Recently (2012-2014), evolution of legislation has been considerable, completing legal coverage to other environmental and food matrices. The appearance of new GC/MS instruments like TQ has opened new possibilities like simplicity, versatility and cost reduction, important for routine labs to enhance their competitiveness in this analysis. This is a clear alternative of screening and even quantitation, to high resolution instruments, which was not possible to think about some years ago.

The aim of this work was to adapt USEPA 1613 method for Polychlorodibenzo-p-dioxins and furans (PCDD/Fs) and Polychlorobiphenyls Dioxin Like (PCBs DL) to include other POPs: PCBs no DL, Polybromodiphenylethers (PBDEs), Short Chain Chloro Paraffins (Chloroalkanes C10-C13, SCCPs) and Nonylphenols (NPs) for screening and quantitation analysis in Biota (fish) at trace levels with a GC/MS/MS TQ system.

Several instrumental parameters have been optimized. Injection conditions, pressure pulse, injection rate have increased sensitivity for all families mainly for high boiling PBDEs and PCDDs. MS/MS parameters were optimized for SRM mode analysis.

Validation results for fish analysis, including CCβ, CCα, Precision and Recoveries were obtained with the developed method. That results achieve compliance according the criteria of EPA1613 and recent legislation for all families except PBDEs.

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AME-P19

DETERMINATION OF DIOXINS AND FURANS IN BIOCHAR AND BIOTAR FROM AGRICULTURAL WASTE

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Last years, biochars, carbonaceous materials produced during the pyrolysis of biomass, have been studied as materials that can contribute positively to the mitigation of climate change, in waste management strategies, in the energy production field and for soil improvement. However, some concern has arisen about the possibility of by-product formation, such as polyaromatic hydrocarbons or polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans. Dioxins and furans have been the target of this work.

Samples studied were the biomass used for the pyrolysis process (hazelnut shells) and the solid (biochar) and liquid (biotar) produced. Two different conditions were tested for the pyrolysis: (A) temperature was increased at 9ºC/min from room temperature to 110ºC (held 50 min), increased at 12ºC/min to 230ºC (held 10 min) and increased at 22ºC/min to 450ºC (held 10 min); (B) temperature was increased at 9ºC/min from room temperature to 110ºC (held 50 min), increased at 8ºC/min to 450ºC (held 30 min). After this temperature programs, the solid remaining (biochar) was collected, as well as the liquid condensed (refrigerated by cold water).

The main steps of the methodology were the following: (1) addition of $^{13}C_{12}$-labelled internal standards, (2) extraction, (3) clean-up, (4) concentration (5) instrumental determination by HRGC-HRMS and (6) quantitation. Biotar was liquid-liquid extracted with hexane and biochar with toluene in a Soxhlet equipment. The clean-up was performed in a multilayer silica column (from top to bottom: anhydrous sodium sulphate, silica modified with sulphuric acid, activated silica, silica modified with sodium hydroxide, activated silica and silica modified with silver nitrate).After the clean-up, fractionation in SPE carbon tubes was performed in order to avoid PCB interferences. Finally, the fractions were concentrated to 15 µl and $^{13}C_{12}$-labelled recovery standards were added. Instrumental determination was performed with an Agilent 6890N gas chromatograph coupled to an Autospec Ultima high resolution mass spectrometer, operating in the SIR mode at 35 eV (EI) and 10,000 resolving power. Two fragments for each compound were monitored in time windows. Quantification was carried out by the isotopic dilution method.

Although the levels of dioxins and furans in the samples analyzed were very low, some differences between them were observed. In addition, profiles of the congeners detected were studied to evaluate the possible formation of PCDD/F or the distribution of them among the biochar and biotar originated in the process.

AME-P20

ANALYSIS OF 1,4-DIOXANE AND RELATED COMPOUNDS IN WATER BY SOLID-PHASE EXTRACTION AND GC-MS

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1,4-Dioxane and related compounds, such as glycol dimethyl ethers (glymes) and ethoxylated alcohols, constitute a new class of emerging environmental pollutants which have been historically used in many industrial and pharmaceutical applications, mostly as solvents and stabilizers, as well as in the production of adhesives, dyes, degreasers and cleaners [1]. 1,4-dioxane has been identified as a probable human carcinogen [2], and several toxicological studies revealed that glymes are toxic for the reproductive system and could lead to infertility and pregnancy problems [3]. The presence of these contaminants in the aquatic environment is a cause of concern and, therefore, there is an interest to dispose of reliable and sensitive methods for the determination of these contaminants in water at low concentration levels.

The aim of this work was to develop a fast and simple method based on solid-phase extraction (SPE) combined with gas chromatography-mass spectrometry (GC-MS) for the analysis of 1,4-dioxane and several glycol ethers in water. For this purpose, different SPE sorbents commercially available were tested and parameters affecting the extraction and desorption of the target compounds were optimized. The proposed method consists on a SPE extraction of 500-mL of water using coconut charcoal as sorbent, elution of the target compounds with dichloromethane and analysis by GC-MS working in selected ion monitoring (SIM) mode. The method was validated for the determination of 1,4-dioxane, mono-, di-, tri- and tetraglymes, and 2-metoxy-, 2-etoxy- and 2-butoxyethanols, in drinking, ground and waste waters. Recoveries for 1,4-dioxane were higher than 95%, while for glycol ethers ranged from 80 to 97%. Quality parameters were established and good precision (RSD <15%) and accuracy (relative error < 10%) with low limits of detection (0.1 - 3 µg/L) were achieved. The method was applied to the analysis of the target compounds in water samples of different origin collected inBarcelona area.

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AME-P21

DEVELOPMENT OF A GAS CHROMATOGRAPHY-MASS SPECTROMETRY METHOD FOR THE DETERMINATION OF UV FILTERS IN BEACH SEDIMENTS

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It is well-known that sun exposure provides many human health benefits, but also that sun overexposure causes adverse effects, such as cutaneous photoaging or even skin cancer. The concern about these health risks has led to an increase in the use of cosmetics containing the so-called UV filters as active ingredients to prevent or minimize the harmful effects of the UV radiation.
The excessive use of cosmetics containing UV filters had led to an appearance of these compounds in the aquatic environment, where they are being accumulated [1]. The high lipophilic characteristics of some of them makes them susceptible to be accumulated in the suspended particles contained in water, sediments, sludge or even biota [1]. Furthermore, different *in vitro* and/or *in vivo* studies show that some UV filters, even at trace levels, present endocrine disrupting activity that might affect the reproduction of fish [2]. For this reason, UV filters are currently considered as emerging contaminants and it is interesting to develop analytical methods that allow their determination in the environment at trace levels.

The aim of this work is to draw on the high potential of the dispersive liquid-liquid microextraction (DLLME) to develop a rapid, selective and sensitive method for the determination of eight typical organic UV filters in beach sediment samples. The developed method, which is expected to be used in environmental surveillance studies, is based on the leaching of the analytes from the sediment sample prior to DLLME and followed by GC-MS analysis.

The variables involved in the leaching and in the DLLME processes were studied to provide the best enrichment factors. Under the selected conditions, the method was successfully validated showinggood intra- and inter-day precision, and limits of detection in the pg g^{-1}level. No significant matrix effects were found, thus external calibration can be used. However, internal calibration was recommended to improve repeatability in both the DLLME and the GC-injection. Moreover, in order to correct losses during the leaching process, the surrogate was added to the samples before the leaching step.The validated method was successfully applied to the analysis of several beach sediment samples from different origin.

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AME-P22

NANOPARTICLE TRACKING ANALYSIS (NTA) AS A CHARACTERIZATION TOOL FOR ENVIRONMENTAL WATERS

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Nanoparticle tracking analysis (NTA) is a recently developed technique devoted to the characterization of nanomaterials suspensions. NTA provides information about the total no. of nanoparticles, their size distribution, and their light –scattering intensity.

In the present study, for the first time, this technique has been applied to real environmental samples: to 36 waters from the Llobregat and the Besòs Rivers and to 6 influents and effluents from 6 different wastewater treatment plants (WWTPs). Nanoparticle concentrations ranged from 10^6 mL^{-1} to 10^8 mL^{-1}. Influent wastewaters showed the largest concentrations with the predominance of small size (10–200 nm) metal/metal oxide nanoparticles. This highlights the significant use nanoparticles in domestic and industrial applications.

During the wastewater treatment, supra-aggregation and flocculation processes decreased the concentration of nanoparticles in the effluents and increased their diameters. No significant impact of wastewater discharges in nearby river waters was observed. Nevertheless, in all the surface waters relatively high nanoparticle concentrations were observed, especially in those located near highways and urban environments, which received the atmospheric deposition input of nanoparticles from traffic emissions. The natural background of nanoparticles in other river samples can be related to minerals weathering, to the biologic activity, to miscellaneous atmospheric inputs and to the minor contribution of WWTPs effluents. NTA results have provided useful supplementary information for the study of the occurrence, behaviour and compartimentation of fullerene aggregates in the same samples.

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AME-P23

ASSESSMENT OF NEW ILLICIT DRUGS IN SEWAGE AND SURFACE WATERS USING UHPLC-QqTOF-MS

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Insufficiently treated municipal wastewater discharge is identified as the route responsible for surface water contamination by compounds of anthropic origin [1]. This situation could bring about potential risks for human health and ecosystems. The aim of this study is to optimize a methodology for the simultaneous extraction, determination and quantification of 16 of new illicit to establish the consumption pattern and their environmental impact by analyzing them at the influent and effluent of wastewater treatment plants (WWTPs) and in surface water samples. The applicability and efficiency of the LC–QqTOF-MS technique in automated IDA-MS/MS for the qualitative and quantitative analysis has been demonstrated by the development of one of the first applications reported of this technique for the simultaneous determination of 16 emerging illicit drugs in wastewater and river water samples.

The selected illicit drugs were ephedrine (EPH), mephedrone (MEP), Methylone (METONE), N-Methyl-1-(3,4-methylenedioxyphenyl)-2-butanamine (MBDB), Dibutylone (bk-MMBDB), 4-Bromo-2,5-dimethoxyphenethylamine (2C-B), Naphyrone (NAPH), methylenedioxypyrovalerone (MDPV), bufotenine (BUF), 1-(3-chlorophenil)piperazine (mCPP), 1-(3-trifluoromethylphenyl)piperazine (TFMPP), α-pyrrolidinopropiophenone (PPP), α-pyrrolidinopentiophenone (alpha-PVP), 4-methyl-α-pyrrolidinohexaphenone (4'-MePHP), 4-methyl-α-pyrrolidinobutiophenone (MPBP) and 4-methoxyphencyclidine (4-MeO-PCP). Compounds were isolated and concentrated from water samples using solid phase extraction (SPE) using Strata-X cartridges (200 mg) and methanol. The recoveries for these compounds ranged from 44.7 to 95.9 % and the method detection limits ranged from 0.01 to 1.54 ng L^{-1}.

The determination of these compounds in the influent of the selected WWTPs shows the presence of stimulant drugs as EPH in 9.5% at concentration up to 13.4 ng L^{-1}. Hallucinogenic drugs as BUF and 4-MeO-PCP (at concentrations up to 334 and 240 ng L^{-1}, respectively) were detected in 100% and 19% of the influents, respectively. The effluent samples analyzed show that all compounds were completely removed except EPH. These new illicit drugs were detected also at 7 sampling points of the Turia River Basin at concentrations ranging from 3.84 to 66.8 ng L^{-1} for BUF and 37.6 ng L^{-1} for 4-MeO-PCP.

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AME-P24

SEPARATION AND CONCENTRATION OF PHTHALATES BY IN TUBE SOLID PHASE MICROEXTRACTION COUPLED TO LIQUID CHROMATOGRAPHY

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Increasing efforts to improve chromatographic determination of phthalates in environmental matrices at low concentration levels are performed because their ubiquity and their estrogenic activity. The separation and concentration using miniaturized systems can be improved in order to achieve a better sensitivity and selectivity. The main problems of the separation of six di-*n*-alkyl-phthalates (dimethyl-(DMP), diethyl-(DEP), dibutyl-(DBP), butylbenzyl-(BBP), 2-di-ethylhexyl-(DEHP) and di-*n*-octyl-phthalate (DOP)) are a remarkable increase of the retention with the number of carbon atoms on alkyl chain and the presence of the three critical pairs (DMP-DEP, BBP-DBP and DEHP-DOP) in diverse chromatographic conditions. Thus, the separations reported in the literature used gradient elution but, the time of analysis is long (around 30 min) or the flow-rate (up to 2mL min^{-1}) is high. Two different columns (monolithic C18 and cyanopropyl silica) and acetonitrile or methanol as modifier were tested. If acetonitrile and monolithic column are used, the separation of critical pairs is achieved in an elution time less than 11 minutes using a flow-rate equal or less 1mL min^{-1}. Similar results are obtained using acetonitrile and cyano column although with broader peaks. Using cyano column and gradient elution with methanol, the separation is also achieved but in 20 minutes.

Due to the different hydrophobicity of the phthalates mixture studied, the use of organic solvent can be a decisive IT-SPME parameter to the phthalates extraction from aqueous samples. Experiments without addition organic modifier, with acetonitrile, methanol and tetrahydrofuran were carried out. The behaviour of phthalates in the IT-SPME has also shown remarkable differences between the three pairs. Acetonitrile was the solvent less suitable to achieve the better compromise conditions. Other IT-SPME parameters as sample volume, conditioning solvent and replacing solvent were examined. The capability of the IT-SPME-HPLC coupling was tested with a method for the determination of polycyclic aromatic hydrocarbons (PAHs). The simultaneous separation and concentration of 16 PAHs and six phthalates were achieved using tetrahydrofuran as modifier. The optimized conditions of separation and IT-SPME were applied to samples of rainwater and aqueous extract with concentration levels of ng mL^{-1}.

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AME-P25

UPTAKE OF PPCPs FROM IRRIGATION WATER BY CROPS

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Reclaimed water can be contaminated with several organic microcontaminants derived from human activities (e.g. pharmaceutical and personal care products (PPCPs). These contaminants can be risky to human health and aquatic ecosystems. For that reason, their determination, for example in food, becomes necessary to evaluate their exposure for risk assessment studies.

The aim of the present study is to evaluate the uptake of selected PPCPs by lettuce (*Lactuca sativa,* L) from irrigation water in a greenhouse experiment and correlate the uptake with their physico-chemical properties. To study the fate of the selected PPCPs, a mesocosm study was used. In different pots with pearlite and sand (2:1; v:v) as a growing medium, twenty lettuces were watered with rainwater spiked at five concentration levels (0, 10, 25, 50 and 100 $\mu g \cdot L^{-1}$). Therefore, the concentration of those microcontaminants in soils, leaves and roots were determined using a gas chromatography (GC) and ultraperformance liquid chromatography (UPLC) coupled to tandem mass spectrometry (MS/MS).

Most of the studied PPCPs were identified at different concentration levels in leaves and roots. Carbamazepine exhibited higher concentrations in leaves than other PPCPs in the four concentrations evaluated. Translocation factors (TSCF) were determined from the ratio between leaves and root and they showed that carbamazepine (TSCF>1) has an active uptake mechanism while the other PPCPs show a TSCF<1 which means they predominant uptake mechanism is based on diffusion (passive transport).

Finally, multiple regression analysis of the obtained data set is performed in order to correlate the TSCF and bioaccumulation factor of microcontaminants to the contaminant physico-chemical properties (e.g. water solubility, log K_{ow}, log D_{ow}, pK_a).

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AME-P26

PRECONCENTRATION STRATEGIES COUPLED TO CAPILLARY ELECTROPHORESIS TO DETERMINE SWEETENERS IN ENVIRONMENTAL WATERS

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Sweeteners are increasingly used as sugar substitutes in foods, beverages and sanitary products. These compounds are not readily metabolized by humans, allowing them to be excreting nearly unchanged by urine and feces [1]. After decades of use of sweeteners, recent studies have documented their widespread environmental occurrence [2]. Hence, it is necessary to develop analytical methods to determine sweeteners in environmental water samples.

Acesulfame (ACE), cyclamate (CYC), saccharine (SAC) and sucralose (SUC) were the mainly compounds found in environmental waters and most methods for their determination at trace levels are based on liquid chromatography coupled to mass spectrometry [3]

To date, to the best of our knowledge, these compounds have not been determined by capillary electrophoresis in environmental waters. However, in the case this kind of matrices a preconcentration step will be needed to reach the concentration levels of these compounds water samples.

The main aim of our study is to evaluate the potential of different preconcentration strategies in combination with CE for the determination of sweeteners in environmental samples [4].

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AME-P27

GREENING FTIR ANALYSIS OF OIL AND GREASE IN WATER

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Infrared spectroscopy is a well-established technique for the determination of oil, grease and hydrocarbon in water. Unfortunately, standard methods have a number of significant drawbacks. These methods use liquid-liquid extraction with volumes of the organic solvent of the order of dL and using only a narrow region of the IR spectrum loosing information that provides the whole middle IR spectrum.

In this work, we have proposed the use of liquid-liquid micro extraction combined with the dry film technique for attenuated total reflectance infrared measurements (DF-ATR-FTIR). 20 mL of water sample contained in conical glass tubes were treated with 500 µL of chloroform (stabilized with amylene) and after vortex mixing during 5 minutes, samples were centrifuged at 3000 rpm for 5 min. Using a zero dead volume microsyringe (serie 7000 from Hamilton, Bonaduz, GR, Switzerland), 5 µL of the organic phase were deposited on the infrared element of an in-compartment ATR DuraSampleIR accessory with a nine reflections diamond/ZnSe DuraDisk (from Smiths Detection Inc., Warrington, UK) and the IR spectra of the dried film obtained after solvent evaporation, with a resolution of 4 cm^{-1}, cumulating 50 scans and with a background of the empty ATR cell measured in the same instrumental conditions..

The aforementioned strategy allows IR to obtain the IR spectra in the region between 4000 and 550 cm^{-1}, with an adequate sensitivity, thus providing additional spectral information that those contained between 4000 and 2800 cm^{-1} commonly used for liquid transmittance measurements. DF-ATR-FTIR permits the chemometric evaluation of the spectra in order to identify the nature and possible source of the oil contamination.

Experimental variables have been evaluated and the method was applied to the study of different sea water samples from Valencia beach and harbor.

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AME-P28

OCCURRENCE OF SHORT-CHAIN CHLORINATED PARAFFINS IN GULL EGGS FROM SPANISH NATURAL PARKS

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Short-chain chlorinated paraffins (SCCPs) are complex mixtures of polychlorinated n-alkanes containing thousands of isomers with carbon chain lengths from C_{10} to C_{13} and a chlorine content from 30 to 70% by weight. Due to their flame retardant properties [1], CP mixtures have been widely used in a wide variety of industrial applications [2]. The presence of SCCPs in the environment is of particular concern because they are persistent, bioaccumulative through the food chain and toxic to aquatic organisms [3]. Consequently, SCCPs are classified as possible carcinogenic to humans (Group 2B) by IARC and are proposed as candidate to new persistent organic pollutant by the Stockholm Convention. Birds have been commonly used as sentinel species for monitoring the levels of environmental pollutants and their presence in bird eggs reflect the contamination burden of the female at the time of egg laying. Although seabird eggs have proven to be suitable to assess the environmental contamination, until now data about levels of SCCPs in gull eggs are very limited.

The aim of the study was to evaluate the occurrence of SCCPs in eggs of yellow-legged gull (Larus michahellis) as bioindicators of environmental pollution from areas of special protection. The study comprised the period 2009-2013 and includes four Spanish natural parks located at Atlantic Islands of Galicia, the Cabrera Archipelago, Ebro Delta, and Chafarinas Islands. The SCCP analysis was carried out using a selective pressurised liquid extraction method in combination with gas chromatography-mass spectrometry operating in negative ion chemical ionisation. The method was validated and applied to the analysis of SCCPs in gull eggs with a good precision (RSD<15%) and low limits of detection (0.5 $ng \cdot g^{-1}$ wet weight, ww). The presence of SCCPs in gull eggs was detected at levels ranging from 1.7 to 24 $ng \cdot g^{-1}$ (ww) and the highest SCCPs concentrations were found at Cabrera and Atlantic Islands of Galicia, although these levels were always at the low concentration range reported for biota samples.

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AME-P29

DETERMINATION OF NPAHS IN AMBIENT AIR. COMPARISON OF CROMATOGRAPHIC METHODS (HPLC-FLU VS. HRGC-MS)

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Nitrated Polycyclic Aromatic Hydrocarbons (NPAHs) are environmental pollutants formed by incomplete combustion of organic matter. Most of them are formed from PAHs by nitration processes during combustion exhaust of vehicles or by gas phase reactions or by heterogeneous interaction between gas-particulates in the atmosphere. In the gas phase reactions, an addition of hydroxyl radicals to PAHs occurs during the day. Here, a reaction with NO_2 takes place and a water molecule is lost. During the night cycle, there is a nitrate radical addition to PAHs, followed by a reaction with NO_2 and consequent loss of nitric acid.

Due to persistence and toxicity of NHAPs (they are carcinogenic, genotoxic and / or mutagenic), concern about the possible environmental and health-related effects is of great importance.

It has been developed a method to determine five NPAHs (1-NPy, 3-NFlu, 9-NPh, 1-NN and 6-NBaPy) in PM10 filters. Chromatographic analysis has been optimized with HPLC-Fluorescence and HRGC-MS.

The workup is based on an ultrasound extraction using dichloromethane as solvent. Sample is concentrated and reconstituted in acetone for analysis by HRGC-MS (EI/ SIM). As internal standard, the corresponding deuterated PAH is used.

For HPLC with fluorescence detector, a reduction process with $NaBH_4$ to obtain the corresponding amino compounds is required after the extraction process. The fluorescence quantum yield of NPAHs is negligible due to the strong withdrawing effect of the nitro group. Therefore, they exhibit only weak fluorescence signals. For fluorescence detection, different wavelengths (excitation/emission) for each amino-compound have been used. Hence, possible matrix interferences are achieved to reduce.

These methods have been validated. Moreover, it has been used to analyze samples from different regions of Catalonia to study the profile according to the different areas and broadcast sources.

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AME-P30

CHROMATOGRAPHIC METHOD TO ANALYZE NON- VOLATILE PAHS BY HRGC/MS (EI/SIM)

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Polycyclic aromatic Hydrocarbons (*PAHs*) are environmental pollutants coming from incomplete combustions of organic matter. Due to their persistence and toxicity, European legislation (2004/107/CE) propose the monitoring of seven of these compounds in the environment: Benzo(a)Anthracene [B(a)A], Benzo(b)Fluoranthene [B(b)F], Benzo(j)Fluoranthene [B(j)F], Benzo(k)Fluoranthene [B(k)F], Benzo(a)Pyrene [B(a)P], DiBenzo(a,h)Anthracene [DiB(a,h)A] and Indeno(1,2,3-c,d)Pyrene [IP].

A chromatographic method with HRGC/MS (EI-SIM) has been developed to identify and quantify the seven *PAHs*included in the legislation plus two more: Chrysene [Chr] and Benzo(g,h,i)Perylene [B(ghi)P].

PAHs to study are characterized by low volatility and the presence of several isomeric compounds. For this reason, the method optimization has been focused on ensuring good *resolution*, *sensibility*and *linearity*.
*Resolution*has been adjusted by evaluating the program temperatures and the type of column employed. Then, *sensibility*has been optimized improving some injection parameters such as the injection volume, the injection temperature, *split* ratio, type of *liner*.

In addition to improve the *sensibility*of the method and ensure good *linearity*, it has been necessary to adjust the transfer line and the ion source temperatures.

Once the optimized method has been developed, some quality parameters have been evaluated: linearity, injection repeatability and LOD/LOQ.

The chromatographic method has been applied to PM10 particulate filters being obtained satisfactory results.

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AME-P31

BIOAVAILABLE FRACTION OF CADMIUM IN MARINE SEDIMENTS MEASURED BY ID-ICP-MS

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When solid samples are analyzed a previous digestion/dissolution step is usually required, which implies risk of contamination and/or loss of analyte. In these cases, isotope dilution inductively coupled plasma-mass spectrometry (DI-ICP-MS) is a pontential primary method of measurement, as it guarantees an optimal accuracy and traceability of the results. DI-ICP-MS is capable of compensating for any loss of analyte during sample preparation, for matrix effects since quantitation is based on ratio measurements and for instrument drift, providing isotopic equilibrium is achieved between the added spike and the endogenous analyte in the sample [1]. Moreover, this technique is very effective for high-precision and high-sensitivity determination of trace elements.

In this work, DI-ICP-MS was used to quantify the bioavailable fraction of cadmium in marine sediments. The parameters affecting the trueness and the precision of the isotope ratio measurements were studied (nonlinearity of the detector, mass bias effects, spectral interferences and amount of spike added to the sample) and the corresponding correction factors calculated.

Cadmium was leached using a fastand simple procedure based on 1 M HCl ultrasound-probe extraction, employing the minimal amount of reagents and reducing the time of analysis. There are many different proposals to assess the bioavailable fraction of metals in sediments.Here, the experimental results were compared to the sum of the 3-step BCR 701 sequential extraction procedure, as it may represent the so-called mobilizable fraction of the metals [2]. A good agreement was achieved (ca. 98% recovery). Sediment samples from the Galician coastline were analyzed using the proposed procedure.

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AME-P32

EVALUATION OF A QUINIDINE-BASED MONOLITHIC COLUMN FOR THE ENANTIOMERIC SEPARATION OF HERBICIDES BY NANO-LC

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Chirality plays an important role in environmental analysis. One reason is that the enantiomers of a chiral agrochemical may have different activities. The use of pure enantiomers as agrochemicals avoids the presence of inactive or even toxic enantiomers in the environment. Analytical methodologies are needed in order to control de optical purity of these compounds.

Nano-liquid chromatography with chiral stationary phases offers several advantages for enantioseparation such as high efficiency, low sample, solvents, and stationary phase consumption and easy coupling with mass spectrometry.

Among the chiral stationary phases, carbamoylated quinidine immobilized on silica microparticles gained great importance due to its outstanding enantioselectivity towards acidic analytes. Lämmerhofer et al. [1] prepared a carbamoylated quinidine monolithic column that joined the enantioselectivity of this group to the easy preparation and good column characteristics of monolithic columns as permeability and efficiency. In this work, a chiral monolithic column based on carbamoylated quinidine was prepared according to the Lämmerhofer method using a re-optimization in the polymerization mixture. The poly (O-9-[2-(methacryloyloxy)-ethylcarbamoyl]-10,11-dihydroquinidine-co-2-hydroxyethyl methacrylate-co-ethylene dimethacrylate) (poly(MQD-co-HEMA-co-EDMA) monolithic column was employed for the enantioseparation of 7 phenoxy-acid herbicides: 2-(3-chlorophenoxy)propionic acid, 2-(4-chlorophenoxy)propionic acid, 2-(4-chloro-2-methylphenoxy)propanoic acid (mecoprop), 2-(2,4-dichlorophenoxy)propanoic acid, 2-(2,4,5-trichlorophenoxy)propionic acid, 2-[4-(6-chloro-1,3-benzoxazol-2-yloxy)phenoxy]propionic acid, and 2-phenoxypropionic acid. Baseline separation was achieved for most of them under optimized mobile phase conditions. An analytical methodology enabling the enantiomeric separation of mecoprop and its simultaneous separation from other three achiral herbicides (4-chloro-2-methylphenoxyacetic acid, 2,4-dichlorophenoxyacetic acid, and 3,6-dichloro-2-methoxybenzoic acid) was developed and applied to the determination of mecoprop in commercial herbicide formulations based on the use of the pure enantiomer (R-mecoprop). Analytical characteristics of the method were evaluated in terms of linearity, accuracy, precision, LODs and LOQs. R-mecoprop was quantified in commercial formulations and the results were in agreement with the labeled content. The enantiomeric impurity content was under the LOD of the method.

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AME-P33

PRESENCE OF TOXIC PRODUCTS IN DRINKING WATER SUBJECTED TO CHLORINATION

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Since 1900, chlorine and its compounds are the principal disinfectants used in the treatment of the water, and is widely proven that this practice has had a positive effect on human health. However, towards the middle of the 1970s it was discovered that chlorine also reacts, under certain operational conditions, with the natural or anthropogenic organic matter in the raw water supply systems, to produce the formation of the so-called disinfection by-products (DBPs). The DBPs can be classified in different groups of synthetic organic compounds including trihalomethanes (THMs) and the haloaceticos acids (HAAs). The emergence of DBPs in chlorinated waters intended for human consumption has attracted growing interest from the perspective of public health, due to the fact that in recent years there has been an accumulation of data that allow associating exposure to these substances with a higher risk of cancer, as well as reproductive disorders. Thus, THMs and some AHAs have been considered as potentially carcinogenic for humans.

This work presents the determination of four THMs in tap waters using dispersive liquid-liquid microextraction with few microliters of decanol (as extraction solvent), and also low amounts of dispersive solvent (acetone) in combination with gas-chromatography coupled to mass-spectrometry. In this sense, this extraction method can be included among the green chemistry requirements.

The relationship between the THMs and their precursors (organic matter, pH, and temperature) has also been studied in water before disinfection processes.

AME-P34

DETERMINATION OF Mo(VI) BY CATHODIC STRIPPING VOLTAMMETRY USING CLIOQUINOL AND FERRON AS CHELATING–ADSORBENT AGENTS

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Molybdenum is an essential element for both animals and plants in concentrations of μgL^{-1}, and possesses low toxicity. Since the concentrations of molybdenum found in natural waters are very low, sensitive, selective and accurate methods are required. Adsorptive stripping voltammetry (AdSV) have important advantages that include speed, high selectivity and sensitivity which depends of working electrode as too the choice of a suitable ligand that forms a complex with adequate net charge, size and solubility. Clioquinol (5–chloro–7–iodo–8–hydroxyquinoline, CQ) is a compound of great interest in the field of analytical, inorganic and bioinorganic chemistry due to complexation properties and the high lipophilicity and could be easily adsorbed on the electrode. On the other hand, changing the chloro for the sulfonic group (ferron), hydrophilic character increase conferring to its metal complexes water solubility.

The aim of this study was to optimize the AdSV technique to determine Mo(VI) in the presence of Cu(II), because copper is usually found with molybdenum, using clioquinol and ferron as complexing and adsorbing agent, and compare their sensitivity and selectivity.

In the presence of CQ a high peak current due to reduction of the Mo-CQ complex is observed to -0.24 V and two small signals at -0.48 and -0.55 V, whereas in the presence of ferron two signals with similar currents are observed at -0.24 and -0.55 V. In both cases the reduction of Mo and Cu are overlapped (-0.24 V). When thiourea was added the signal of copper was displaced to negative potentials; with ferron was not necessary because the signal at -0.55 V was used. On the other hand, nitrate catalyzes the reduction of the Mo-CQ complex and not Mo-ferron complex. With CQ: peak current is proportional to Mo concentration until 18.0 μgL^{-1}, with a 3sdetection limit of 53 ngL^{-1}; whereas with ferron, peak current is proportional to Mo concentration until 40.0 μgL^{-1}, with a 3sdetection limit of 78 ngL^{-1} (pH 2.7; E_{ads} -0.50 V; t_{ads} 60 s). The methods were validated by determining Mo in spiked synthetic sea water (ASTM D665), certified reference water (TMDA–61) and were applied to the determination of Mo in sea water samples.

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AME-P35

DETERMINATION OF PHARMACEUTICALS AN PERSONAL-CARE PRODUCTS IN SEA WATER AND SEDIMENTS BY LC-MS TQ

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An exceptional sensitive LC-MS TQ method has been developed for the analysis of pharmaceuticals and personal-care products (PPCPs) in samples of sea water and sediments. The achieved sensitivity permitted the sub-ppb analysis for all compounds under study, and sub-ppt for some of them. The dynamic linear range were from 0.05 to 100 ng mL^{-1} with good linearity in all cases (r^2>0.99). Recoveries studies of spiked samples at two different levels yielded values from 82 – 130 % and 70 – 124 % for water and sediments, respectively

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DIA-P02

HIGH TEMPERATURE SEC OF POLYOLEFIN COPOLYMERS USING IR DETECTION: SENSITIVITY CHANGES WITH COMONOMER TYPES

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Size Exclusion Chromatography (SEC) is the technique routinely used to analyse the molar mass distribution in many natural and synthetic polymers, including polyolefins. Due to the semi-crystalline nature of these polymers, high temperatures (140-160ºC) are used to dissolve them in organic solvents (1,2,4-trichlorobenzene or *o*-dichlorobenzene), before injection in the GPC columns for fractionation. Equipment able to keep the injection system, columns, detectors and interconnecting lines at a controlled high temperature is required, in order to prevent polymer precipitation in the system. A filter-based infrared (IR) detector has demonstrated to be highly useful to detect the concentration of polymer, as well as its chemical composition after separation according to molar mass distribution [1]. The analytical signal given by the ratio of absorbance values at two selected bands in the MID-IR is calibrated to chemical composition of the polyolefin in methyl per one thousand total carbon units. A small set of reference materials with known chemical composition can be used given the high linearity and precision of the method [2,3]. In this work, different sets of reference copolymers of different types were used to study the IR detector response variation with comonomer type. The observed differences can be attributed to the different length of the side chains introduced by the comonomer and the spectral differences due to the different distance to the terminal methyl group to the polyolefin backbone [4]. The study included several ethylene/α-olefins copolymers of propylene, 1-butene, 1-hexene, 1-octene and 1-octadecene, and was performed with an HT-GPC instrument, model GPC-IR (Polymer Char, Paterna, Valencia).

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DIA-P03

ANALYSIS OF BIOLOGICAL FLUIDS BY CAPILLARY- AND NANO-LIQUID CHROMATOGRAPHY WITH SYNCHRONIZED GRADIENT ELUTION

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Instruments with two rather different designs, namely split-flow and splitless-flow or syringe pumped, are used to generate the tiny flow rates required in capillary- (cHPLC) and nano-liquid chromatography (nHPLC). In split-flow systems, the splitting of a primary flow provides the much smaller secondary flow required at the injection device and analytical column. In a previous work, a procedure for the accurate synchronization of sample injection and gradient elution in these systems was developed and applied to the cHPLC separation of alkylbenzenes [1].

Two operations are required in system synchronization: (i) to switch the injection valve back to bypass at the $t_V$time after the injection, that is, immediately after the whole sample plug has entered the valve-column path, and (ii) to start the gradient either before or after the injection, thus to prevent the late or early arrival of the gradient front to the valve, respectively. Accordingly, starting of the gradient should be performed at the match time, t_M, which is the time required to match the entrance of the gradient front to the valve-column path with the arrival of the end of the sample plug. Both $t_V$and $t_M$are functions of both the primary and secondary flow rates, also varying significantly with the backpressure. Simple experiments to measure $t_V$and $t_M$in the actual conditions under which the gradient must be started (i.e. with the column and the same mobile phase and flow-rate) were described.

In this work, this synchronization technique was first extended to a splitless-flow system. Then, two systems, namely a split-flow cHPLC and a splitless-flow nHPLC, were used to separate relevant bioactive substances (including endocrine disruptors), inhuman urine and serum. Both packed columns and poly(buty-co-ethylenedimethylmethacrylate) polymeric monolithic columns were used. The advantages of synchronization over the normal operation mode were demonstrated.

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DIA-P04

A MICROSTRUCTURED CAPILLARY AS CE-LIF SEPARATION COMPONENT FOR NITROCELLULOSE DETECTION FROM DYNAMITE SAMPLES

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Instrumentation development is a current trend in analytical chemistry, focused, among other purposes, in the improvement of detection capability. Regarding one of the most important separation techniques, capillary electrophoresis (CE) is widely used in many analytical fields, including forensic science.

Our previous research in both the use of MSCs as main separation component in CE **[1]** and nitrocellulose derivatization processes **[2]** allowed us the detection of this macromolecule in real samples of dynamite (GOMA 2-ECO) by employing a microstructured capillary (MSC) as separation platform. The MSC, consisted of 6 holes of 25 µm id and 300 µm od. It was manufactured by using the stack-and-draw technique and was made of pure silica covered by a transparent polymer to avoid the creation of a detection window. Samples of dynamite (2mg) were derivatized with APTS and analysed by CE-LIF. The nitrocellulose profile was evidenced when signlas were compared to a blank analysed in the same conditions (Lt, 31 cm, T_{sample}, 15ºC, $T_{cartridge}$, 20ºC, Injection, 4 psi during 6 s, Separation Voltage, -10 kV). This study confirms the use of MSCs as separation platform in commercial CE equipment by detecting, for the first time, the nitrocellulose contained in dynamite.

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DIA-P05

METHOD DEVELOPMENT FOR THE SIMULTANEOUS DETERMINATION OF METHYLMERCURY AND INORGANIC MERCURY IN SEAFOOD

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Within the elements that are toxic for humans and the environment, mercury is a well-known pollutant due to the high toxicity of its species. The toxicity of metals and their bioavailability depend on the chemical form of the metals. All Hg forms are toxic, with the organic species being in most cases more dangerous than the inorganic ones. Bioaccumulation occurs in most cases of human exposure. Seafood is responsible for the highest source of Hg, especially methylmercury ($MeHg^+$). Thus, an accurate analytical method for Hg speciation in seafood is required to assess the real toxicity of samples [1, 2].

This work reportsthe method development for the simultaneous determination of methylmercury ($MeHg^+$)and inorganic mercury (iHg) species in seafood samples. The study focused on the extraction and quantification of $MeHg^+$ (the most toxic species) by liquid chromatography coupled to on-line UV irradiation and cold vapour atomic fluorescence spectroscopy (LC-UV-HG-AFS), using HCl 4 mol L^{-1} as the extractant agent.

Accuracy of the method has been verified by analysing three certified reference materials and different spiked samples. The values found for total Hg and $MeHg^+$ for the CRMs did not differ significantly from certified values at a 95% confidence level, and recoveries between 85% and 97% for $MeHg^+$, based on spikes, were achieved. The detection limits (LODs) obtained were 0.001 mg Hg kg^{-1} for total mercury, 0.0003 mg Hg kg^{-1} for $MeHg^+$ and 0.0004 mg Hg kg^{-1} for iHg. The quantification limits (LOQs) established were 0.003 mg Hg kg^{-1} for total mercury, 0.0010 mg Hg kg^{-1} for $MeHg^+$ and 0.0012 mg Hg kg^{-1} for iHg. Precision for each mercury species was established, being ≤ 12 % in terms of RSD in all cases.

Finally, the developed method was applied to 24 seafood samples from different origins and total mercury contents. The concentrations for Total Hg, $MeHg^+$ and iHgranged from 0.07–2.33, 0.003–2.23 and 0.006–0.085 mg Hg kg^{-1}, respectively. The established analytical method allows obtaining results for mercury speciation in less than one hour including both, sample pretreatment and measuring step.

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DIA-P06

UHPLC-ESI-QqQ(MRM) MULTICOMPONENT METHOD FOR THE DETERMINATION OF PHTHALATES, PARABENS AND BISPHENOL A IN COSMETICS

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Due to the widespread use of phthalates (PAEs), parabens and bisphenol A (BPA) in daily use products, and its certainty of reproductive toxicity and estrogenic activity[1], lists of priority substances[2], limitations on concentrations[3] and tolerable daily intakes[4] has been published. For these reasons and for its large presence in the environment, it is necessary to develop rapid and sensitive multicomponent methods for the determination of these endocrine disruptors in a single chromatographic run.

A method based on ultra-high performance liquid chromatography coupled to a triple quadrupole mass analyser working in the multiple reaction monitoring mode (UHPLC-ESI-QqQ(MRM)) for the fast and simultaneous determination of five phthalates (*dimethyl phthalate, diethyl phthalate, dibutyl phthalate, butyl benzyl phthalate, diethyl hexyl phthalate*), seven parabens(*methyl paraben, ethyl paraben, n-propyl paraben, iso-propyl paraben, n-butyl paraben, iso-butyl paraben, benzyl paraben*)and BPA was developed using a Box-Wilson Central Composite experimental Design.The analytical characteristics of the developed method were studied in terms of linear range, limits of detection, instrumental precision (repeatability and intermediate precision), and robustness. The suitability of the developed method was demonstrated through its application to the analysis of commercial cosmetics (*perfumes, hairsprays, hair foams, shower gels and shaving products*), being possible to determine the simultaneous presence of PAEs, parabens and BPA.

To keep contamination to a minimum, any type of plastic, which could contain phthalates, has been avoided during the treatment of the samples. For liquid samples, a direct 1:10 dilution with MeOH:water (75:25, v/v) was performed. For solid samples, 0.5 g sample was dissolved in 5 mL of MeOH and a portion of 10 µL of this solution was subjected to the same dilution.

The concentration levels and profiles found were different for each type of sample. Perfumes showed the highest concentration of phthalates (60-4976 ng mL^{-1} of sample), hairsprays presented quantifiable concentrations of BPA (0.3-3.9 ng mL^{-1} of sample) and parabens are mainly present in gels (<LOQ-648 ng g^{-1}), shaving products (24-30 ng g^{-1}), and in one of the hair foams analysed (16507 ng g^{-1}).

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DIA-P07

ONLINE MONITORING BY FID OF THERMAL DEGRADATION OF SUNFLOWER OIL AND QUANTIFICATION BY SPE-GC-MS

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Heating of oil produces alterations of its physical properties (colour [1], viscosity) and chemical characteristics [2]. Numerous studies examine the composition and characteristics of the oil after heating it [1, 3-5]; nevertheless, few studies examine the chemical composition of the fumes generated during this process [2, 6].

Thermogravimetry has been used to study the effect of heating on degradation of oil [7].In this work, a Flame Ionization Detector (FID) has been used as a new, alternative and complementary method to thermogravimetry to monitor the degradation of oil. High oleic sunflower oil has been heated and the volatile compounds have been carried to the FID. In addition, these compounds have been trapped with Solid Phase Extraction and analyzed by Gas Chromatography Mass Spectrometry. Both studies have been made using nitrogen and air as purge gas.

Signal of FID curves when it is purged with nitrogen increases at temperature higher than 300 ºC. However, when air is used, the starting point is at less temperature (200ºC). In this case, three steps can be distinguished. In the first step, the graphic is a straight line, in the second step the slope of the curve increases and in the last step the increase is higher and the slope is similar to obtained with nitrogen.

Forty five compounds have been identified during heating process with the analysis by GC-MS. All of them appear when air is used but only 20 compounds when the purge gas is nitrogen. Moreover, concentration of compounds released with nitrogen is lower than concentration of compounds when air is used. Differences between nitrogen and air curve with FID could be explained for those reasons.

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DIA-P08

QUALITATIVE METHOD FOR THE DETECTION OF EXOGENOUS ANABOLIC STEROIDS IN URINE BY GC-(APCI)QqQ MS/MS

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Androgenic anabolic steroids (AAS) are the most frequently detected group of compounds in doping control analysis and one of the widest problems in sport. Doping control laboratories have to develop adequate analytical approaches to detect their misuse, dealing with the presence of a large number of endogenous compounds in a complex matrix like urine [1].

Due to their inherent sensitivity and selectivity, analytical methodologies using chromatographic techniques coupled to mass spectrometry with triple quadrupole (QqQ) are adequate for the target determination of AAS in urine. Nowadays, two techniques are implemented in laboratories: methods based on LC-API-MS, which allow the detection of thermolabile compounds at low LODs simplifying sample preparation; and the traditional GC-EI-MS methods which present high fragmentation in the source [2]. This high fragmentation can hamper the choice of adequate precursor ions in the selected reaction monitoring (SRM) transitions in QqQ instruments which undermines the specificity/selectivity of the method due to the effect of interferences coming from the urine. The use of a softer ionization source that allows the selection of more specific precursor ions could alleviate this issue.

An atmospheric pressure chemical ionization (APCI) source, developed for gas chromatography [3], has been used to detect seventeen trimethylsylil-AAS in urine samples. This interface promotes soft ionization in GM-MS with very little fragmentation similar to the obtained by LC-API-MS. The resulting base peak are $[M+H]^+$ ions (using water as modifier) which allow the selection of abundant and specific precursor ions. A SRM target method has been developed in a QqQ instrument. Since the mere occurrence of an exogenous steroid has to be reported as an adverse analytical finding, qualitative methods are needed. The proposed method consists on an enzymatic hydrolysis of conjugates, a liquid-liquid extraction, a derivatization step [4] and the detection by GC-(APCI)QqQ MS/MS. The method has been validated by spiking ten different urines at five different concentration levels and its applicability has been tested in positive samples.

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DIA-P09

DEVELOPMENT OF A METHOD BASED ON GC-(APCI)QqQ MS/MS FOR THE DETECTION OF DIOXIN-LIKE PCBs IN COMPLEX-MATRIX SAMPLES

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Dioxin-Like polychlorinated biphenyls (DL-PCBs) have been typically determined by HRGC-EI-HRMS, as they allow the identification and quantitation of coeluting dl-PCBs congeners at concentration levels as low as 0.009 mg/kg. However, this technique presents some disadvantages as the need for trained personnel and frequent maintenance (together with the high purchasing costs), so the development of alternative, more economical technologies as TOF(MS), ion trap and triple quadrupole have been used for this purpose, with reported sensitivity performances ranging from 0.1 to 0.3 mg/kg [1].

This work studies the capabilities of triple quadrupole (QqQ) mass spectrometers using the novel atmospheric pressure chemical ionization (APCI) source [2]. Thus, an analytical methodology for the simultaneous determination of 12 DL-PBCs in complex samples by GC-MS/MS using a QqQ has been developed.

Ionization and fragmentation behaviour of PCBs by APCI under charge transfer conditions have been studied. Favouring the formation of a highly abundance molecular ion has been pursued because of the specificity added when choosing the molecular ion as a precursor ion in tandem MS experiments. Then, *m/z* ions corresponding to M+• isotopic cluster were fragmented in the collision cell. Main product ions corresponded to the loss of two ^{35}Cl atoms, $[M-^{35}Cl_2]^+$ at collision energies of 35eV and a cone voltage of 30V. In addition, the fact that the APCI source does not produce remarkable in-source fragmentation greatly reduced the possibility of interferences from higher chlorination degree congeners.

Accuracy, linearity, repeatability and LODs have been evaluated during method validation, obtaining instrumental LODs near to 0.5 fg in the worst case.

The final step in method development and evaluation has been the application to real samples (animal feed, fish and ashes). Several DL-PCBs congeners have been detected and quantitated in different matrices in the range of 0.08-10 ppt. The concentration values obtained were in good agreement with those reported by GC-HRMS determination. Special attention was given to the confirmation of the identity of compounds in order to avoid reporting false positives making use of the q/Q ratio as confirmation parameter. The specificity of the acquired transitions and the sensitivity of the system show this technique as an alternative to the current GC-(HRMS).

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DIA-P10

DEVELOPMENT OF A TANDEM MASS SPECTROMETRY METHODOLOGY FOR THE ANALYSIS OF DIOXANES AND DIOXOLANES IN WATER

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Dioxanes and Dioxolanes are volatile compounds that come from industrial processes. These compounds go through waste water treatment plants and spread along the rivers. Several odor events caused by Dioxanes and Dioxolanes have taken place in our rivers in the last years [1,2]. It has been shown that these compounds can reach tap water, being responsible of complaints from water consumers due to their odor. The most odorous dioxane is 2EDD, which has a threshold of odor between 5-10 ng / L [3].Recently, an episode of odor because of these compounds was detected in the Llobregat River at intake the Drinking Water Treatment Plant (DWTP).

In this work, a new methodology for the identification and quantification at trace levels of these compounds in waters, using Closed Loop Stripping analysis (CLSA) followed by GC-MS/MS, has been optimized. The instrumental parameters had been optimized and two transitions have been monitored for each compound. At these working conditions four identification points were obtained as required by EU guidelines. Validation parameters have been reached according to ISO 17025: Instrumental quantification limits varied from 1 to 25 pg, calibration curves have been obtained with correlations coefficients > 0.99, and recoveries at 10, 50 and 100 ppt have been evaluated.

Finally the optimized methodology was applied to analyse dioxanes and dioxolanes in wastewaters, surface and drinking waters and it helped to determine which concentration levels of dioxanes can be removed by DWTP.

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DIA-P11

UV FILTERS IN COSMETICS: COMPARATIVE PERFORMANCE OF GC AND HPLC COUPLED TO TRIPLE QUADRUPOLE-MASS SPECTROMETRY

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To guaranty consumer's health, UV filters are essential ingredients in cosmetic formulations. The use of these additives is extended to almost the total variety of leave-on personal care products, and not only to the solar cosmetics. The high spread use at high levels, together with some aspects related to toxicity, has made them gaining the consideration as emerging pollutants. Although the levels in cosmetics are high, the complexity of the matrices, the prohibition of some of these substances, and the incessant introduction of amendments in the Cosmetic Regulation makes necessary the analysis of these personal care product (PCP) ingredients at low levels. On the other hand, the environmental concern requires their control at very low levels. Therefore, the development of high sensitive and high selective analytical methods is necessary.

In the present work, two sensitive and selective methodologies based on gas chromatography-triple quadrupole tandem mass spectrometry (GC-TQ/MS), liquid chromatography-triple quadrupole tandem mass spectrometry (LC-TQ/MS) are proposed for the simultaneous analysis of different classes of UV filters including benzophenones, salicylates,methoxycinnamates, p-aminobenzoic acid derivatives, and others commonly used in cosmetic products. Considering the broad variety of highly complex matrices, sensitive detection of the target analytes could be achieved working in the selected reaction monitoring (SRM) mode. After chromatographic performance evaluation, both methods were tested in real sample extracts to assess the matrix effects, and different experimental conditions were evaluated to mitigate it. The performance of both techniques was evaluated in terms of detection limits (LODs), precision and linear working range. For most compounds, higher sensitivity was obtained using LC-TQ MS, with LODs at the low pg mL^{-1}. In general, LC-tandem MS provided better performance than GC-tandem MS for the analysis of the target UV filters. Some compounds such as homosalate and ethylhexyl salicylate could not be adequately determined using LC-ESI-TQ/MS, whereas other compounds like benzophenones underwent significant improvement when using LC-TQ/MS. Both LC and GC coupled to TQ/MS detectors have demonstrated to be adequate for the analysis of the majority of target compounds.

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DIA-P12

USING MALDI-ToF-MS FOR IDENTIFICATION AND CHARACTERIZATION OF DIFFERENT HOMO-POLYMERS

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Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-ToF-MS), first developed to study peptides and proteins, has also been applied to synthetic polymers analysis. This technique requires that the polymer has a relatively narrow molecular weight distribution (MWD) [1250-8000].

MALDI-TOF is ideally suited for polymer analysis because of simple acquisition of the mass spectra which show mainly single-charged quasi-molecular ions with hardly any fragmentation. Simple sample preparation, fast analysis times, the variety of available matrices, low sample consumption, and particularly the formation of singly charged ions, are only a other advantages of the MALDI technique.

The application of different analytical softwares to process the raw data has allowed us to unequivocally identify the studied polymers, because of characteristic repeating units.

Here, we present the results obtained from the analysis of different commercially available biodegradable homo-polymers (polylysine, poly(caprolactone)diol 1250 and poly(caprolactone)diol 2000. These polymers have been analyzed using the MALDI-ToF-MS in different matrices and cationizing agents; In addition, the proportions of matrix and cationizing agent have been optimized for each polymer investigated.

DIA-P13

POLYMERIC PHOSPHONIUM IONIC LIQUIDS AND GRAPHENE OXIDE AS STATIONARY PHASES IN GAS CHROMATOGRAPHY

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Eight new functionalized polymerizable phosphonium ionic liquids were synthetized and applied for the preparation of polymeric stationary phases in gas chromatography (GC). These coated GC columns exhibit exceptional thermal stability (220-360ºC) and column efficiencies between 3200 and 3900 plates m^{-1} and have been characterized using the Abraham model in order to understand the effects of the polymeric cation and the anion on the system constants. These stationary phases exhibited unique selectivity for organic compounds such as alcohols, amines and polycyclic aromatic hydrocarbons (PAHs) with good symmetries (less to 1.5 in all cases). Moreover, graphene oxide (GO) sheets were covalently bonded onto the inner wall surface of fused silica capillary columns using 3-aminopropyl-diethoxymethylsilane (3-AMDS) as a cross-linking agent. The use of GO in the preparation of the capillary columns enhanced their efficiency, improving peak symmetries because of the reduction of the unspecific absorptions. The resulting excellent separation efficiencies proved that ionic liquids do not lose their dual nature when polymerized.

OQA-P01

USING NIR-HSI AND CHEMOMETRICS TO DETECT EXPLOSIVES ON HUMAN HANDPRINTS

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The use of improvised explosive devices (IEDs) against civilian populations has been intensely increased during the last years. This fact can be due to the production of IEDs is relatively easy and cheap. Consequently, their use is quickly spread and the information related to their development and improvements is also published on internet.

In this study near infrared hyperspectral imaging (NIR-HSI), combined with partial least squares discriminant analysis (PLS-DA) is used to provide a fast, non-contact, non-invasive and non-destructive method for the analysis of five different explosive residues on human handprints. Volunteers manipulated individually each of these explosives and after deposited their handprints on plastic sheets. Common explosives potentially used as part of IEDs as ammonium nitrate, black powder, single- and double-base smokeless gunpowders and dynamite were studied. PLS-DA models were built to detect and classify the presence of explosive residues in handprints. High levels of sensitivity of specificity for all classes defined were obtained, allowing the development of a preliminary library and facilitating the direct and *in-situ* detection of explosives by NIR-HSI. In this study [1], we want to highlight how the proposed HSI-PLS-DA will offer the possibility of determining whether a person has been manipulating dynamite or smokeless gunpowder explosives by the direct analysis of his/her handprints. We have demonstrated that HSI-NIR combined with chemometrics is a promising forensic tool for the detection of explosives residues contained in human handprints avoiding the influence of sweat or dirtiness commonly present on hands.

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OQA-P02

A SENSIBLE METHOD FOR ENDOCRINE DISRUPTING CHEMICALS ANALYSIS IN HUMAN MILK BASED ON A SIMPLE EXTRACTION PROCEDURE

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In recent decades, the overall development has led man to have available a lot of manufactured products with a wide applicabilitythat have significantly eased the life. Nevertheless, this development has brought an important inconvenient to the population: the exposure to a high variety of xenobiotics that could cause negative health effects. Among these compounds, endocrine disrupting chemicals (EDCs), that cover an important range of substances able to alter the normal hormone function of wildlife and humans, have become in a special concern [1]. Synthetic chemicals such as are bisphenol A and its chlorinated derivatives, benzophenone-UV filters and parabens have been implicated in endocrine disruption. Developmental exposure to EDCs is particularly important in the first stages of life because of the increased susceptibility of the brain and other organs to estrogens during this period [2]. It has been postulated that EDCs accumulate in human tissues and their effects might pass to the offspring [3]. Breastfeeding mothers exposed may be unknowingly exposing their children to harmful levels of these compounds. In this context, it is particularly important to develop sensitive analytical methods to monitor EDCs in human milk in order to evaluate the exposure with the final objective of establishing, in an accurate way, relationships between EDCs and the harmful health effects observed.

In this work, a method based on a simplified sample treatment involving steps of precipitation, evaporation and clean-up of the extracts with C18 followed by ultra high performance liquid chromatography-tandem mass spectrometry (UHPLC-MS/MS) analysis for the determination of bisfenol A and its chlorinated derivatives, four PBs (methyl-, ethyl-, propyl- and butylparaben) and six BPs (benzophenone-1, -2, -3, -6, -8 and 4-hydroxybenzophenone) in human breast milk samples is proposed and validated. The limits of detections ranged from 0.02 to 0.05 ng mL^{-1}. The method was validated using matrix-matched standard calibration followed by a recovery assay with spiked samples. Recovery rates ranged from 91% to 110% and the precision (evaluated as relative standard deviation) was lower than 15 % for all compounds. The method was applied for the determination of these compounds in samples collected from 10 randomly selected women.

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OQA-P03

EVALUATION OF IONIC LIQUID STATIONARY PHASES FOR THE GC-MS ANALYSIS OF CARBOHYDRATES

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Due to the high resolution, sensitivity and structural information that gas chromatography coupled to mass spectrometry (GC-MS) provides, this technique has been widely applied to the analysis of low molecular weight carbohydrates (LMWC). Ionic liquids (ILs) have been introduced as novel GC stationary phases since they present some advantages over classical phases prepared with polysiloxanes and poly(ethylene glycols) such as lower column bleed, higher thermal stability, etc.[1].Moreover, the different selectivity as compared to conventional phases and their noteworthy capacity to resolve complex mixtures has made commercial ILs stationary phases very versatile for different applications [1-3]. However, to the best of our knowledge, these stationary phases have not been previously used for carbohydrate analysis. Thus, the aim of this study was to evaluate the usefulness of 5 commercial IL capillary columns of different polarities (SLB^{TM}-IL59, 60, 76, 82 and 100) for the analysis of LMWC, including mono-, di- and trisaccharides, inositols and iminosugars. Two classical GC stationary phases (100% methyl polysiloxane and poly(ethylene glycol)) were also included in this study for comparative purposes.

Comparable GC temperature programs were used for the different columns. Retention indices for the trimethylsilyl-oximes of the LMWC under study were obtained. No carbohydrate was eluted in SLB^{TM}-IL100 while SLB^{TM}-IL59, SLB^{TM}-IL60 and SLB^{TM}-IL76 columns allowed mono- di-, trisaccharides and inositols to be eluted; however, iminosugars could not be determined in any of them. SLB^{TM}-IL82 allowed the satisfactory analysis of all the studied carbohydrates. The effect of temperature conditions (programmed and isothermal) on resolution, peak width and tailing factor of target carbohydrates was evaluated in SLB^{TM}-IL82. Finally, the optimized chromatographic conditions were applied to the analysis of different real samples rich in LMWC. In all cases the simultaneous analysis of sugars, iminosugars and inositols was feasible.

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OQA-P04

FIELD-FLOW FRACTIONATION AND CAPILLARY ELECTROPHORESIS OF FUNCTIONALIZED FULLERENES

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Fullerenes are carbon-cage nanoparticles with widespread commercial and industrial application. Nowadays, fullerenes functionalized with polar groups are produced in high quantities, especially for use in pharmaceutical and clinical applications (e.g. as drug carriers, tumor inhibitors). Fullerenes are increasingly studied in relation to their potential risk for the environment and human health. However, they show a strong tendency to aggregate into clusters, which alters their reactivity, toxicity, fate and transport in the environment. In this context, it is important to develop specific analytical methods for (functionalized) fullerenes and especially for their aggregates. In this study asymmetrical flow field-flow fractionation (AF4) and capillary electrophoresis (CE) are used to fractionate and characterize functionalized fullerene aggregates.

AF4 is a versatile technique that allows the separation and characterization of aggregates over a wide size range, from nano- to micrometers. Till now, AF4 has been used mostly for the characterization of pristine fullerene aggregates in water (aqu/C_{60}) [1]. Another technique that can be used for the physicochemical characterization and separation of species from low molecular weight (inorganic ions) to complex organic molecules (proteins, nucleic acid, peptides, etc) is capillary electrophoresis (CE) and its application to the analysis of fullerene compounds has been previously reported [2]. In this work, AF4 with multi-angle light scattering (MALS) detection and CE-UV were used to study the aggregation behavior of functionalized fullerenes (polyhydroxyfullerenes and carboxylic C_{60}-derivatives). The AF4-MALS results showed that the retention of the fullerenes increased with the ion strength due to a decrease of the electrostatic repulsion between the channel wall and the fullerenes. Polyhydroxyfullerenes showed small particle sizes (≈10 nm) with increasing aggregation with the ionic strength. In contrast, the size of the carboxylic C_{60}-derivative aggregates was significantly larger (≈ 300 nm) in pure water, but decreased with the addition of salt, possibly due to the higher hydrophobicity of these compounds compared with polyhydroxyfullerenes. The electrophoretic behavior of functionalized fullerenes was studied at different pH values and ionic strengths. The ionic strength affected significantly the shape of the electrophoretic peaks due to a change in the size of the aggregates, as was also demonstrated by the AF4-MALS results.

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OQA-P05

DETERMINATION OF Sb^{3+} USING AdSV. EFFECT OF SULFONIC ACID SUBSTITUDED LIGANDS ON THE SENSITIVITY OF THE METHODS

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Anodic stripping voltammetry (ASV) and adsorptive stripping voltammetry (AdSV) have been the most widely used electroanalytical techniques for metal ion determination.

The choice of ligand must be adequate for a substantial accumulation of the complex on the electrode surface during the accumulation step. Neutral and less polar compounds are adsorbed on the electrode surface, while charged compounds are adsorbed to a lower extent. With the aim of decreasing the positive charge of the metal in the complex and increasing the latter's adsorption, ligands with anionic groups can be used. The sulfonic acid group is a possibility because it has a low pK_a, and therefore in water it is deprotonated and contributes with a negative charge in the complex.

In the present work quercetin (Q) and 8-hydroxyquinoline (HQ), with their corresponding sulfonic acid derivates (quercetin-5`-sulfonic acid (QS) and 8-hydroxyquinoline-5-sulfonic acid (HQS)) were studied as complexing agents for the determination of antimony(III) by adsorptive stripping voltammetric in water samples.

The experimental parameters pH, ligand concentration, potential, and accumulation time were optimized. The optimum ligand concentrations for sulfonic acid derivatives in both cases are higher than those of complexing agents without sulfonic groups, and the negative charge of the sulfonic acid group increases their solubility in water, thereby decreasing the adsorption of sulfonic ligands on the electrode surface. Calibration plots were made under the optimal experimental parameters, and the linear range and detection limits were determined.

For the HQ and HQS pair the linearity was maintained until 12.0 μgL^{-1} in both cases, and the detection limits were 0.1 μgL^{-1} and 0.014 μgL^{-1}, respectively, with 30 s of accumulation time. The slopes of the calibration plots were 2.6 and 5.8 $nA(\mu gL^{-1})^{-1}$, respectively.

In the case of Q and QS, the linearity was maintained until 10 μgL^{-1} in both cases, and the detection limits were 0.076 μgL^{-1} and 3.6 ngL^{-1}, respectively, with 60 s of accumulation time. The slopes of the calibration plots were 2.6 and 44.0 $nA(\mu g\ L^{-1})^{-1}$, respectively.

The developed methods using ligands with sulfonic acid groups presented higher sensitivities and lower detection limits than unsubstituted ligands, and they may increase the sensitivity of AdSV methods for some other metal ions.

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OQA-P06

ELECTROCHEMICAL BEHAVIOR OF Cu(I) AT Pt ELECTRODE IN IONIC LIQUID 1-BUTHYL -3-METHYLIMIDAZOLIUM CHLORIDE

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The electrochemical behaviour of $CuCl_x^{1-x}$ solutions in 1-buthyl-3-methylimidazolium chloride (BMIMCl) ionic liquid, has been investigated on a platinum electrode at 343.15 K, by different electrochemical techniques (i.e. square wave voltammetry (SWV), cyclic voltammetry (CV), convolutive potential sweep voltammetry (CPSV), chronoamperometry (CA), and chronopotentiometry (CP)).

Figure 1.- Electrochemical behavior of Cu(I) on Pt electrode in BMIMCl at 353,15 K.
Two electrochemical systems have been detected (Figure 1) corresponding to the electrochemical exchanges:

$CuCl_4^{3-} + 2Cl^- \rightarrow CuCl_6^{4-} + 1e^-$
$CuCl_4^{3-} + 1\ e^- \rightarrow Cu(0) + 4\ Cl^-$

The electro-oxidation of Cu(I) to Cu(II) follows a simple mechanism, that has been found as reversible or quasi-reversible depending on the work conditions (i.e. scan rate). The intrinsic rate constant of charge transfer, k^0, and the charge transfer coefficient, a, have been calculated for the first time in the mentioned ionic liquid, by simulation of the cyclic voltammograms, logarithmic analysis of the convoluted curves and from the steady-state current potential curves by applying the Gauss–Newton non-linear square method.

The diffusion coefficient of $CuCl_4^{3-}$ has been also calculated by CV, CPSV, CP and CA.

Electro-crystallization of cooper plays an important role in the electrodeposition process. The experimental chronoamperometric curves are compared with theoretical models based on instantaneous and progressive nucleation.

Keywords Cooper, BMIMCl, Electrochemical behavior, Diffusion Coefficient, Kinetic parameter

Acknowledgements.- This work was supported by the Ministerio de Ciencia e Innovación (Spain) Project CTQ2010-19912.

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OQA-P07

ELECTROCHEMICAL BEHAVIOR OF EU(III) AT INERT ELECTRODES IN IONIC LIQUID 1-BUTHYL -3-METHYLIMIDAZOLIUM CHLORIDE

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The electrochemical reduction of Eu(III) on Glassy Carbon (GC) and Platinum (Pt) electrodes in the ionic liquid 1-buthyl-3-methylimidazolium chloride (BMIMCl), has been investigated at 343-373 K by square cyclic voltammetry (CV), convolutive potential sweep voltammetry (CPSV), square wave voltammetry (SWV), chronoamperometry (CA), and chronopotentiometry (CP).

On both electrodes, the electro-reduction of Eu (III) takes place between dissolved species, there are not chemical reactions coupling to the charge transfer step, neither adsorption process, being similar the diffusion coefficients of Eu(III) and Eu (II).

The intrinsic rate constant of charge transfer, k^0, and the charge transfer coefficient, a, have been calculated, for the first time in the mentioned ionic liquid, by simulation of the cyclic voltammograms, logarithmic analysis of the convoluted curves and from the steady-state current potential curves by applying the Gauss–Newton non-linear square method. Taken into account the Matsuuda and Ayabe criteria the exchange Eu(III)/Eu(II) can be qualified as quasi-reversible.

The diffusion coefficient (D) has been also calculated by CV, CPSV, CP and CA.

Figure 1.- Cyclic voltammograms of Eu(III)/Eu(II) on GC electrode in BMIMCl at 353,15 K.

Keywords: Europium, BMIMCl, Electrochemical behavior, Diffusion Coefficient, Kinetic parameters

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OQA-P08

ELECTROCHEMICAL BEHAVIOUR OF TERBIUM IN THE EUTECTIC LICl-KCl IN Cd LIQUID ELECTRODES

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The electrode reaction of Tb(III)/Tb couple in the eutectic LiCl-KCl, at Cd liquid electrodes (i.e a Cd pool and a Cd coated W electrodes) was investigated in the temperature range of 673-823K. In both electrodes, the electrochemical reduction of Tb(III) was observed at less cathodic potential values than at the surface of an inert W electrode, due to the decrease of Tb activity in the metal phase.

Cyclic voltammetry, using a Cd bulk electrode, suggest a quasi-reversible behaviour of the system Tb(III)/$Tb_{(dissolved\ in\ liquid\ Cd)}$, and the values of the kinetic parameters, k^0 and *a*, as well as the reversible half wave potential, $E^r_{1/2}$, have been obtained. The differences between the equilibrium potential adopted by a Tb electrode and the $E^r_{1/2}$ observed with the same Tb(III) solution at the Cd pool electrode, were used to calculate approximate values of the excess Gibbs energy change of Tb in liquid metal, and hence the activity coefficient of Tb in Cd.

The formation of intermetallic compounds was also studied. Electromotive force, *emf,* measurements for five intermetallic compounds in two-phase coexisting states were carried out using a Cd coated tungsten electrode. The activities and relative partial molar Gibbs energies of Tb were obtained for $TbCd_6$, $TbCd_{45/11}$, $TbCd_3$, $TbCd_2$ and TbCd. The formation energy of each intermetallic compound, and the global formation constants were also calculated. The linear dependence of the Gibbs free energies with temperature yields to the enthalpies and entropies of formation of the five intemetallic compounds.

Analysis of the samples after electrolysis runs by scanning electron microscopy (SEM) with energy dispersive X-ray allowed the identification of $TbCd_6$, $TbCd_3$, $TbCd_2$ and TbCd.

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OQA-P09

OXOACIDITY BEHAVIOUR OF Tb(III) AND ELECTROCHEMICAL FORMATION OF Tb-Ni ALLOYS IN THE EUTECTIC LiCl-KCl

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Rare earth (RE) metals and their alloys are increasing in importance, particularly in the fields of magnetism, energy and high technology. The use of molten salts as reaction media provides a unique opportunity for the electrowinning and electrorefining of high purity RE metals, as well as for the electrochemical synthesis of their alloys. Another important issue concerning REs and molten salts is pyrochemical reprocessing of nuclear fuel. The transmutation of the more hazardous radionuclides in the nuclear waste into less hazardous or shorter lived elements would significantly reduce the volume and the required storage time for the waste, and can be done only after separation of minor actinides (Ans) from other fission products, specially lanthanides (Lns). This separation process can be carried out in molten salt media, whose properties allow high actinide content, shorter cooling times and inherent proliferation resistance.

Ans-REs separation in molten chlorides contemplates a two-step process: (i) selective extraction of Ans and (ii) extraction of (REs) for decontamination of the salt. Our studies are devoted to the acquisition of fundamental data of REs to allow design and assessment of reprocessing processes involving: (i) electrolytic extraction using inert (e.g. W and Mo) and reactive (e.g. Cd, Bi, Ni or Al) cathodes and (ii) selective dissolution/precipitation of rare earth oxides.

The electrochemical formation of Tb-Ni alloys was investigated at 723K in the eutectic LiCl-KCl. On reactive Ni electrode, the electrochemical system Tb(III)/Tb(0) was observed at less cathodic potential values that on an inert W electrode, this potential shift is caused by the decrease of Tb activity in the metal phase due to the formation of Tb-Ni intermetallic compounds. Analysis of the samples after electrolysis by X-ray diffraction and SEM with EDX, allowed the identification of different intermetallic compounds.

The identification of the Tb-O compounds as well as the determination of their solubility products were carried out by potentiometric titration using an yttria stabilised zirconia membrane electrode (YSZME). The results indicated the stability of TbOCl and Tb2O3. The best chlorinating conditions have been extracted from the comparison of the E-pO2- diagram corresponding to the Tb-O compounds and that of some chlorinating mixtures.

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OQA-P10

DIRECT INJECTION METHOD TO DETECT β-BLOCKERS AND METABOLITES IN URINE BY UPLC-MS/MS IN DOPING CONTROL

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β-Adrenergic antagonists (β-blockers) are drugs prohibited by the World Antidoping Agency (WADA) in some sports and, therefore, laboratories need fast and reliable methods to detect their use. The objective of the study was to develop a direct injection method for the detection of 21 b-blockers and their metabolites in urine, including compounds excreted in free form as well as metabolites conjugated with glucuronic acid or with sulphate.

The method consisted on a dilution (1:5) of the urine sample with a mixture of deionized water, acetonitrile and formic acid containing the internal standard. The analysis was carried out by ultraperformance liquid chromatography coupled to tandem mass spectrometry using a C18 column (100 mm × 2.1 mm i.d., 1.7 µm particle size), with a total run time of 6 minutes. Electrospray ionization in positive mode was used. Specific ion transitions were monitored for each metabolite under study.Optimization of the mass spectrometric detection conditions to detect sulphate and glucuronoconjugated metabolites, which are not commercially available as reference standards, was performed using urines collected after administration of the drugs.The method was validated for the free metabolites according to international quality standards (limit of detection, selectivity, intra-assay precision, carry over were evaluated). The limit of detection was 50 ng/mL for all the analytes which is in agreement with the minimum performance limits established by WADA. The usefulness of the method was validated using urines obtained after the administration of the drugs.

In the lasts years, “dilute and shoot” techniques have being applied by the antidoping control laboratories to screen for some substances and this is the first time that a “dilute and shoot” method to screen for b-blockers in urine including free and conjugated metabolites is described.

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OQA-P11

DIRECT POLYETHYLENE FINGERPRINTING BY PYROLYSIS-COMPOUND SPECIFIC ISOTOPE ANALYSIS (Py-CSIA)

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A low-density green polyethylene was studied using conventional analytical pyrolysis (Py-GC/MS), bulk C, N, H, O isotopic ratio (TC/EA-IRMS) and direct pyrolysis compound specific isotope analysis (Py-CSIA) of stable light elements C, N, and H (Py-GC- (FID)-C/TC-IRMS). Py-GC/MS (500 ºC) released series of *n*-alkane, α-alkene and α,ω-diene (C8 to C37). A peak at *c.* min. 6 was identified as o-Chloroaniline (1-Amino-2-chlorobenzene) corresponding to the plastic's green dye. Bulk plastic isotopic values (TC/EA-IRMS) were $\delta^{13}C$=-30.16±0.60 ‰ δD=-79.23±0.28 ‰ and $\delta^{18}O$=+15.33±0.59 ‰ $\delta^{15}N$ was not detected due to a relative low signal contribution from the sole N bearing dye compound. Py-CSIA confirmed a similar $\delta^{13}C$ (-30.13±0.60 ‰) for the three homologous series (*n*-alkane -29.48±0.69 ‰ α-alkene -29.86±0. 36 ‰; α,ω-diene -30.26±0.54 ‰) but different from that *o*-Choloroaniline (-27.13±0.56 ‰). Only for this molecule $\delta^{15}N$ could be measured (+21.87±1.97 ‰). These signatures are in line with tabulated values for synthetic materials but indicate that polyolefin and dye are probably from two distinct origins. In the range where it was possible to unambiguously measure isotope ratio (no co-elution zone between C12 and C19), Py-CSIA for hydrogen revealed significant different compound specific δD values for the three structures (*n*-alkane -98.87±5.40 ‰; α-alkene -74.74±1.50 ‰; α,ω-diene -67.38±2.98 ‰). A significant enrichment in the heavy isotope with chain length was observed for *n*-alkanes, best explained by the quadratic equation $\delta D=0.59Cx^2-16.38Cx+11.01$ (r^2=0.959). The original structure of the casted plastic have tertiary carbons with higher polarity, our results suggests that these may act as deuterium concentrators. The incorporation of the most probable isotope (light ^1H) into the *n*-alkane chains when cracking may be the cause of the observed decrease of the hydrogen isotopic values in short chain molecules. This effect is less obvious with increasing chain length due to a "dilution" effect and long chain *n*-alkanes tend to the isotopic signature of the unsaturates α,ω-dienes and α-alkenes. This finding is to be taken in consideration when measuring compound specific δD in polymeric materials using this new hyphenated Py-GC-TC-IRMS technique.

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OQA-P12

DETERMINATION OF NON-VOLATILE MIGRANTS FROM FOOD PACKAGING INKS BY UPLC-MS(QTOF). STUDY OF EXTERNAL LACQUERS EFFECT

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Inks are commonly used in food packaging materials and therefore, migration of ink components to food must be studied. Even though inks are commonly placed in the external side of packaging, ink components can migrate to food due to a set-off effect that takes place during packaging materials storage [1].

In this work, migration test from different multilayer materials containing inks to 2 food simulants (ethanol 95% and Tenax®) were performed and non volatile migrants were analyzed by UPLC-MS(QTOF). A total of 17 migrants coming from inks due to the set off effect were detected in migration from multilayer material [ink/PET/aluminum/polyethylene], such as some plasticizers or slip agents. The number of migrants decreased dramatically when a lacquer layer was added in the external side of packaging [lacquer/ink/PET/aluminum/polyethylene], and especially when ink was placed before PET [lacquer/PET/ink/aluminum/polyethylene]. Some new migrants appear by the reaction between ink and lacquer.

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OQA-P13

STUDY OF SET OFF IN MULTILAYER MATERIALS USED IN FOOD PACKAGING. DETERMINATION OF VOLATILE MIGRANTS BY GC-MS

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Most of food packaging multilayer materials contain inks, and eventhough there is no specific legislation for inks, final material must fullfil Directive UE No.1935/2004 and Directive EU/10/2011 for food contact materials and ink components must be included in EUPIA list [1].
In order to determine migration of ink components in different multilayer materials and to evaluate the effect on migration of applying an external lacquer layer, two sets of multilayer materials were selected for this study. Set A was composed by multilayer materials manufactured with polyethylene terephthalate, aluminum, polyethylene, lacquer and ink, and set B was composed by multilayer materials manufactured with paper, polypropylene, aluminum, polyethylene and ink.

The aim of this work was to study migration of volatile ink components from these materials to four different food simulants (acetic acid 3%, ethanol 95%, isooctane and tenax). After migration test, solutions were analyzed by GC-MS. Results showed that more than 20 compounds migrated from each of the materials. Comparison among migration solutions allowed determining those compounds coming from ink such as some plasticizers, curing agents or pigment components.

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OQA-P14

CAPILLARY ELECTROPHORESIS TO SELECT DEVICES TO STORE GLYCOPROTEINS

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Glycoproteins play an important role in many biological processes. Moreover, analyzing differences in the forms of glycoproteins could be useful for doping control and quality control of biopharmaceuticals. Also, these differences could be useful as biomarkers.

Capillary electrophoresis (CE) is an adequate technique to separate isoforms (peaks containing one or several glycoforms) of glycoproteins [1].

Usually glycoproteins of interest are in human samples at low concentrations, which is a problem for their manipulation and conservation. It is known that the adsorption isotherms of proteins to a given material are dependent on concentration; the adsorption effect is more significant for diluted solutions.

Thus, the devices used to store the glycoprotein samples have to be carefully selected to avoid adsorption of the analyte, which would decrease its concentration in the sample to be analyzed.

The objective of this work is to select the most appropriate commercial device to store different glycoproteins relevant in biomarker, biopharmaceutical, or doping fields.

Adsorption of each glycoprotein on commercial low-volume vials has been studied trying to simulate the conditions that the protein solution would experience during storage. To carry out this study, a low concentration of each glycoprotein has been chosen, so that a decrease in concentration caused by adsorption to the vial can be clearly observed by CE. Freshly made solutions of glycoproteins have been stored for several days in the refrigerator, analyzed during storage by CE, and the size of the isoforms (height, corrected peak area) measured.

The results show that adsorption in the different vials is dependent on the glycoprotein considered. For some of the vials tested glycoprotein adsorption is evident for storage as short as 24 hours. The information obtained in this study could be of practical value not only for glycoprotein handling for CE, but also in choosing the storage vial for each glycoprotein to be analyzed by other techniques.

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OQA-P15

ANALYSIS OF GLYCINE BETAINE BY HPCE-UV

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Glycine betaine, an amino acid derivate from sugar-beet, is a widely used compound in cosmetics and pharmaceuticals. Its multifunctional properties such as providing better skin feeling reducing stickiness, giving a long lasting moisturizer and its low toxicity makes glycine betaine an ideal compound for formulation in personal care field.

This study presents an analysis methodology for the determination of glycine betaine by capillary electrophoresis (CE) using UV detection. The methodology was applied for the direct analysis of glycine betaine, without any previous derivation reaction, in oil-in-water emulsions for a concentrations range between 0.3 and 5% (w/w). The analysis was performed at low pH and the detection was done by diode-array at 195 nm. The methodology proposed represents a simple, rapid and reliable technique for the determination of glycine betaine and represents an interesting proposal for further betaines analysis. The analytical characteristics of the proposed method were established by evaluating its selectivity, linearity, precision and accuracy.

In addition, other interesting properties for the optimization of the chromatographic conditions were studied. Considering that glycine betaine is a small N-trimethylated amino acid existing in zwitterionic form at a neutral pH (pka=1.83), a deeply study of the pH conditions was design. The main interest was to evaluate the dependency between the pH conditions and the mobilities of the species along the analysis. The successful results demonstrate the crucial importance of pH on the selectivity of the method.

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OQA-P16

IDENTIFICATION OF NEW MARKERS IN CHOLESTEROL METABOLISM RELATED DISEASES IN RAT LIVER BY UPLC-ESI-MS/QTOF

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Cholesterol performs essential functions in the living beings. The metabolism of cholesterol and their related metabolites is regulated mainly by the liver through three different processes: controlling the synthesis, absorbing the intestinal contribution of diet cholesterol, and managing the degradation processes.

Oxysterols are formed during cholesterol degradation processes. They are potent regulators of lipid homeostasis and they are considering as a markers of some cardiovascular diseases and other metabolic disorders [1]. In order to find new markers of these metabolic problems, rats with faulty cholesterol metabolism were generated (KO, *Knock Out*), and results were compared with those obtained for healthy rats (WT, *Wild Type*).

Tissue samples were obtained by liver biopsy and then triturated. Bligh/Dyer extraction was performed followed by a solid phase extraction [2]. Finally, samples were analyzed by ultra-performance liquid chromatography coupled to quadrupole time-of-flight mass spectrometry (UPLC-ESI-MS/QTOF).

Principal components analysis (PCA) was carried out with software Markerlynx ® from Waters. Markerlynx®. This software allows extracting the main markers (defined as retention time–exact mass pairs) and carrying out a principal components analysis (PCA) with them. In this way, it is possible to detect any possible sample grouping and also markers responsible of it.
Clear differences were observed between KO rats and WT rats. KO rats showed an enhancement in the expression of some metabolites which participate in cholesterol degradation pathway. This finding contributed to explaining part of its distinct pathogenic role.

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OQA-P17

ION MOBILITY SPECTROMETRY AS AN ALTERNATIVE ANALYTICAL TECHNIQUE IN ROUTINE LABORATORY

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Traditional analytical techniques such as atomic absorption spectroscopy, gas or liquid chromatography and mass spectroscopy present some disadvantages like time-consuming, are expensive and normally a pre-concentration of samples is needed[1]. Then, is necessary improve the analytic methods in order to apply in ordinary analysis such as in process of quality control in industry.

The Ion Mobility Spectrometry (IMS) is proposed as an alternative technique to employ in routine laboratory. The main advantages of IMS are the high sensitivity and fast data-acquisition[2]. The minimal solvent consumption and the low waste generation convert IMS in to a low cost analytical technique. In addition, the sample normally does not need pre-treatment.

The aim of this work is show the results obtained using IMS as analytical technique to determine volatile and semivolatile compounds in different samples. The results denote that IMS can be used as an alternative rapid and efficient technique in front of standard techniques in detection of illegal drugs in ordinary controls, analysis of compounds in process of quality control in industry and in environmental analysis.

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OQA-P18

EFFECT OF CPB ON As(III) TRACE AS DDTP COMPLEX BY AdSV DETERMINATION IN PRESENCE OF COPPER IONS

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Arsenic is a ubiquitous element present in atmosphere, soil and rocks, natural waters and organisms. Natural processes and anthropogenic activities are triggers of As emission and that may be mobilized in the surface. The most common route entry to the body is through the intake of arsenic in water or food and respiratory for dust. Arsenic toxicity depends on chemical forms and oxidation states. However, it is known that As^{3+} is more toxic that other arsenicals species.

Cathodic stripping voltammetry (CSV) at a hanging mercury drop electrode (HMDE) has been used to determine arsenic in natural and drinking waters. This method requires the presence of Cu(II) in acid media, as involves the pre-concentration of a copper–arsenic intermetallic compound at the mercury electrode and then stripped cathodically. In order to improve the sensitivity, has been incorporated the use of ligands, which form complexes with the metal. These complexes may interact with adequate surfactant adsorbed on the surface of electrode increasing concentration in the step of accumulation and increasing the sensitivity of the methodology [1,2].

In this work, the effect of cetylpyridinium bromide (CPB) on the arsenic trace level in the presence of copper ions using HMDE was evaluated. Furthermore, sodium dimethyldithiophosphate (DDTP) was used as ligand. Supporting electrolyte, potential and time in the accumulation step (E_{acc}, t_{acc}), and Instrumental parameters were optimized in order to obtain the better current signal for the As^{3+}.

The best experimental conditions were C_{DDTP} 1.6 $\mu molL^{-1}$ (As^{+3} 20 μgL^{-1}), C_{CPB} 10 $\mu molL^{-1}$, t_{ads} 60 s, E_{ads} -0.10 V. When CPB was added the peak current of As increased until 15 $\mu molL^{-1}$ and then decreased slightly. Peak current is proportional to As concentration over the 0.5–15.0 μgL^{-1} range, with a 3σ detection limit of 10 ngL^{-1}. Under these working conditions, Ni, Mo, Cd, Pb, Tl, Bi, Be and Sb until 150 μgL^{-1}, and Co and Zn until 10 μgL^{-1} no interference were found (As:10 μgL^{-1}). The method was validated using water spiked with As^{3+}.

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OQA-P19

ENANTIOSEPARATION OF *N*-DERIVATIZED AMINO ACIDS BY NANO-LC WITH CARBAMOYLATED QUINIDINE MONOLITHIC STATIONARY PHASE

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The stereochemistry of amino acids plays an important role in their biological and pharmacological properties.Therefore, the enantioseparation of *N*-derivatized amino acids remains a hot research topic even if well advanced. In previous studies, poly (O-9-[2-(methacryloyloxy)-ethylcarbamoyl]-10,11-dihydroquinidine-*co*-2-hydroxyethyl methacrylate-*co*-ethylene dimethacrylate) (poly(MQD-*co*-HEMA-*co*-EDMA)) monolithic columns exhibited very good enantioselectivity and column efficiency in the CEC mode for several *N*-derivatized amino acids, such as carbazole-9-carbonyl (CC)-Alanine, CC-Serine, and 3,5-dinitrobenzoyl (DNB)-Leucine [1]. However, their applicability to nano-LC separations has not been reported so far.

In this work, in order to obtain satisfactory column permeability, efficiency and selectivity for nano-LC, a poly(MQD-*co*-HEMA-*co*-EDMA) capillary monolithic column was re-optimized. The monolithic column showed excellent morphology, good permeability, reproducibility, mechanical and chemical stability and satisfactory chromatographic performance in nano-LC. The column was used to successfully enantioresolve a wide range of N-derivatized amino acids including alanine, leucine, methionine, threonine, phenylalanine, valine, serine, isoleucine, tryptophan, and cysteine. The influence of the mobile phase parameters, such as the organic solvent type and concentration, the apparent pH, and buffer concentration, on retention and enantioseparation of N-derivatized amino acids was investigated. The highest enantioresolution values were observed for 3,5-DNB-derivatives, followed by 3,5-dichlorobenzoyl amino acids. For instance, α value of ~ 6.98 and R_s value of ~ 8.74 for 3,5-DNB-Isoleucine enantiomers were obtained. The chemoselectivity of the monolithic column for a multicomponent mixture of *N*-derivatized amino acids was also investigated.

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OQA-P20

CHARACTERIZATION OF LASER-INDUCED PLASMAS OF ORGANICS BY SPATIAL- AND TEMPORALLY RESOLVED EMISSION SPECTROMETRY

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The large majority of laser-induced plasmas experiments are performed on metals in air at atmospheric pressure, where recombination mechanisms do not play a significant role, as the primary emission lines of interest are significantly more intense than those derived from recombination with air, particularly those yielding oxides. Due to the large number of electronic transitions commonly attainable on metals, many intense emission lines are recorded and different regions of interest useful for identification and quantification purposes may be assigned.

The main difficulties in the interpretation of the molecular emission of species containing C, N, O or H relies on the questions concerning their origin: direct release from native bonds or recombination with ambient constituents. In other words: does the resultant spectrum mimic the structure of a molecule or the molecular information gets lost in the course of the secondary reactions? Considering that the spectrum observed is always a convolution of primary and secondary processes, experiments in vacuum or in controlled atmospheres may help to address such questions.

The present work shows detailed experiments where spatially- and temporally-resolved optical emission spectroscopy of laser-produced plasmas on organic compounds has been performed. The experiments cover a pressure range from 1000 mbar to 10-3 mbar that allows a precise observation of the effect of the surrounding atmosphere in the formation of species by recombination.

NDP-P01

EVALUATION OF A DIRECT SAMPLE INTRODUCTION METHOD FOR PHTHALATE ESTERS DETERMINATION IN CLEANING PRODUCTS BY GC-MS

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Phthalates are mainly employed as plasticizers, but also as additives to detergents. These compounds have become widespread contaminants as result of their migration from their original containers to the surrounding environment, and their estrogenic characteristics, affecting reproductive capacity and endocrine regulation. The presence of phthalates in cleaning products has been previously assessed [1], and in this work, a method using direct sample introduction (DSI) coupled to GC-MS has been developed for the determination of six of them in these products.

DSI is a sample introduction procedure related with large volume injection. In DSI sample is placed in a glass microvial that is submitted to a temperature program in a thermal desorption unit. Volatile compounds are vaporized and transferred to the GC column, while non-volatile interfering matrix components remain in the vial [2]. Different variables involved in the DSI step, like venting time and temperature, vaporization time and temperature, PTV heating temperature and gas flow rate and pressure, were evaluated and optimized using Taguchi orthogonal arrays.

The proposed method showed good linearity in the concentration range 5-500 ng g^{-1} and good repeatability, with RSD values ranging from 3.5 to 5.7%. Detection limits (calculated for a signal-to-noise ratio of 3) ranged between 0.12 and 0.49 ng g^{-1}. Recovery assays (performed at 20 and 50 ng g^{-1}) provided values from 83 to 115%. Twenty seven household cleaning products were analyzed using the DSI-GC-MS procedure, being four phthalates (dimethyl, diethyl, dibutyl and diethylhexyl phthalate) found at concentration levels in the 0.1-21 ng g^{-1} range.

A classic direct injection procedure was conducted for comparison purposes. DSI procedure provided larger peak areas (21-30 fold), and lower detection limits (3-8 fold) than the direct injection method. The higher sensitivity is related to the greater injected volume (50 µL vs. 2 µL) and the reduction of the noise associated with non-volatile matrix components, which remain retained in the sample microvial.

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NDP-P02

OPTIMIZATION OF A NEW DLLME METHOD FOR THE DETERMINATION OF QUINOLONES AND β-LACTAMS IN MILK BY UHPLC-MS

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Antibiotics are widely used in the veterinary field for the treatment of diseases in food-producing animals such as cows, pigs or chicken. The widespread use represents a potential risk to human health, because residues of these substances may be present in edible tissues and milk destined for human consumption. To protect human health, the EU has established safe maximum residue limits (MLRs) for veterinary drugs in animal tissues and milk destined for human consumption (EU Regulation 37/2010).

For the determination of these antibiotic residues in milk, it is necessary to develop methods of extraction and analysis that are sensitive enough to ensure that such residues are not present at levels that may pose health risks to the public.

An analytical method based on a sample treatment by dispersive liquid-liquid microextraction (DLLME) followed by ultra high performance liquid chromatography-tandem mass spectrometry analysis (UHPLC-MS/MS) for the determination of quinolones and *β*-lactams (penicillins and cephalosporins) in raw cow milk,was validated according to the European guidelines (Decision 2002/657/EC).

The extraction efficiency of the DLLME depends on several parameters such as the nature and volumes of extractant and dispersive solvents, pH, concentration of salt, shaking time and time of centrifugation. These variables were accurately optimized using multivariate optimization strategies. A Plackett-Burman design to select the most influential parameters and a Doehlert design to obtain the optimum conditions have been applied. Two different pH values were used for the extraction of compounds (pH = 3 for acidic quinolones and β-lactams and pH = 8 for amphoteric quinolones).

The method was validated using matrix-matched standard calibration followed by a recovery assay with spiked samples. The LOQfound ranged from 0.3 μg $kg^{-1}$for amoxicillin to 6.6 μg $kg^{-1}$for ciprofloxacin, and the precision was lower than 15%. Recoveries higher than 72% were obtained. The decision limits (CC_α) ranged between 4.1 and 104.8 μg kg^{-1}, while detection capabilities (CC_β) from 4.2 to 109.7 μg kg^{-1}, for the studied antibiotics. Finally, in order to evaluate the applicability of method, 28 raw cow milk samples were analysed. 28% of the samples were positive but only 11% were considered non-compliant with the current EU legislation.

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NDP-P03

DETERMINATION OF PERSONAL CARE PRODUCTS BY VORTEX-ASSISTED EMULSIFICATION MICROEXTRACTION AND UHPLC-UV

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Personal care products (PCPs) refer to a group of organic chemicals recently categorized as emerging contaminants due to probable endocrine disrupting activity and even possible carcinogenic effects in humans.

They are present in a wide variety of dairy products such as gels, lotions, or cosmetics. Once PCPs are applied onto the human body, they can directly or indirectly reach the environment. PCPs are not completely removed from wastewater treatments plants, thus being retained in the sewage sludge or accumulated in the effluents. Therefore, humans are exposed to a variety of PCPs sources other than those coming from personal direct use [1].

PCPs can be classified attending to their specific utilization: preservatives (as parabens), ultraviolet filters (as benzophenones), antimicrobials (as triclosan), musk fragrances, insect repellents (as DEET) and siloxanes.

Given their low levels in environmental samples, it results of enormous interest the development of sensitive analytical methods for their monitoring. Within the analytical trends, it is also advisable the establishment of methods able to fulfill characteristics of greenness, low organic solvent consumption and short analysis time.

In this work, it has been developed a vortex-assisted emulsification microextraction which does not require the use of organic solvent acting as dispersive agents. This liquid-phase microextraction method is used in combination with ultra-high performance liquid chromatography with ultraviolet detection for the determination of 10 PCPs in different environmental waters. Overall, the method is characterized for low requirements of organic solvent in the extraction step (few microliters), keeping characteristics of sensitivity (low part per billion levels) and reproducibility, with short time requirements.

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NDP-P04

USE OF Mn-DOPED ZnS QUANTUM DOT – MOLECULARLY IMPRINTED POLYMERS FOR COCAINE FLUORESECENCE SCREENING IN URINE SAMPLES

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A novel method based on the quenching of fluorescence emission from Mn-doped ZnS quantum dots (QDs) – molecularly imprinted polymer (MIP) by cocaine and analogues has been developed for cocaine screening in urine samples. Mn-doped ZnS QDs were synthesized in inert atmosphere followed by polyethileneglycol (PEG) modification and synthesis of molecularly imprinted polymer onto the QD surface by precipitation method. Cocaine was used as a template; whereas, ethylene dimethacrylate (EDMA) and divinylbenzene (DBV) were used as a monomer and as a cross-linker, respectively. 2-2'-azoisobutyronitrile (AIBN) was used as an initiator. The PEG-QD-MIP material was found to be selective for cocaine and the main metabolites (benzoylecgonine, BEC; and ecgonine methyl ester, EME). Fluorescence operating conditions imply an excitation wavelength of 297 nm, an emission wavelength of 590 nm, 100 mg PEG-QD-MIP, a pH of 5.5 (use of sodium dihydrogen phosphate/disodium hydrogen phosphate buffer), and 15 min as delay time before fluorescence measurement.

Urine samples were subjected to an optimized solid phase extraction method (Bond Elute Certify cartridges) by loading 1 mL of sample, followed by four rinsing stages with ultrapure water (3 mL), 0.1 M hydrochloric acid (3 mL), methanol (9 mL) and 0.3 M ammonium hydroxide (3 mL). Elution was performed by passing 3 mL of a chloroform-isopropanol (4:1) mixture. After N_2 stream evaporation to dryness, the residue was re-dissolved with 100 µL of sodium dihydrogen phosphate/disodium hydrogen phosphate buffer (pH 5.5). Matrix effect was found to be negligible, and aqueous calibration could be used for measurements. The limit of detection (LOD) and the limit of quantification (LOQ) were 0.0042 and 0.014 mg L^{-1}, respectively. The method was validated in accordance with FDA guidance. In addition, the screening procedure was finally applied to several cocaine positive urine samples, and results were statistically compared to those obtained for confirmative purposes by well-established HPLC-MS/MS methodologies.

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NDP-P05

DISPERSIVE LIQUID–LIQUID MICROEXTRACTION METHOD BASED ON SOLIDIFICATION OF FLOATING ORGANIC DROP

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In the last years, interest in faster, simpler, cheaper and more environmentally-friendly extraction methods than traditional liquid–liquid extraction and solid-phase extraction is continuously increasing. Dispersive liquid-liquid microextraction (DLLME) is a novel extraction technique easy to operate, allows high enrichment factors, requires low solvent volumes and it is fast and inexpensive so it is highly suitable to be used for routine monitoring control. The operational and analytical benefits of DLLME have encouraged some authors to employ it for the extraction of organic pollutants from aqueous samples [1]. DLLME is based on a three-component solvent system: a high-density solvent (extraction solvent), a water-miscible polar solvent (disperser solvent) and the aqueous sample. To overcome some of the disadvantages of conventional DLLME, some variations such as the use of solvents with density lower than water, the use of more environmentally-friendly solvents or the solidification of the organic drop has been proposed (*dispersive liquid–liquid microextraction based on the solidification of floating organic drop*, DLLME-SFO).

In this work, a novel, simple, rapid and sensitive DLLME-SFO method combined with high-performance liquid chromatography–mass spectrometry has been developed and validated for the determination of five phenolic compounds (nonylphenol, bisphenol A and methyl-, ethyl- and propylparabens), four estrogens (17α-ethinylestradiol, 17b-estradiol, estriol and estrone), six perfluoroalkylated compounds (perfluorooctane sulfonic acid and five perfluoroalkyl carboxylic acid), and the brominated flame retardant hexabromocyclododecane in surface and tap water. Parameters optimized werethe type and volume of the extraction and disperser solvents, extraction time, ionic strength and sample pH.

The precision of the method, expressed as relative standard deviation, ranged from 1 to 16%. Method detection limits varied between 0.001 and 1.126 μg L^{-1} in surface water and from 0.001 to 1.031 μg L^{-1} in tap water. The applicability of the proposed method was demonstrated analyzing surface and tap water samples from Seville (South of Spain). Most of pollutants were detected at concentration levels between 0.894 μg L^{-1} (nonylphenol in surface water) and 0.012 μg L^{-1} (perfluorohexanoic acid) in surface water.

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NDP-P06

NOVEL SOLID-PHASE MICROEXTRACTION SORBENT COATINGS BASED ON TWO-LAYER POLYMERIC IONIC LIQUIDS

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The monitoring of organic compounds at trace levels, in environmental and industrial samples, demands rapid, cheap, and safe preconcentration and extraction methods. Solid-phase microextraction (SPME) is a solvent free sample preparation technique that possesses many advantages such as rapidity, simplicity and an easy operation. The simple design of SPME fibers allows quick and cost-effective extractions and the analytes can be easily delivered to chromatographic or electrophoretic systems. In the last years, polymeric ionic liquids (PILs) have emerged as a new class of SPME sorbent coatings. PILs typically exhibit high viscosity that prevents them from flowing into the gas-chromatography (GC) injector, at high operation temperatures, and high thermal stability.In comparison to commercial coatings, PILs possess the major advantage of structural tunability for the selective extraction of target analytes [1].

In this work, two-layer PIL-based SPME sorbent coatings were developed for the extraction of 24 analytes including alcohols, ketones, aldehydes, esters, amines, alkyl halides and aromatic compounds from aqueous samples. GC-MS was used for the detection of the analytes. Two-layer coatings were used in order to improve selectivity and fiber protection.Two previously synthesized PILs,were combined in different positions and tested as sorbent coatings for SPME-GC: poly(1-vinyl-3-hexylimidazolium) chloride (poly([VHIM][Cl-])) and poly(1-vinyl-3-hexadecylimidazolium) bis[(trifluoromethyl)sulfonyl]imide (poly([VHDIM][NTf_2])). Polymerization of the IL monomers was carried out by free-radical polymerization via ultraviolet photoinitiation on a fused silica support. Mixtures composed by various amounts of the IL cross-linker, UV initiator (DAROCUR 1173), and IL monomer were dip-coated onto an etched and derivatized fused-silica support and placed into a high-capacity UV reactor.

An enhancement of the extraction efficiency was observed for most of the analytes when the fiber with (poly([VHDIM][NTf_2]) in the external layer was used. This effect was less pronounced for polar analytes. This fact indicates that the longer hydrocarbon chain substituent on the PIL poly([VHDIM][NTf_2]) located on the external layer exhibits higher extractive power, due to its dispersive forces, than the hydrogen-bonding basicity derived from the poly([VHIM][Cl]).

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NDP-P07

IONIC LIQUIDS AND DERIVATIVES IN DISPERSIVE LIQUID-LIQUID MICROEXTRACTION FOR DETERMINING Cu IN WATERS BY AAS

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Ionic liquids (ILs) are non-molecular solvents with low melting points (below 100ºC). They are formed only by ions: mainly asymmetric organic cations like imidazolium or pyridinium, together with organic or inorganic anions. ILs present unique properties such as high thermal stability, low to negligible vapor pressure at room temperature, and tuneable solvation ability. These qualities make ILs adequate substitutes of organic solvents in extraction procedures, as greener solvents. Among interesting derivatives of ILs, polymeric ionic liquids (PILs) and ionic liquid-based surfactants (ILBSs) can be included.

Recent trends in analytical chemistry are focused not only to the employment of greener reagents and solvents, but also to the elimination, or at least minimization, of the organic solvent consumption in the methods. Thus, dispersive liquid-liquid microextraction (DLLME) has been shown to be a successful liquid-phase microextraction method, in which the amount of organic solvent required as extractant is limited to few microliters.

ILs have been successfully employed as extraction solvents in DLLME [1], for determining a wide variety of organic compounds and metals in a number of samples. There are four main modes to accomplish the DLLME method: conventional, temperature-assisted, ultrasounds-/vortex-/microwaves-assisted, and *in situ*.

This work compares the performance of an optimized and validated DLLME method for the determination of Cu^{2+} in waters, followed by atomic absorption spectrometry (AAS), using a neat IL such as 1-butyl-3-methylimidazolium hexafluorophosphate ($C_4MIm\text{-}PF_6$) as extractant, or using an ILBS such as 1-hexadecyl-3-butylimidazolium bromide ($C_{16}C_4Im\text{-}Br$). The neat IL is used under the convention IL-DLLME mode, in which acetonitrile is needed as dispersive solvent. On the other hand, the ILBS is used under the *in situ* IL-DLLME mode, which requires an anion-exchange reagent but avoids the necessity of a dispersive solvent.

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NDP-P08

IMPROVING SAMPLE PREPARATION TECHNIQUES: PRE-CONCENTRATION OF CD BY HOLLOW FIBER LIQUID PHASE MICROEXTRACTION

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Cadmium is considered to be one of the most toxic metals in the environment, as it is reflected in the Priority Pollutants List of the Environmental Protection Agency. Its presence in natural waters comes from both natural and anthropogenic sources, with deleterious effects on living organisms even at very low concentrations. In this sense, some of the most frequently available analytical techniques, such as spectrometry, have not the appropriate sensitivity and, therefore, a sample pre treatment step is usually required.

Along the different steps of a chemical analysis, sample pre-treatment consumes solvent and chemicals the most. For this reason, huge efforts have been directed towards improving this crucial part of the analysis.

To date, several microextraction techniques have been successfully used for the determination of metals in environmental samples. Along with Dispersive Liquid-liquid Microextraction (DLLME), and Single Drop Liquid Phase Microextraction (SDLPME), Hollow Fiber liquid Phase Microextraction (HF-LPME) can be considered as a feasible extraction technique.

In this work a HF-LPME process for the pre-concentration of Cd in natural waters has been optimisedusing a multivariate methodology. The hollow fiber employed was Accurel PP S6/2 with the pores filled by the extracting agent Cyanex 272 dissolved in dihexyl ether (DHE), and the lumen with nitric acid. The hollow fibers were immersed in the sample solutions containing 0.1 µg L^{-1} Cd(II) at pH 6.4. The response variable was the enrichment factor (EF), defined as follows:

$$EF = [Cd]_{Strip}/[Cd]_{Feed}$$

with $[Cd]_{strip}$ and $[Cd]_{Feed}$ the Cd concentration in the receiving solution and initial Cd concentration in the sample, respectively.

First of all, a factorial design was performed to obtain those variables which affected EF the most. Afterwards, a response surface methodology was applied to obtain optimum conditions: 4.26 h agitation time, 0.041M HNO_3 concentration, and 1.057M Cyanex 272 dissolved in DHE.

Under these optimum conditions, the proposed methodology was successfully applied to the determination of cadmium in different natural waters.
The authors thank the Spanish Ministry of Economy and Competitiveness for the finantial support in this work.

NDP-P09

SPE USING MOLECULAR IMPRINTED POLYMERS FOR PHTHALATE DETERMINATION IN WATER AND WINE SAMPLES BY LC-MS

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A method for the determination of four phthalates in water and wine samples by Liquid Chromatography-Mass spectrometry has been developed. The four phthalates studied were dibutyl phthalate (DBP), butyl benzyl phthalate (BBP), diethyl phthalate (DEP) and dimethyl phthalate (DMP). A preconcentration step was necessary due to the low levels of these compounds in these samples. Solid phase extraction (SPE) using Molecular Imprinted Polymer (MIP) was selected as a preconcentration technique. The MIP was prepared via precipitation polymerization using DBP as template, methacrylic acid (MAA) as a monomer, ethyleneglycol dimethacrylate (EDMA) as crosslinking agent, acetonitrile as porogen and 2,2´-azobisisobutyronitrile (AIBN) as iniciator.

The experimental parameters for SPE extraction in column mode, such as sample volume, sample load rate, elution rate, etc... were optimized. The sample volumes selected were 25 mL and 100 mL for water and wine samples, respectively. Four milliliters of methanol were used for the quantitative extraction of the phthalates studied.

Phthalates were analyzed in the extract by high performance liquid chromatography (HPLC)-electrospray ionization-mass spectrometry, working in positive mode. Phthalates were separated by HPLC using a ZORBAX Eclipse XDB-C_8(3.5 µm particle size, 2.1 mm i.d. x 50 mm length) column, working in gradient mode with acetonitrile-ultrapure water starting from 5% to 75% acetonitrile in 5 minutes, followed by isocratic elution for 27 min. The method was sensitive (LOD< 3 µg L^{-1}), precise (RSD<8%) and accurate.

The developed method was applied to the phthalate determination in water and wine samples.

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NDP-P10

DETERMINATION OF PHENOLIC COMPOUNDS IN AIR BY USING CYCLODEXTRIN-SILICA HYBRID MICROPOROUS COMPOSITE SAMPLERS

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An analytical method for the determination of phenolic compounds in air samples based on the use of cyclodextrin-silica hybrid microporous composite samplers is proposed.

The nano-micrometric organization of these solid phases consists in well dispersed and accessible cyclodextrins trapped in the interconnected cage-like micropore system of a silica xerogel. Details on the synthesis procedure and characterization have been described previously in detail [1]. β-$CD_{0.0007}SiO_{1.5}(OH)_{0.5}$.0.7H2O was selected as solid phase based on the recovery of phenols and the solubility of the cyclodextrin in the desorption solvent. The porosity and easy accessibility to CD molecules was supported by textural parameters such as total area (352.2 m^2/g), pore volume (0.16 cm^3/g) and pore size (1.18 nm). Moreover, NMR data confirm that the β-CD structure is preserved and does not undergo degradation under the preparative and working conditions.

The method allows the determination of phenol, guaiacol, cresols, eugenol, 4-ethylphenol and 4-ethylguaiacol in workplaces according to the Norm UNE-EN 1076:2009 for active sampling. Therefore, the proposed method offers an alternative for the assessment of the occupational exposure to phenol and cresol isomers. The detection limits of the proposed method are lower than those for the NIOSH Method 2546. Recovery values for phenol, guaiacol, o-cresol, m-cresol, p-cresol, 4-ethylguaiacol, eugenol and 4-ethylphenol are 109%, 99%, 102%, 94%, 94%, 91%, 95% and 102%, respectively with a coefficient of variation below 6%.

The method has been applied to the assessment of exposure in different areas of a farm and regarding the quantification of these compounds in the vapours generated by burning incense sticks and an essential oil marketed as air fresheners. Air samples were analyzed by HPLC. The other samples, due to the complexity of the chromatograms, were analyzed by GC/MS. The acquired results are comparable with those provided from a reference method for a 95% of confidence level.

On the other hand, the volatile compounds generated by fresheners were identified from their mass spectra and their retention index. Many of the compounds identified are terpenes, compounds that form part of essential oils such as linalool, borneol, camphor or eucalyptol. Moreover, some studies related contact dermatitis with some compounds found in studied fresheners.

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[1] Sp. Patente 201100594, 2013.

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NDP-P11

EVALUATION OF A CYCLODEXTRIN-SILICA HYBRID MICROPOROUS COMPOSITE FOR THE SOLID-PHASE EXTRACTION OF PAHs

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Solid-phase extraction (SPE) coupled with HPLC fluorescence detection were employed to detect trace polycyclic hydrocarbons in water samples. The use of cartridges containing cyclodextrin-silica hybrid microporous solid phases is proposed herein.

Recently we described a new family of solid phases based on cyclodextrin-silica hybrid microporous nanocomposites [1]. The stoichiometry of these materials, which can incorporate a diversity of cyclodextrins in variable amounts, correspond to the general formula (CD)xSiO1.5(OH)0.5.0.7H2O. A preliminary part in the present work concerned CD selection. For this screening process we used the recovery of benzo[a]pyrene as key parameter. We observed that β-HPCD led to better recovery.

The resulting solid-phase architecture consisted of an inorganic silica network containing well dispersed β-HPCD (x=0.0013) trapped molecules inside cage-like interconnected micropores.

The porosity and easy accessibility to CD molecules was supported by textural parameters such as total area (535.7 m2/g), pore volume (0.25 cm3/g) and pore size (1.21 nm). Moreover, NMR studies confirmed that no β-HPCD degradation occurred under the preparative working conditions.

The method provided recoveries of between 77% and 117% with relative standard deviations of below 15%. Detection limits recorded were 12, 1.2, 12, 38, 4, 6 and 4 ng L-1 for benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[g,h,i]perylene, indeno[1,2,3-c,d]pyrene, benzo[a]pyrene, dibenzo[a,h]anthracene and benzo[a]anthracene, respectively. The major advantages of the cyclodextrin-silica hybrid microporous solid phases are that they reduce solvent consumption and toxicity and improve expediency of the sample treatment step.

From the study reported here, it can be concluded that the cyclodextrin-silica hybrid microporous solid phases are an alternative to other sorbents used for solid-phase extraction.

The proposed procedure can be used to determine PAHs in drinking water and for the quality control of waters in accordance with 2008/105/EC and 98/83/CE directives as the detection limits are below tabulated values. Moreover, the detection limits of the proposed procedure are similar to those obtained using other procedures.

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NDP-P12

APPLICATION OF ELECTROMEMBRANE EXTRACTION TO SILVER ANALYSIS IN WATER SAMPLES

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In 2006, Pedersen-Bjergaard et al. observed the extraction of basic drugs through a supported liquid membrane by the application of an electrical potential of 300V establishing the bases of electromembrane extraction (EME) [1]. The process of EME consists in the extraction of analytes from an aqueous solution to other solution located in the lumen of a polypropylene hollow fiber through an organic solvent immobilized in the pores of the fiber by the application of an electrical potential. This electrical potential is applied placing one platinum electrode in the sample solution and another one in the acceptor phase inside the lumen of the hollow fiber. The main advantage of this approach is a reduction in the extraction time due to the improvement of extraction process. Nevertheless, only a few papers with EME applications can be found in the literature and they are mainly related with the extraction of organic compounds.

In this work, the application of an electrical potential in a hollow fiber liquid phase microextraction system previously optimized for the extraction of silver from natural waters was tested, achieving higher enrichment factors for short extraction times. Then, a fractional factorial design was applied to identify the most influent parameters in the extraction process. The effect of six parameters on the enrichment factor was studied: triisobutyl phosphine sulfide (TIPBS) concentration in the organic solution,sodium thiosulphate concentration in the receiving solution, potassium nitrate concentration in the sample solution, extraction time, stirring rate and electrical potential. Only four of them had a significant effect on enrichment factor including extraction time, stirring rate, electrical potential and, to a lesser extent, sodium thiosulphate concentration in the receiving solution. The optimal conditions obtained from a Draper-Lin small response surface design were: a thiosulphateconcentrationof 0.03 M, an extraction time of 22 min, a stirring rate of 1000 rpm and an electrical potential of 74 V.

Under optimized conditions, the application of EME to the analysis of silver in water samples with different salinities was tested.

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NDP-P13

EXTRACTION OF BIOACTIVE CARBOHYDRATES FROM FOOD BYPRODUCTS USING A MICROWAVE ASSISTED EXTRACTION PROCEDURE

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Extraction of bioactive carbohydrates from food byproducts has special relevance, as they could be used as food ingredients. Among them, inositols exhibit activities connected to insulin-related diseases [1] and prebiotics allow specific changes in the composition and/or activity in the gastrointestinal microbiota that confer benefits upon host well-being [2]. Inulin is considered a prebiotic carbohydrate and is used as a technological ingredient. It is present in relatively high concentrations in common vegetable foodstuffs, and is composed of fructose unit chains of various lengths, terminated by a glucose unit [3].

Microwave Assisted Extraction (MWAE) is a fast and efficient technique for extraction of bioactives which generally provides higher yields and shorter extraction times than conventional solid-liquid extraction (SLE). However, this technique has been scarcely applied to the extraction of bioactive carbohydrates and to the best of our knowledge, there are no studies focused on the simultaneous extraction of inositols and prebiotics. Therefore, in this work, a MWAE method has been optimized to obtain high yields of bioactive carbohydrates (both inositols and inulin) from artichoke external leaves, as an agro-industrial by-product.

Water (10 mL) was used as the most appropriate solvent for the extraction of both types of carbohydrates. A Box-Behnkenexperimental design for response surface methodologywas used to optimize the extraction method. Extraction time (5-30 min), temperature (50-150ºC) and dry sample amount (0.5-1 g) were considered as variables. Inositols and other low molecular weight carbohydrates were converted to their trimethylsilyl oximes and analysed by GC-FID. The inulin content was calculated according to Schütz *et al.*[4] as the difference between the glucose and fructose content before and after hydrolysis with inulinase (Novozymes, 55 ºC, 48 h).A compromise between time and temperature was necessary to achieve good yields of both bioactives (inositols and inulin). The optimized method resulted to be a good alternative to conventional SLE for the production of enriched inositols and inulin extracts from food-grade byproducts.

Acknowledgments: This work was financed by projectsCTQ2012-32957 (MINECO) and P11-AGR-7626 (Junta de Andalucía).

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NDP-P14

ENZIMATIC HYDROLYSIS FOR THE DETERMINATION OF OXYSTEROLS IN RAT PLASMA BY SPE-LC-MS

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Oxysterols are formed during cholesterol catabolism. They are potent regulators of lipid homeostasis and play fundamental roles in the development of some cardiovascular diseases and other metabolic disorders.
Hepatic activity is crucial for oxysterols conversion into bile acids, because their accumulation is toxic for the organism in different kind of cells. In the reproductive tract, the enzyme metabolizes androgens that antagonize estrogen action. The role of oxysterolsin brain is under investigation; but there are recent studies that show some neuropathies caused by the accumulation of these analytes [1].

The esterified form of these analytes is the most abundant in plasma [2], so their determination requires hydrolysis prior to other steps of the analytical process.
The standard protocol starts with a Bligh/Dyer extraction followed by an alkaline hydrolysis which involves high temperatures, basic environment and finally a rigorous extraction process. After that,free oxysterols were isolated by solid phase extraction and analysed by liquid chromatography–mass spectrometry. Due to the harsh conditions of this hydrolysis and the fact thatcholesterol is thousand times more abundant than the oxysterols, sample stability and process efficiency are not ensured [3].

The problem was overcome using a cholesterol esterase enzyme which has the ability to hydrolyze oxysterols ester bond. Sample treatment is reduced to an enzymatic hydrolysis, Bligh/Dyer extraction, solid phase extraction and the instrumental analysis. As a consequence, the oxidation and degradation of the sample is avoided as well asglobal efficiency process is increased. The detection and quantification limits for 25 and 27 hydroxycholesterol were within 12-15 pg/mL and 40-49 pg/mL, respectively. The precision of the method, expressed as intra-day precision was 6 %.To conclude, the proposed method can be used to assess the metabolism of these compounds.

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NDP-P15

DETERMINATION OF PHTHALATE ESTERS IN CLEANING AND COSMETIC PRODUCTS BY DLLME AND LC-DAD-ESI-IT-MS/MS

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Phthalates or phthalic acid esters (PEs) are chemicals used in a multitude of everyday products, being widely used in industry and commerce. They may be classified into two groups, low molecular weight PEs, which are highly polar, being used in a variety of personal-hygiene and cosmetic products, detergentsand fragrances as scent stabilizers or carriers, and highmolecular weight PEs, being used in plastic tubing, food packaging... Most cleaning products contain phthalates, listed on the ingredients as fragrance. Most methods for phthalate esters analysis are based on gas chromatography (GC) and liquid chromatography (LC) using conventional or miniaturized extraction techniques

In the present study, a procedure coupling ultrasound assisted extraction (UAE) and DLLME asgreen sample preparation techniques for the efficient determination of dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DBP), bis(2-ethylhexyl) phthalate (DEHP), butyl benzyl phthalate (BBP) and di-n-octyl phthalate (DOP), using LC coupled to both diode array detection (DAD)and electrospray ionization-ion trap-tandem mass spectrometry (ESI-IT-MS/MS) is proposed.

An ultrasonic probe and acetonitrile were selected for extraction of the PEs, while for DLLME, the influencing parameters were 3mL of acetonitrile (disperser solvent), 150 µL carbon tetrachloride (extraction solvent) and 10 mL aqueous solution. The organic phase was evaporated, reconstituted with 50 µL acetonitrile and injected into reversed-phase liquid chromatography (LC) with a mobile phase composed of acetonitrile:10 mM ammonium acetate (pH 4) under gradient elution and a C_{18} stationary phase. The flow-rate was 0.4 mL min^{-1}. The DAD detector was operated at 225 nm. ESI was selected for ionization. Maximum sensitivity was obtained operated in positive ion mode for all compounds, obtaining the protonated molecular $[M+H]^+$ as the dominant precursor ions. Good sensitivity and selectivity was achieved when operated in the multiple-reaction monitoring (MRM) mode, which was selected. Two or three transition products were monitored for each compound. Quantification was carried out by the standard addition method using matrix-matched standards. Detection limits were calculated and the recoveries obtained were in the 84-106% range, with RSDs lower than 10%. The ESI-MS/MS spectra, in combination with UV spectra, permitted the correct identification of PEs in cleaning and cosmetic products.

NDP-P16

FINDING OUT AND CORRECTING UNACCURACIES IN THE TWO-PHASE POTENTIOMETRIC TITRATION OF ANIONIC SURFACTANTS

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Industrial quality control of anionic surfactants in raw materials and cleaners is frequently carried out by potentiometric titration with an ion-selective electrode (ISE) which is sensitive to large ions. Large quaternary ammonium compounds, as benzethonium chloride (Hyamine® 1622), are used as titrating agents. In an official method (EN14699/2005), the titrations are performed in a two-phase system constituted by an emulsion of water, methyl-isobutyl ketone (MIBK) and alcohols. The titrant gives rise to ion-pairs with the anionic surfactants. Extraction of the ion-pairs in the organic phase enhances the potential jump. The titrant is standardized at pH 3 with sodium dodecyl sulfate (SDS). As far as we know, a study of the accuracy of the method has not been done.

Dodecylbenzene sulfonates (DBS) and alkylether sulfates (LESNa) are also titrated at pH 3. We have not found any significant systematic error at this pH. However, the samples may also contain soaps, which are formed by adding an alkali to oleins (mixtures of fatty acids of vegetal origin). Soaps are titrated together with DBS and LESNa at pH 11.5. The olein concentration is established by difference between the measurements at pHs 11.5 and 3. When cleaners are titrated at pH 11.5, systematic errors which can be as large as +10% are sometimes found for the sum olein + DBS + LESNa. This is significantly higher than the coefficient of variation of ca. 2% of the method. This positive error is always present for all anionic surfactants and their mixtures, but its magnitude varies with the composition of the mixture to be titrated. The systematic error is higher for olein, which is calculated by difference.

The main problem seems to be the partial titration of other anions also present in the medium (as hydroxyl) or formed at the surface of mixed micelles by partial ionization of alcohols, including non-ionic surfactants, is possible. The systematic errors are reduced by titrating in a sodium carbonate / bicarbonate buffer of pH 10.

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NDP-P17

BIOACTIVE NATURAL EXTRACTS OBTAINED BY PRESSURIZED SOLVENT EXTRACTION (PSE)

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Nowadays there is an increased interest in natural products, like fruits or vegetables, due to their bioactive compounds associated to health benefices. They have been recently studied because of their possible prevention of cardiovascular diseases and cancer, among others.

Some of these good properties have been attached to a large group of compounds: polyphenols. Some of these compounds are present in different natural materials, which have been investigated to get profitable extracts. Researchers have mostly carried out the extraction of natural resources by conventional process that may not extract all the polyphenolic content.

In this context characterization of some plants and vegetable residues have been done by an efficient technique: Pressurized Solvent Extraction (PSE). Samples from *Cytisus scoparius*, *Hibiscus sabdariffa* and grape marc [1] have been extracted by PSE, optimizing the extraction processes by chemometric tools. Total polyphenolic content was measured by Folin-Ciocalteu assay, while antioxidant activity was determined using DPPH reagent. In addition, individual polyphenols were identified and quantified by HPLC-DAD and LC-MS-MS.

Results show that PSE improves the extraction of polyphenols from all the different raw materials considered, confirming the high extraction efficiency of the process. However, different optimized conditions have been found for these three natural sources of polyphenols, becoming the optimization a necessary step in the procedure development. All the materials studied show high and similar polyphenols content, but not the same composition. This is reflected in the different antioxidant capacity of the different extracts.

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NDP-P18

DETERMINATION OF DYES IN COSMETIC PRODUCTS BY MATRIX SOLID PHASE DISPERSION AND LC-MS/MS

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Synthetic dyes are added to cosmetic preparations in order to colour the cosmetic itself and/or the body as a whole or certain parts thereof, by absorption or reflection of visible light. They are widely used in personal care products in spite of many studies confirming their negative influence on human organism.

The Regulation (EC) No 1223/2009 establishes the rules to be complied with by any cosmeticproduct available on the market, in order to ensure a high level of protection of human health.It includes the prohibited substances, which must not be integrated in the cosmetic formulations, as well as the restrictions applied to othersubstances [1]. Synthetic dyes are regulated in Annex IV.

Matrix Solid Phase Dispersion (MSPD) has been successfully proposed by our group for the analysis of several families of additives in personal care products and cosmetics [2,3]. A method based on micro-MSPD followed by high performance liquid chromatography-electrospray ionization tandem mass spectrometry has been developed for the simultaneous determination of several water-soluble dyes including Tartrazine, Sunset Yellow FCF, Allura Red AC, Ponceau SX, Brilliant Blue FCF, Quinoline Yellow, Acid Orange 7, Acid Red 92 and Acid Violet 43, in different cosmetic matrices. The sample extraction conditions were optimized by means of experimental design. The method performance has been studied and it was applied to the analysis of real cosmetics, including care and decorative products.

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NDP-P19

ANALYSIS OF REGULATED INGREDIENTS AND ADDITIVES IN COSMETICS USING MICRO-MSPD AND GC-MS/MS

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Cosmetics composition is very complex. To assure human health protection, regulation in EU establishes limits and prohibitions of hundreds of compounds [1]. Among the regulated compounds, fragrances considered as suspected allergens are frequently used in cosmetics and personal care products; musks and plasticizers are also usually present, although many of them are considered harmful to health; preservatives are added to cosmetic preparations to inhibit the development of microorganisms (parabens are the most frequently used and recently five of them have been banned). Therefore, cosmetics control requires new efficient and cost effective analytical methodology.

A simple and low cost sample preparation method based on micro-matrix solid-phase dispersion (MSPD) followed by gas chromatography-triple quadrupole-mass spectrometry (GC TQ-MS) analysis is proposed for the rapid simultaneous determination of more than 70 chemicals commonly used in cosmetics and personal care products. The use of a triple quadrupole working under MS/MS mode allows to reach lower detection limits than single quadrupole-MS and significantly improves selectivity.

The validated method was applied to a variety of cosmetics, including leave-on and rinse-off products such as shampoos, body milks, toothpastes, lipsticks, shower gels...

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NDP-P20

ANALYSIS OF UV FILTERS IN COSMETICS BY PRESSURIZED LIQUID EXTRACTION-GAS CHROMATOGRAPHY TANDEM MASS SPECTROMETRY

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UV filters are substances that are exclusively or mainly intended to protect the skin against certain UV radiations by absorbing, reflecting or scattering them. However, in spite of being required for this reason, they can cause some adverse effects. Therefore, the EU established a specific Regulation (EC) Nº 1223/2009 laying down the rules that must follow all marketed cosmetic products in order to ensure a high level of protection of human health. Sunscreens allowed for use in cosmetic products are gathered in Annex VI of this regulation [1]. The analytical control of these compounds is necessary toguarantee compliance withthese rules.

A methodology based on pressurized liquid extraction (PLE) followed by gas chromatography–tandem mass spectrometry (GC–MS/MS) has been developed for the simultaneous analysis of different classes of UV filters including methoxycinnamates, benzophenones, salicylates, p-aminobenzoic acid derivatives, and others in cosmetic products. The extractions were carried out in 1 mL extraction cells and the amount of sample extracted was only 100 mg. The experimental conditions, including the acetylation of the PLE extracts to improve GC performance, were optimized by means of experimental design tools.Main factors affecting the PLE procedure such as solvent type and extraction temperature were assessed. Good linearity (R^2> 0.9971), quantitative recoveries (>80% for most of compounds) and satisfactory precision (RSD < 10% in most cases) were obtained at the optimal conditions. The validated methodology was successfully applied to the analysis of different types of cosmetic formulations including sunscreens, hair products, nail polish, and lipsticks, amongst others.

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[1] Regulation (EC) No 1223/2009 of the European Parliament and of the Council of 30 November 2009 on cosmetic products (recast), Official Journal of the European Union L342/59.

NDP-P21

DISPERSIVE LIQUID-LIQUID MICELLAR MICROEXTRACTION USING UHPLC-DAD FOR THE DETERMINATION OF PHARMACEUTICAL COMPOUNDS

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A liquid-phase microextraction (LPME) procedure is presented for the analysis of five pharmaceuticals compounds (two anti-inflammatory compounds, naproxene and ketoprofen, an antibiotic, ornidazole, an antiepileptic, carbamazepine, and a stimulant, caffeine) in wastewater samples. These compounds are widely used and they are not eliminated in the wastewater treatment plants (WWTPs) and could reach the environment through different ways.

The methodology is based in the dispersive liquid–liquid microextraction (DLLME) but replacing the conventional organic solvent by a micellar medium, which has been satisfactorily used to develop methods for the extraction-preconcentration from different type of matrices [1-2].

This dispersive liquid–liquid micellar microextraction (DLLMME) is coupled with Ultra High Performance Liquid Chromatography (UHPLC) using DAD detector. The parameters envolving the extraction procedure, such as time and temperature extraction, ionic strength and surfactant and organic solvent volume were optimized using an experimental design in order to obtain the higher extraction efficiency. Under these optimized conditions, this procedure allows enrichment factors up to 47 times. The detection limit of the method ranged from 0.1 to 2.0 μg·L−1 for the different pharmaceuticalsand the repeatability expressed as Relative Standard Deviations (RSD) were satisfactory. The procedure was applied to samples from final effluent collected from wastewater treatment plants (WWTPs) in Las Palmas de Gran Canaria (Spain),and two compounds (ketoprofen and naproxene) were measured at 67 and 113 μg·L−1in one of them.
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NDP-P22

CORE-SHELL POLY(DOPAMINE) MAGNETIC NANOPARTICLES FOR THE DSPE OF ESTROGENIC COMPOUNDS FROM WATERS PRIOR TO LC-MS

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Certain groups of nanoparticles (NPs) are sorbents widely applied nowadays in sample preparation since they have a high surface area-to-volume ratio that provide a much greater extraction capacity and efficiency compared with other sorbents used in this field. Particularly, magnetic NPs (m-NPs) have a special interest because they can be attracted to a magnetic field which simplifies their separation from different matrices without additional filtration or centrifugation [1].

Dispersive solid-phase extraction (dSPE) constitutes a different approach of conventional SPE in which the sorbent is not retained in a cartridge, disk or needle, but is directly dispersed in the liquid sample. Compared with classic SPE methods, pre-conditioning of the sorbent is not necessary, simplifying its performance as well as reducing the extraction time without decreasing its effectiveness [2]. The properties of m-NPs allow them to act as interesting and faster alternatives as dSPE sorbents. In this sense their coating have been achieved not only to stabilize them and to prevent their oxidation but also to increase sample extraction selectivity.

The aim of this work, was to evaluate the use of laboratory synthesized core-shell poly(dopamine) m-NPs as dSPE sorbents for the extraction of a group of three natural (i.e. estrone, 17α-estradiol and 17β-estradiol), four synthetic (i.e. ethynylestradiol, diethylstilbestrol, dienestrol and hexestrol) and five mycoestrogens (i.e. zearalenone, α-zearalanol, β- zearalanol, α-zearalenol and β-zearalenol) from water samples prior to LC-MS analysis. Parameters that affect the extraction efficiency were studied by means of a step-by-step approach in order to obtain optimum extraction conditions. Preliminary results showed that core-shell poly(dopamine) m-NPs can be good sorbents to provide a simple, reproducible and effective methodology for the extraction of estrogens from water samples.

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NDP-P23

EVALUATION OF TWO MOLECULAR IMPRINTED POLYMERS FOR THE SPE OF ESTROGENIC COMPOUNDS FROM WATERS PRIOR TO LC-MS

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Natural estrogens are sex steroid hormones which main function is the development of female characteristics and the regulation of the menstrual cycle of humans and, in general, the estrous cycle of mammals. Among these natural organism-synthesized compounds, also known as *endoestrogens*, the most important are estrone (E_1), estradiol (E_2) and estriol (E_3). Apart from them, there is a wide group of substances called *exoestrogens* that also have an important estrogenic activity. Within this group, ethynylestradiol (EE_2), which is a human contraceptive, or stilbenes like dienestrol (DS), hexestrol (HEX) or diethylstilbestrol (DES), which are illegally used as growth promoters, can be highlighted. In addition, mycoestrogens like zearalenone (ZEN), zearalanols (ZALs) and zearalenols (ZELs) can also be included, since they also have an important estrogenic activity [1].

It is well known that all these compounds may reach aquatic ecosystems through humans' and animals' wastes. In fact, they are normally found at trace levels; that is the reason why a preconcentration step is necessary. Such procedure is frequently carried out by solid-phase extraction (SPE) in which a high selectivity of the sorbent for the target analyte is highly desirable [2].

In this work we have compared the selectivity of two commercial molecular imprinted polymers (MIPs) which have been designed for the extraction of natural estrogens like estradiol and zearalenol derivatives. For this purpose, twelve estrogenic compounds (i.e. 17β-E_2, 17α-E_2, E_1, HEX, EE_2, DES, DS, ZEN, α-ZAL, β-ZAL, α-ZEL and β-ZEL) were extracted from water samples. High performance liquid chromatography (HPLC) coupled with ion trap mass spectrometry with electrospray ionization was used for their determination. Contrary to what it was expected, results show that although both MIPs cartridges were specifically designed for different groups of analytes they nearly have the same extraction performance (recoveries in the range 65-101%) for the same analytes in Milli-Q water. However, when more complex water samples were analyzed, it was clear that they only extract those compounds for which they have specifically designed. Validation of the proposed methodology revealed that the extraction was repeatable and the final LODs of the proposed method were in the low ng/L range.

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CTQ-P01

SELECTIVITY MODULATION WITH SERIALLY-COUPLED COLUMNS IN RPLC FOR THE ANALYSIS OF COMPLEX SAMPLES

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In many fields of modern Analytical Chemistry, including analysis of pharmaceuticals and foods, as well as clinical and environmental samples, the demand for methods capable of analyzing increasingly complex samples has increased. Often, a separation technique using a sensitive and selective detector is required (as diode-array or mass spectrometry). The use of these detectors is needed, because the separation technique is often unable to completely resolve the compounds of interest. However, it is always desirable that sufficient resolution be provided to obtain the maximal benefit from the detectors. This is the reason that the interest in developing separation methods with increasing performance has not decayed. The combination of two or more different separation mechanisms may increase, significantly, the resolution of some samples.

The idea of using mixtures of stationary phases for analyzing complex samples appeared in the early development of chromatography (particularly in gas chromatography). Garay describes the effect achieved in a very graphical way, stating that "it is similar to the technique of a painter preparing a green paint by mixing blue and yellow colors, and amending the tone by altering the ratio of the two paintings". In the context of chromatography, we would talk about polarity, or more broadly, selectivity, instead of color: quasi-continuous transitions between the selectivity of two stationary phase that are mixed can be achieved by performing different combinations. The term "modulation" has been associated with these transitions or combinations.

This communication presents recent advances developed in our laboratory with the serial columns and the optimization of the eluent composition, and the nature and length of the coupled columns, using both isocratic and gradient elution [1,2]. The developments are illustrated with the separation of complex mixtures of sulphonamides and diuretics. The structure of software prepared for these applications, which allows reliable predictions of chromatographic resolution by incorporating the peak profile (width and asymmetry) in the modeling step, is described. The attractive results obtained in isocratic elution are especially relevant. The results are closer to two-dimensional liquid chromatography in terms of resolution, and to gradient elution in terms of analysis time, using a simpler and more accessible instrumentation to most laboratories.

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CTQ-P02

REVERSED-PHASE LIQUID CHROMATOGRAPHY WITH BRIJ-35: A CHROMATOGRAPHIC MODE WITH WATER AND SOAP

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Polyoxyethylene(23)lauryl ether ($(C_2H_4O)_{23}C_{12}H_{25}OH$,known as Brij-35) is a non-ionic surfactant, which has been considered as an alternative to the extensively used in micellar liquid chromatography (MLC) anionic surfactant sodium dodecyl sulphate (SDS), for the analysis of drugs and other types of compounds [1–3]. Brij-35 is also the most suitable non-ionic surfactant for MLC, owing to its commercial availability, high purity, low cost, low toxicity, high cloud temperature and low background absorbance. However, it has had a minor use in MLC, due to its irreversible adsorption on C_{18} and C_8 stationary phases and lower efficiencies. However, it has been the surfactant of choice in quantitative retention-activity relationships (QRAR), since it mimics with high reliability diverse biopartitioning processes [4,5].

In this work, we gather several results obtained in our laboratory with groups of flavonoids, sulfonamides, β-blockers and tricyclic antidepressants, concerning the use of Brij-35 as unique modifier in reversed-phase liquid chromatography (RPLC). The less polar character of Brij-35 increases the retention of polar compounds and the polyoxyethylene chain with its end hydroxyl group allows the establishment of hydrogen-bond interactions that modify the retention of aromatic compounds with hydroxyl groups. The result is the possibility to use pure aqueous solutions of Brij-35 as mobile phases in RPLC (solutions of water and soap), which is an interesting “green” strategy in an effort to minimize pollution and wastes, increasing thus sustainability.

The work includes the examination of the performance of isocratic and gradient elution with pure aqueous solutions of Brij-35, and the possible need of a small amount of an organic solvent to reduce the retention and improve the peak profiles. The effect of the modifiers and temperature on the retention and peak profile of several types of analytes is examined.

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CTQ-P03

STUDY OF THE PERFORMANCE OF A SILICA-BASED MONOLITHIC COLUMN UNDER FLOW PROGRAMMING

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A usual problem that RPLC must cope with is the separation of complex mixtures of analytes within a wide range of polarities. Acceptable separations are considered to be in the range $1 < k < 20$. In many cases, isocratic elution hardly can meet this requirement with an acceptable degree of resolution, which is called the "general elution problem of RPLC". The solution to this problem is usually the use of gradient elution with programming changes of organic modifier, to provide a gradual increase in the elution strength of the mobile phase entering the column. Thus the initial bands have their migration rates decreased and are separated under more optimal conditions, while the final bands have their relative migration rates increased to values near the optimal range. Thus, adequate resolution is achieved in acceptably short analysis times. Flow programming, where the flow rate increases as a function of time, is an alternative to reduce the analysis time. However, this approach has been scarcely applied in liquid chromatography, due to the relatively small range of modification of this factor for the usual microparticulate columns.

Monolithic columns allow different flow rates beyond those suitable for conventional microparticulate packed columns. This is possible due to the lower backpressures and higher efficiencies at high flow rates. Particularly interesting is the use of a silica-based monolithic column patented by Merck (Darmstadt, Germany) with the trade name Chromolith, which show the reproducibility required for routine analysis. The second generation Chromololith shows increased performance, especially with regard to the efficiency. In view of the nature of these columns, flow-rate becomes an important factor to be considered, in addition to the mobile phase composition, in order to achieve good resolution at sufficiently low analysis time. In this work, the effect on chromatographic peaks (retention, width and asymmetry) with changes in the organic modifier content and flow rate is studied, in both isocratic and gradient modes. The final goal is to describe the combined effect on resolution of coupling flow programming with the most classical gradients of organic modifier, with the purpose of improving the separation performance.

CTQ-P04

VARIABLE GENERATION FROM MONO-CHANNEL RECORDINGS USING OVERLAPPED BLIND WINDOWS IN TANDEM WITH PRINCIPAL COMPONENTS

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In instrumental chemical analysis and most other experimental techniques, information is obtained as peaks standing out the baseline noise. To extract the relevant information, automatic rather than manual peak recognition and integration is most convenient. Further, unsupervised processing is the only practical way of using all the available information contained in complex recordings, as those having large noise levels, partially resolved peaks or a large number of peaks. Variables can be generated by using either peak searching or "blind" window (BW) strategies. In BW methods the variables are automatically generated without taking into account the actual location and width of the peaks. The large number of variables which are created is reduced by the subsequent application of principal component analysis (PCA) or any other soft-modelling technique.

In this work, simulated recordings along a single scanned variable were used to study the best way of applying a BW-PCA method. The recordings imitated those obtained with any mono-channel detector when either wavelength (as in spectroscopy) or time (as in chromatography) is scanned. Recordings with differently spaced peaks of different widths were generated. The variables created by BW-PCA were used to classify the recordings into four categories by linear discriminant analysis (BW-PCA-LDA). Prediction quality was estimated as the percentage of correct classifications in cross-validation (leave-one out) conditions, *P%*.

This study showed that, for all the simulated experiments and in all situations, *P%* increased steadily with the degree of overlapping of consecutive windows, δ. The quality of the prediction models also depended on the window size (Δt_w), showing optimal regions which depended on both the average peak width and the spacing between consecutive peaks. Within small ranges of both Δt_w and δ, wandering *P%* values were found; however, at large δ values and within the optimal Δt_w region, the theoretically maximal *P%* values were always reached, and much lower values were never obtained. The quality of the predictions also improved when baseline regions having no significant peaks were excluded. Thus, for real recordings a value of $\delta > 0.9$ is recommended. On the other hand, a simulation method as that here reported, but applied to recordings that imitate the real ones to be processed, can be of help in establishing the optimal Δt_w region.

CTQ-P05

A NEW PARAMETRIC FUNCTION FOR THE MULTIVARIATE CURVE RESOLUTION OF HIGHLY ASYMMETRIC VOLTAMMETRIC SIGNALS

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Voltammetric techniques are useful in studies of heavy metal binding by a variety of ligands. In many cases, univariate analysis by using classical equations (e.g. Deford - Hume) provides acceptable results. However, other systems (often with biomolecules acting as ligands) produce intricate voltammograms with numerous overlapping signals, which requires the use of strategies of multivariate analysis.

This work aims to develop a methodology to improve the performance of the multivariate algorithm GPA (Gaussian Peak Adjustment), previously developed in our research group for non-linear voltammetric data [1]. GPA is based on the adjustment of peak-shaped signals to a set of two Gaussian functions, one on each side of the maximum, with different widths. This provides good results in relatively symmetrical peaks, but exhibits limitations in the analysis of strongly asymmetric signals as these obtained in Linear Sweep Voltammetry (LSV). For this purpose, asymmetric logistic function has been tested [2], but the adjustment is not robust. Thus, in this work a simpler function is tested, again consisting of a double Gaussian but with a more gradual (sigmoid) change of the parameter governing the width on both sides of the peak. The new function has been successfully applied to LSV measurements on the Cd(II)-cysteine system.

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CTQ-P06

VAPOR CORRECTIONS IN INFRARED SPECTROSCOPY DETERMINATION

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The objective of this study was the assessment of a flexible and automated method taking acetone as target compound, for avoiding the spectral interferences of organic vapors in FTIR spectra measured in vapor phase. Acetone is one of the many substances that can be falsely identified and measured as ethanol by some breathalyzer machines. Other situation where the acetone can produce spectral interference is in the determination of BTEX in industries when the acetone is present in the atmosphere. Hence, is interesting to eliminate the acetone contribution to the FTIR spectra sample and for this reason, both BTEX and ethanol spectra in vapor phase with different levels of acetone in the atmosphere were acquired and corrected.
To avoid the presence of spectral interferences, a correction method developed by our research team was used, employing an algorithm based on the measurement of acetone reference spectrum followed by the automatic estimation of spectral contribution of interference in the spectrum of the sample to be corrected. After that, the contribution of acetone was compensated by a simple spectral subtraction.
To compare spectral similarities, three parameters were used: the correlation coefficient (R), the Fisher's Z transformation and the noise level. R and Z values were calculated by comparing different spectra regions between vapor phase spectra in the absence of interfering of sample and: i) final one also without interferencesmeasured at the end of the experiment to know the maximum similarities after time analysis, ii) spectra with acetone interference and, iii) sample spectra after acetone correction. The spectral noise was also calculated in different spectra regions to evaluate the performance of correction method applied. Stundent's test was used to compare mean value between sample spectrum without interferences and sample spectrum after interference correction. In all cases, the two mean values do not differ significantly for 95% confidence level, and it confirmed the high spectral similarity in all regions between spectra in the absence of interference and corrected spectra.

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CTQ-P07

UNDERSTANDING THE BEHAVIOUR OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN HPLC-UV BY MEANS OF QSRR

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Polycyclic Aromatic Hydrocarbons (PAHs) is a large family of chemical compounds of high interest due to their carcinogenic and mutagenic activity. For this reason, their analysis, detection and control are very important, but the large number of compounds that include this family and the lack of standards for their identification difficult their study.

The Quantitative Structure Retention Relationship (QSRR) methodology permits the development of mathematical models to predict the chromatographic retention time of chemical compounds. After a training stage, by using experimental data of known molecules, QSRR methods allow the identification of unknown compounds of the same chemical family in real samples.

Liquid chromatographic analysis (HPLC-UV) of PAHs standards is performed to obtain the retention times. In order to correlate experimental data with molecular structure, we calculate for each compound a set of molecular descriptors. These mathematical representations of molecular properties are used to create a linear (PLS) and non-linear (e.g. Artificial Neural Networks) regression models. The combination of the number of carbon atoms, the number of aromatic rings and the energy of the HOMO orbital permit to obtain the best model.

The QSRR predictive model has been validated and therefore tested on a real emission samples, which contain PAHs whose retention time is unknown, in order to identify and assign them.

A robustness studied has also been carried out in order to determine the applicability of the QSRR model in other analytical techniques. The predictive ability has been evaluated when elution gradient of liquid chromatography is modified, and when the analysis is carried out by ultra-high performance liquid chromatography (UHPLC) and gas chromatography (HRGC). The results show that the QSRR predictive model is independent of the analytical technique used, and selected molecular descriptors are able to describe the PAHs experimental behavior.

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