

XXIV Reunión Nacional y VIII Congreso Ibérico de ESPECTROSCOPIA

ABSTRACT BOOK



**XXIV RNE – VIII CIE
ESPECTROSCOPIA**

Logroño, 9-11 de julio de 2014

ORGANIZAN



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PRESENTACIÓN

El Comité Organizador de la **XXIV Reunión Nacional de Espectroscopia-VIII Congreso Ibérico de Espectroscopia** os da la bienvenida a esta cita bianual de la espectroscopia ibérica que se celebra en Logroño (La Rioja) del 9 al 11 de julio de 2014. Tras la última edición celebrada en Córdoba en septiembre de 2012, tomamos animados el testigo de su organización con la esperanza de ser, de nuevo, la gran cita para los científicos y profesionales de la Península Ibérica interesados en los avances de la espectroscopia y en sus aplicaciones. En esta edición contamos con la participación de más de ciento sesenta inscritos procedentes de veintitrés universidades españolas, cuatro universidades extranjeras y doce casas comerciales de instrumentación espectroscópica.

La belleza y singularidad de Logroño –enclave estratégico del Camino de Santiago, punto de encuentro de peregrinos, y capital de la afamada región de La Rioja por la excelencia de sus vinos y productos– representan un marco idóneo en el que fortalecer los lazos de la espectroscopia ibérica animados por su riqueza monumental y gastronómica.

El principal objetivo de la XXIV RNE-VIII CIE es presentar los avances más recientes en el campo de la espectroscopia, a través de conferencias plenarias e invitadas, contando con la participación de científicos internacionales de reconocido prestigio, y al mismo tiempo, estimular las relaciones y futuras colaboraciones entre los participantes. Paralelamente al programa científico, tendrá lugar una exposición comercial en la que estarán presentes las principales empresas del sector de la instrumentación científica relacionada con la espectroscopia que nos mostrarán, de primera mano, las novedades del mercado. Además, durante este congreso está prevista la celebración de las asambleas de socios la Sociedad de Espectroscopia Aplicada (SEA) y la Sociedad Española de Óptica (SEDOptica).

El Comité Organizador ha hecho un esfuerzo especial para ofrecer cuotas muy reducidas a los estudiantes y favorecer la participación de jóvenes investigadores, los futuros científicos y profesionales de la espectroscopia y de ediciones venideras de la RNE-CIE. Esto no hubiera sido posible sin la ayuda económica de las instituciones y el patrocinio de las empresas, a las que estamos muy agradecidos.

Después de las sesiones científicas, hemos preparado un programa social para mostraros lo más típico de Logroño. El miércoles degustaremos unos pinchos en la famosa calle Laurel y el jueves visitaremos y cenaremos en una bodega.

Estamos encantados de contar con vuestra presencia y deseamos que disfrutéis al máximo tanto del programa científico como de vuestra estancia en La Rioja.

¡Muchas gracias por vuestra participación!

El Comité Organizador

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D. Antonio Sola Díaz, Organizador XXIII RNE – VII CIE

PROGRAMA

Martes 8 de julio

17:00-19:00 Recogida de documentación

19:30 **Vino de bienvenida**

Miércoles 9 de julio

09:00 Sesión de apertura

Sesión I, presidida por M^a Paz Sevilla Sierra

09:30 Conferencia Plenaria

PL-1. Concepción Domingo

Raman Spectroscopy, a “broad-spectrum” tool: from rock art to Mars exploration; from graphene-based materials to medical diagnosis or cosmetics industry

10:15 Conferencia Invitada

IL-1. Martín Resano

Non-invasive methods for clinical elemental analysis. Direct analysis of dried matrix spots for diagnosis and control

10:45 **Café**

Sesión II, presidida por Maria Paula Marques y Belén Maté Naya

11:15 Conferencia Invitada

IL-2. Helena Vieira Alberto

Spectroscopy of a muonium atom formed inside a semiconductor

11:45 Comunicaciones Orales: Nanotecnología

O-01. Diameter selection of carbon nanotubes in arrays of polymer/SWCNT nanowires by template wetting

M.C. García-Gutiérrez, C. Domingo

O-02. Synthesis and study of plasmonic properties of gold-silver nanostructures: From a spherical nanoparticles to ultrathin nanowires

J. Crespo, A. Falqui, J.M. López-de-Luzuriaga, M. Monge, M. E. Olmos, M. Rodríguez-Castillo, M. Sestu, K. Soullantica

O-03. Gaps induced by molecular linkage of plasmonic nanoparticles in colloidal suspensions for SERS enhanced pesticide sensing

S. Sánchez-Cortés, J. Kubackova, D. Jancura, J.V. García-Ramos

O-04. An ICPMS-based analytical platform for the determination of nanoparticles released from nanocomposites

E. Bolea, I. Abad-Álvaro, J. Jiménez-Lamana, N. Manninen, A. Cavaleiro, S. Carvalho, F. Laborda, J.R. Castillo

O-05. A novel quantum dot-based phosphorescent immunoassay for PSA detection in human serum: signal amplification strategies based on ICP-MS

M. García-Cortés, M.T. Fernández-Argüelles, J.M. Costa-Fernández, J. Ruiz Encinar, A. Sanz-Medel

O-06. *Bioconcentration and toxicity studies of titanium dioxide nanoparticles by zebrafish embryos*

R. Muñoz-Olivas, A. López-Serrano, J. Sanz, S. Rainieri, C. Cámara

O-07. *Experimental observation of Fano- and Lorentz-like line shapes in the optical extinction of plasmonic nanorods*

F. López-Tejeira, N. Verellen, R. Paniagua-Domínguez, D. Vercruysse, D. Denkova, L. Lagae, P. Van Dorpe, V.V. Moshchalkov, J.A. Sánchez-Gil

13:30 **Comida**

Sesión III, presidida por Manuel Hernández Córdoba y María Teresa Tena Vázquez de la Torre

15:30 Conferencia Plenaria

PL-2. Demetrios Anglos

Art and Archaeology through the spectroscopic looking glass

16:15 Comunicaciones Orales: Plasmas

O-08. *Biomedical applications of laser induced breakdown spectroscopy in bacterial identification*

S. Manzoor, S. Moncayo, F. Navarro-Villoslada, J.A. Ayala, R. Izquierdo-Hornillos, F.J. Manuel de Villena, J.O. Cáceres

O-09. *LIBS quantitative analysis of fluorite ores (CaF₂) through the measurement of CaF molecular emission bands*

C. Álvarez, J. Pisonero, N. Bordel

O-10. *Different approaches for the generation of chemical maps of complex samples by laser-induced plasma spectroscopy*

M.P. Mateo, G. Nicolás

17:00 Comunicaciones orales: Casas comerciales I

O-11. *MIR-FIR spectroscopy in one step – wide range infrared technology*

C. Villar Pascual, G. Zachmann

O-12. *Spectral interferences removal in multiple isotope selenium and iodine determinations using an ICP-MS triple quadrupole in MS/MS mode*

N. Sugiyama, Y. Shikamori, K. Nakano, S. Kakuta, F. Tobalina

17:30 **Café**

17:30-19:30 **Sesión de carteles 1**
Exhibición Comercial

20:30 **Visita a la calle Laurel (bono-pincho)**

Jueves 10 de julio

Sesión IV, presidida por María Cruz Moreno Bondi y José Manuel Costa Fernández

09:00 Conferencia Plenaria

PL-3. Luca Prodi

Dye doped silica nanoparticles as luminescent organized systems for nanomedicine

09:45 Conferencia Invitada

IL-3. Fernando Rull

Applications of Raman spectroscopy: from the historical heritage to the space exploration

10:15 Comunicaciones Orales: Alimentos y sensores

O-13. *β -Cyclodextrin modified CdSe/ZnS quantum dots as a vanillin-sensor*

A. Ríos, G.M. Durán, A.M. Contento

O-14. *Furfural selective colorimetric sensors for beer ageing monitoring*

A. Rico-Yuste, E. Benito-Peña, V. González-Vallejo, M.C. Moreno-Bondi

O-15. *Determination of technological maturity of grapes and total phenolic compounds of grape skins in red and white cultivars during ripening by near infrared hyperspectral image: A preliminary approach*

J. Nogales-Bueno, J.M. Hernández-Hierro, F.J. Rodríguez-Pulido, F.J. Heredia

11:00 **Café**

11:30-13:30 **Sesión de carteles 2**
Exhibición Comercial

13:30 **Comida**

Sesión V, presidida por Santiago Sánchez Cortés y Santiago MasPOCH Andrés

15:30 Conferencia Invitada

IL-4. Manuel Montejo

Molecular and supramolecular chirality by VCD spectroscopy and quantum chemical calculations

16:00 Comunicaciones Orales: Análisis forense y bioquímico

O-16. *Double confirmation of MDMA abuse: saliva analysis*

S. Armenta, S. Garrigues, M. de la Guardia, J. Brassier, M. Alcalá, M. Blanco

O-17. *Evaluation of confocal Raman spectroscopy to identify gunshot residue particles*

M. López-López, C. García-Ruiz

O-18. *Porous membrane protected molecularly imprinted polymer based microsolid phase extraction for cocaine and metabolites assessment in human plasma by HPLC-MS/MS*

S. García-Carballal, J. Sánchez-González, A.M. Bermejo, M.J. Tabernero, P. Bermejo-Barrera, A. Moreda-Piñeiro

O-19. *Determination of lidocaine in urine at low ppm levels using dispersive microextraction and attenuated total reflectance-Fourier transform infrared measurements of dry films*

A. Sánchez-Illana, D. Pérez-Guaita, S. Garrigues, M. de la Guardia

17:00 **Café**

Sesión VI, presidida por José Miguel Vadillo Pérez

17:30 Comunicaciones orales: Casas comerciales II

O-20. Supercontinuum fiber lasers: White light with laser brightness. A new tool for advanced spectroscopy

P. Pérez-Millán, E. Ribes, J.L. Cruz, A. Díez, Y.O. Barmenkov, M.V. Andrés

O-21. Time-resolved spectroscopy using streak cameras

J. Sobrino

O-22. AFM for high resolution and high speed chemical imaging and first fully-integrated Raman Imaging + Scanning Electron microscope (RISE)

E. Bailo, J. Toporski, U. Schmidt

O-23. Improving analysis of large isotopes ratios using high sensitivity ICPMS

P. Cano, M. Hamester, R.Chemnitzner

18:30 **Asambleas de Sociedades**

19:30 Salida de autobuses desde Edificio Quintiliano

20:00 Visita y cena en bodega Campo Viejo

Viernes 11 de julio

Sesión VII, presidida por Pilar Bermejo Barrera y Luis Batista de Carvalho

09:30 Conferencia Plenaria

PL-4. Mario Berberan-Santos

Thermally activated delayed fluorescence. Fundamentals and applications in optical sensing and in OLED materials.

10:15 Comunicaciones Orales: Análisis ambiental

O-24. Molecularly imprinted polymer based – solid phase extraction for mercury speciation in seawater by HPLC-ICP-MS

M.P. Rodríguez-Reino, R. Domínguez-González, P. Bermejo-Barrera, A. Moreda-Piñeiro

O-25. First insights into mercury speciation in aquatic plants using coupled techniques based on gas chromatography and atomic fluorescence detection

M. Jiménez-Moreno, M.A. Lominchar, M.J. Sierra, R. Millán, R.C. Rodríguez Martín-Doimeadios

O-26. FAPA-APGD as ion source for VOCs detection by a novel ion differential mobility analyser

M. Bouza, J. Orejas, S. López-Vidal, J. Pisonero, N. Bordel, R. Pereiro, A. Sanz-Medel

O-27. Analytical environmental nanoscience: A new challenge for Analytical Chemistry in the XXI century

J.R. Castillo, P. Bermejo-Barrera, F. Laborda, E. Bolea, M.S. Jiménez, M.T. Gómez, G. Cepriá, A. Moreda, M.C. Barciela

11:15 **Café**

Sesión VIII, presidida por Concha Domingo y Carmen Cámara Rica

11:45 Comunicaciones Orales: Estructura atómica y molecular, materiales avanzados y otros

O-28. *Unveiling the early history of ultrafast laser ablation: Design, construction and evaluation of a femtosecond-resolved phase-change microscope*

I.M. Carrasco-García, M. López-Claros, J.M. Vadillo, J.J. Laserna

O-29. *Copper(II) complexes of cinnamic and caffeic acids: A Raman study*

N.F.L. Machado, M.P.M. Marques

O-30. *Crystal disruption in novel titanias for enhanced photocatalytical applications*

M. Rico-Santacruz, E. Serrano, A. Sepúlveda, E. Lalinde, J. Berenguer, J. García-Martínez

O-31. *Trimeric gold-mercury containing species as fluorescence quenchers*

D. Pascual, J.M. López de Luzuriaga, M. Monge, M.E. Olmos

O-32. *Insights into the coordination chemistry in the system $[Zn(l-Lac)(H_2O)_2]^+$ from DFT, NBO and QTAIM: Structure/vibrational spectra relationship*

M.C. Ramírez Aví, A.A. Márquez García, F. Partal Ureña

O-33. *SCA methodology for the analysis of deposited atmospheric particles on the surface of outdoors exhibited steel sculptures*

J. Aramendia, L. Gómez-Nubla, K. Castro, J.M. Madariaga

O-34. *Raman, SERS and DFT analysis of mauve dye and its components*

M.V. Cañamares, J.R. Lombardi

13:30 **Clausura y entrega de premios**

CONFERENCIAS PLENARIAS

Raman spectroscopy, a “*broad-spectrum*” tool: from rock art to Mars exploration; from graphene-based materials to medical diagnosis or cosmetics industry

C. Domingo.

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The “Raman effect” discovered in 1928 independently in India (C.V. Raman and K.S Krishnan) and in Russia (G.S. Landsberg and L.I. Mandelshtam), which led C.V. Raman to receive the Nobel Prize in Physics in 1930, has generated the development of several Raman Spectroscopy techniques. Acronyms such as SERS, CARS, ROA, TERS, TRS, SORS, ... and terminology (Raman microscopy, Raman imaging, ...) have burst into the scientific journals and even into the “analytical instrumentation” market, illustrating their *excellent* capabilities with *extraordinary* applications of Raman spectroscopy in so different areas as biomedicine, geology, semiconductors, Cultural Heritage, pharmaceutical industry or homeland security, among others. The long way since 1928 till now, when Raman Spectroscopy occupies an outstanding position among the materials characterization techniques, is paved with a great deal of basic research carried out by “Raman spectroscopists”, successfully accompanied by hard and extensive collaborative work for (relatively) fast integrating the scientific and technological progresses made in other research fields. In this sense, the commercialization of gas lasers more than 45 years ago, as sources of monochromatic and intense light able to efficiently excite the extremely weak Raman effect, was the beginning of a new age (*first renaissance*) for (Laser) Raman spectroscopy. Likewise, the huge advances in optics, microelectronics, computing science, etc. arisen since the mid-1990s have allowed a *second renaissance* for Raman Spectroscopy.

Consequently Raman instrumentation can be presently found not only in research laboratories of Universities and related Centers but also: as *on-line* tool in-process control monitoring of different industries (pharmaceutical, petrochemical, cosmetics, etc.); in the carbon materials - either diamond, carbon nanotubes or graphene -quality control premises; in the Restoration and Conservation laboratories of the most important Museums and Libraries all around the world; in the Mars planetary mission; in the security controls of airports; in the anatomic pathology divisions of hospitals or in Institutes of legal medicine and forensic sciences. And, please, don’t forget to look for “a *light Raman*” among the portable instrumentation carried off by the field archeological teams!. Moreover, such instrumentation can be mostly routinely used due to the existing Raman spectra databases, the application of multivariate components statistical analysis and the embedded software developed by the Raman instruments manufacturers.

The main *Strengths* of Raman spectroscopy lie in its non-destructive and non-invasive character and in the small quantity of sample (no/scarce preparation) needed for the analysis, with the important added value of providing molecular information beyond the elemental analysis made available by other analytical techniques. Further, it can be practically applied to all states of matter, even in extreme conditions such as high pressure or temperature. The *Weaknesses* of the “conventional” Raman technique, as the low intrinsic sensitivity and, sometimes, the strong competition of the much more intense fluorescent background, can be overcome using another one.

Bearing in mind that not all the present Raman techniques enjoy a similar *popularity*, I will present an overview of relevant applications together with a reasonable near-future outlook for Raman spectroscopy, daring also to comment some *Opportunities* and *Threats*.

Having worked as “Raman spectroscopist” (or having been closely bound to Raman techniques) during the last 42 years, I consider myself a “privileged witness” of the advances undergone by them, and can satisfactorily endorse that “*behind are the days when Raman spectroscopy was considered a difficult technique reserved to a few research laboratories*”. Nevertheless, in my opinion it is imperative to seriously continue supporting the so-called *basic studies* carried out in Research Centers, which are definitely at the base of the often mentioned and demanded “*Innovation*” which should allow broadening the applications of Raman Spectroscopy.

Art and archaeology through the spectroscopic looking glass

D. Anglos^{1,2}

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The scientific study and safeguarding of heritage objects relies largely on our capabilities to identify and quantify materials, understand corrosion or degradation processes and environmental impact and apply efficient restoration or preventive conservation treatments. And as it turns out, this is a highly challenging task, considering the inherently complex, multi-component nature of materials in such objects, which calls for elaborate and quite often case-specific analysis and conservation procedures. Furthermore, given the value and sensitivity of works of art, analysis needs to be carried out non-invasively, often directly on the object itself or, in certain cases, on increasingly small samples.

In recent years, analytical spectroscopies based on the use of laser sources have been proven capable to illuminate complex diagnostic problems. By tuning the wavelength of the laser source and/or by controlling the flux of photons it is possible to realize many different types of light-matter interactions and therefore to probe the composition of materials from different perspectives. Linear and non-linear spectroscopies, remote sensing methods and laser-assisted sampling-excitation schemes evidence the versatility offered by laser sources. Examples to illustrate how art materials can be looked at through the spectroscopic “looking glass” will be described with emphasis on the development of mobile and hybrid instrumentation that permit the collection of enhanced analytical information as well as access to highly valued artworks and objects in museums or excavation sites.

References

[1] D. Anglos, S. Georgiou, C. Fotakis. Lasers in the analysis of cultural heritage materials. *Journal of Nano Research* **8** (2009) 47.

[2] A. Nevin, G. Spoto, D. Anglos. Laser spectroscopies for elemental and molecular analysis in art and archaeology. *Appl. Phys. A* **106**, (2012) 339; doi: 10.1007/s00339-011-6699-z.

Dye doped silica nanoparticles as luminescent organized systems for nanomedicine

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Silica nanoparticles are versatile platforms with many intrinsic features, including a low toxicity. Proper design and derivatization yield particularly stable, very bright nanosystems displaying multiple functions, which can be used for either photoluminescence (PL) or electrochemiluminescence (ECL) sensing, labelling or imaging applications. [1,2] For these reasons silica nanoparticles already offer unique opportunities, and further improvement and optimization can substantially increase their applications in fields of high impact, such as medical diagnostics and therapy, environmental and food analysis, and security. This contribution describes silica-core/PEG-shell multi-component nanoparticles (NPs), tailored for optimization of processes such as directional energy transfer, which provide those systems with extremely valuable functions: high light-harvesting capability, signal-to-noise maximization, multiplex output, signal amplification, [1-5] also for in vivo imaging (figure 1).

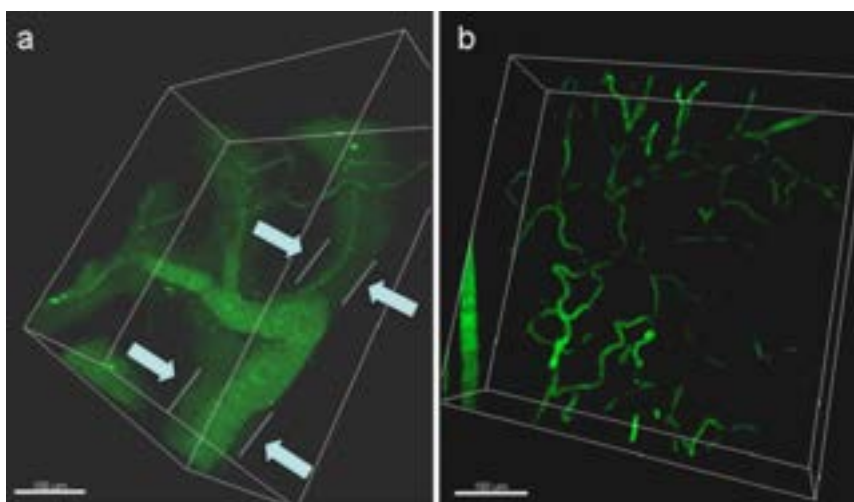


Figure 1: In vivo microscopic images of silica-core/PEG-shell multi-component nanoparticles in tumour (panel a) and in ear (panel b). [5]

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References

- [1] S. Bonacchi, D. Genovese, R. Juris, M. Montalti, L. Prodi, E. Rampazzo, N. Zaccheroni. Luminescent silica nanoparticles: extending the frontiers of brightness. *Angew. Chem. Int. Ed.* 50 (2011) 4056.
- [2] M. Montalti, L. Prodi, E. Rampazzo, N. Zaccheroni. Dye Doped Silica Nanoparticles as Luminescent Organized Systems for Nanomedicine. *Chem. Soc. Rev.*, in press.
- [3] E. Rampazzo, S. Bonacchi, D. Genovese, R. Juris, M. Sgarzi, M. Montalti, L. Prodi, N. Zaccheroni, G. Tomaselli, S. Gentile, C. Satriano, E. Rizzarelli. A versatile strategy for signal amplification based on Core/Shell Silica Nanoparticles. *Chem. Eur. J.* 17 (2011) 13429.
- [4] M. Soster, S. Bonacchi, D. Genovese, R. Juris, M. Montalti, E. Rampazzo, N. Zaccheroni, P. Garagnani, F. Bussolino, L. Prodi, S. Marchiò. Targeted dual-color silica nanoparticles provide univocal identification of micrometastases in preclinical models of colorectal cancer. *Int. J. Nanomedicine* 7 (2012) 4797.
- [5] E. Rampazzo, F. Boschi, S. Bonacchi, R. Juris, M. Montalti, N. Zaccheroni, L. Prodi, Calderan, B. Rossi, L. S. Becchi, A. Sbarbati. Multicolor Core/Shell Silica Nanoparticles for in vivo and ex-vivo Imaging. *Nanoscale* 4 (2012) 824.

Thermally activated delayed fluorescence. Fundamentals and applications in optical sensing and in OLED materials

Mario Berberan-Santos

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Thermally Activated Delayed Fluorescence (TADF) following optical excitation has been studied by us both theoretically and in relation with fullerenes [1-5]. Recently, TADF became relevant in temperature and oxygen optical sensing [6-9] and in the Organic Light-Emitting Diode (OLED) field, leading to outstanding results (3rd generation OLED materials) [10]. In the last case both the singlet and the triplet are directly excited. We will contrast the kinetics for optical excitation and for electron-hole recombination, and will also refer the nature and significance of the unique ¹³C isotope effect observed in the TADF of fullerenes [4,5,9].

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References

- [1] M.N. Berberan-Santos, J.M.M. Garcia, Unusually strong delayed fluorescence of fullerene C₇₀, J. Am. Chem. Soc. 118 (1996) 9391.
- [2] C. Baleizão, M.N. Berberan-Santos, Thermally activated delayed fluorescence as a cycling process between excited singlet and triplet states. Application to the fullerenes, J. Chem. Phys. 126 (2007) 204510.
- [3] C. Baleizão, M.N. Berberan-Santos, Thermally activated delayed fluorescence in fullerenes, Ann. N. Y. Acad. Sci. 1130 (2008) 224.
- [4] C. Baleizão, M.N. Berberan-Santos, The brightest fullerene. A new isotope effect in molecular fluorescence and phosphorescence, ChemPhysChem 12 (2011) 1247.
- [5] T. Palmeira, A. Fedorov, M.N. Berberan-Santos, Temperature dependence of the phosphorescence and of the thermally activated delayed fluorescence of ¹²C₇₀ and ¹³C₇₀ in amorphous polymer matrices. Is a second triplet involved? Methods Appl. Fluoresc. 2 (2014) xxxx.
- [6] C. Baleizão, S. Nagl, S.M. Borisov, M. Schäferling, O.S. Wolfbeis, M.N. Berberan-Santos, An optical thermometer based on the delayed fluorescence of C₇₀, Chemistry Eur. J. 13 (2007) 3643.
- [7] S. Nagl, C. Baleizão, S.M. Borisov, M. Schäferling, M.N. Berberan-Santos, O.S. Wolfbeis, Optical Sensing and Imaging of Trace Oxygen with Record Response, Angew. Chem. Int. Ed. 46 (2007) 2317.
- [8] C. Baleizão, S. Nagl, M. Schäferling, M.N. Berberan-Santos, O.S. Wolfbeis, Dual Fluorescence Sensor for Trace Oxygen and Temperature with Unmatched Range and Sensitivity, Analytical Chemistry 80 (2008) 6449.
- [9] S. Kochmann, C. Baleizão, M.N. Berberan-Santos, O.S. Wolfbeis, Sensing and imaging of oxygen with ppb limits of detection and based on the quenching of the delayed fluorescence of ¹³C₇₀ fullerene in polymer hosts, Anal. Chem. 85 (2013) 1300.
- [10] C. Adachi, Third-generation organic electroluminescence materials, Jpn. J. Appl. Phys. 53 (2014) 060101.

CONFERENCIAS INVITADAS

Non-invasive methods for clinical elemental analysis. Direct analysis of dried matrix spots for diagnosis and control

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The analysis of biological fluids, such as blood or urine, presents a certain number of problems throughout all steps of the analytical process. In this regard, collection and preservation of such samples as well as transportation to the analytical lab may be especially problematic, particularly when the patients live in isolated areas, requiring a considerable amount of resources and difficulties to properly dispose of all materials that have been in contact with the samples. The deposition of biological fluids onto clinical filter paper, producing a dried matrix spot (DMS), is a methodology that has become increasingly popular in the years to date and is nowadays deployed in a wide variety of bioanalytical contexts, such as screening for metabolic diseases in newborns, therapeutic drug monitoring, pharmacokinetic or toxicological and forensic studies.¹ This popularity is a consequence of the significant advantages brought by this methodology, that permits the development of minimally or non-invasive collection approaches, and results in specimens (DMS) that are very stable and can be easily transported and stored.

However, there is still a very limited number of works exploring its potential for elemental analysis. In part, this can be explained considering that the transformation of a liquid sample (e.g., blood or urine) into a solid one (DMS) often implies additional problems for the analyst, such as lower sensitivities or enhanced matrix effects. Fortunately, there are analytical techniques that permit direct analysis of these types of solid samples and are capable of offering an excellent performance.

In this presentation, the different characteristics of Dried Urine Spots (DUS) and Dried Blood Spots (DBS) will be examined, with the aim of developing methodologies that permit the elemental and isotopic analysis of both types of samples using either high-resolution continuum source graphite furnace atomic absorption spectrometry (HR CS GFAAS) or laser ablation-inductively coupled plasma-mass spectrometry (LA-ICPMS). In particular, the benefits deriving from the use of a fs-LA unit capable of operating at a high repetition rate (up to 100 000 Hz) in order to achieve fully quantitative information will be highlighted.

The usefulness of these approaches and its application to a variety of situations, such as i) fast screening of large populations;² ii) monitoring of chronic patients,³ and iii) early detection of disease associated with the metabolism of some metals⁴ will be discussed in detail.

Acknowledgements

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References

- [1] S. Tanna, G. Lawson, Analytical methods used in conjunction with dried blood spots, *Anal. Meth.* 3 (2011) 1709.
- [2] M. Resano, L. Rello, E. Garcia-Ruiz, M.A. Belarra, Minimally-invasive filter paper test in combination with solid sampling-graphite furnace atomic absorption spectrometry for Pb determination in whole blood, *J. Anal. At. Spectrom.* 22 (2007) 1250.
- [3] M. Aramendía, L. Rello, F. Vanhaecke, M. Resano, Direct trace-elemental analysis of urine samples by laser ablation-inductively coupled plasma-mass spectrometry after sample deposition on clinical filter papers, *Anal. Chem.* 84 (2012) 8682.
- [4] M. Resano, M. Aramendía, L. Rello, M. L. Calvo, S. Bérail and C. Pécheyran, Direct determination of Cu isotope ratios in dried urine spots by means of fs-LA-MC-ICPMS. Potential to diagnose Wilson's disease, *J. Anal. At. Spectrom.* 28 (2013) 98.

Spectroscopy of a muonium atom formed inside a semiconductor

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Muonium is a bound state of a positive muon and an electron. When positive muons are implanted in a semiconductor, a fraction of them form muonium. The muonium atom acts as a light isotope of hydrogen, exhibiting its typical splitting of the lowest energy level due to the hyperfine interaction between the electron and the nucleus spins [1].

At low temperatures (of the order of tens of mK) and high magnetic fields (1-2 T) the relative population of the hyperfine energy levels corresponding to spin up and spin down electrons can be measured using the muon spectroscopy technique (μ SR). This ratio is found to be very sensitive to the defect content of the sample in semiconductors like CdTe, CdS or Si [2,3].

The muonium formation probability is also an important parameter, yielding local information on the electron processes occurring inside a semiconductor. Muonium formation inside a p-n junction for example, can be used as a local probe giving spatially resolved information on electron charge dynamics [4].

Selected examples of muonium formation in semiconductors will be presented and the relevant physical information conveyed by its spectroscopy study will be discussed.

Acknowledgements

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References

- [1] S. F. J. Cox, Muonium as a model for interstitial hydrogen in the semiconducting and semimetallic elements, Rep. Prog. Phys., 72 (2009) 116501.
- [2] H. V. Alberto, A. Weidinger, R. C. Vilão, J. Piroto Duarte, J. M. Gil, J. S. Lord, S. F. J. Cox, Mechanisms of electron polarization of shallow muonium in CdTe and CdS, Phys. Rev. B, 81 (2010) 245205.
- [3] H. V. Alberto, R. C. Vilão, J. Piroto Duarte, J. M. Gil, A. Weidinger, J. S. Lord, and S. F. J. Cox, Electron polarization and formation probability of bound muonium in CdS and Si, Phys. Rev. B 86, (2012), 035203.
- [4] R.C. Vilão, H.V. Alberto, J.M. Gil, J. Leitão, A. Cunha, T. Prokscha, Muonium study of a CZTS-based p-n junction, PSI Experimental report 20121651 (2013).

Applications of Raman spectroscopy: From the historical heritage to the space exploration

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Raman spectroscopy is a powerful tool allowing the structural analysis of matter in either the solid, liquid or gas state in a fast, reliable and non destructive way.

In the last years Raman spectroscopy experienced a huge expansion multiplying its capabilities in a wide range of applications such as material science, chemistry, geology, biology, etc.

The combination of miniaturisation in optical components, developments on optical fibres and electronics leaded recently to the possibility to built small and powerful spectrometers able to analyse samples without any preparation at the field, at the industry or inside the museums.

In this context the present work intend to illustrate how this technique can supply relevant information on the structural characterisation of materials on the basis of several examples related with our historical heritage and with the future missions to Mars.

In the historical heritage, results from the analysis of minerals, artworks, frescoes and manuscripts will be presented and discussed [1-3].

For the future missions to Mars the current state of the Raman spectrometer for Exomars mission under development inside our group together with the future development of remote combined Raman-LIBS for the NASA 2020 mission will be presented and discussed.

In addition, several results obtained at the field and laboratory using prototypes of the proposed instruments will be used to discuss the scientific potential of the technique in the planetary exploration on the solar system [4-6].

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References

- [1] J. Dubessy, M.C. Caumon, and F. Rull, Editors. EMU notes in Mineralogy Volume 12 -- Raman Spectroscopy Applied to Earth Sciences and Cultural Heritage. 504 pp. ISBN 978 0 903056 31 1, (2012).
- [2] S. E. Jorge Villar, H.G.M. Edwards, J. Medina, F. Rull Pérez "Raman Spectroscopic Analysis of Mediaeval Wall Paintings in the Palencia Region, Spain", Journal of Raman Spectroscopy, 37, 238-245 (2005).
- [3] H G M Edwards, F Rull Pérez, A R David "Raman microscopy in Art and Archaeology: illumination of historical mysteries. Inst. Phys. Conf. Ser. No. 165. 85-86, (2000).
- [4] Fernando Rull, Jesús Martínez-Frías "Raman spectroscopy goes to Mars" Spectroscopy Europe, vol 18, nº 1(2006),
- [5] F. Rull, M. J. Muñoz-Espadas, R. Lunar and J. Martínez-Frías, Raman spectroscopic study of four Spanish shocked ordinary chondrites: Cañellas, Olmedilla de Alarcón, Reliegos and Olivenza, Phil. Trans. R. Soc. A 368, 3153-3166. (2010)
- [6] Grégory Bazalgette Courrèges-Lacoste, Berit Ahlers, Erik Boslooper, Fernando Rull-Pérez, Sylvestre Maurice "Combined Raman spectrometer/ Laser-Induced Breakdown spectrometer design concept" Procc. 6th International Conference Space Optics, ESTEC, 27-30 July 2006

Molecular and supramolecular chirality by VCD spectroscopy and quantum chemical calculations

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The so-called classic vibrational spectroscopy techniques (i.e. IR and Raman) have been extensively used during the last 30 years for the structural characterization and conformational analysis of a wide range of molecular systems in multidisciplinary works where other experimental techniques as well as quantum chemical calculations were also implemented.

The use for this task of chirality sensitive vibrational spectroscopies, such as vibrational circular dichroism (VCD), is an expanding field, arising from the middle of the 90's decade of the last century. During this period, VCD has been used in studies aiming the spectroscopic characterization of chiral molecular systems of biological (such as peptides or carbohydrates) and technological (polymers, liquid crystals etc.) interest.

The systems studied can be divided in two different groups, depending on the type of chirality exhibited. Thus, on one hand, there are systems presenting chirality *per se*, i.e. molecular chirality.

Moreover, there exist certain molecular assemblies in which the chirality arises as a consequence of the adequate orientation of non-covalent interactions established among isolated units (molecules) being these chiral or not, hence speaking of supramolecular chirality.

In the specific case in which two isolated chiral units interact according to a substrate-receptor model, their stereochemistry will control the nature and strength of the binding forces, influencing the stability of the subsequent complex. This is called chiral molecular recognition, phenomenon which controls a number of biological processes such as enzymatic activity or drug action. If the interacting units are not chiral, supramolecular chirality may be induced photochemically or by the presence of certain solvents or other species in the medium.

Up to date, our research group has used the VCD technique for the structural characterization, conformational analysis or even the assessment of the absolute configuration of systems presenting either molecular or supramolecular chirality, always in a frame of work involving, likewise, the use of quantum chemical calculations and other spectroscopic techniques (IR, Raman). From the first group of systems, the conformational landscape of some amino acids [1] and terpenes [2] (among other species) has been explored.

Concerning supramolecular chirality, the selectivity of a chiral substrate (namely the all-S diastereomer of the crown ether called 18c6H₄) towards the L and D forms of the amino acid serine, has been analysed.[3] Further, other systems with supramolecular chirality have been subject of study, such as some azopolymer liquid crystals species [4] and several 1H-indazole derivatives [5], the latter allowing the observation of the phenomenon of spontaneous resolution of chiral crystalline structures.

References

- [1] M.M. Quesada, A.A. Márquez, J.R. Avilés, J.J. López González. Conformational landscape of l-threonine in neutral, acid and basic solutions from vibrational circular dichroism spectroscopy and quantum chemical calculations. *Tetrahedron:Asymmetry*. 24 (2013) 1537.
- [2] J.R. Avilés, F. Partal, J.J. López González. Conformational preference of a chiral terpene: vibrational circular dichroism (VCD), infrared and Raman study of S-(–)-limonene oxide. *Phys. Chem. Chem. Phys.* 11 (2009) 2459.
- [3] J.R. Avilés, M.M. Quesada, J.J. López González, B. Martínez Haya. Chiral Recognition of Amino Acid Enantiomers by a Crown Ether: Chiroptical IR-VCD Response and Computational Study. *J. Phys. Chem. B* 117 (2013) 9362.
- [4] R.M. Tejedor, L. Oriol, J.L. Serrano, F. Partal, J.J. López González. Photoinduced Chiral Nematic Organization in an Achiral Glassy Nematic Azopolymer. *Adv. Funct. Mater.* 17 (2007) 3486.
- [5] J.R. Avilés, M.M. Quesada, J.J. López González, R.M. Claramunt, C. López, I. Alkorta, J. Elguero. Self-Assembly Structures of 1H-Indazoles in the Solution and Solid Phases: A Vibrational (IR, FIR, Raman, and VCD) Spectroscopy and Computational Study. *ChemPhysChem* 14 (2013) 3355.

COMUNICACIONES ORALES

Diameter selection of carbon nanotubes in arrays of polymer/SWCNT nanowires by template wetting

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Flexible electronics offer a wide-variety of novel applications such as flexible circuits, flexible displays, touch screens and implantable medical devices [1]. Although devices composed of individual carbon nanotubes (CNTs) have been considered as an option to enable some of these applications, they have been deemed impractical for commercialization due to the difficulty of manipulation and placing individual CNTs at desired locations. One alternative for CNTs manipulation and transfer to industrial production are polymer/CNT nanocomposites, adding to the system good viscoelastic properties and processability. The key to transfer the unique electrical conductivity and mechanical strength of CNTs to polymer nanocomposites is to control both the dispersion and percolation of CNTs within the polymer matrix.

One step more in the application of polymer/CNT nanocomposites in flexible electronics is the fabrication of arrays of nanostructures. Arrays of polymer/SWCNT nanowires supported by a residual nanocomposite film have been prepared by melt wetting, using porous anodic aluminum oxide (AAO) as a template. By Raman spectroscopy we have quantified SWCNT aggregation by analyzing their Raman radial breathing modes (RBMs) [2]. In addition, probing the cross section of the samples by Raman microscopy the RBMs reveal that as we enter into the membrane some carbon nanotubes are filtrated indicating a diameter selection of SWCNTs by the AAO membrane allowing mainly the infiltration of thinner nanotubes into the nanopores and excluding the thickest ones.

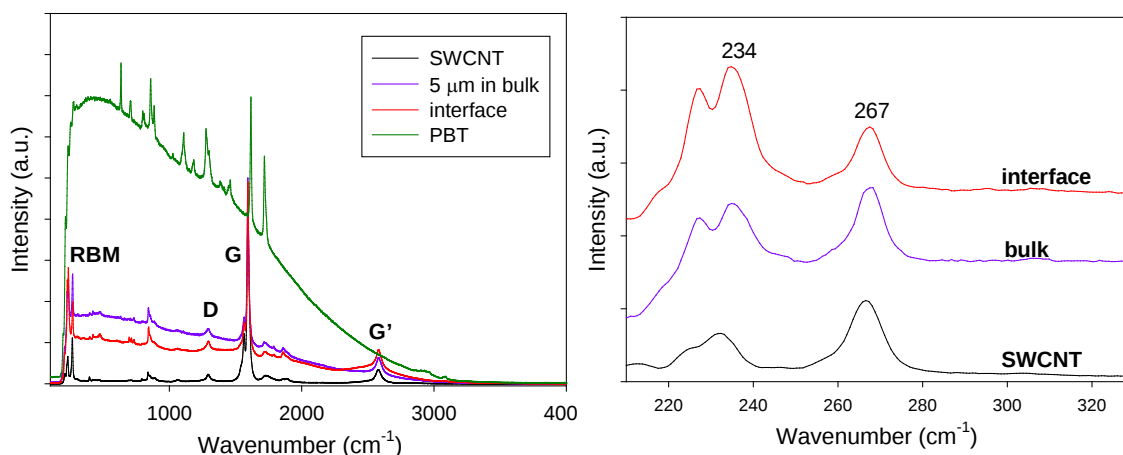


Figure 1. Raman spectra obtained from poly(butylene terephthalate) (PBT) without carbon nanotubes, from native SWCNTs, from the residual PBT/SWCNT film (bulk) and from the interface between the residual nanocomposite film and the nanoarray into the AAO template (left). Zoom of the radial breathing modes (RBMs) region of Raman spectra (right).

Acknowledgements

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References

- [1] S. Park, M. Vosguerichian, Z. Bao. A review of fabrication and applications of carbon nanotube film-based flexible electronics. *Nanoscale* 5 (2013) 1727.
- [2] D.A. Heller, P.W. Barone, J.P. Swanson, et al. Using Raman spectroscopy to elucidate the aggregation state of single-walled carbon nanotubes. *J. Phys. Chem. B* 108 (2004) 6905.

Synthesis and study of plasmonic properties of gold-silver nanostructures: From a spherical nanoparticles to ultrathin nanowires.

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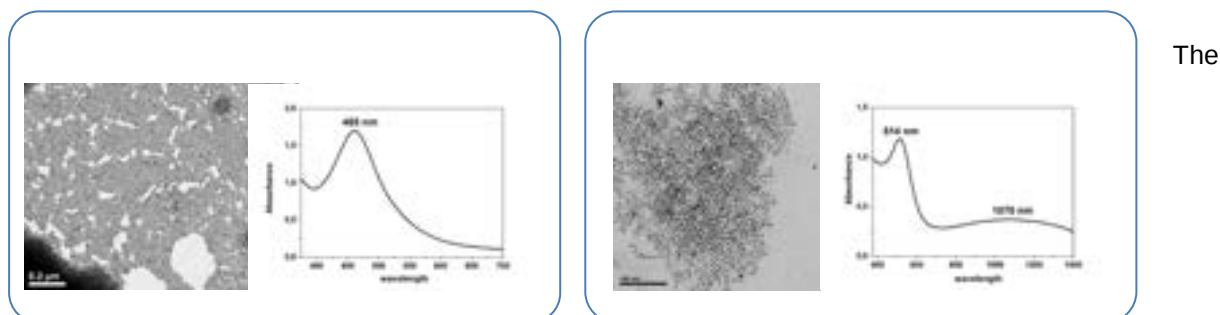
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The plasmon resonances and other optical properties of noble metal nanoparticles have generated enormous scientific interest. There are numerous applications for plasmon-active nanoparticles, especially in areas such as biological microscopy, medicine, and sensors [1]. We have developed an organometallic approach that allows the synthesis of nanoparticles using mild conditions by the chemical reduction of perfluoroaryl metal precursors in the presence of different capping agents. This methodology permits to exert a delicate control over the size, shape and composition of the nanostructures [2]. Bimetallic gold-silver nanoparticles have been obtained through the reduction of the organometallic complex $[\text{Au}_2\text{Ag}_2(\text{C}_6\text{F}_5)(\text{Et}_2\text{O})_2]_n$. Small spherical alloy nanoparticles are obtained when hexadecylamine is used as capping agent, whereas ultrathin nanowires are obtained when oleic acid is used as stabilizing agent (see Figure).



gold-silver bimetallic nanoparticles obtained display very interesting plasmonic properties. Thus, when hexadecylamine is used as capping agent the composition-controlled gold-silver alloyed nanoparticles permits the tuning of the Localized Surface Plasmon Resonance (LSPR) in the 400-530 nm range. When ultrathin nanowires are obtained the LSPR is kept around 500-510 nm, but the different nanowire length permits the tuning of the longitudinal plasmon resonance in the near-infrared region. Several spectroscopic techniques such as UV-Vis-NIR absorption, ^{19}F nuclear magnetic resonance or energy dispersive X-ray and advanced electron microscopy techniques have been used in the characterization of the nanomaterials.

Acknowledgements

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References

- [1] M.B. Cortie, A. M. McDonagh. Synthesis and Optical Properties of Hybrid and Alloy Plasmonic Nanoparticles. Chem. Rev. 111 (2011) 3713.
- [2] J. Crespo, A. Falqui, J. García-Barrasa, J. M. López-de-Luzuriaga, M. Monge, M. E. Olmos, M. Rodríguez-Castillo, M. Sestu, K. Soulantica. Synthesis and Plasmonic Properties of Monodisperse Au-Ag Alloy Nanoparticles of Different Compositions from a Single-Source Organometallic Precursor. J. Mat. Chem. C (2014) DOI: 10.1039/C3TC32577F.

Gaps induced by molecular linkage of plasmonic nanoparticles in colloidal suspensions for SERS enhanced pesticide sensing

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Linear α,ω -dithiols with aliphatic nature have been used in this work as linkers to control the aggregation of silver nanoparticles and to induce the formation of interparticle gaps. The interest of these gaps resides in the well-known fact that when plasmonic surfaces are within a close distance, their plasmon modes couple [1]. This event affects the electromagnetic field distribution in a manner that a drastic enhancement occurs in the gaps leading to the creation of *hot spots*. As a result, the optical response of substances situated inside the hot spots is strongly increased, which is highly valuable for their use in surface-enhanced spectroscopies. In this work we present a study of the formation and the characterization of the gaps formed by using dithiols of different lengths, where both thiol groups are connected by a linear aliphatic chain with 6, 8 and 10 CH_2 groups. This characterization was done by using plasmon resonance and transmission electron microscopy (TEM). The Surface-Enhanced Raman Scattering (SERS) technique was employed in the investigation of the adsorption of these dithiols on the metal surface by analysing key structural spectral markers of the adsorption, metal coordination, orientation, ordering and interfacial packing of these molecules on surfaces of silver and gold NPs [2]. The fingerprint character of SERS spectra, the propensity rules of SERS [3] and the high sensitivity of this technique make this study possible even at the very low concentration of dithiols sufficient to induce the NPs linking. Dithiol-linked nanoparticles were employed as sensors in the detection of the pesticides aldrin, dieldrin, endosulfan and linden at very low concentrations, taking advantage of the high affinity of these pollutants for aliphatic-like membranes. The sensing ability of these substrates was optimized by varying the surface coverage of dithiols (Figure 1).

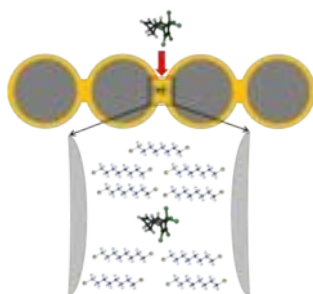


Figure 1: Detection of pesticide molecules (aldrin) by insertion into interparticle gaps induced by nanoparticle linking with dithiols.

Finally, the adsorption of pesticides on the functionalized metal surfaces was studied by obtaining the adsorption isotherms, which provided the affinity constant and the linearity curve to relate the SERS intensity to the pollutant concentration. According to the results, the functionalization with dithiols induces the formation of chain-like aggregates where the hot spots are localized in the interparticle gaps induced by the multi-layered adsorption of dithiols, which in turn are able to link the pesticide molecules.

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References

- [1] S. Sheikholeslami, Y.W. Jun, P.K. Jain, A.P. Alivisatos, Coupling of Optical Resonances in a Compositionally Asymmetric Plasmonic Nanoparticle Dimer, *Nano Lett.* 10(2010)2655.
- [2] I. Izquierdo-Lorenzo, J. Kubackova, D. Manchon, A. Mosset, E. Cottancin, S. Sanchez-Cortes, Linking Ag Nanoparticles by Aliphatic α,ω -Dithiols: A Study of the Aggregation and Formation of Interparticle Hot Spots, *J. Phys. Chem. C* 117(2013)16203.
- [3] M. Moskovits, *J Chem Phys, Surface Selection-Rules*, 77(1982)4408.

An ICPMS-based analytical platform for the determination of nanoparticles released from nanocomposites

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The lack of reliable methods to determine nanoparticles identity, characteristics and concentrations, as well as their transformations in complex systems (environmental and biological) is one of the most significant troubles in nanosciences. In the case of environmental nanosciences, analysis at environmentally relevant concentrations adds an extra level of difficulty.

Inductively coupled plasma mass spectrometry (ICPMS) is a multielemental-specific technique, which is used routinely for the quantification of the elemental content of nanoparticles and nanomaterials. However, novel approaches based on the use of ICPMS are emerging. Direct analysis based on the detection of individual nanoparticles (single particle-ICPMS) [1] and hyphenation of flow field flow fractionation (FIFFF) techniques to ICPMS [2] are two of the most promising ones. Whereas FIFFF-ICPMS allows the separation and quantification of nanoparticles according to their size, single particle detection ICPMS provides information about dissolved and nanoparticle forms of an element, size distributions, and number and mass concentration without previous separation. The use of ultrafiltration in combination with ICP-MS analysis allows to fractionate an element in a suspension as dissolved and nanoparticle forms, complementing and supporting the information provided by the two other methods.

A platform of analytical methods based in ultrafiltration-ICPMS, single particle-ICPMS and FIFFF-ICPMS is proposed to face and solve different types of nanometrological problems, which are current challenges in nanosciences, as well as in analytical chemistry.

State of the art of the cited above methodologies will be presented, discussing their performance, challenges, limitations and complementarity. Application to selected cases about releasing of nanoparticles from nanocomposites will also be presented.

Acknowledgements

This work was supported by the Spanish Ministry of Economy and Competitiveness, project CTQ2012-38091-C02-01.

References

[1] F. Laborda, E. Bolea, J. Jimenez-Lamana. Single Particle Inductively Coupled Plasma Mass Spectrometry: A Powerful Tool for Nanoanalysis. *Anal. Chem.* 2014, 86, 2270–2278

[2] E. Bolea, J. Jimenez-Lamana, F. Laborda, I. Abad-Alvaro, C. Blade, L. Arola, J. R. Castillo. Detection and characterization of silver nanoparticles and dissolved species of silver in culture medium and cells by AsFIFFF-UV-Vis-ICPMS: application to nanotoxicity tests. *Analyst* 139 (2014) 914.

A novel quantum dot-based phosphorescent immunoassay for PSA detection in human serum: Signal amplification strategies based on ICP-MS detection

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Photoluminescent techniques have aroused great interest in the development of new bioanalytical methodologies, as these analytical techniques have great advantages in terms of sensitivity and selectivity. Moreover, the luminescent signal is localized being specially suited for optical imaging studies without the need of perform a biopsy for analytical detection. In particular, within the different photoluminescent techniques, phosphorescence stands out for having very advantageous properties such as large separation between absorption and emission wavelength, long lifetime of the triplet excited state, autofluorescence of biological media can be easily avoided, etc.

Although analytical methods based on photoluminescence are highly interesting, their development is limited due to the lack of luminescent compounds sensitive to the species of interest, problems of photostability and limited quantum yields typical from conventional organic luminescent species. With the recent development of nanotechnology, different nanomaterials have reached great interest in analytical chemistry; among these colloidal semiconductor nanoparticles (QDs) have improved luminescent properties and biocompatibility that make them excellent materials for use as indicators in the development of bioanalytical applications [1].

Moreover, in bioanalytical methodologies that involve QDs, Inductively Coupled Plasma Mass Spectrometry (ICPMS) is especially attractive due to high advantages of this technique such as its extreme sensitivity for the detection of metals, low matrix effects, and simultaneous multielemental and isotopic detection, so it has a high potential for multiplex analysis [2].

In this context, a phosphorescent Mn doped ZnS QDs-based immunoassay is presented for the detection of Prostate Specific Antigen (PSA) as analyte model in biological samples. Phosphorescent and metal detection were carried out and their analytical figures of merit were compared. ICPMS is able to improve phosphorescent detection limits due to elemental amplification of these nanoparticles composed by hundred of atoms. In this sense, these Mn doped ZnS QDs would allow phosphorescent and elemental detection with the same immunological strategy depending on detection limits required.

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References

- [1] J.M. Costa-Fernández. Optical sensors based on luminescent quantum dots. *Anal. Bioanal. Chem.* 384 (2006) 37.
- [2] A.R. Montoro, L.Traipella, J. Ruiz Encinar, J.M. Costa-Fernández, R. Pereiro, A. Sanz-Medel. Elemental and molecular detection for Quantum Dots-based immunoassays: A critical appraisal. *Biosens. Bioelectron.* 33 (2012) 165.

Bioconcentration and toxicity studies of titanium dioxide nanoparticles by zebrafish embryos

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The production of (TiO₂NPs) for commercial applications has increased extraordinarily over the last years and so its potential risk for human health. Information on the behavior of these nanoparticles in the environment and their potential toxicity to aquatic organisms is very scarce, and there is greater concern regarding their release into the environment. Bioaccumulation serves as a good integrator to assess chemical exposure in aquatic systems and is dependent on factors such as the exposure routes, the diet, and the aqueous medium. Here, we calculated the experimental bioaccumulation capability of ionic titanium and TiO₂NPs by zebrafish (*Danio rerio*) eleutheroembryos through bioconcentration factors (BCFs), after 48 or 72 hours of exposure. The stability of both chemical forms in an aquatic medium was fully characterized for further bioconcentration studies. Several stabilizing agents (for anatase and rutile, the two isoforms of TiO₂NPs, were evaluated to check the evolution of the 48-72 hour aggregation process. A high percentage of TiO₂NPs remained disaggregated under simulated environmental conditions with addition of 50 mg·L⁻¹ of humic acids. However, the presence of eleutheroembryos in the exposure medium increased TiO₂NPs aggregation during the experimental tests. BCFs values below 100 were obtained indicating there was low bioaccumulation of both titanium chemical forms in early life stages of zebrafish at the concentrations tested. Toxicity tests were performed on the embryos at different exposure concentrations of TiO₂NPs (ranging from 2 to 100 ppm). No acute toxicity was detected in these conditions. To evaluate possible sub-acute effects, expression analysis was performed on a variety of genes; of these only *fos* and *nfkβ* were significantly induced with respect to the control, indicating a possible effect of this compound on cellular processes such as proliferation and apoptosis.

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Experimental observation of fano- and Lorentz-like line shapes in the optical extinction of plasmonic nanorods

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Metallic nanorods are widely used as generic plasmonic dipole antennas operating at optical and near-infrared frequencies, forming an analogue to classical half-wave dipole antennas. The fundamental dipole and higher order antenna modes have been extensively studied experimentally using optical spectroscopy and a broad range of mapping techniques. Likewise, theoretical investigations have elucidated the antenna modes' scaling properties, their dependence on the shape, size, and dielectric environment by using a variety of methods. Despite this large interest in nanorods, only very few theoretical reports address the scattering behavior with a focus on the spectral line shape [1-3].

Plasmon resonance, as a wave phenomenon, is expected to present interference characteristics. For localized surface plasmon resonances, interference of spectrally overlapping and coupled modes is well recognized to affect the scattering behavior of the nanostructure under investigation [4, 5]. In particular, the interference of a broad background continuum state with spectrally sharp higher order resonances can lead to a spectral response with asymmetric Fano-like line shapes in a variety of nanoparticle configurations. Only recently, it was indicated that Fano resonances may appear for individual nanorods provided that interacting modes overlap in both spatial and frequency domains [1, 2]. Interestingly, the narrow asymmetrical line shape of a nanorod's Fano interference is, for example, more favorable for label-free biosensing than broader Lorentzian resonances [3].

In our present work [6], we study the spectral line shapes of metallic nanorod antennas in detail, using extinction spectroscopy and finite element simulations. Surface plasmon resonances of odd mode parity present Fano interference in the scattering cross-section resulting in asymmetric spectral lines. Contrarily, modes with even parity appear as symmetric Lorentzian lines. The emergence of either constructive or destructive mode interference is explained with a semi-analytical 1D line current model. This simple model directly explains the mode-parity dependence of the Fano-like interference. Plasmonic nanorods are widely used as half-wave optical dipole antennas. Our findings offer a perspective and theoretical framework for operating these antennas at higher order modes.

References

- [1] J. M. Reed, H. Wang, W. Hu, S. Zou. Shape of Fano resonance line spectra calculated for silver nanorods. *Opt. Lett.* 36 (2011) 4386.
- [2] F. López-Tejeira, R. Paniagua-Domínguez, R. Rodríguez-Oliveros, J. A. Sánchez-Gil. Fano-like interference of plasmon resonances at a single rod-shaped nanoantenna. *New. J. Phys.* 14 (2012) 023035.
- [3] F. López-Tejeira, R. Paniagua-Domínguez, J. A. Sánchez-Gil. High-Performance Nanosensors Based on Plasmonic Fano-like Interference: Probing Refractive Index with Individual Nanorice and Nanobelts. *ACS Nano* 6 (2012) 8989.
- [4] B. Luk'yanchuk, N. I. Zheludev, S. A Maier, N. J. Halas, P. Nordlander, H. Giessen, C. T. Chong. The Fano resonance in plasmonic nanostructures and metamaterials. *Nature Mater.* 9 (2010) 707.
- [5] V. Giannini, Y. Francescato, H. Amrania, C. C. Phillips, S. A. Maier. Fano resonances in nanoscale plasmonic systems: a parameter-free modeling approach. *Nano Lett.* (2011) 2835.
- [6] N. Verellen et al., 2014 (submitted).

Biomedical applications of laser induced breakdown spectroscopy in bacterial identification

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Antibiotic resistant bacterial strains belonging to same species were identified and discriminated using laser induced breakdown spectroscopy (LIBS) and neural networks (NN) algorithm. The method has been applied to identify 40 bacterial strains i.e. *Escherichia coli* (Ec), *Pseudomonas aeruginosa* (Pa), *Klebsiella pneumoniae* (Kp), *Salmonella typhimurium* (St), *Salmonella pullorum* (Sp) and *Salmonella salamae* (Ss). The bacterial samples analyzed included strains isolated from clinical samples and constructed in laboratory. The strains differed from each other in mutations as a result of their resistance to one or more antibiotics. Kp, Ec and Pa strains showed multidrug antibiotic resistance and multiple genes mutations, whereas St, Sp and Ss were resistant to kanamycin and differed in only one gene.

LIBS is a non-microbiological technique which has been used in various studies to deal with rapid bacterial identification based on the elemental composition of bacterial cells [1-4]. In a previous study by our group [4], LIBS/NN has shown to be a promising methodology to classify and predict bacterial samples at genus level. This work is an extension of the previous study in order to investigate the application of LIBS/NN to discriminate different antibiotic resistant strains of same bacterial species and address its use as a rapid potential diagnostic methodology. The objective was to determine if genetic variations between bacterial strains of the same bacterial species, even when there is a difference in only one gene, generate sufficient or significant changes in their atomic composition which can be detected by LIBS/NN method in order to achieve their identification and discrimination. Single shot LIBS measurements combined with supervised neural network method were sufficient for a clear identification and classification of bacterial strains differing in multiple and even single mutation. Identification of strains with such minute differences i.e. even a single gene shows the high capacity of the proposed methodology. The results demonstrate the potential of this method to be used for continuous monitoring of the bacterial infections and identify pathogenic bacteria at an early stage of infection, which can be significant towards an early treatment of the infections.

References

- [1] D. Marcos-Martinez, J.A. Ayala, R.C. Izquierdo-Hornillos, F.J.M. de Villena, J.O. Caceres, Talanta, 84 (2011), 730–737
- [2] S.J. Rehse, Q.I. Mohaidat, S. Palchaudhuri, Appl. Opt. 49 (2010) C27–C35.
- [3] M. Baudelet, J. Yu, M. Bossu, J. Jovelet, J.P. Wolf, T. Amodeo, E. Frejafon, P. Laloi, Appl. Phys. Lett. 89 (2006). (163903/1-163903/3).
- [4] S.J. Rehse, J. Diedrich, S. Palchaudhuri, Spectrochim. Acta, Part B 62 (2007) 1169–1176.

LIBS quantitative analysis of fluorite ores (CaF₂) through the measurement of CaF molecular emission bands

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Fluorite (or fluorspar) is a mineral composed of calcium fluoride (CaF₂) that is mainly used for the production of hydrofluoric acid, which is the principal feedstock for the vast majority of fluorine related chemicals. Other uses of this mineral include the production of aluminum fluoride, iron and steel casting, manufacture of abrasives compounds, welding items and high quality optical elements manufacturing [1]. The measurement of the mineral purity in the processing of the fluorite ore is a key point in mining industry. Therefore, the development of robust, fast, simple and cheap analytical methods to evaluate the composition of the fluorite ores is highly demanded.

Approaches for fluorine chemical determination, such ion selective electrode, atomic absorption spectroscopy, as ICP-OES and ICP-MS, show great analytical potential but require the samples to be dissolved [2]. Direct solid analysis methods, such as neutron activation techniques, could be employed [3]. However, these methods involve radioactive installations where samples are bombarded by neutrons and gamma photons are measured from the radioactive products. As an alternative, LIBS (Laser Induced Breakdown Spectroscopy) is a powerful and versatile analytical technique that provides fast, in-situ analysis with minimum sample preparation requirements [4].

It is possible to determine fluorine mass-content as an indirect indicator of the fluorite concentration in ore powdered samples. In this sense, fluorine detection with LIBS is usually carried out in a helium atmosphere in order to enhance the emission signal from the F(I) elemental line at 685.6 nm [5].

In this work, it is presented a complementary LIBS analytical methodology to measure the concentration of fluorite samples in air atmosphere, avoiding in this way the use of helium and simplifying the experimental set-up. This method is based on combining the LIBS spectral measurement of the emission signals from CaF molecular bands and those from minor analyte elemental lines (e.g. Si(I) and Mg(I)). It is shown that the use of this approach significantly improve the quantitative analysis of fluorite ores, in terms of analysis time, accuracy and precision.

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References

- [1] Mineral Commodity Summaries 2013, U.S: Geological Survey, Reston, Virginia, 2013.
- [2] R. B. Fulton, M. M. Miller, "Fluorspar," in J.E. Kogel, N.C. Trivedi, M. J. Barker, S.T. Krukowsk (Eds.) Industrial Minerals and Rocks, 7th ed., Society for Mining, Metallurgy and Exploration, Inc. (ME), 2006, pp. 461–473.
- [3] M. P. Castro-García, T. Alonso-Sánchez, M. A. Rey-Ronco. Study of the gamma spectrum of ¹⁶N with a BGO detector, for the purpose of calibration and of determining the fluorine grade of mineral samples, J. Radioanal. Nucl. Chem. 298 (2013). 915
- [4] D.W. Hahn, N. Omenetto. Laser-induced breakdown spectroscopy (LIBS), part II: review of instrumental and methodological approaches to material analysis and applications to different fields., Appl. Spectrosc. 66 (2012). 347
- [5] D.A. Cremers, L.J. Radziemski. Detection of Chlorine and Fluorine in Air by Laser-Induced Breakdown Spectrometry. Anal. Chem. 55 (1983). 1252

Different approaches for the generation of chemical maps of complex samples by laser-induced plasma spectroscopy

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Analytical techniques able to perform spatially resolved analysis are highly demanded in the surface analysis and material science fields. Laser-induced plasma spectroscopy (LIPS) can furnish information on the surface and in-depth distribution of the constituent elements of a sample at the micrometric level. In this sense, 2D and 3D compositional maps, tomographic analyses and depth profiles can be performed in air at atmospheric pressure without the need of an auxiliary ion beam [1]. No or minimal sample preparation is required, and the analysis of any sample without restrictions on the size or conductive nature can be performed in a matter of seconds. Despite plasma spectroscopy has some advantages over other surface techniques, the development of high-technology and complex materials has impelled the improvement and tweak of LIPS technique for mapping purposes. In this work, several strategies are explored to address the compositional mapping of samples of different complexity and nature which cannot be analyzed by conventional LIPS. One of these strategies consists, in the case of specimens with complex shape, of a laser displacement sensor employed to maintain both a constant laser fluence, as well as to keep an invariable distance between the light collection system and the sample surface during the LIPS measurements [2]. In order to illustrate the instrumental modifications and methodology changes which are evaluated in this work, samples of different nature, metallic alloys of non-flat shapes [3], ceramic coatings with concentration gradient and biological specimens of interest in fields like quality control and failure inspection, manufacture industry and environment, between others, will be characterized.

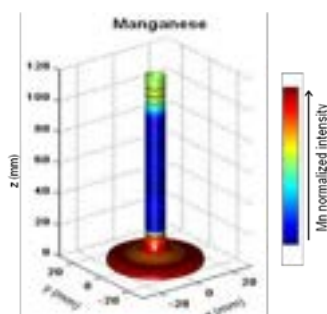


Figure 1. 3D LIPS chemical map of Mn on the surface of an engine valve.

References

- [1] V. Piñón, M.P. Mateo, G. Nicolas. Laser induced breakdown spectroscopy for chemical mapping of materials. *Appl. Spectrosc. Rev.* 48 (2013) 357.
- [2] G. Nicolas, M.P. Mateo, V. Piñón. 3D chemical maps of non-flat surfaces by laser-induced breakdown spectroscopy. *J. Anal. At. Spectrom.* 22 (2007) 1244.
- [3] I. Lopez, V. Piñón, M.P. Mateo, G. Nicolas. Mapping of mechanical specimens by laser induced breakdown spectroscopy method: application to an engine valve. *Spectrochim. Acta B* 74-75 (2012) 109.

MIR-FIR spectroscopy in one step – wide range infrared technology

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The extension of the mid IR towards the far IR spectral range below 400 cm^{-1} is of general interest for molecular vibrational analysis for inorganic and organometallic chemistry, for geological, pharmaceutical, and physical applications, polymorphs and crystallinity analysis as well as for matrix isolation spectroscopy.

The achievable spectral range of an FTIR spectrometer is defined by the intersection of the efficiency ranges of the used source, beam splitter, and detector. The lower limit of the spectral range is very dependent upon the beam splitter, and is typically limited to 350 cm^{-1} . To extend the spectral range further into the far IR and THz spectral ranges one or more additional far IR beam splitters and detectors are required and because of this the user has to pause the measurement and as needed manually open the spectrometer optics bench.

Now available for the first time is the Bruker **VERTEX FM** wide range infrared technology for VERTEX 70 and 70v FT-IR spectrometers which combines two Bruker innovative optic components the wide range MIR-FIR beam splitter [1] and the wide range DLaTGS detector. The **VERTEX FM** option [2] enables in connection with the standard IR source the spectral range from 6000 cm^{-1} down to ca. 50 cm^{-1} in one step for all types of transmittance, reflectance and ATR measurements. Utilizing the external water cooled mercury arc high power lamp the spectral range can be ultimately extended down to 10 cm^{-1} .

References

[1] Bruker Optics Product Note M143-03/13.

[2] Bruker Optics Application Note AN118 2014.

Spectral interferences removal in multiple isotope selenium and iodine determinations using an ICP-MS triple quadrupole in MS/MS mode

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The accurate elemental analysis at low concentrations levels using the ICP-MS technique can be challenging for some elements when measurements have to be done in variable matrices. Results in these conditions can be influenced by other ions in the plasma even when some of them are at low concentrations, as double charged isotopes, noble gases impurities in the plasma argon flow, or polyatomic species.

Recent developments on ICP-MS triple quadrupole technologies allowed us to use collision-reaction cells capable to work very effectively with reactive gases in MS/MS mode though a better control of the reaction processes inside the cell. The mass filtering done through the first and third quadrupoles controlling the entrance and exit of the collision-reaction cell improves the efficiency of the interference removal, specially in reaction mode, in a way that can not be matched by any single quadrupole instrument, removing interferences that even high resolution instruments can not handle in some applications.

In this communication we show examples for accurate Se determinations in environmental, geological, and food samples using on-line isotope dilution and reaction gases in MS/MS mode in a single set of instrumental conditions. We also show accurate measurements for ^{129}I and $^{129}\text{I}/^{127}\text{I}$ ratios in environmental samples as those performed for evaluation and control of contamination resulted from nuclear weapons testing and accidental releases from nuclear power plants and spent nuclear fuel reprocessing plants.

References

- [1] N. Sugiyama, The accurate measurement of selenium in twelve diverse materials using on-line isotope dilution with the 8800 Triple Quadrupole ICP/MS in MS/MS mode. Agilent Technologies, Application Note, 2013.
- [2] Y. Shikamori, K. Nakano, N. Sugiyama, S. Kakuta. The ultratrace determination of iodine 129 using the Agilent 8800 Triple Quadrupole ICP/MS in MS/MS mode. Agilent Technologies, Application Note, 2013.

β -Cyclodextrin modified CdSe/ZnS quantum dots as a vanillin-sensor

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The use of quantum dots (QDs) for the development of sensors is one of the most promising fields of nanotechnology today. Their fluorescence efficiency is sensitive to the presence and nature of adsorbates at their surface. Therefore, molecular recognition at the surface of QDs can be used in the development of fluorescent-based sensors [1]. For this purpose, cyclodextrins (n-CDs), one of the best host molecules, have been selected to QDs surface modification for vanillin determination.

In the n-cyclodextrin modified QDs procedure, the hydrophobic pockets of the cyclodextrin molecules interact with the aliphatic chains of the trioctylphosphine oxide (TOPO) present on the nanoparticle surface from the QDs synthesis. Nevertheless, the immobilized cyclodextrins retain their capability of engaging molecular recognition. Their cavity-shaped cyclic phenol molecules are capable of forming host-guest complexes with a variety of organic molecules. Cyclodextrins coating ensures the high emission efficiency and the smaller size of QDs and provides selectivity. Thus, this work reports an optical sensor for vanillin in food samples using CdSe/ZnS (QDs) modified by β -cyclodextrin (β -CD). This vanillin-sensor is based on the selective host-guest interaction between vanillin and β -CD. The procedure for the synthesis of β -cyclodextrin-CdSe/ZnS (β -CD-QDs) complex has been optimized, and its fluorescent characteristics have been also reported. It was found that the interaction between vanillin and β -CD-QDs complex produced the quenching of the original fluorescence of β -CD-QDs, according to the Stern-Volmer equation. The mechanism of interaction is discussed.

The potential application of the proposed method using the designed sensor for determination of vanillin in food samples has been demonstrated. Recoveries obtained were in the 91-111% range. Detection limits of 1 mg L^{-1} , lineal range between $2 - 20 \text{ mg L}^{-1}$ and precision (% RSD) of 1.12% for five replicates of 4.1 mg L^{-1} vanillin solution were obtained as analytical performance characteristics.

This approach is simple and sensitive and opens up new possibilities for developing analytical method using QDs for the detection of additives in foods, as it is the case for vanillin.

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References

[1] Gema M.Duran, Ana M. Contento, A. Rios. Use of CdSe/ZnS Quantum Dots for sensitive detection and quantification of Paraquat in water samples. *Anal.Chim.Acta* 801 (2013) 84.

Furfural selective colorimetric sensors for beer ageing monitoring

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Beer, together with water and tea, is the one of the most popular drinks in the world and the alcoholic beverage most widely consumed nowadays as well. Beer ageing during storage may strongly affect the quality and taste of this beverage therefore maintenance of the quality of beer from the production to the consumption stages is one of the main concerns in the brewing industry. The formation of volatile carbonyl compounds has been correlated with beer ageing [1,2] as these compounds have a great flavor potential. In this respect, furfural has been identified as one of the main markers of flavor instability. This compound is formed during the Maillard reactions and its concentration increases substantially with the storage time.

Current methods for the analysis of furfural in beer involve gas-liquid chromatography (GC) or liquid chromatography (LC) with mass spectrometry (MS) detection after a clean-up and preconcentration steps by liquid-liquid or solid-phase extraction (SPE). These techniques are time consuming and require specialized personnel and instrumentation therefore; there is a great demand for fast, cheap and reliable sensors that can be used in situ at the brewery plants to control beer ageing during storage.

The present contribution reports the development of fiber-optic based colorimetric sensors for the determination of furfural and its application to the evaluation of ale beers ageing [3]. Selective methacrylate-based polymeric layers were prepared in the form of thin films (0.5 mm). In the presence of furfural, a pink-colored derivative is formed, as a result of the condensation reaction of the reactive aniline groups in the polymer and the target aldehyde [4]. The product absorbs at 537 nm and the signal change was monitored using a portable fiber optic spectrometer. Several parameters influencing assay performance have been optimized to improve sensor sensitivity including: polymer composition and thickness, reagents concentrations, reaction time, and effect of the ethanol content in the samples. In the optimized conditions the sensors provided a linear response range from 39 to 500 µg/L with a detection limit of 12 µg/L, improving the performance of established methods for the detection of this compound. Sensor selectivity has been assessed measuring the cross-reactivity of the polymeric films to other volatile aldehydes that have been detected during beer ageing including, hydroxymethylfurfural, 2-methyl-propanal, hexanal, benzaldehyde, phenylacetaldehyde, *trans*-2-nonenal and acetaldehyde.

The usefulness of this approach for furfural analysis has been demonstrated by its application to the analysis of ale beer samples with different storage times. A linear correlation between the concentration of the aldehyde and the time elapsed since beer production of has been obtained. The results have been validated by HPLC-DAD. The developed sensor has proven to be a very useful and cost-effective device for the control of beer quality and can be easily implemented at the brewery plants.

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References

- [1] S. Malfliet, F. Van Opstaele, J. De Clippeleer, E. Stryn, K. Goiris, L. De Cooman, G. Aerts. Flavour Instability of Pale Lager Beers: Determination of Analytical Markers in Relation to Sensory Ageing. *J. Inst. Brew.* 114 (2008) 180.
- [2] J. J. Baert, J. De Clippeleer, P. S. Hughes, L. De Cooman, G. Aerts. On the Origin of Free and Bound Staling Aldehydes in Beer. *J. Agric. Food. Chem.* 60 (2012) 11449.
- [3] M. C. Moreno Bondi, M. E. Benito Peña, M. V. González de Vallejo Rodríguez, A. Rico Yuste, J. Peña Bahamonde, B. Fité Luis, J. Lluís Tartera. Membrana polimérica, procedimiento de obtención, usos de la misma y método de detección de furfural y/o 5-hidroximetilfurfural. P201430002, Jan 02, 2014 (Submitted)
- [4] T. E. Friedemann, P. K. Keegan, N. F. Witt. Determination of Furan Aldehydes. Reaction with Aniline in Acetic and Hydrochloric Acid Solutions. *Anal. Biochem.* 8 (1964) 300.

Determination of technological maturity of grapes and total phenolic compounds of grape skins in red and white cultivars during ripening by near infrared hyperspectral image: A preliminary approach

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Grape harvest time is one of the most fundamental aspects that have influence on the future of wine quality. A number of factors have influence on this decision, among them technological and phenolic maturity of grape, especially grape skins phenolic maturity. Technological maturity is mainly connected with sugar concentration, titratable acidity and pH. The sugar concentration determines the potential alcoholic strength. The titratable acidity and pH help to control the wine quality and colour. Phenolic maturity shows the ripeness degree for the skins, pulp and seeds taking into account its phenolic composition [1,2].

Hyperspectral images of intact grapes during ripening were recorded using a near infrared hyperspectral imaging system (900 - 1700 nm). Spectral data have been correlated with grape skin total phenolic concentration, sugar concentration, titratable acidity and pH by modified partial least squares regression (MPLS) using a number of spectral pre-treatments and different sets of calibration. The obtained results (RSQ and SEP respectively) for the global model of red and white grape samples were: 0.89 and 1.23 mg g⁻¹ of grape skin for total phenolic concentration, 0.99 and 1.37 °Brix for sugar concentration, 0.98 and 3.88 g L⁻¹ for titratable acidity and for pH 0.94 and 0.12. Moreover, separate calibration models for red and white grape samples were also developed and better results were obtained for the red grape model. The obtained results present a good potential for a fast and reasonably inexpensive screening of these parameters in intact grapes and therefore, for a fast control of technological and phenolic maturity [3].

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References

- [1] E. Meléndez, M. C. Ortiz, L. A. Sarabia, M. Íñiguez, P. Puras. Modelling phenolic and technological maturities of grapes by means of the multivariate relation between organoleptic and physicochemical properties. *Anal Chim Acta* 761 (2013) 53.
- [2] R. Ferrer-Gallego, J. M. Hernández-Hierro, J.C. Rivas-Gonzalo, M. T. Escribano-Bailón. Influence of climatic conditions on the phenolic composition of *Vitis vinifera* L. cv. Graciano. *Anal Chim Acta* 732 (2012) 73.
- [3] J. Nogales-Bueno, J. M. Hernández-Hierro, F. J. Rodríguez-Pulido, F. J. Heredia. Determination of technological maturity of grapes and total phenolic compounds of grape skins in red and white cultivars during ripening by near infrared hyperspectral image: A preliminary approach. *Food Chem.* 152 (2014) 586.

Double confirmation of MDMA abuse: Saliva analysis

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Drug abuse remains a significant public health issue worldwide. In many European countries, amphetamines, including ecstasy, is the second most commonly used illicit substance after cannabis [1]. Ecstasy refers to synthetic substances that are chemically related to amphetamines, but which differ to some extent in their effects, being the best-known member of the ecstasy group the 3,4-methylenedioxy-methamphetamine (MDMA).

It can be assessed that the main objectives of drug-of-abuse testing are the detection, identification, and/or deterrence of substance abuse or misuse. Drug testing has been conducted primarily on blood and urine, but, recently, there is a high interest in their replacement by alternative biological specimens which can be collected using noninvasive sampling techniques, such as saliva.

We propose the use of two analytical technologies based on different chemical principles, sequentially or in combination, to accomplish fast and accurate detection, identification and semi-quantification of MDMA from saliva samples. It is expected an improvement of on-site drug testing by the application of two analytical methods of categories A and B of the Scientific Working Group for the Analysis of Seized Drugs [2] such as infrared spectroscopy (IR) and ion mobility spectrometry (IMS). The order of the analytical methodologies in the aforementioned sequence is fixed taking into consideration the high sensitivity of the IMS to identify positive samples combined to the high selectivity of the IR procedure to confirm positive results (see Figure 1).

Different sample pretreatment strategies, including direct analysis, protein precipitation, micro liquid-liquid extraction (μ LLE) and solid phase extraction (SPE) have been evaluated for MDMA extraction from saliva samples. Using the most appropriate measurement conditions, the analytical features of merit of the methodology, such as precision, accuracy, limit of detection (LOD) and identification (LOI), recoveries and the effect of potential interferents on the MDMA signals were established.

The proposed two tier method was applied to the identification of MDMA in saliva of different individuals, non-consumers and consumers, providing comparable results with those obtained by a reference procedure and indicating possibility to distinguish between consumers and those who consumed MDMA.

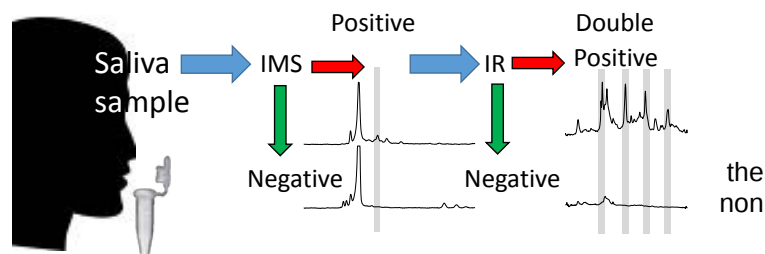


Figure 1. Scheme of the proposed procedure for the double confirmation of MDMA in saliva samples.

Acknowledgements

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References

- [1] 2012 Annual report on the state of the drugs problem in Europe, EMCDDA, Lisbon, 2012. <http://www.emcdda.europa.eu/publications/annual-report/2012>.
- [2] Scientific Working Group for the Analysis of Seized Drugs. <http://www.swgdrug.org/>.

Evaluation of confocal Raman spectroscopy to identify gunshot residue particles

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When a weapon is fired a set of burned and unburned particles, called gunshot residues (GSR) are transferred to the shooter, the weapon, the victim, or the surrounding environment. Therefore, the ability to unequivocally identify a GSR is a very important and crucial part of crime scene investigation. Nowadays, the method of choice for analyzing GSR is Scanning Electron Microscopy with Energy Dispersive X-ray spectroscopy (SEM-EDS). However, this technique has a limitation in the GSR identification of the new “lead-free” or “nontoxic” ammunition. This fact has led to a search for complementary techniques of SEM-EDS in order to obtain additional information.

In this work, Raman spectroscopy is proposed as a fast and complementary tool for the analysis of GSR and its potential was evaluated by determining the memory effect of the weapon. First, six different types of ammunition were fired at short distances into cloth targets, and the Raman spectra produced by the GSR were measured and compared with the spectra from the unfired gunpowder ammunition. Surprisingly, the GSR spectra showed high similarity to the spectra of their corresponding unfired ammunition, and discrimination between two types of ammunition was easily performed on the basis of their stabilizers. Additionally, other substances that might be found on the victim’s, shooter’s or suspect’s clothes and might be confused with GSR, such as sand, dried blood, or black ink from a common ballpoint pen, were analyzed to test the discrimination capability of the Raman technique [1]. Second, the memory effect of the weapon was studied by analyzing the GSR particles from ammunition with the stabilizer ethyl centralite (EC) after previously firing cartridges of ammunition with diphenylamine (DPA) [2]. The results obtained suggested that the memory effect of the weapon has not a significant influence when the organic analysis of macroscopic GSR on targets by Raman spectroscopy is performed. These results are essential to establish a link between GSR found and the ammunition fired.

These findings suggest that Raman spectroscopy is a good complementary analytical technique to SEM-EDS for the analysis of GSR, especially to deal with the analysis of lead-free ammunition.

References

- [1] M. López-López, C. J. Delgado, C. García-Ruiz, Ammunition Identification by Means of the Organic Analysis of Gunshot Residues Using Raman Spectroscopy, *Anal Chem* 84 (2012) 3581.
- [2] M. López-López, C. J. Delgado, C. García-Ruiz, Analysis of macroscopic gunshot residues by Raman spectroscopy to assess the weapon memory effect, *Forensic Sci. Int.* 231 (2013) 1.

Porous membrane protected molecularly imprinted polymer based microsolid phase extraction for cocaine and metabolites assessment in human plasma by HPLC-MS/MS

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Molecularly imprinted polymers (MIP) for selective cocaine recognition were packed inside a polypropylene membrane, and the protected MIP was then used for pre-concentrating cocaine and metabolites (benzoylecgonine and cocaethylene) from human plasma before high performance liquid chromatography – tandem mass spectrometry (HPLC-MS/MS). MIP synthesis was performed by the precipitation method (N_2 atmosphere, constant stirring at 40 rpm, 60°C for 24 hours) using cocaine as a template, ethylene dimethacrylate (EDMA) as a monomer, divinylbenzene (DVB) as a cross-linker, and 2-2'-azoisobutyronitrile (AIBN) as an initiator. Variables affecting the MIP-MIMSPE (batch mode, 50 mg MIP) process were fully studied. Optimum loading (retention) conditions were: plasma (5 mL) pH adjustment at 5.5 (sodium dihydrogen phosphate/sodium hydroxide buffer), and mechanical stirring at 150 rpm at 40°C for 10 minutes. Target elution was performed with 5 mL of hexane/2-propanol/ammonium hydroxide 72:20:8 under ultrasounds irradiation for 5 minutes. The eluates were further N_2 evaporated to dryness, and the residue re-dissolved in 100 μ L of mobile phase (2 mM ammonium acetate methanol). A pre-concentration factor of 50 was achieved.

HPLC-MS/MS targets separation/detection was achieved under a gradient elution which involves two mobile phases: aqueous 2 mM ammonium acetate, pH 7.5 (A) and 2 mM ammonium acetate methanol (B). The flow rate (Phenomenex Kinetex C18 column) was set at 0.20 mL min⁻¹, and the gradient program consisted of 0% A for 0.5 minutes, followed by a 1 minute ramp until 30% A, 2.5 minutes ramp until 0% A, and 1 minute hold at 0% A. The developed method was fully validated and applied to several plasma samples.

Acknowledgements

The authors wish to thank the *Dirección Xeral de I+D – Xunta de Galicia* (Project number 10CSA209042PR) for financial support.

Determination of lidocaine in urine at low ppm levels using dispersive microextraction and attenuated total reflectance-Fourier transform infrared measurements of dry films

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IR spectra provide valuable information about biological systems and can be obtained with compactable and affordable instruments, and requiring minimum treatment of samples. Nevertheless, the lack of sensitivity of this technique hampers its use in the determination of drugs in clinical fluids, where those exogenous compounds are normally present at very low concentration levels. Taking lidocaine as a target molecule, in this work we introduced a methodology for determining drugs in urine samples using IR spectroscopy. The lack of sensitivity of the IR was compensated with the combination of an effective and straightforward dispersive liquid-liquid micro-extraction and the measurement of the dry film of the organic extracts through attenuated total reflectance (ATR) (see Figure). The method developed improves the sensitivity by eliminating the solvent and preconcentrating the analyte in the surface of the ATR crystal. Urine samples were taken from 15 volunteers and 9 samples were spiked at 6 concentration levels ranging from 0 to 33 mg L⁻¹. Although univariate calibration provides a good adjust (see Figure), when different urine matrices are compared there are a significant spectral interference, and it is necessary to employ multivariate calibration strategy. Multivariate models based on partial least squares regression and science based calibration were performed and validated with a separated set of spiked urine samples from other patients, obtaining ratio prediction to deviation (RPD) values higher than 3.5. The limit of detection values obtained were 0.4 mg L⁻¹ for the univariate calibration and 1.7 mg L⁻¹ for a reliable multivariate calibration. Therefore, the procedure is limited to only medium and high levels of lidocaine, but serves as an untargeted, fast and versatile screening tool which maintains all the advantages of the widespread application of the IR spectroscopy to the clinical analysis; such as simplicity, compactability and minimum use of reagents and solvents.

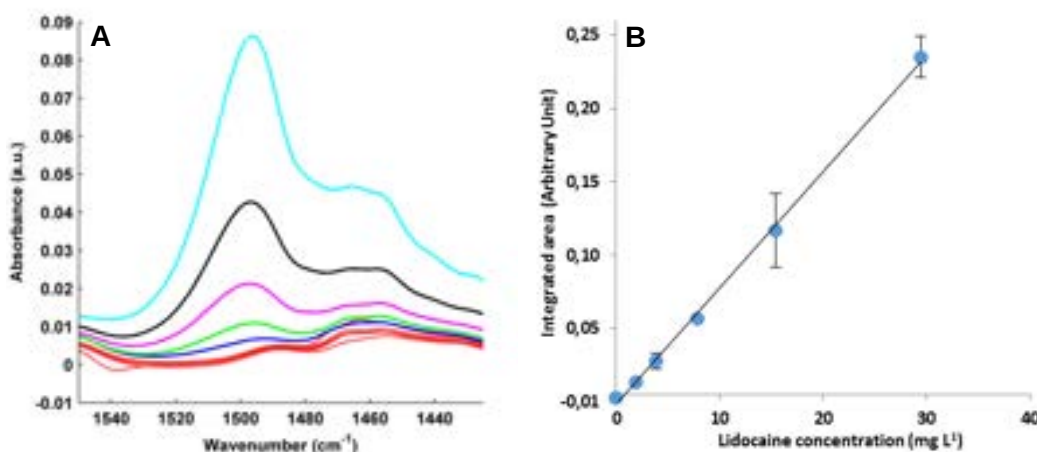


Figure: Univariate calibration of lidocaine by ATR-FTIR after extraction. (A) Dried film ATR-FTIR spectra of spiked lidocaine samples and blanks and (B) the univariate calibration curve obtained for a urine sample spiked with different concentrations of lidocaine (from 0 mg L⁻¹ to 30 mg L⁻¹).

Acknowledgements

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Supercontinuum fiber lasers: White light with laser brightness. A new tool for advanced spectroscopy

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VIS and NIR - range Broadband Spectroscopy (e.g. Optical Absorption Spectroscopy, Inspection of fiber optic components or Hyperspectral Imaging) relies on incandescent and fluorescent lamps as optical sources. Limitations of these sources (such as thermal influence on the sample, low capacity of penetration, low fluence on illumination of small samples, low spatial coherence, size and positioning rigidity with respect to sample) might be overcome with laser sources. However, lasers are usually monochromatic, hence a set of different lasers at specific wavelengths are required to cover a broad spectrum. Supercontinuum fiber lasers overcome this limitation: they deliver an ultrabroadband white-light spectrum (covering simultaneously up to a range from 400 nm to 2400 nm) in a singlemode beam with the properties of spatial coherence, directionality and brightness of a laser. Consequently they are often called "white lasers".

Supercontinuum generation is the formation of broad continuous spectra by propagation of high peak power pulses through nonlinear media. First observed in 1970 [1], the efficiency of its generation has been dramatically enhanced in the last years by the use of photonic crystal fibers [2] as nonlinear media, to the point that supercontinuum lasers are nowadays available commercially with affordable prices.

In this communication a revision of supercontinuum generation techniques and their application in different spectroscopic techniques will be presented. A new method for noninvasive inspection of whole dried fruit nuts by hyperspectral analysis using a FYLASC500 Supercontinuum Laser will be presented as a case of success.

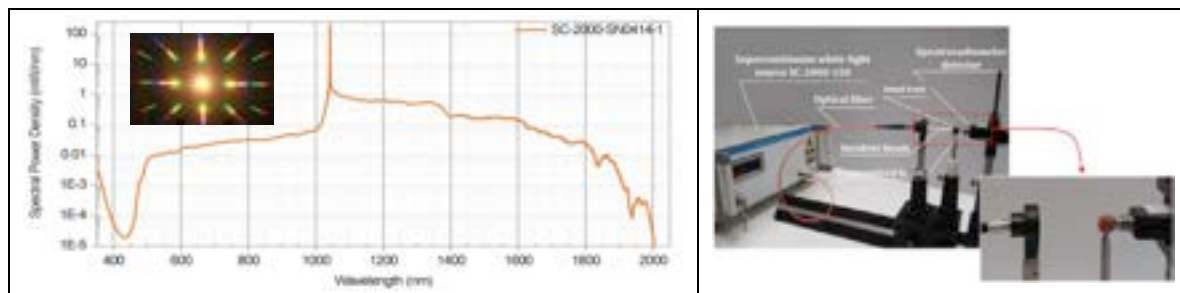


Fig.1. Left: Spectrum of a Supercontinuum Laser FYLASC500 model, spectral power density (mW/nm) versus wavelength (nm). Left (Inset): Diffraction pattern of the supercontinuum laser spot after passing through a 2D diffraction grating, demonstrating the spatial coherence nature of its white light as well as continuity of its spectral components. Right: Experimental setup for noninvasive inspection of whole dried fruit nuts by hyperspectral analysis using a FYLASC500 Supercontinuum Laser.

Acknowledgements

This work was supported by the Spanish Ministry of Economy and Competitiveness, MINECO (Torres Quevedo grant PTQ_12_05593).

References

- [1] R. R. Alfano and S. L. Shapiro, "Emission in the region 4000 to 7000 Å via four-photon coupling in glass" *Physical Review Letters* 24, 584 (1970).
- [2] A. Birks, J. C. Knight, and P. S. Russell, "Endlessly single-mode photonic crystal fiber" *Opt. Lett.* 22, 961 (1997).

Time-resolved spectroscopy using streak cameras

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Streak Cameras are one of the fastest instruments in measuring the variation of a light pulse's intensity over time. This unique feature on top of their imaging capability have made them extremely suitable and precise for the study of dynamic processes in materials by means of spectroscopic techniques when used with a spectrometer.

Therefore a streak camera setup is a complex set of instruments which need to be precisely synchronized in order to obtain the best time-resolution, which depending on the camera type can be down to the femtosecond range.

In this talk I will briefly introduce streak camera technology and give a detailed description of the different items a streak system needs. An overview of the different streak camera types will be presented. Besides an example of a possible configuration for performing Time-resolved spectroscopy measurements will be described.

AFM for high resolution and high speed chemical imaging and first fully-integrated Raman imaging + Scanning electron microscope (RISE)

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Knowledge about the morphology and chemical composition of heterogeneous materials on a sub-micrometer scale is crucial for the development of new material properties for highly specified applications. Such materials can either have mono-atomic flat surfaces or a roughness of several hundred micrometers or millimeter. In the past two decades, AFM (atomic force microscopy) was one of the main techniques used to characterize the morphology of nano-materials spread on nanometer-flat substrates. From AFM images it is possible to gain information about the physical dimensions of the material on the nanometer scale, without additional information about their chemical composition, crystallinity or stress state. On the other hand, Raman spectroscopy is known to be used to unequivocally determine the chemical composition of a material. By combining the chemical sensitive Raman spectroscopy with high resolution confocal optical microscopy, the analyzed material volume can be reduced below $0.02 \mu\text{m}^3$, thus leading to the ability to acquire Raman images with diffraction limited resolution from very flat surfaces. The combination of confocal Raman microscopy with Atomic Force Microscopy (AFM) is a breakthrough in microscopy. Using such a combination, the high spatial and topographical resolution obtained with an AFM can be directly linked to the chemical information provided by confocal Raman spectroscopy.

RISE Microscopy is a novel correlative microscopy technique that combines confocal Raman Imaging and Scanning Electron (RISE) Microscopy within one integrated microscope system. A new dimension in imaging: ultra-structural SEM complemented with chemical compound information and molecular Raman imaging.

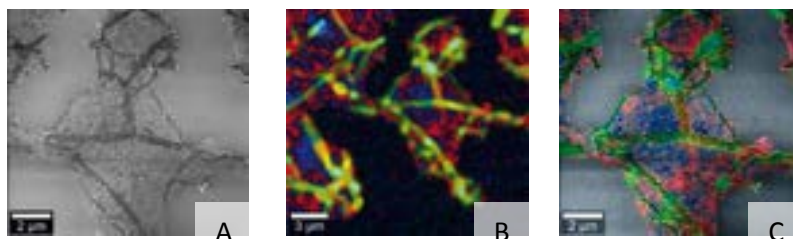


Fig. 1 - (A) SEM image of a graphene sample. (B) Color-coded confocal Raman image. The colors display the graphene layers and wrinkles. Image parameters: $20 \mu\text{m} \times 20 \mu\text{m}$, 150×150 pixels = 22,500 spectra, integration time: 0.05 s/spectrum. (C) SEM image overlaid with the confocal Raman image.

Improving analysis or large isotopes ratios using high sensitivity ICPMS

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Scientific disciplines like Food Chemistry, Geochemistry, environmental sciences and Paleontology are not only interested in the total concentration of an element but also in the isotope ratio of either two or more isotopes of the same element or isotopes of different elements. In principle three instrumental ICP-MS solutions exist: Quadrupole based ICP-MS, single collector magnetic sector field ICP-MS and multicollector magnetic sector field ICP-MS. General assumption is that precision and accuracy for isotope ratio measurements increases with complexity of technology used. In this work we will present data with the improved performance of new Single Quadrupole ICPMS systems, Bruker Aurora ELITE which allow isotope ratio determination with excellent sensitivity, speed and stability.

The sensitivity of an ICP-MS is an indispensable performance characteristic and will enable the instrument to achieve highest isotope ratio precisions even at low, down to single digit ppt levels. High sensitivity is on one hand important to measure isotope ratios with high precision despite of low concentrations, and/or to measure large isotope ratios to achieve high precision for low abundant isotopes. Beside the stability of an instrument and the precision of the detector calibration the abundance sensitivity is an important parameter for the accuracy of isotope ratio determinations. This is especially important for minor isotopes in the presence of neighbouring intense ion beams.

The presentation will discuss the figures of merit of a high sensitivity quadrupole ICP-MS, and will demonstrate the capability for different isotope ratios determinations with emphasize on large isotope ratios. At this point the possibility to use Q-ICPMS more affordable systems for this application will open the use of isotope ratio determination to classical and new applications fields, being affordable for many labs in a routine basis.

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Meike Hamester, René Chemnitzer Bruker application Laboratory in Bremen

Molecularly imprinted polymer based – solid phase extraction for mercury speciation in seawater by HPLC-ICP-MS

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A molecularly imprinted polymer (MIP) based – solid phase extraction (SPE) has been optimized for assessing traces of inorganic mercury (Hg^{2+}), methyl mercury (CH_3Hg^+) and ethyl mercury ($\text{CH}_3\text{CH}_2\text{Hg}^+$) in surface seawater samples. The polymeric material was synthesized by the precipitation method using CH_3Hg^+ as a template, phenobarbital as a non-vinylated monomer, methacrylic acid (MAA) as a vinylated monomer, ethylene dimethacrylate (EDMA) as a cross-linker, and 2-2'-azoisobutyronitrile (AIBN) as an initiator. Variables affecting the MIP-SPE (column mode, 250 mg MIP) process were fully studied. Optimum loading (retention) conditions were: sample pH adjustment (ammonium chloride / ammonium hydroxide buffer) 8.0, and loading flow rate of 2 mL min^{-1} . Elution was performed with 4 mL of a water/2-mercaptoethanol/methanol 84.2:0.8:15 (pH 3.0) mixture. A pre-concentration factor of 25 was achieved (sample volume of 100 mL).

Mercury species separation/detection was performed by high performance liquid chromatography coupled to inductively coupled plasma – mass spectrometry (HPLC-ICP-MS). Separation was achieved under isocratic conditions (0.70 mL min^{-1} as a flow rate; water/2-mercaptoethanol/methanol 89.6:0.4:10 pH 2.5 as a mobile phase) by using a Phenomenex Kinetex C18 column. The three mercury species were resolved in 5 minutes (retention times of 2.151, 1.61, and 4.257 min for Hg^{2+} , CH_3Hg^+ , and $\text{CH}_3\text{CH}_2\text{Hg}^+$, respectively). The developed method was fully validated and applied to several surface seawater samples. Inorganic mercury and methyl mercury were the major mercury species quantified in the analyzed surface seawaters.

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First insights into mercury speciation in aquatic plants using coupled techniques based on gas chromatography and atomic fluorescence detection

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Mercury (Hg) is a global pollutant that negatively impacts human health and the environment. One of the major problems related to Hg is the production of the highly toxic organomercury compounds (such as monomethylmercury, MeHg) in the aquatic environment and its possibility of bioaccumulation and biomagnification along the aquatic food chain. It is commonly accepted that fish and seafood are the main sources of MeHg exposure to humans. Nevertheless, recent studies revealed that plants such as rice are the major source of MeHg intake from food in part of the population from Asia.

In this sense, the knowledge of speciation and partitioning of toxic metals such as Hg becomes crucial for the better understanding of Hg species accumulation and transformation pathways in plants. However, few studies have been focused on metal speciation in this matrix and little information is available about Hg species distribution in plants. So far, certified methods for extraction of Hg species in environmental matrixes do not include specific procedures for plants and even less considering the differences related to the type of plant material (i.e. ligneous, macrophyte, algae, etc.). Thus, MeHg concentrations in plants reported in previous studies are likely to be underestimated since no quantitative MeHg extraction from plants could be achieved. Accordingly, the development of a validated methodology for Hg speciation in plants which enables to detect Hg species in low concentrations and to control MeHg artifact generation becomes a challenge due to the different analytical drawbacks especially related to the non-quantitative extraction of Hg species from the plant. Therefore, the aim of this work has been to develop a quantitative method for MeHg analysis in plants using a hyphenated technique based on gas chromatography coupled to atomic fluorescence detection after closed-vessel microwave heating extraction and derivatization of Hg species by ethylation. The influence of different parameters related to both extraction (such as type and concentration of extractant agent, irradiation temperature and time) and derivatization (volume of extract used for derivatization, concentration of ethylating reagent) have been evaluated using not only field samples spiked with MeHg but also certified reference materials. Hence, the application of this methodology will enable having a better estimation of Hg species accumulation and transformations in plants for risk assessment.

FAPA-APGD as ion source for VOCs detection by a novel ion differential mobility analyser

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Ion mobility spectrometry has become an area of increasing research activity as denoted by the growing number of publications resorting to techniques based on the velocity of gas-phase ions in an electric field [1] to classify chemical substances. There are three main approaches using ion mobility in gas phase as the separation principle, typically known as Ion Mobility Spectrometry (IMS), Differential Mobility Spectrometry (DMS) and Differential Mobility Analysis (DMA), the newest one.

Although ion mobility was initially conceived for the detection of volatile organic compounds (VOCs), chemical warfare agents, and explosives [2], innovative applications have been appearing along the last years in areas as diverse as proteomics and environmental analysis [3]. Its coupling with ion sources such as electrospray ionization, matrix assisted laser desorption ionization, or different types of discharges, has contributed to extend the applications of the techniques which use electric mobility as separation principle.

Several discharges have been used as ionization sources for IMS. The first introduced was the corona discharge (CD). Its advantages versus the most traditional ion sources used in IMS are the lack of radioactive elements (like the ⁶³Ni ionization source) and the broader range of ionizable molecules compared to UV-photoionization sources. Corona discharges have been applied to several types of compounds: aliphatic and aromatic hydrocarbons, explosives, alkaloids, and alcohols among others.

An alternative to CD are atmospheric pressure glow discharges (APGD), like that known as helium flowing atmospheric-pressure afterglow (FAPA). These discharges offer similar characteristics to CDs in terms of range of ionizable compounds, but with higher electron densities which presumably improve ionization efficiency compared to CDs. The FAPA-APGD used in the present work generates a rich variety of reactant ions that are able to ionize the analyte; this fact implies the appearance of multiple peaks in the spectra. In this context, the aim of this work is to evaluate an atmospheric pressure glow discharge with this specific design (FAPA) for VOCs analysis by DMA[4].

Acknowledgements

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References

- [1] S. Armenta, M. Alcalá, M. Blanco, A review of recent, unconventional applications of Ion Mobility Spectrometry (IMS), *Anal. Chim. Acta.* 703 (2011) 114.
- [2] G.A. Eiceman, Z. Karpas, *Ion Mobility Spectrometry*, 2nd ed., Taylor & Francis Group, Florida, 2005. [3] R. Guevremont, High-field asymmetric waveform ion mobility spectrometry: A new tool for mass spectrometry, *J. Chromatogr. A*, 1058 (2004) 3.
- [4] J.P. Santos, E. Hontañón, E. Ramiro, M. Alonso, Performance evaluation of a high-resolution parallel-plate differential mobility analyzer, *Atmos. Chem. Phys.* 9 (2009) 2419.

Analytical environmental nanoscience: A new challenge for Analytical Chemistry in the XXI century

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Whereas nanomaterials are playing an increasing role in many fields, the knowledge about their potential impact on human health and the environment as well as the development of regulations and legislation for their control is being outpaced. It is recognized that innovative analytical approaches are necessary for monitoring the presence of nanomaterials in environmental and biological media, assessing their potential impact and supporting regulations. In this context, Analytical Chemistry is facing new challenges by regarding nanomaterials as analytes and not just as samples. In comparison with conventional analytes, the metrology of nanomaterials involves not only their detection and quantification but also their physicochemical characterization. One of the first challenges arises from the solid-state properties of nanomaterials. In addition to their chemical composition, a number of physical properties can be used for their characterization, which includes size, shape, surface charge, or surface area.

In the context of regulations, the recommendation on the definition of nanomaterials published by the European Commission is a paradigm of the situation described above. The definition states that: "Nanomaterial means a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm–100 nm". The correct implementation of this definition requires appropriated analytical methods that are able to determine the number size distribution of particles at least in the 1–100 nm size range. At present, there is no single technique able to fulfil satisfactorily and routinely this regulatory definition.

On the other hand, the role of Analytical Environmental Nanosciences is key to the understanding the mobility, bioavailability and toxicity of nanomaterials themselves and their possible association with other chemicals too. These studies can be focused to engineered or natural nanomaterials

An outstanding example of natural materials is the femtoplankton which plays an important role in the ocean's carbon cycle. It is responsible for about half the photosynthetic fixation of carbon (primary production) on Earth, and it is a primary producer of dissolved organic matter (DOM) in oceans.

We are going to present a new analytical methodological platform for characterizing engineered and natural nanomaterials according to their chemical composition, size and shape with combined separation and spectroscopic techniques trough the work developed in two coordinated CTQ projects (2009, and 2012) of the analytical groups from University of Zaragoza and University of Santiago de Compostela

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Unveiling the early history of ultrafast laser ablation: Design, construction and evaluation of a femtosecond-resolved phase-change microscope

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The chronology of laser ablation - from the first photons reaching the sample to the end of all the transient effects on the surface - occurs in less than a few microseconds. Regardless the final process taking place (from sample discoloration to plasma formation), the early stages of ablation process acquire a relevant role for describing and understanding the parameters and physicochemical constants implied in the subsequent processes. Laser-plasma interactions under nanosecond pulses, impairs the visualization of such early processes. However, their absence during ultrafast ablation allows the following of the dynamic of ablation and the possibility of performing deeper studies on the physical and spectroscopic characteristics of materials.

A femtosecond-resolved phase-change microscope, based on a conventional pump-probe setup has been designed, constructed and evaluated. The instrument allows the recording of wavelength-specific images and optical emission spectra with temporal and spatial resolution. To achieve this, the amplified pulse from a Ti:Sa laser (35 fs, 4 mJ/pulse) is splitted into two branches. The pump beam, centered at 800 nm, is focussed to the sample with an angle of incidence of 45°. The probe beam is frequency doubled to obtain emission at 400 nm, and shines the sample surface after being focussed through a 20x microscope objective at the same position of the pump probe, but at normal incidence. The light reflected from the sample travels back across a microscope. A dichroic mirror rejects the 800 nm component from the reflected light, and sends the rest of the spectral components to a CMOS camera. Different band-pass filter allows the obtention of wavelength-selective images. The pump and probe branches can be independently adjusted in energy and polarization angle. The use of two independent linear stages with retroreflectors, allow precision in the delay of 30 fs.

The temporal evolution of the surface reflectivity of silicon is shown in the image, where the temporal scale indicates the time delay between the pump and probe laser. In all the situations, a single pulse is observed. The origin and dynamics of the patterns observed, as well as the implications of such structures will be commented.

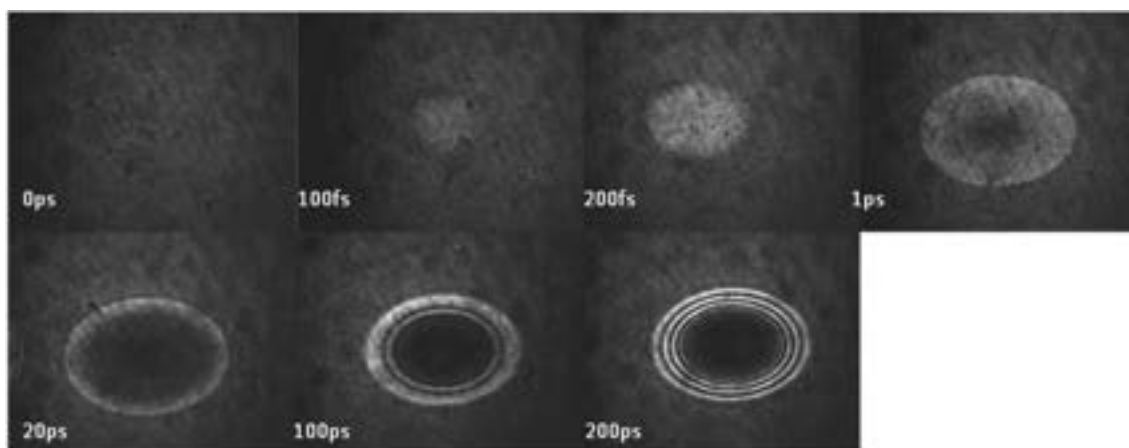


Figure 1. Temporal evolution after femtosecond laser irradiation at 150 μ J on a silicon sample

Copper(II) complexes of cinnamic and caffeic acids: A Raman study

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Cinnamic acid and its hydroxylated derivatives, present in most fruits and vegetables, display a huge variety of biological functions such as antioxidant capacity (through their radical scavenging activity), anti-inflammatory action and carcinogenesis modulation [1]. Furthermore the capacity to form complexes with metal ions, therefore reducing their toxicity, is another recognised ability of these compounds, strictly related to their biological activities [2]. Therefore, the assessment of the way in which they coordinate metal ions, and the structure of the complexes formed, arises as an important issue regarding the understanding of their ability to act as scavengers of potentially toxic species.

Within this scope, a Raman study of the copper(II) complexes of cinnamic acid, and its hydroxylated derivative caffeic acid, was undertaken, with particular emphasis on the assessment of the functional groups that coordinate the Cu(II) cation (carboxyl vs. hydroxyl).

Cu(II) complexes of cinnamic and caffeic acids (the latter containing a catechol group) were synthesised and analysed by Raman spectroscopy. A complete assignment of the spectra was carried out, both for the complexes and the phenolic acids, in the light of the corresponding calculated wavenumbers. These were obtained at the Density Functional Theory level, with resort to the B3LYP hybrid functional and Pople basis sets, using the Gaussian 03 package [3]. In order to accurately evaluate the structure of the complexes, a complete conformational analysis was also performed for the different possible geometries, as well as for the free ligands, and the corresponding frequencies were predicted for all the minimum energy conformations.

For phenolic acids containing a catechol group, such as caffeic acid, it was verified that the Cu(II) complex is formed either through the carboxylic group or the hydroxylated moiety, while for cinnamic acid metal coordination can only occur via the carboxylate.

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References

- [1] P. De, M. Baltas, F. Bedos-Belval. Cinnamic acid derivatives as anticancer agents - a review. *Curr. Med. Chem.* 18 (2011) 1672.
- [2] F. Borges, J. Lima, I. Pinto, S. Reis, C. Siquet. Application of a Potentiometric System with Data-Analysis Computer Programs to the Quantification of Metal-Chelating Activity of Two Natural Antioxidants: Caffeic Acid and Ferulic Acid. *Helv. Chim. Acta* 86 (2003) 3081.
- [3] M. Frisch, *et al.* Gaussian 03 Revision B.04, Gaussian Inc., Pittsburgh, 2003.

Crystal disruption in novel titanias for enhanced photocatalytical applications

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Nanocrystalline titanium dioxide materials are attracting much attention worldwide due to their potential applications in environmental protection, solar energy conversion, nonlinear optics, and heterogeneous photocatalysis^[1]. The reduction of the band gap of these materials, enabling the absorption in the visible range, is of prime importance for improving their efficiency. Two main strategies, i.e. doping and partial reduction of Ti(IV), are the available alternatives up to date. Herein it is present a new synthetic strategy for the obtention of novel titania materials via crystal disruption, with photocatalytic activities up to 100% better than the bare titania. These photoactive materials have been prepared by co-condensation of a titanium precursor, TBOT, with several adequate organic compounds (4,6-dihydroxypyrimidine (DHP) and *p*-phenylenediamine (PPD)) or a ruthenium complex, in mild conditions and in absence of surfactant.^[2] This new strategy allows the homogeneous incorporation of organic and metallic moieties (disruptors) within the crystal structure of titania. By using PDD and the Ru complex as disruptors, two titanias have been obtained with a remarkable reduction of its band gap, exhibiting outstanding photocatalytic activity under visible light.

References

- [1]** (a) L. Saadoun, J. A. Ayllon, J. Jimenez-Becerril, J. Peral, X. Domenech, R. Rodriguez-Clemente, *Mat. Research Bull.*, 35 (2000) 193; (b) A. Fujishima, T.N. Rao, A. Donald, *J. Photoc.: Photochemistry Reviews* 1 (2000) 1; (c) T. Aarthi, G. Madras, *Ind. Eng. Chem. Res.*, 46 (2007) 7; (d) A.L. Linsebigler, G. Lu, J.T. Yates, *Chem. Rev.*, 95 (1995) 735.
- [2]** M. Rico-Santacruz, A.E. Sepúlveda, E. Serrano, J.R. Berenguer, E. Lalinde, J. García-Martínez, *Spanish Patent 20130535*, 2013.

Trimeric gold-mercury containing species as fluorescence quenchers

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One of the most productive activities we are developing is the study of the optical properties of organometallic and coordination gold containing complexes. During the last years, our efforts have been addressed to the synthesis and study of gold-heterometal complexes displaying "weak" intermetallic interactions. Thus, we have been successful in obtaining complexes displaying unsupported interactions with a great structural diversity with different compositions as, for instance, gold(I) and silver(I), thallium(I), bismuth(III) and, lately, mercury(II) [1-2]. Previously, we carried out quenching experiments of naphthalene fluorescence with the complex $[\{\text{Hg}(\text{C}_6\text{F}_5)_2\}\{\text{Au}(\text{C}_6\text{F}_5)\text{PMe}_3\}]$, resulting in a static quench in which the complex formation model suited well [3]. This result is interpreted in terms of that the presence of gold in the molecule give rise to an orientation of the rings, due to the short metallophilic interaction, and therefore allowing the naphthalene approach to the mercury center and promoting the quench.

In this communication we show a next step, which is the introduction of a gold center in a complex with probed quenching abilities and study of the role of gold in the quenching experiment. To do that we chose the complex $[\text{Hg}_3(\text{C}_6\text{F}_4)_3]$, previously tested by other groups and proposed as naphthalene fluorescence quencher through a static quenching mechanism. Starting from this compound we prepared another complex built with two trimers of formula $\text{NBu}_4[\text{Hg}_3(\text{C}_6\text{F}_4)_3][\text{AuHg}_2(\text{C}_6\text{F}_4)_3]$, and we carried out quenching. We found a static quenching process, with a different mechanism. Other fluorophores tested as biphenyl or pyrene confirm a novel quench model with long range efectivity.



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References

- [1] J. M. López-de-Luzuriaga, M. Monge, M. E. Olmos, D. Pascual, T. Lasanta. Amalgamating at the molecular level. A study of the strong closed-shell $\text{Au(I)}\cdots\text{Hg(II)}$ interaction. *Chem. Commun.* 47 (2011) 6795.
- [2] J. M. López-de-Luzuriaga, M. Monge, M. E. Olmos, D. Pascual. Experimental and Theoretical Comparison of the Metallophilicity between $d^{10}-d^{10}$ $\text{Au}^{\text{I}}-\text{Hg}^{\text{II}}$ and d^8-d^{10} $\text{Au}^{\text{III}}-\text{Hg}^{\text{II}}$ Interactions. *Inorg. Chem.* 53 (2014) 1275.
- [3] T. Lasanta, J. M. López-de-Luzuriaga, M. Monge, M. E. Olmos, D. Pascual. Experimental and Theoretical Evidence of the Existence of Gold(I)···Mercury(II) Interactions in Solution through Fluorescence-Quenching Measurements. *Chem. Eur. J.* 19 (2013) 4754.

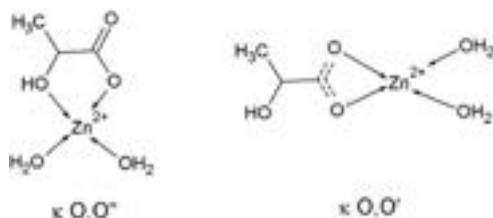
Insights into the coordination chemistry in the system $[\text{Zn}(\text{l-Lac})(\text{H}_2\text{O})_2]^+$ from DFT, NBO and QTAIM: Structure / vibrational spectra relationship

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α -Hydroxycarboxylic acids are ubiquitous in nature, playing a key role in many biological processes, as Krebs (citrate, isocitrate and malate) and Cori (lactate) cycles and in the active transport of metals across cell membranes. For example, Zn^{2+} cation complexed with citrate anion is transported by *Bacillus subtilis* and *Pseudomonas fluorescens*. On the other hand, they and their derivatives are widely used in pharmacy, cosmetics, production of food and other general chemical fields. In addition, small anions of them are able to behave as more complex natural ligands [1]. However, the coordination chemistry of such complexes are relatively poorly understood [2,3].

In the present work, we study as a model the $[\text{Zn}(\text{l-Lac})(\text{H}_2\text{O})_2]^+$ complex (with coordination number fixed at 4 [4,5] and two coordination patterns, see figure).



A thorough analysis of the conformational landscape is carried out at DFT level [6]. A previous conformational analysis is done at the MM level. In order to test the influence of the functional in the number and molecular structure of predicted conformers, all the obtained conformers were optimized using two well-known global-hybrid GGA (B3LYP and B3PW91), two global-hybrid

meta-GGA (M06 and M06-2X) and three long-range corrected hybrid (ω B97, ω B97X and ω B97X-D) ones. In all cases, the basis set chosen was the LACVP+** (LANL2DZ ECP for Zn plus 6-31+G(d,p) for the rest of elements) [7]. Those calculations were carried out using Spartan08 [8].

In order to test the influence of taking into account solvent effects in predicted structures and vibrational spectra, conformers from B3LYP, M06-2X and ω B97X-D were newly optimized with the 6-311++G(2d,2p) basis set and IEF-PCM, C-PCM and SMD solvent continuum models. Gaussian09 software [10] was used for this task. The characterization of the different bonding types in the complexes is carried out applying NBO analysis [10] and QTAIM [11]. NPA charges are used to study the metal-ligand charge transfer.

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References

- [1] E. Bermejo, R. Carballo, A. Castiñeiras, A. B. Lago, Coord. Chem. Rev. 257 (19-20) (2013) 2639.
- [2] J. J. Lensbouer, R. P. Doyle, Critical Rev. Biochem. Mol. Biol., 45 (5) (2010) 453.
- [3] B. Huta, J. J. Lensbouer, A. J. Lowe, J. Zubietta, R. P. Doyle, Inorg. Chim. Acta 393 (2012) 125.
- [4] L. Rulíšek, J. Vondrášek, J. Inorg. Biochem. 71 (1998) 115.
- [5] M. Dudev, J. Wang, T. Dudev, C. Lim, J. Phys. Chem. B 110 (2006) 1889.
- [6] C. J. Cramer, D. G. Truhlar, Phys. Chem. Chem. Phys. 11 (2009) 10757.
- [7] Y. Yang, M. N. Weaver, K. M. Merz, Jr., J. Phys. Chem. A 113 (2009) 9843.
- [8] Spartan08 for Windows, Macintosh and Linux. Wavefunction, Inc., Irvine, CA USA.
- [9] Gaussian 09, Frisch M. J. et al., Gaussian, Inc., Wallingford CT, 2009.
- [10] F. Weinhold, C. L. Landis Discovering Chemistry with Natural Bond Orbitals, Wiley, Hoboken, New Jersey, 2012.
- [11] R. W. Bader Atoms in Molecules. A Quantum Theory, Oxford University Press, Oxford UK, 1990 (Reprinted 2003).

SCA methodology for the analysis of deposited atmospheric particles on the surface of outdoors exhibited steel sculptures

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The weathering steel is a special kind of steel that was designed for its exposure outdoors. It is a high strength-low alloy steel which, due to the development of a protective rust layer, resists to the weathering phenomenon [1]. However, it is well known that the presence of some pollutants in high concentrations can degrade the structure reducing its characteristic protective ability and its lifetime [2]. Moreover, it has been reported that the presence of some atmospheric particles on the surface of the steel can affect to the normal development of the protective rust layer. For instance, silicate matter induces the retard of the transformation of the active form of iron oxyhydroxide (lepidocrocite, γ -FeOOH) into the passive form (goethite, α -FeOOH) [3] and therefore, the passivation of the rust layer. This passivation is crucial for the protection function of this layer. In this work, several weathering steel sculptures exposed to the urban atmosphere of Bilbao city (Northern Spain) have been analyzed by means of SCA (Structural Chemical Analyzer) in order to detect the deposited atmospheric material and to characterize it. This technique is based on the combination of micro-Raman spectroscopy and Scanning Electron Microscopy/Energy Dispersive X-Ray Spectroscopy (SEM-EDS), and it allows the characterization of the particles elementally and molecularly simultaneously. In this way, several kind of silicates and aluminosilicates have been identified on the steel surface. In addition, other atmospheric particles such as calcite, charcoal, chromium rich particles, etc have been identified. This technique also makes easier the assessment of the marine airborne impact on the steel surface by SEM-EDS images. Finally, several compounds coming from the reaction of the steel and the deposited particles with the acid gases of the atmosphere of Bilbao city have been observed. The presence of all these compounds can affect to the normal evolution of the protective rust layer and even, they can also react with the raw material damaging it seriously. Taking all this into account, it can be affirmed that for this kind of samples and for the mentioned aim, the choice of this technique has been very successful.

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References

- [1] M. Kimura, H. Kihira. Nanoscopic Mechanism of Protective Rust Formation on Weathering Steel Surfaces. Nippon Steel Tech. Rep. 91 (2005) 86.
- [2] J. Aramendia, L. Gomez-Nubla, I. Arrizabalaga, N. Prieto-Taboada, K. Castro, J.M. Madariaga. Multianalytical approach to study the dissolution process of weathering steel: The role of urban pollution. Corros. Sci. 76 (2013) 154.
- [3] U. Schwertmann, R. M. Taylor. The influence of silicate on the transformation of lepidocrocite to goethite. Clay Clay Miner. 20 (1972) 159.

Raman, SERS and DFT analysis of mauve dye and its components

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Mauveine was the first synthetic organic dyestuff to be manufactured industrially. William Henry Perkin discovered this purple dye by chance when trying to synthesize quinine, the only known remedy for malaria. Perkin's synthesis of mauve and the establishment of a factory to produce it commercially mark the beginnings of the modern dye industry [1]. The main components of mauveine are mauveine A and B; other components such as mauveine B2 and C were also discovered in 2007 [2].

In this study we endeavoured to study the Raman and SERS spectra of the dye and its components in order to determine their interaction with Ag nanoparticles. Ordinary Raman and Surface-enhanced Raman Scattering (SERS) spectroscopies are well established techniques for the analysis of artists' pigments and dyes [3]. DFT (Density Functional Theory) calculations of the four mauveine molecules were carried out to aid in the assignments of the vibrational normal modes.

The Raman spectrum of mauve was recorded on a gold mirror at 633 nm. No Raman spectra of the mauveine molecules could be obtained. The SERS (Surface-Enhanced Raman Spectroscopy) measurements of the dye were carried out in a water/methanol solution by the use of Ag nanoparticles prepared by reduction with trisodium citrate [4]. However, the SERS spectra of the mauveine molecules were obtained directly on a TLC (Thin Layer Chromatography) plate. A previous separation of the different components of the dye was needed before the acquisition of the SERS spectra [5]. DFT calculations were carried out using the B3LYP/6-31+G* basis set. The geometry of the mauveine molecules was optimized and the Raman spectra were simulated.

Some differences between the Raman and SERS spectra of mauve were found. Thus, a chemical interaction between the dye and the Ag nanoparticles was concluded.

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References

- [1] P. Ball. Chemistry: Perkin, the mauve maker. *Nature* 440 (2006) 429.
- [2] J. S. De Melo, S. Takato, M. Sousa, M. J. Melo, A. J. Parola. Revisiting Perkin's dye(s): the spectroscopy and photophysics of two new mauveine compounds (B2 and C) *Chem. Comm.* (2007) 2624.
- [3] M. V. Cañamares, M. Leona, M. Bouchard, C. M. Grzywacz, J. Wouters, K. Trentelman. Evaluation of Raman and SERS analytical protocols in the analysis of Cape Jasmine dye (*Gardenia augusta* L.) *J. Raman Spectrosc.* 41 (2010) 391.
- [4] P. C. Lee, D. Meisel. Adsorption and Surface-Enhanced Raman of Dyes on Silver and Gold Sols. *J. Phys. Chem.* 86 (1982) 3391.
- [5] F. Pozzi, N. Shibayama, M. Leona, J. R. Lombardi. TLC-SERS study of Syrian rue (*Peganum harmala*) and its main alkaloid constituents. *J. Raman Spectrosc.* 44 (2013) 102.

COMUNICACIONES EN CARTEL

Stability assessment of virgin olive oils enriched with new natural antioxidants using spectrophotometric color monitorization

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Today there is a growing interest in the development of functional foods, which are those able to provide beneficial effects on health, in addition to their nutritional or energetic values. Usually these products are traditional foods enriched with one or several components promoting beneficial effect on human health.

Lutein is a yellow natural pigment of the carotenoid family that is selectively accumulated in different parts of the human eye, and is especially abundant at the centre of the human eye retina (macula), displaying important biological activities (i.e. antioxidant, blue light filter). The interest in lutein (macular pigment) has recently increased on the basis of different studies suggesting the protective effect resulting from an adequate intake of this pigment in the prevention and evolution of human-degenerative eye diseases (i.e. age-related macular degeneration, cataracts and maculopathy) [1,2]. The estimated daily lutein uptake by eating fruits and vegetables (1.5 mg/day) is not enough to reach the recommended value (6 mg/day). Therefore, for risk groups (elderly population) and people in general it would be important an adequate lutein intake through functional foods.

In the present paper, we describe the stability of virgin olive oils (VOOs) enriched with lutein obtained from the microalga *Scenedesmus almeriensis* using a previously described methodology [3]. Different varieties of VOOs have been enriched with lutein extract (5 mg/ml) obtaining a new functional food which seems a suitable conduction medium to provide this antioxidant to human organism in order to prevent eye diseases. In this sense, we have obtained VOOs enriched between 0.1 and 0.21 mg lutein/ml oil. This concentration range allows administering the daily-recommended lutein intake taking into account the estimated VOOs average consumption (30 ml per habitant and day).

We focus on the stability of a set of 10 VOOs as a function of three main degradation variables (time, temperature and light exposure) considering lutein-enriched VOOs in comparison with control VOOs (oils without antioxidant added). As it is well known, oil stability depends on chemical composition, which can be tracked using spectrophotometric color determinations. So, we used an application-based approach, employing the CIELAB color space rather than the analysis of transmittance spectra to assess the observed color changes (ΔE^*_{ab}). The results obtained were different depending on VOOs utilized but, in all cases, the VOOs enriched with lutein were more stable than the control ones. These results show that lutein-enriched VOOs could be successfully used like functional foods with additional health properties as an alternative way in the fight against some specific human degenerative diseases.

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References

- [1] A. Kijlstra, Y. Tian, E. Kelly, T. Berendschot. Lutein: more than just a filter for blue light, Progress in Retinal and Eye Research (2012) 31, 303-315.
- [2] F. Granado, B. Olmedilla, I. Blanco, I. Nutritional and clinical relevance of lutein in human health. British Journal of Nutrition, (2003) 90:487-502.
- [3] J.M. Fernández-Sevilla, F.G. Gabriel Acien-Fernández, E. Molina. Biotechnological production of lutein and its applications, Appl. Microbiol. Biotech. (2010) 86, 27-40.

Multielemental analysis of plant samples by total reflection X-ray fluorescence together with linear discriminant analysis to identify the anatomical part

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Spices and herbs like tea are widely used to season food, as medicinal plants, and also in pharmacy, cosmetology and perfumes. Thus, a quality control is required in order to ensure the identity, purity and content, thus guaranteeing the safe consumption of these products, avoiding the presence of heavy metals, agrochemicals or microbial contaminants [1].

Nowadays, there is an increasing demand for multielemental analysis of plants on a routine basis and following the green trends when developing new methods, *i.e.*: i) use of low sample mass; ii) use of low amounts of reagents; iii) rapidity and iv) safety of the procedure. Ultrasound-assisted extraction (UAE) [2] in combination with total reflection X-ray fluorescence (TXRF) [3] is proposed as a fast and simple method for multielemental analysis (P, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn and Pb) of plants (Fig. 1). Different extractant media (acids and oxidants) and sonication times were tried. A mixture of diluted $\text{HNO}_3 + \text{HCl} + \text{HF}$ was selected as the preferred option for the achievement of complete extractions. Accurate and precise results can be reached in most cases with a high sample throughput.

The proposed analytical approach was applied to unknown seasoning, aromatic and medicinal plants. Since different parts of plants may have different properties, unambiguous identification of the commercial plant preparation is required for quality control. Plant classification has been reported in accordance with the origin, the family and the anatomical part of the plant. The discrimination on the basis of the anatomical part of the medicinal plant (flower, leaves, fruits, herbs, barks and roots) is important because an specific part of a medicinal plant is used for culinary or therapeutic (it contains the active principle) purposes. In this work, linear discriminant analysis was applied to discern the anatomical part of commercial plant preparations (*i.e.*, flower, leaf, and fruit) available for consumers.

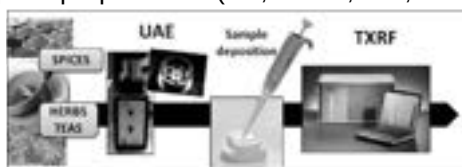


Figure 1. Scheme of the employed procedure.

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References

- [1] WHO (1998). World Health Organization (WHO) Quality control methods for medicinal plant materials. Available from <<http://whqlibdoc.who.int/publications/1998/9241545100.pdf>>.
- [2] Bendicho, I. De La Calle, F. Pena, M. Costas, N. Cabaleiro, I. Lavilla. Ultrasound-assisted pretreatment of solid samples in the context of green analytical chemistry. *Trends. Anal. Chem.* 31 (2012) 50.
- [3] I. De La Calle, N. Cabaleiro, V. Romero, I. Lavilla, C. Bendicho. Sample pretreatment strategies for total reflection X-ray fluorescence analysis: A tutorial review. *Spectrochim. Acta Part B* 90 (2013) 23.

Classification of Spanish red wines according to their designation of origin using laser-induced breakdown spectroscopy and neural networks

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The system of quality assurance to control fraud and preserve the Protected Denomination of Origin (PDO) and special characteristics of wines is regulated by law [1]. The amount and relative proportion of the mineral elements as Mg, Ca, K and Na in red wine depends on several factors such as the vineyard, grape type, climate, water availability and quality, soil type and the way in which the wine is elaborated and stored [2,3].

In this work, a quick and cost effective method based on Laser Induced Breakdown Spectroscopy (LIBS) and Neural Networks (NN) has been developed and applied to the identification of the PDO and quality control of red wines. Instant identification of the samples is achieved using a spectral library, which was obtained by analysis of representative samples using a single laser pulse and treatment by NN. The samples used belonged to the most important Spanish PDOs. The results obtained allow the identification of the red wines tested with a certainty of above 98%. Single-shot measurements were enough for clear identification of the samples. The method can be developed for automatic real time, fast, reliable and robust measurements and the system can be packed into portable system.

References:

- [1] Regulation (CE) 1151/2012 of the European Parliament and Council, November 21, 2012.
- [2] F. Pizarro, F.A. Vargas, E. Agosin, A system biology perspective of wine fermentation, *Yeast* 2007, 24, 977.
- [3] R.S. Jackson, 6 - Chemical Constituents of Grapes and Wine, in: R.S. Jackson (Ed.), *Wine Sci. Second Ed.*, Academic Press, San Diego, 2000: pp. 232–280.

Determination of resveratrol, piceatannol and oxyresveratrol isomers in wines using stir bar sorptive extraction and gas chromatography-mass spectrometry

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Stilbenoids are polyphenolic phytoalexins produced by plants as defence substances against stress. Due to their antioxidant activity, they have a wide range of beneficial effects, including anticancer, anti-inflammatory, and anti-microbial. These compounds have been found in several plants, although the highest concentrations are reached in grapes and derived products, such as wine [1].

A simple and highly sensitive procedure based on the combination of stir bar sorptive extraction coupled and gas chromatography-mass spectrometry by means of a thermal desorption unit (SBSE-TD-GC-MS) has been proposed for the first time for the simultaneous determination in wine samples of the *cis/trans* isomers of the three more representative stilbenoids: resveratrol, piceatannol and oxyresveratrol [2]. Vines synthesize *trans*-stilbenols in response to stress situations whereas *cis*-isomers are produced during the wine making process [3].

For the quantification of the *cis*-isomers, a novel and very effective procedure for the generation of the standards, in which isomerization takes place by irradiation of the corresponding *trans*-species once they have been preconcentrated on the SBSE extraction phase, has been employed. This isomerization procedure has been compared with that using direct UV irradiation of the *trans*-isomers solution, showing great advantages.

So as to improve the extraction efficiency and the chromatographic response of the studied compounds, an acetylation derivatization step has been included prior to SBSE extraction. Different factors affecting this derivatization reaction as well as other parameter related with the SBSE extraction and the subsequent thermal desorption steps, were investigated using multivariate optimization based on Plackett-Burman designs.

Quantification of the samples was carried out against aqueous standards, using bisphenol F as internal standard. Repeatability, expressed as relative standard deviation of 10 successive analyses was between 5 and 9%, confirming the high precision attained under the optimized conditions. Satisfactory recovery values of between 79 and 109% were obtained for spiked samples in the 0.2-1.0 $\mu\text{g L}^{-1}$ concentration range, depending on the compound.

The method was employed for the analysis of 15 wine samples (white, rosé and red), being *trans*-resveratrol the most abundant, with concentrations in the range 3-230 $\mu\text{g L}^{-1}$, depending on the type of wine.

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References

- [1] M.A. Carluccio, L. Siculella, M.A. Ancora, M. Massaro, E. Scoditti, C. Storelli, F. Visioli, A. Distanti, R. De Caterina, "Olive Oil and Red Wine Antioxidant Polyphenols Inhibit Endothelial Activation: Antiatherogenic Properties of Mediterranean Diet Phytochemicals" *Arterioscl. Thromb. Vas.* 23 (2003) 622.
- [2] H.Y. Sun, C.F. Xiao, Y.C. Cai, Y. Chen, W. Wei, X.K. Liu, Z.L. Lv, Y. Zou, "Efficient Synthesis of Natural Polyphenolic Stilbenes: Resveratrol, Piceatannol and Oxyresveratrol" *Chemical & Pharmaceutical Bulletin* 58 (2010) 1492.
- [3] R. Montes, M. García-López, I. Rodríguez, R. Cela, "Mixed-mode solid-phase extraction followed by acetylation and gas chromatography mass spectrometry for the reliable determination of *trans*-resveratrol in wine samples" *Anal. Chim. Acta* 673 (2010) 47.

Development of multivariate models for quantifying microbial load in goat milk by near infrared spectroscopy

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Goat milk has a lower lactose content in comparison to bovine milk, making it more suitable for individuals with lactase deficit. Furthermore, it also has a lower content of the α S1-casein protein fraction, one of the main allergens in bovine milk [1]. Quality and food safety of goat milk cheese greatly depends on the initial microbial contamination in the goat milk used for its manufacture. The Near Infrared Technology (NIR) has been proved to be an useful tool to detect microorganisms in food matrices [2]. Therefore, the objective of this study was to investigate the potential of NIR spectroscopy, as rapid, non-destructive and reliable method for quantification of microbial load in goat milk.

The procedure consisted of collecting milk samples from different milk producers in Zuheros (Córdoba, Spain), which is a region devoted to produce different milk product, specially different varieties of cheese. Then, samples were incubated at different temperatures (5, 10 and 15 °C) and microbial concentration changes were measured over time by plate count method as reference method and NIR technique based on diffuse reflectance integrating sphere in a region 1100 – 2500 nm. Thickness of the sample was 0.5 mm. Different models were compared on 50 samples in range 3.7-8.6 log CFU/ml. Final predictive models were developed based on continuum regression, and parameters were set in a two-stage optimization procedure.

Models developed for the different temperatures showed good performance to predict bacterial contamination in goat milk over time. In order to estimate the prediction capacity of the model, Mean Square Error were computed on independent validation set, obtaining a value of 0.5 log CFU/ml which evidenced the great accuracy obtained by the model. This value is quite similar to the typical error associated with the reference method used in this study. In addition, this method allows determination of microbial load in real time, with a similar accuracy which enables to take corrective measures immediately when high microbial load is detected in milk samples. In conclusions, results in this work suggest NIR technology as a suitable method for rapid detection of bacterial contamination, improving efficiency of the production process and food safety of this commodity.

References

[1] B.M. Exl, R. Fritsché. *Nutrition* 17 (2001) 642.

[2] F. Cámara-Martos, G. Zurera-Cosano, R. Moreno-Rojas, R.M. Garcia-Gimeno, F. Pérez-Rodríguez. *Food Anal Meth* 5 (2012) 19.

Spectroscopical study of compounds emitted by household ovens

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It is known that many compounds as aldehydes, organic acids, volatile organic compounds (VOC's), etc. are emitted during the cooking process in a domestic oven. Some of them are odorous, providing the cook useful information of the state of the roasted food. But there are also hazardous compounds that can pollute the air of the kitchen/room where the oven is located [1]. For that reason, in recent years there has been an increase in the studies about these emissions in order to prevent negative effects on the health and to provide safe home and workplace environments [2]. Many of the methods used in the determinations of these compounds are based on chromatographic techniques, for batch measurements, or inespecific methods prone to interferences.

In this work, we propose to continuously monitoring the cooking by UV-VIS-NIR absorption spectroscopy in order to get information about the evolution of the process in real time. Besides, since our oven is supplied with a self-cleaning program we have also monitored the pyrolysis cycle during which all the remains of roasted food are burnt at higher temperatures and transformed into ashes. The final objective is the development of an optical sensor to prevent unpleasant or burnt odours.

For this purpose we have implemented several systems in different locations of the oven:

1.- A UV-VIS-NIR Diode Array Spectrometer adapted with a cylindrical quartz cuvette. In this case all the vapours that come from inside the oven cavity are collected by a piping and directed to the cuvette. This method allows to get a wider and precise information of the process.

2.- A scattering sensor device located at the end of the extraction piping that works at different wavelengths. In this case, we obtain information about the particles that are generated.

3.- A portable fiber optic system coupled to a CCD spectrometer placed at the bottom part of the door where the vapours are extracted. The compounds that are detected in this location can be different from the ones inside the oven owing to the decrease in the temperature

4.- A polyaniline sensor film (PANI) situated in the optical path of the fiber optics. We can evaluate if there is a change in the pH of the vapours.

We present the main results obtained.

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References

- [1] E. Kabir, K.-H. Kim. An investigation on hazardous and odorous pollutant emission during cooking activities. J Hazard Mater 188 (2011) 443.
- [2] K. Duarte, C. I. L. Justino, A. C. Freitas, A. C. Duarte, T. A. P. Rocha-Santos. Direct-reading methods for analysis of volatile organic compounds and nanoparticles in workplace air. Trends Anal. Chem. 53 (2014) 21-32.

Migration and characterization of nanosilver particles from food containers by AF4-ICP-MS

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The most active area of food nanoscience is packaging, where nanoparticles are easily incorporated into polymers to produce functional materials that contribute to extend and improve food life time [1]. Among them, silver nanoparticles (AgNPs) are the most frequently used due to their recognised antimicrobial properties [2]. However, their environmental fate and final impact on human health is still widely unknown.

In this work, silver migration from commercial food containers was studied according to the European Regulation 10/2011. Several experimental parameters affected silver release: food simulant, temperature, exposition time and sampled bag area. Results demonstrated a significant AgNP migration into aqueous and acidic food simulants. The amount of silver migrated increased with storage time and temperature, although in general, AgNPs showed a low tendency to migrate into food simulants (17 ng/g). However, the food simulant did not seem to be a real outstanding variable for long term storage, which is probably a significant finding to be considered in risk assessment studies.

AF4-ICP-MS was used to confirm the presence of AgNPs in the investigated simulants. The low limit of detection achieved (0.4 µg/L) allowed identification of AgNPs and their size characterization (40-60 nm). Finally, SEM-EDX analysis, of both the extracts and the raw material, suggested a transformation of the AgNPs during migration assays due to association with other ligands, such as chlorine and sulfur, present in the original containers. These transformations could modify AgNPs properties and toxicity and, therefore, it would be essential to evaluate their potential risks for humans and the environment.

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References

- [1] H. Althues, J. Henle, S. Kaskel. Functional inorganic nanofillers for transparent polymers. *Chem. Soc. Rev.*, 36(2007)1454.
- [2] S.N. Luoma. *Silver Nanotechnologies and the Environment: Old Problems or New Challenges*, Woodrow Wilson International Center for Scholars: Project of Emerging Nanotechnologies, Washington, DC. (2008).

Direct determination of essential elements in food and dietary supplements by high-resolution continuum source atomic absorption spectrometry

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Elements, such as iron, calcium, magnesium, copper or silicon are required by living organisms or have a role in health. These minerals are usually obtained through diet and its deficiency in food may cause many diseases, such as anaemia. In order to compensate the deficiencies of these macro and trace elements in the human diet, multivitamin -multimineral dietary formulations with different compositions are available.

Analytical methodologies that permit the determination of these elements directly in the sample, without pretreatment steps, increase the speed of analysis and reduce the risk of contamination and loss of volatile analytes of the samples. In addition, these methods are considered analytical approaches more environmentally-friendly than the traditional methodologies based on the digestion of solid samples. High-resolution continuum source atomic absorption spectrometry (HR-CS AAS) provides significant advantages in comparison to traditional line source AAS, such as improved capabilities to the detection and correction of spectral interferences from the matrix sample, as well as the possibility of simultaneous multi-element determination. In addition, it is possible to decrease the sensitivity to the required levels and therefore expand the working range without the need to carry out additional measurements, by recording the absorption only at the line wings [1-3].

This work aims to explore the possibilities of HR-CS AAS using flame and graphite furnace atomizers for the fast and direct determination of essential elements in food and dietary supplements. To achieve this purpose, measurement parameters such as selection of the absorption line, burner height, flame composition or temperature program of the graphite furnace are optimized. The presence of molecular interferences are evaluated and corrected. Owing to the expected high content of these elements in some samples, the use of less sensitive lines and the approach of side pixel registration have been also evaluated. The principal analytical figures of merit are estimated and then the methodology is used to determine these elements in commercial samples.

References

- [1] B. Welz, S. Mores, E. Carasek, M.G.R. Vale, M. Okrus, H. Becker-Ross. High-Resolution Continuum Source Atomic and Molecular Absorption Spectrometry: A Review. *Appl. Spectrosc. Rev* 45 (2010) 327.
- [2] B. Gomez-Nieto, M.J. Gismera, M.T. Sevilla, J.R. Procopio. Simultaneous and direct determination of iron and nickel in biological solid samples by high-resolution continuum source graphite furnace atomic absorption spectrometry. *Talanta* 116(2013) 860.
- [3] M. Resano, M.R. Florez, E. Garcia-Ruiz. High-resolution continuum source atomic absorption spectrometry for the simultaneous or sequential monitoring of multiple lines. A critical review of current possibilities. *Spectrochim. Acta B* 88 (2013) 85.

Determination of caffeoylquinic acids in feed and related products by focused ultrasound solid-liquid extraction and ultra-high performance liquid chromatography-mass spectrometry

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The interest in using natural products with therapeutic properties as additives has increased in recent years. Chlorogenic acid (CQAs) and caffeoylquinic acids are naturally present in herbs, which are usually used as additive in feed industry due to their health-promoting properties. CQAs have been shown to possess a multitude of preservative and pharmacological activities, such as antioxidant, antiviral, antibacterial, anti-inflammatory, reduction of the relative risk of cardiovascular disease and diabetes type 2, antispasmodic activities, inhibition of the mutagenicity of carcinogenic compounds, etc. [1].

In this communication, CQAs determination in three sources (feed, feed additive, herbal extract) using a novel method based on Focused Ultrasound Solid-Liquid Extraction (FUSLE) followed by Ultra-high Performance Liquid Chromatography (UPLC) coupled to quadrupole-time of flight mass spectrometry is presented.

First, chromatographic separation and mass detection conditions were studied and optimised for both, mono- and di- caffeoylquinic acids. The selected UPLC conditions allowed the isolation of the CQAs isomers in only seven minutes. The optimisation of QToF parameters for the mass 353.09 (mono-CQAs) and 515.12 (di-CQAs) provided a signal increase that improved method sensitivity.

Second, FUSLE variables such as extraction solvent, power and time were optimised by a central composite design. Under optimal conditions, FUSLE extraction was performed with 8 mL of 80:20 methanol:water for 20 seconds at a power of 60%. Only two extraction steps were found necessary to recover analytes quantitatively.

Sensitivity, linearity, accuracy and precision were also established. Matrix effect was studied for each batch. Matrix effects were not detected for mono-CQAs, whereas the 1,3-dicaffeoylquinic signal was strongly decreased due to ionization suppression in presence of matrix components; so the quantification by standard addition was mandatory for the determination of di-caffeoylquinic acids.

Finally, the method was applied to the analysis of feed, feed additives and herbal extracts. In all samples, 5-caffeoylquinic acid (chlorogenic acid) were the predominant CQAs, followed by 4-caffeoylquinic acid, 3-caffeoylquinic acid and 1,3-dicaffeoyl quinic acid.

The method developed in the present study allows an efficient determination of CQAs with good recovery rates. Therefore, it may be used for screening of raw material and for process and quality control in the feed industry.

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References

[1] A. Farah, M. Monteiro, C.M. Donangelo, S. Lafay. The Journal of Nutrition 138 (2008) 2309.

Using spectroscopy Vis/NIR to determinate quality parameters in *Prunus avium* “Chelan” sweet cherries

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The objective of this study was to evaluate the use of Vis/NIR spectroscopy as a non-destructive method to estimate some quality parameters during the ripening process of *Prunus avium* ‘Chelan’ sweet cherries.

In this experiment, 282 cherries were collected from a commercial orchard in La Almunia de Doña Godina (Zaragoza). Vis/NIR spectra were kept from samples picked up every 2 days during 2 weeks. In the same fruits, soluble solids contents (SSC) and firmness were measured by traditional destructive methods. Spectra from intact cherries were measured with a Multispec reflectance modular equipment (range: 400-1060 nm).

PLS calibration methods were used to create the statistical model to predict SSC and firmness [1]. Good results were obtained when PLS calibration was applied. The r_p^2 values obtained were 0.73 for firmness and 0.94 for SSC, which are higher than other reported in the literature for the same commodity [2, 3].

Acknowledgements

This work has been partially supported by the AGL2009-08501/AGR project from National Program of Research Projects.

References

[1] The Unscrambler® X.1. CAMO Software AS

[2] R. Lu. Predicting firmness and sugar content of sweet cherries using near infrared diffuse reflectance spectroscopy. *Trans ASAE* 44 (2001):1265-1271

[3] P.Carlini, R. Massantini, F. Mencarelli. Vis-NIR measurement of soluble solids in cherry and apricot by PLS regression and wavelength selection. *J Ag Food Chim*, 48 (2000) pp. 5236-5242.

Cloud point extraction with silver nanoparticles for the determination of very low amounts of cadmium by electrothermal atomic absorption spectrometry

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The determination of very low concentrations of cadmium is nowadays of relevance since this element is highly toxic to animals, plants and humans, and accumulates in different organs. The concentrations currently found in foods and environmental samples are extremely low so that they may even be below the detection limit of the most sensitive analytical techniques. This difficulty can be overcome taking advantage of the present knowledge of microextraction techniques, that allow the analytes to be preconcentrated thus obtaining solutions that can be measured by means of techniques commonly present in the analytical laboratory. Sometimes the microextraction stage is carried out by using a neutral complex with a suitable organic reagent. This is the case of ammonium pyrrolidine dithiocarbamate (APDC) that has been used for the extraction of metals with different microextraction methodologies [1-2]: ionic liquids, solid phase with activated carbon, organic solvents, ultrasonic emulsification, flow systems and hollow fibers. The extraction of the neutral Cd-APDC complex with supramolecular systems has already been proposed (decanoic acid plus tetrahydrofuran [3] or octyl ether and phenol polyethylene glycol [4]). In these cases the final measurement was carried out by using flame atomic absorption spectrometry after a dilution stage to increase the volume of the extract, and thus render the introduction into the flame atomizer possible. Consequently, the preconcentration factors were low (22 and 48), respectively.

In the work here presented, silver nanoparticles (AgNPs) are used together with APDC in the presence of Triton X-114 [5] in such a way the neutral Cd-APDC complex is extracted into the surfactant-rich phase obtained by cloud point extraction (CPE). The experimental data clearly show that AgNPs are essential in order the total extraction of the metallic complex to be achieved. The optimal experimental conditions to rapidly obtain the CPE of the complex are studied. The final measurement is carried out by electrothermal atomization atomic absorption spectrometry (ETAAS). Thus, since the extract is directly injected into the atomizer without the need for a dilution stage, a high sensitivity is achieved. A very high preconcentration factor (close to 1000) is obtained which, in addition to the low detection limit inherent to ETAAS, results in a highly sensitive procedure. The procedure optimized is applied to the preconcentration and determination of cadmium in water, wine and beer samples with a detection limit of 1 ng L^{-1} .

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References

- [1] I. López-García, Y. Vicente-Martínez, M. Hernández-Córdoba, *Determination of lead and cadmium using an ionic liquid and dispersive liquid-liquid microextraction*, *Talanta*, 110 (2013) 46-52.
- [2] P. Viñas, N. Campillo, I. López-García, M. Hernández-Córdoba, *Dispersive liquid-liquid microextraction in food analysis. A critical review*, *Anal. Bioanal. Chem.* (2014) DOI 10.1007/s00216-013-7344-9
- [3] S. Jafarvand, F. Shemirani, *Supramolecular-based dispersive liquid-liquid microextraction: determination of cadmium in water and vegetable samples*, *Anal Methods*, 3 (2011) 1552-1559.
- [4] H.Y. Han, Y.Y. Xu, C. Zhang, *Determination of Available Cadmium and Lead in Soil by Flame Atomic Absorption Spectrometry after Cloud Point Extraction*, *Commun. Soil Sci. Plant Anal.*, 42 (2011) 1739-1751.
- [5] P.-H. Liao, S.-J. Jiang, A.C. Sahayam, *Cloud point extraction combined with flow injection vapor generation inductively coupled plasma mass spectrometry for preconcentration and determination of ultra trace Cd, Sb and Hg in water samples*, *J. Anal. At. Spectrom.*, 27 (2012) 1518-1524.

Determination of lead in wine samples by means of dispersive liquid-liquid microextraction and graphite furnace atomic absorption detection

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Continuous intake of small Pb amounts has a negative impact on human health. Foods are the main sources of this element for humans and, as a consequence, several international organizations have regulated maximum allowed levels of this element [1]. Wine is a widely consumed beverage around the world with significant Pb levels. The source of Pb in wine is mainly related to atmospheric precipitation, pesticides and materials used in production, transport and storage [2].

Lead analysis is usually performed by means of spectroscopic techniques such as Graphite Atomic Absorption Spectrometry (GFAAS) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) due to its lower limits of detection [3]. However, results are strongly affected by the occurrence of both spectral and non-spectral interferences. To mitigate wine matrix effects, several sample pre-treatment strategies such as dilution or acid digestion have been employed. Alternatively, liquid-liquid extraction [4] and solid phase extraction [5] have also been recommended to separate the analyte from the matrix and improve limits of detection. Nonetheless, these methodologies suffer from several shortcomings: (i) use of toxic solvents; (ii) high solvent consumption; (iii) high residue generation; (iv) labour intensive; (v) volume changes (i.e. swelling or shrinking) on the sorbent material; and, (vi) deactivation of the surface and/or loss of functional groups. In order to make the extraction/preconcentration step greener, miniaturized extraction techniques (e.g. dispersive liquid-liquid microextraction, DLLME) and the use of ionic liquids have been recommended instead [6,7]. However, the use of these methodologies for trace and ultra-trace analysis in food and beverages has been limited.

The goal of this work is to develop a new methodology for Pb determination in wine by means of GFAAS after an extraction/preconcentration procedure based on the simultaneous use of DLLME and ionic liquids (1-butyl-3-methylimidazolium hexafluorophosphate). To this end, the influence of extractant volume, dispersant, pH and ionic strength on Pb detection has been investigated.

Acknowledgements

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References

- [1] V.A. Lemos, M. de la Guardia, S. L.C. Ferreira, An on-line system for preconcentration and determination of lead in wine samples by FAAS, *Talanta* 58 (2002) 475
- [2] <http://www.oiv.int/oiv/info/en/publication/oiv?lang=en>, accessed in February, 23, 2014.
- [3] G. Grindlay, J. Mora, L. Gras, M.T.C. de Loos-Vollebregt, Atomic spectrometry methods for wine analysis: a critical evaluation and discussion of recent applications, *Anal. Chim. Acta* 691 (2011) 18.
- [4] R. Cerdeira de Campos Costa, A. Nova Araújo, Determination of Fe(III) and total Fe in wines by sequential injection analysis and flame atomic absorption spectrometry, *Anal. Chim. Acta* 438 (2001) 227.
- [5] M. Tuzen, M. Soylak, L. Elci, Multi-element pre-concentration of heavy metal ions by solid phase extraction on Chromosorb 108, *Anal. Chim. Acta* 548 (2005) 101.
- [6] V. Andruch, I.S. Balogh, L. Kocúrová, J. Šandrejová, The present state of coupling of dispersive liquid-liquid microextraction with atomic absorption spectrometry, *J. Anal. At. Spectrom.* 28 (2013) 19.
- [7] E.M. Martinis, P. Berton, R.P. Monasterio, R.G. Wuilloud, Emerging ionic liquid-based techniques for total-metal and metal-speciation analysis, *Trends Anal. Chem.* 29 (2010) 1184.

A novel method for evaluating flavanols in grape seeds by near infrared hyperspectral imaging

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Grape seeds constitute a small part of the berry, but they affect extensively the sensory properties of wine. Their phenolic compounds are responsible of these properties and they change in a qualitative and quantitative manner during ripening [1,2]. The most representative of them in grape seeds, flavanols, include flavan-3-ol monomers (catechin, epicatechin and epicatechin gallate) and procyanidins, which are polymers comprised of flavan-3-ol terminal and extension subunits [3]. Phenolic composition of grapes depends on multiple factors, including climate, variety, soil, and degree of ripeness, being this phenolic maturity decisive for the production of quality red wines. In order to control the features of wines, the condition of seeds is becoming an important factor for deciding the moment of harvesting by winemakers. Sensory analysis is not easy to carry out and chemical analysis needs lengthy procedures, reagents, and it is destructive and time-consuming.

In the present work, near infrared hyperspectral imaging has been used to determine flavanols in seeds of red (cv. Tempranillo) and white (cv. Zalema) grapes (*Vitis vinifera* L.). As reference measurements, the flavanol content was estimated using the p-dimethylaminocinnamaldehyde (DMACA) method [4]. Not only total flavanol content was evaluated but also the quantity of flavanols that would be extracted into the wine during winemaking. A like-wine model solution was used for this purpose. Calibrations were performed by partial least squares regression and they provide coefficients of determination $R^2=0.73$ for total flavanol content and $R^2=0.85$ for predicting flavanols extracted with model solution. Values up to $R^2=0.88$ were reached when cultivars were considered individually.

Though it is not yet a substitute for conventional chemical analysis, it arises as an attractive alternative due to its simplicity and quickness. By establishing the variables that affects each cultivar, this could become a reference method to assess the chemical characteristics of grape seeds during maturation, being very useful for vine growers and wineries [5].

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References

- [1] Y. Cadot, M. T. Miñana-Castelló, M. Chevalier. Anatomical, Histological, and Histochemical Changes in Grape Seeds from *Vitis vinifera* L. cv Cabernet franc during Fruit Development. *J. Agric. Food Chem.* 54 (2006) 9206.
- [2] B.S. Sun, T. Pinto, M.C. Leandro, J.M. Ricardo-Da-Silva, M.I. Spranger. *Am. J. Enol. Vitic.* 50 (1999) 179.
- [3] R. Ristic, P.G. Iland. Relationships between seed and berry development of *Vitis Vinifera* L. cv Shiraz: Developmental changes in seed morphology and phenolic composition. *Aust. J. Grape Wine Res.* 11 (2005) 43.
- [4] N. Vivas, Y. Glories, L. Lagune, C. Saucier, M. Augustin. Estimation du degré de polymérisation des procyanidines du raisin et du vin par la méthode au p-diméthylaminocinnaldéhyde. *J. Int. Sci. Vigne Vin* 28 (1994) 319.
- [5] F.J. Rodríguez-Pulido, J.M. Hernández-Hierro, J. Nogales-Bueno, B. Gordillo, M.L. González-Miret, F.J. Heredia. A novel method for evaluating flavanols in grape seeds by near infrared hyperspectral imaging. *Talanta* 122 (2014) 145.

Application of the characteristic vector method to the reconstitution of red grape NIR spectra

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Characteristic vector method has been applied in a number of studies to the reconstitution of visible spectra [1-4]. In the present study red grape absorbance spectra in the near infrared region have been reconstituted using characteristic vectors. For this purpose, 99 Tempranillo and Syrah grape samples were collected and their spectra were recorded using a near infrared hyperspectral system (900 – 1700 nm). To develop characteristic vector analysis, experimental spectra were split into three equal regions and 1, 2, 3 and 4 wavelengths were selected for each region. In this way, spectra were reconstituted from 3, 6, 9 and 12 characteristic vectors respectively.

The goodness of this reconstitution method was tested using the method described by Nogales-Bueno et al. [5]. This method use near infrared hyperspectral imaging to develop calibration models in order to predict total phenolic concentration in grape skins and sugar concentration, titratable acidity and pH in grape must. Original and reconstituted spectra (from 3, 6, 9 and 12 vectors) were used to develop calibration models and the aforementioned parameters were predicted. It was found similar Standard Error of Prediction (SEP) for calibration models developed using experimental and reconstituted spectra from 12 characteristic vectors. However, higher SEP values were obtained using the reconstituted spectra from 9, 6 and 3 characteristic vectors.

In conclusion, characteristic vector analysis allows to reconstitute near infrared spectra using only a few wavelengths and the reconstituted spectra keep almost all spectral information. To our knowledge, this is the first time that the aforesaid method has been applied to near infrared spectra.

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References

- [1] F. Ayala, J. F. Echavarri, A. I. Negueruela. A new simplified method for measuring the color of wines. III. All wines and brandies. *Am. J. Enol. Vitic.* 50 (1999) 359.
- [2] M. L. Gonzalez-Miret, F. Ayala, A. Terrab, J. F. Echavarri, A. I. Negueruela, F. J. Heredia. Simplified method for calculating colour of honey by application of the characteristic vector method. *Food Res Int.* 40 (2007) 1080.
- [3] A. J. Melendez-Martinez, F. Ayala, J. F. Echavarri, A. I. Negueruela, M. L. Escudero-Gilete, M. L. Gonzalez-Miret, I. M. Vicario, F. J. Heredia. A novel and enhanced approach for the assessment of the total carotenoid content of foods based on multipoint spectroscopic measurements. *Food. Chem.* 126 (2011) 1862.
- [4] M. J. Moyano, F. Ayala, J. F. Echavarri, J. Alba, A. I. Negueruela, F. J. Heredia. Simplified measurement of virgin olive oil color by application of the characteristic vector method. *J. Am. Oil Chem. Soc.* 78 (2001) 1221.
- [5] J. Nogales-Bueno, J. M. Hernández-Hierro, F. J. Rodríguez-Pulido, F. J. Heredia. Determination of technological maturity of grapes and total phenolic compounds of grape skins in red and white cultivars during ripening by near infrared hyperspectral image: A preliminary approach. *Food Chem.* 152 (2014) 586.

Feasibility study on the use of near infrared hyperspectral imaging for the screening of anthocyanins in intact grapes during ripening

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Phenolics are secondary metabolites which present important roles in the plant kingdom [1, 2]. Among them, anthocyanidins are responsible for tissue pigmentation and provide colours that range from reddish to purplish ones [1]. Grapes are a non-climateric fruit that follow three growing phases and contain several phenolic compounds, which include anthocyanins in the case of red cultivars. Anthocyanins are responsible for the colour of red wines and their interactions with other phenolic compounds largely determine the colour changes observed during ageing [3-5].

The potential of near infrared hyperspectral imaging to determine anthocyanins in intact grape has been evaluated. The hyperspectral images of intact grapes during ripening were recorded using a near infrared hyperspectral imaging covering the spectral range between 900 and 1700 nm. Reference values of anthocyanins were obtained by HPLC-DAD. A number of spectral pre-treatments and different mask development strategies were studied. Calibrations were performed by modified partial least squares regression (MPLS) and present a good potential (RSQ of 0.86 and SEP values of 2.62 and 3.05 mg g⁻¹ of grape skin for non-acylated and total anthocyanins respectively) for a fast and reasonably inexpensive screening of these compounds in intact grapes [6].

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References

- [1] A. Crozier, M. N. Clifford, H. Ashihara. *Plant Secondary Metabolites. Occurrence, Structure and Role in the Human Diet*. Blackwell Publishing: Garsington Road, Oxford, UK, 2006.
- [2] R. E. Koes, F. Quattrocchio, J. N. M. Mol. The flavonoid biosynthetic pathway in plants: Function and evolution. *BioEssays* 16 (1994) 123.
- [3] R. Boulton. The Copigmentation of Anthocyanins and Its Role in the Color of Red Wine: A Critical Review. *Am. J. Enol. Vitic.* 52 (2001) 67.
- [4] M. V. Moreno-Arribas, C. Polo. *Wine Chemistry and Biochemistry*. Springer New York: New York, NY, 2008.
- [5] M. T. Escribano-Bailon, C. Santos-Buelga. Anthocyanin Copigmentation - Evaluation, Mechanisms and Implications for the Colour of Red Wines. *Curr. Org. Chem.* 16 (2012) 715.
- [6] J. M. Hernandez-Hierro, J. Nogales-Bueno, F. J. Rodriguez-Pulido, F. J. Heredia. Feasibility Study on the Use of Near-Infrared Hyperspectral Imaging for the Screening of Anthocyanins in Intact Grapes during Ripening. *J. of Agric. and Food Chem* 61 (2013) 9804.

Determination of the geographical origin of cocoa beans by means spectrometric methods and chemometrics

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Cocoa, i.e., the fatty bean of *Theobroma cacao* L., is among the top most commercially cultivated cash crops for many countries worldwide (above 40 million people depend upon cocoa for their livelihood). In addition, cocoa bean is becoming a very interesting product because its numerous health benefits. World cocoa producer countries are located in West Africa (Ivory Coast, Ghana, Nigeria and Cameroon), Central and South America (Brazil, Mexico, Colombia, Ecuador and Dominican Republic) and Asia (Indonesia and Malaysia).

The origin of cocoa bean has become an extremely relevant issue because it determines the chemical and organoleptic properties of its derivate products (chocolates, cocoa beverages and confectionary products) as recognized by consumers and food industry [1-3]. As a consequence, the geographical origin determines the cocoa bean price. Traceability of cocoa bean quality is, therefore, an essential activity for controlling fraud and accidental or deliberate mislabelling and adulteration.

A wide variety of analytical methods have been reported for determining the geographical origin of foods [4]. Among them, GC [5], MS [6] or electronic tongue technology [7] have been applied to determine the geographical origin of cocoa beans. It is well known that the content of selected elements in foods clearly reflects the geographical origin of food samples. Nevertheless, in spite of its analytical advantages, the use of elemental analysis techniques has not been reported for this purpose in cocoa bean samples. In addition, information on the elemental composition of cocoa beans is relatively scarce. Recently, a rapid and inexpensive method based on the use of FT-Raman spectroscopy has been successfully applied for determining the origin of palm date (*Phoenix dactylifera* L.) samples [8].

The purpose of the present study is to develop different analytical methods based on the use of spectrometric techniques (i.e., Inductively Coupled Plasma Mass Spectrometry and Raman spectroscopy) to identify cocoa beans from different geographical origins. To this end, twenty three cocoa bean samples from different countries (i.e., Belize, Bolivia, Dominican Republic, Ecuador, Ghana, Madagascar, Nicaragua, Papua New Guinea, Peru and Venezuelan) and varieties (i.e., Criollo, Trinatario and Forastero) were analysed by means of Inductively Coupled Plasma Mass Spectrometry and Raman Spectroscopy. Principal component analysis was used to predict cluster trends.

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References

- [1] M. Torres-Moreno, A. Tarrega, E. Costell, C. Blanch, Dark chocolate acceptability: influence of cocoa origin and processing conditions, *J. Sci. Food Agric.*, 92 (2012) 404.
- [2] S. Jinap, P.S. Dimick, R. Hollender, Flavour evaluation of chocolate formulated from cocoa beans from different countries, *Food Control*, 6 (1995) 105.
- [3] R. Saltini, R. Akkerman, S. Frosch, Optimizing chocolate production through traceability: a review of the influence of farming practices on cocoa bean quality, *Food Control*, 29 (2013) 167.
- [4] D.M.A.M. Luykx, S.M. van Ruth, An overview of analytical methods for determining the geographical origin of food products, *Food Chem.*, 107 (2008) 897
- [5] A.Cambrai, C. Marcic, S. Morville, P.S. Houer, F. Bindler, E. Marchioni, Differentiation of chocolates according to the cocoa's geographical origin using chemometrics, *J. Agric. Food Chem.*, 58 (2010) 1478
- [6] B.S. Radovic, M. Lipp, E. Anklam, Classification of cocoa butters using pyrolysis-mass spectrometry, *Rapid Commun. Mass Spectrom.*, 12 (1998) 783
- [7] E. Teye, X. Huang, F. Han, F. Botchway, Discrimination of cocoa beans according to geographical origin by electronic tongue and multivariate algorithms, *Food Anal. Methods* 7 (2014) 360
- [8] S.S. Abdrabo, L. Gras, G. Grindlay, J. Mora, Classification of palm dates (*Phoenix Dactylifera* L.) by Fourier Transform Raman Spectroscopy and chemometrics, *J. Agric. Food Chem.*, submitted

Time-course evolution of catechin, gallic acid and resveratrol in vinification process by ^1H NMR spectroscopy

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Since its discovery, Nuclear Magnetic Resonance (NMR) spectroscopy has not ceased to experience an increase in their use and applications. Chemical structure elucidations and medical diagnostic have been important scopes for NMR. In the last years its use in the detection, quantification and checking of metabolites has been significantly improved and this fact has favored a relevant growth in the implementation of this spectroscopy technique in grape derived products research [1].

Pauli and co-workers set up the methodology of quantification by ^1H NMR spectroscopy in different complex matrix [2] and our research group developed its use for monitoring and controlling biological processes such as the alcoholic and malolactic fermentations of wine [3].

In this work, we focused on the evolution of polyphenol compounds along the vinification process. Catechin, gallic acid and resveratrol were monitored and quantified by ^1H NMR spectroscopy during the alcoholic and malolactic fermentations and oak barrel aging.

The samples were collected from Bodegas Altanza. To ensure the traceability of the wine, three tanks through alcoholic fermentation, two in malolactic fermentation and several barrels in the oak barrel aging were explored. The quantification method used was the external standard developed in wine by our research group [3].

The time-course evolution of these compounds along the wine production process was tracked perfectly by this technique. With this work we have demonstrated the enormous potential of ^1H NMR spectroscopy as a tool for monitoring and controlling polyphenols evolution during the vinification and the oak barrel aging processes.

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References

- [1] C. Fotakis, K. Kokkotou, P. Zoumpoulakis, M. Zervou. NMR metabolite fingerprinting in grape derived products: An overview. *Food Res. Int.* 54 (2013) 1184.
- [2] a) G. F. Pauli, B. U. Jaki, D. C. Lankin. Quantitative ^1H NMR: Development and Potential of a Method for Natural Products Analysis. *J. Nat. Prod.* 68 (2005) 133. b) C. Simmler, J. G. Napolitano, J. B. McAlpine, S.-N. Chen, G. F. Pauli. Universal quantitative NMR analysis of complex natural samples. *Curr. Opin. Biotech.* 25 (2014) 51.
- [3] a) A. Avenoza, J. H. Busto, N. Canal, J. M. Peregrina. Time course of the evolution of malic and lactic acids in the alcoholic and malolactic fermentation of grape must by quantitative ^1H NMR (qHNMR) spectroscopy. *J. Agric. Food Chem.* 54 (2006) 4715. b) E. López-Rituerto, S. Cabredo, M. López, A. Avenoza, J. H. Busto, J. M. Peregrina. A thorough study on the use of quantitative ^1H NMR in the Rioja red wine fermentation processes. *J. Agric. Food Chem.* 57 (2009) 2112.

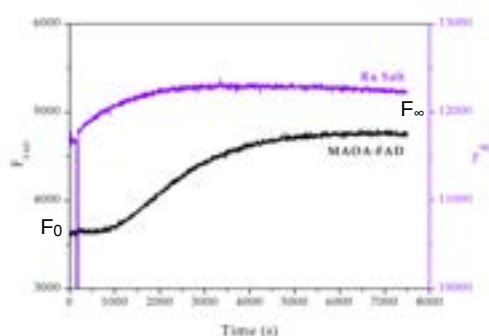
Neurotransmitters determination based on the auto-indicating properties of enzymes

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The work addresses the development of a new methodology, which could then be implemented in biosensors, for the analysis of a series of neurotransmitters, especially serotonin and dopamine. It will be presented the auto-indicating properties of Monoaminoxidase type A (MAOA) and their use to determine serotonin, as model substance, and those of Tyrosinase or Laccase (two Cu containing enzymes) which will be used for dopamine determination.

The fluorescent properties of FAD in flavoenzymes have been used in previous works for the determination of different analytes [1]. During this type of enzymatic reactions, FAD is reduced to FAD.H₂ (less fluorescent), which is finally re-oxidated to FAD by oxygen. These properties have been used for serotonin oxidation by MAOA (Monomine oxidase-A, a flavoenzyme) in combination with an O₂ sensitive fluorophore (Ru salt). The following figure shows the fluorescence profiles of the FAD-MAOA ($\lambda_{\text{exc}}=450$ nm; $\lambda_{\text{em}}=520$ nm) and the Ru salt ($\lambda_{\text{exc}}=450$ nm; $\lambda_{\text{em}}=600$ nm) during the enzymatic reaction with serotonin ($7.5 \cdot 10^{-5}$ M; pH=7.4)



After analyte addition, the initial fluorescence of FAD (F_0) is kept constant over the first seconds of reaction, then the intensity increase slowly to a higher value (F_∞). In order to understand the mechanism, the concentration of dissolved O₂ has been monitorized through the fluorescence changes of the Ru salt. After analyte addition, the initial fluorescence of Ru increases due to the consumption of O₂ which finally decreases to the initial value. Despite no changes in the FAD fluorescence during the beginning of the reaction, this result confirms the reduction of FAD and the later re-oxidation process.

The differences between the initial and the final fluorescence of FAD could be due to a mixture of the FAD/FAD.H₂ forms in MAOA. Currently, additional studies for method optimization are being developed.

In the case of dopamine it has been studied both, the autoindicating optical properties of Tyrosinase and Laccase [2] which intrinsic absorption signals change during the enzymatic reaction. However, only in the case of working with Laccase at pH=4.5, it has been possible to determine dopamine in the range from $2.5 \cdot 10^{-5}$ to $2.5 \cdot 10^{-4}$ M. When studying the enzymatic reaction at pH=6.0, the changes on the intrinsic properties of the enzyme are weakly observed, due to the product formation (which absorbs at 470 nm). In order to increase the sensibility of the determination, Laccase is being immobilised in a polyacrylamide film as the base of a biosensor film which will allow to continuous follow the enzymatic reaction based on the changes of the absorption signal of the enzyme.

Preliminary studies of the fluorescence signal of Lac and Tyr are also being developed.

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References

- [1] J. Galbán, I. Sanz-Vicente, E. Ortega, M. del Barrio and S. de Marcos. Reagentless fluorescent biosensors based on proteins for continuous monitoring systems. *Anal Bioanal Chem* 402 (2012) 3039.
- [2] J. Sanz, S. de Marcos, J. Galbán. Autoindicating optical properties of Laccase as the base of an optical biosensor for phenol determination. *Anal. Bioanal. Chem.* 404 (2012) 351.

Impact of a dietary antioxidant in cancer cells: A Raman microspectroscopy study

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Oxidative stress conditions – disruption of the homeostatic balance between free radical generation and the production of natural antioxidants – are recognised to be directly linked to damage in numerous cell targets (DNA, lipids, proteins) which can finally result in severe diseases, such as cardiovascular and neurodegenerative disorders, or cancer. Phytochemicals, although not considered as essential nutrients, may act as effective chemopreventive agents towards unwanted oxidative processes, due to their well-recognised antioxidant capacity [1-4].

The development of novel and more efficient chemotherapeutic or chemopreventive agents requires, apart from a thorough characterisation of the compound, methodologies capable of yielding information at the cellular and sub-cellular level, for an accurate understanding of the pharmacokinetic and pharmacodynamic profiles, which are pivotal in improving efficacy and limiting potential side effects. Vibrational microspectroscopy (infrared and Raman) is one of the few techniques available nowadays with high sensitivity, non-invasiveness and real-time molecular imaging capability without the need for contrast agents or dyes. The interplay between vibrational microscopic imaging and spectra-structure correlation yields quantitative and readily comprehensible information even for inhomogeneous biological samples. Raman microspectroscopy, in particular, with negligible interference from water and very high spatial resolution, constitutes an unmatched approach for probing cellular environments and monitor a compound's *in vitro* bioavailability and biodistribution after administration [5-7].

This study reports a microRaman investigation of the impact of a dietary antioxidant – quercetin – on the cellular chemical fingerprint, the lipids being the main cellular metabolite affected by interference with this flavone.

The human amelanotic melanoma cell line A375 was used, for a concentration of quercetin equal to 30 μ M and an incubation time of 48 h (according to previous studies by the team [3]). Several experimental conditions were tested in order to attain the following optimised protocol: cells were fixed in 4% formalin in PBS after 4 days of seeding, and placed onto 2% gelatin-covered quartz disks ($\varnothing$ 20 mm) for Raman analysis.

The Raman spectra were obtained at room temperature, in a Jobin-Yvon T64000 Raman system (focal distance 0.640 m, aperture f/7.5) with a direct configuration, equipped with an holographic grating of 1800 grooves. mm^{-1} and a BH-2 Olympus microscope with a 60X water immersion objective (work distance 1.00 mm). The detection system was a liquid nitrogen cooled non-intensified 1024 $\times$ 256 pixel (1") Charge Coupled Device (CCD) chip, the entrance slit having been set to 200 μ m. The 514.5 nm line of an Ar⁺ laser in backscattering geometry was used as the excitation radiation, providing ca. 15 mW at the sample position. Spectra were acquired for 45 different sites in each sample, in the 600-1800 cm^{-1} interval, with an integration time of 120 s and 2 scans *per run*.

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References

- [1] Y. Surh, *Nature* 3 (2003) 768.
- [2] P. Fresco et al., *Curr Pharm Design*, 16 (2010) 114.
- [3] M.M. Dias et al., *Food&Function* 2 (2011) 595.
- [4] N.F.L. Machado et al., *Vib.Spec.* 63 (2012) 325.
- [5] M.P.M. Marques et al., "Raman Microspectroscopy: Applications in Life Sciences", in: "Image Analysis in Life Sciences", C. Diniz (Ed.), Research Signpost, Kerala, 2009, pp. 55 - 97, ISBN 978-81-308-0312-8.
- [6] A. Angela Kallenbach-Thieltges et al., *J. Biophotonics* 6 (2013) 88.
- [7] H. Nawaz et al., *Analyst* 138 (2013) 6177.

Determination of biochemical parameters in human serum by near-infrared spectroscopy

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NIR offers multiple advantages for serum analysis, permitting a fast and direct determination of several parameters simultaneously, with low sample handling and without the need of reagents during the measurement step. The aim of this work was to provide an evaluation of this technique in a real world scale, for the simultaneous determination of several parameters and based on a considerable number of samples. Direct near infrared (NIR) absorbance measurements were used to determine the concentration of clinical parameters in human serum that are required in routine biochemical tests. Total protein, albumin, total cholesterol, high-density lipoprotein (HDL cholesterol), low-density lipoprotein (LDL cholesterol), and very low-density lipoprotein (VLDL cholesterol), triglycerides, urea and glucose were determined in 447 serum samples obtained randomly from the clinical laboratory of the University Hospital Doctor Peset in Valencia (Spain). NIR spectra from 12500 to 4000 cm^{-1} obtained with a 1 mm optical path length were evaluated by using partial least squares regression models (PLS) built from the spectra of samples with known concentrations provided by the hospital. Root mean square error cross validation (RMSECV) was used for selecting the number of factors, spectral regions and spectra pre-processing considered to build the models, that were evaluated from their prediction capability using the relative root mean square error of prediction (RRMSEP) of a series of around 30 independent samples, not used for the calibration. For some analytes such as total protein, albumin, total cholesterol and triglycerides, errors obtained were 2.3, 4.4, 5.1, 6.2 % respectively, evidencing that the proposed methodology could compete with the enzymatic reference methodologies. However in the case of urea, glucose, HDL and LDL, average errors obtained were 16.0, 16.2, 18.0 and 11.0% respectively, and therefore NIR methodology proposed is limited as a screening tool. With the use of a considerable number of samples for calibration, this study confirms that the proposed green and cost-effective methodology is ready for scaling up from the bench to the real world.

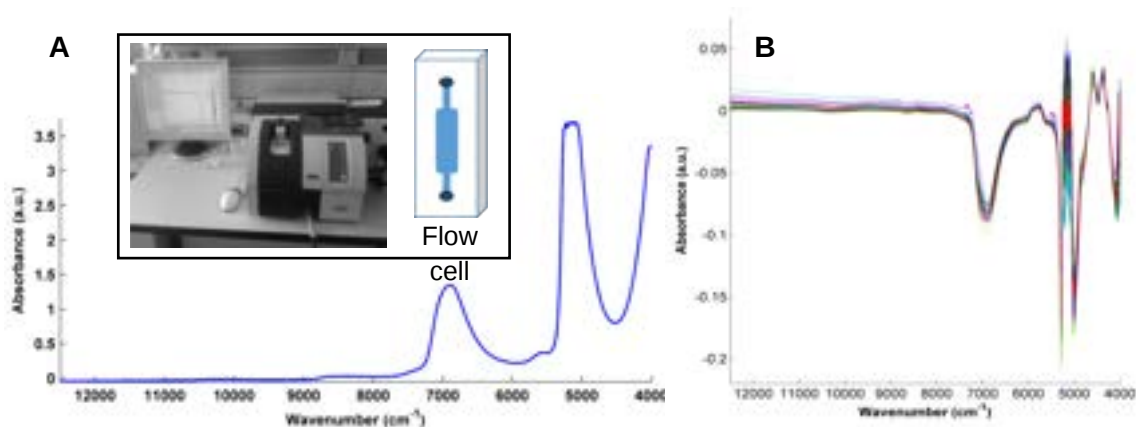


Figure: NIR spectrum of a serum sample obtained using empty flow cell as background (A) and some serum absorption spectra after water subtraction (B). Insert: The setting and the cell employed for NIR spectra acquisition.

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Bioavailability, bioaccessibility and speciation of As and other heavy metal elements in contaminated areas of Chile

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ABSTRACT

Our study on As and heavy metal contamination, bioavailability, bioaccessibility, As speciation of more toxic species, and action of local microorganisms on As species transformation, has been centralized on a little area of Chiu Chiu region of Chile, where vegetables are grown for consumption by the indigenous population. In this study, we have chosen to address: i) the bioavailability of the As and other heavy metals such as Cr, Cu, Pb, Mn and Cd contained in impacted soil and sediments through labile, reduced, oxidized and residual fractions, ii) the total As and heavy metals content in the edible and non-edible parts of carrots, beets and quinoa growing in the area where soil samples were taken, and where the indigenous population live, iii) the As bioaccessibility from edible parts of these vegetables under "*in vitro*" digestion process, iv) determination of inorganic As and its main methylated forms in the edible parts of vegetables; v) As speciation in the extracts from "*in vitro*" digestion of these vegetables and vi) action of microorganisms in transformation of As species. These studies provide a clearer understanding on the impact that As has in this contaminated region. Wherever possible, the results obtained from these studies have been compared with those obtained from reference materials, to validate the methodology employed, and/or with analogous non stressed samples.

Advanced analytical techniques for chemical extraction such as ultrasound probes, microwave extraction, and multielement or specific analytical techniques such as LC-ICP-MS, ESI-MS, etc. have been used.

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Troubleshooting in arsenic species analysis in human urine by high-performance liquid chromatography inductively coupled plasma-mass spectrometry

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High performance liquid chromatography coupled to inductively coupled plasma – mass spectrometry (HPLC–ICP–MS) was used to separate and detect arsenical species (arsenite, As(III); arsenate, As(V); monomethylarsonic acid, MMA; dimethylarsinic acid, DMA; arsenobetaine, AsB; trimethylarsine oxide, TMAO; and arsenocholine, AsC) in human urine. Arsenical species separation was achieved by a pH-gradient anion exchange HPLC method in a single chromatographic with two mobile phases (Milli-Q water / methanol, 98:2; 80 mM aqueous nitric acid / methanol, 98:2, pH 1.8). The mobile phase flow rate was set at 1.35 ml min⁻¹. DMA, AsB and MMA were the major As species quantified in the urine samples. In addition, several unknown and artifacts As species were also identified and characterized by HPLC coupled to mass spectrometry (HPLC–MS). Accuracy of the developed procedure was tested by analyzing the NIST 2669 (Arsenic Species in Frozen Human Urine) certified reference material, which offers certified contents for all arsenic species. The developed arsenic speciation method was also applied to several human urine samples.

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Determination of thiametoxam by a multicommutated flow-through optosensor based on photochemically induced fluorescence

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The determination of thiametoxam, a widely known neonicotinoid pesticide, by a multicommutated optosensing device implemented with photochemically induced fluorescence (PIF) is reported. The combination of both methodologies allows, on one hand a quick on-line photodegradation of thiametoxam, and on the other hand, the preconcentration, quantification and desorption of the fluorescent photoproduct generated on a suitable support placed in a commercial flow cell.

Although fluorescence has found a significant application as the basis for the analysis of pesticides with many different strategies, up to date, the fluorimetric determination of thiametoxam has not been reported. As this compound is a non-fluorescent pesticide, its fluorimetric determination will need a previous derivatization step. The generation of fluorophores from non-fluorescent analytes by UV irradiation presents inherent advantages over ordinary chemical reactions such as quicker reaction rate, less chemical involved and smaller dilution factor. The combination of multicommutation with PIF is usually carried out with UV light and measuring the fluorescence of one of the photodegradation products generated. To our best knowledge, no photochemical reaction has been reported to date for the quantitative determination of thiametoxam.

The completely automated optosensor is based on the use of three-way solenoid valves conveniently operated by means of a home-made multicommutation software written in Java language. On the other hand, the use of an active solid support placed inside the flow cell of the system allows the retention of the analyte and its continuous monitoring at 358/411 nm ($\lambda_{exc}/\lambda_{em}$, respectively). This methodology, combines advantages such as simplicity, high sensibility and high selectivity. The optosensor will be applied to the determination of thiametoxam in the industry of food.

Identification and discrimination of bones remains by laser induced breakdown spectroscopy and neuronal networks

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Many methods are used in Disaster Victim Identification (DVI) to deal with the forensic cases. The identification process involves a multidisciplinary group of experts and techniques, i.e. fingerprint analysis, forensic pathology, forensic odontology and DNA analysis. When the bodies are non-decomposed the methods used in DVI include physiognomic data analysis such as scars or marks, personal effects, matching of fingerprints and dentition pattern [1-3]. In approximately 42% of cases, common methods for human identification are not sufficient, due to the lack of ante-mortem data and body decomposition. In such cases, DNA identification is required [4,5] which provides the opportunity to identify unknown human remains by a comparative analysis with relatives[6]. However, when the number of remains is high as in natural disasters, accidents and mass burial sites, the identification by DNA poses a high temporal and economic cost. Also, the contamination and degradation of the sample makes the DNA extraction process more difficult.

A new methodology that provides simple, direct, cost-effective and non-invasive method based on Laser Induced Breakdown Spectroscopy (LIBS) has been developed. A comparative study was done to classify the remains using two methods; relations between the elements (Mg/Ca; Na/Ca) that constitute the bones and Neural Networks (NN) bone classification.

Several studies demonstrate that trace elements in bones may provide complementary information to associate bone fragments or discriminate between individuals [7]. In our investigation we demonstrate that the elemental ratios were not sufficient to separate commingled human remains in mass burial sites, but it could be a complementary method that provides information to discriminate with NN.

Result obtained on twenty five bones from five individuals, collected from a local graveyard located in Segovia (Spain) will be presented and discussed.

References

- [1] D. Sweet. Solving certain dental records problems with technology –The Canadian solution in the Thailand tsunami response, *Forensic Sci.* (2006) Int. 159S S20–S23.
- [2] S. Blau, C.A. Briggs. The role of forensic anthropology in Disaster Victim Identification (DVI), *Forensic Sci. Int.* 205 (2011) p. 29.
- [3] A.J. Hill, I. Hewson, R. Lain. The role of the forensic odontologist in disaster victim identification: Lessons for management. *Forensic Sci.* (2011) Int. 205 p. 44.
- [4] J. Ye, A. Ji., EJ Parra, et. al. A simple and efficient method for extracting DNA from old and burned bone. *J Forensic Sci.*, (2004). 49(4): p.754
- [5] Š. Anđelinović, D. Sutlović, I.E. Ivkošić, et. al. Twelve-year experience in identification of skeletal remains from mass graves. (2005) *Croat Med J.* 46 p. 530.
- [6] M.J. Schoeninger, K.M. Moore, M.L. Murray et. al. Detection of bone preservation in archaeological and fossil samples. *Applied Geochemistry* (1989). 4(3): p. 281
- [7] W. Castro, J. Hoogewerff, C. Latkoczy et al. Application of laser ablation (LA-ICP-SF-MS) for the elemental analysis of bone and teeth samples for discrimination purposes. *Forensic Sci. Int.* (2010) 195 p. 17

Deepening on analysis of glass samples by LA-ICP-MS for forensic pairwise comparisons

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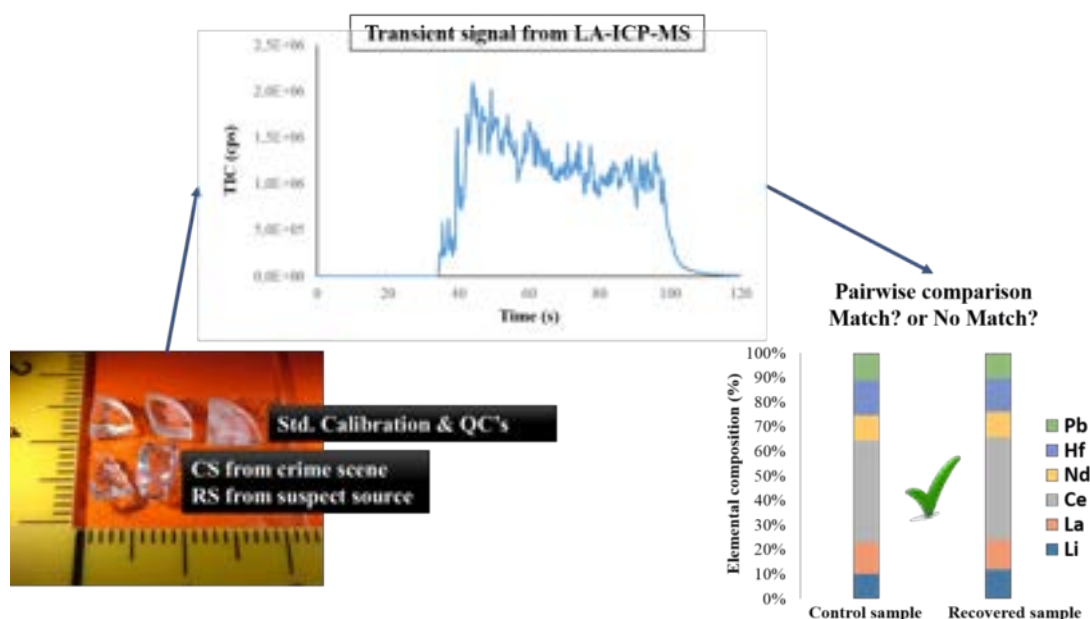
A methodology on the analysis of glass samples through LA-ICP-MS has been recovered from the literature and subjected to intra-laboratory validation with forensic purposes. Samples studied have been collected from real forensic caseworks, inter-laboratory test samples, blind samples and a NIST certified reference material (float glass).

In addition to quality controls in each sequence of samples analyzed,, tests which guarantee both the proper status of the instrument and the correct precision of the method have been also used. Besides, the detection limits (LODs) have been estimated. A protocol to normalize the data treatment with the aim of obtaining reliable conclusions for the forensic expert inform when comparing forensic glass samples, has been developed. Graphic representations to see at a glance are proposed for enabling non **experts** in forensic sciences to understand the results; this may be very useful for presenting the scientific evidence in court.

The main difference between this forensic methodology and a classic quantitative method relies on the fact that the first one is focused on the characterization of samples by pairwise comparisons. The objective of the established methodology lies not in achieving traceable quantitative results but obtaining comparable results with high confidence levels in order to avoid mistakes in criminal cases.

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Synthesis, characterization and application of Mn-doped ZnS quantum dot – molecularly imprinted polymers for fluorescence detection of cocaine and analogues in urine

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A novel method has been developed for cocaine and metabolites (benzoylecgonine, BEC; and ecgonine methyl ester, EME) assessment based on the quenching of fluorescence emission from Mn-doped ZnS quantum dots (QDs) – molecularly imprinted polymer (MIP) by cocaine and analogues. Mn-doped ZnS QDs were synthesized in inert atmosphere followed by polyethyleneglycol (PEG) modification under ultrasounds irradiation (37 kHz). After PEG-QDs isolation by centrifugation, and oven drying, molecularly imprinted polymerization (precipitation method) was performed by using cocaine as a template, ethylene dimethacrylate (EDMA) as a monomer, divinylbenzene (DBV) as a cross-linker, and 2-2'-azoisobutyronitrile (AIBN) as an initiator. The PEG-QD-MIP material was further characterized by X-ray diffraction spectrometry, IR spectrometry, and electronic microscopy.

Under optimum conditions [excitation wavelength of 296 nm, emission wavelength of 590 nm, 100 mg PEG-QD-MIP, pH 5.5 (sodium dihydrogen phosphate/disodium hydrogen phosphate buffer), and 15 min as delay time before fluorescence measurement], the calibration graph was linear up to 1 mg l⁻¹ for cocaine, 5 mg l⁻¹ for BEC, and 1.5 mg l⁻¹ for EME. The measured Stern-Volmer constants were 0.066, 0.032, and 0.039 for cocaine, BEC and EME, respectively. The imprinting effect was tested by synthesizing PEG-QD-NIP (polymerization in absence of cocaine as a template), and quenching phenomena was not observed up to 3.0 mg l⁻¹ for cocaine, BEC and EME. These findings proved specific interaction between targets (cocaine, BEC and EME) and the prepared PEG-QD-MIP nanoparticles. In addition, cross-reactivity experiments by measuring the fluorescence quenching when mixing PEG-QD-MIP (PEG-QD-NIP) with other drugs of abuse / metabolites such as morphine, codeine, and 6-monoacetylmorphine (heroin abuse), and Δ^9 -tetrahydrocannabinol, 11-hydroxy- Δ^9 -tetrahydrocannabinol, cannabidiol, and cannabitol (cannabis abuse), showed the selective recognition for cocaine and analogues by the prepared nanomaterial.

The limit of detection (S/N=3) was 0.09 mg l⁻¹, which is a concentration lower than 0.15 mg l⁻¹ proposed by the European Workplace Drug Testing Society and by the American Substances Abuse and Mental Health Services Administration as a cut-off level for cocaine in urine.

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Novel electrospinning-produced turn-on fluorescence microfibre mat encapsulating a rhodamine 6G derivative for Hg²⁺ determination in water samples

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Mercury is considered as one of the most hazardous pollutants and it is present in the environment in several different forms. Therefore, it is important to monitor Hg²⁺ levels in aquatic ecosystems as a potential source of contamination [1]. Among other methods, the fluorescence-based chemosensors represent a simple but sensitive technique for fast controlling Hg²⁺ in many samples, and turn-on responses are preferred due to enhanced sensitivity and the ubiquitous nature of fluorescence quenching. Although the number of examples of molecular probes reported for Hg²⁺ is high, there are only few examples of probes immobilized in solid supports that concern Hg²⁺ detection [2].

The use of a spirocyclic phenylthiosemicarbazide Rhodamine 6G derivative (FC1) for Hg²⁺ determination in water and fish samples [3], and its immobilization into poly(2-hydroxyethyl methacrylate-co-methyl methacrylate) [4] was previously reported.

This Communication describes a highly selective Hg²⁺-sensing microfibre mat based on the encapsulation of FC1 into polymeric microfibrils produced by electrospinning.

The Hg²⁺ selective microfibre mat possesses very high specific surface and excellent mechanical properties, as it is easily manipulated and it has high mechanical strength, high consistency and high flexibility. In addition, it is highly hydrophilic but insoluble in aqueous media as well as in nonpolar solvents. Furthermore, the encapsulated FC1 preserves its sensing ability, displaying intense turn-on fluorescence in the presence of mercury (II). It responds to Hg²⁺ concentrations in water between 0.4 and 4 µM, with a detection limit of 0.1 µM Hg²⁺ which is 2.6 times better than those of the same chemodosimeter immobilized into a classical polymeric sensing film [4]. Finally, the response time of the proposed mat is 15 min, which is lower than the response time provided by FC1-classical polymeric sensing film (50 min). Therefore, it is possible to conclude that the use of electrospinning increases the sensitivity and decreases the response time in the use of FC1 to determine Hg²⁺. To test the predictive ability of the microfibre sensing mat, two water samples were evaluated with satisfactory results, by measuring the fluorescence at $\lambda_{\text{ex}}/\lambda_{\text{em}} = 540/562$ nm: one sample of tap drinking water from the city of Granada and one mineralized water sample commercialized in Spain.

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References

- [1] T. Syversen, P. Kaur, The toxicology of mercury and its compounds, J. of Trace Elements in Medicine and Biology, 26 (2012) 215.
- [2] M.J. Culzoni, A. Muñoz de la Peña, A. Machuca, H.C. Goicoechea, R. Babiano, Rhodamine and BODIPY chemodosimeters and chemosensors for the detection of Hg²⁺, based on fluorescence enhancement effects, Anal. Methods, 5 (2013) 30.
- [3] D. Bohoyo Gil, M. I. Rodríguez-Cáceres, M. C. Hurtado-Sánchez, A. Muñoz de la Peña, Applied Spec., 64 (2010) 520.
- [4] F.J. Orriach-Fernández, A.L. Medina Castillo, J.F. Fernández-Sánchez, A. Muñoz de la Peña, A. Fernández-Gutiérrez, Hg²⁺-selective sensing film based on the incorporation of a rhodamine 6G derivative into a novel hydrophilic water-insoluble copolymer, Anal. Methods., 5 (2013) 6642.

Use of microextraction by packed sorbents in the determination of brominated flame retardants in sewage sludge

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Brominated diphenyl ethers (BDEs) are part of brominated flame retardants that have been widely used since the early 1970s. These compounds have been classified as persistent organic pollutants (POPs). BDE toxicity stems from their adverse effects on the endocrine system, particularly thyroid hormone regulation and neurodevelopment [1]. The analysis of BDEs in sewage sludge is important to provide information about chemical pollution in the aqueous environment and the risk associated with the reutilisation of sewage sludge as bio-solids for land application. However, it is a difficult task due to the complexity of the matrix and wide of variety of compounds which can act as interference in the analysis.

MicroExtraction by Packed Solvents (MEPS), introduced by M. Abdel-Rehim [2], is a miniaturized solid-phase extraction connected on-line with LC or GC. Approximately 1-2 mg of the solid packing material (C2, C8, C18, Silica, molecular imprinted polymers (MIPs), etc.) are inserted into a syringe (100-250 μ L) between the barrel and the needle as a cartridge. For the extraction, the sample is pumped up and down through the cartridge by an autosampler. MEPS technique allows the simultaneous enrichment of target analytes, the clean-up of the sample and the transfer of target analytes to a solvent that can be injected into the GC. As it is a miniaturized and completely automated technique, the MEPS based methods are faster, simpler and they consume lower solvent volume than the classic sample preparation techniques (SPE, liquid extraction, etc.).

In this work, the development, optimisation and validation of a selective pressurised liquid extraction (sPLE), followed by MEPS and GC-MSMS for the determination of BDEs in sewage sludge is described. The influence of MEPS factors affecting the extraction, such as elution volume, elution speed, injection speed, extraction speed, number of draw-eject cycles, number of drying cycles, were optimized. Also, the absence of carry over effects was checked.

MEPS before GC-MSMS analysis provides a sensitivity enhancement, resulting in a decrease of detection limits, below 0.4 ng g⁻¹ dw, significantly lower than those previously reported for the determination of BDEs in sewage sludge. Besides, it provides automated extract clean-up that improves detection and protects GC-MS from dirt. Good relative standard deviation values below 10% and recovery values between 92 and 102% were. Finally, the analysis of several sewage sludge samples of La Rioja showed levels of total BDEs between 53.9 and 76.8 ng g⁻¹, similar to those previously reported in Sweden and Mexico.

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References

- [1] L.G. Costa, G. Giordano, *Neurotoxicology* 28 (2007) 1047.
- [2] M. Abdel-Rehim, *J. of Chromatogr. B* 801 (2004) 317.

Dissolution of natural scorodite in a waste pile and its role as arsenic carrier evaluated by EXAFS, TEM and single particle - ICPMS detection

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Scorodite ($\text{FeAsSO}_4 \cdot 2\text{H}_2\text{O}$) often occurs as a secondary mineral in oxidized waste rocks and mine tailings rich in arsenopyrite. With a low dissolution rate, scorodite is considered one of the least soluble arsenate phases in many mine tailing systems.

However, under strongly acid conditions, scorodite dissolves congruently releasing equimolar concentrations of As and Fe, while at pH higher than 6, it does incongruently, releasing free Fe(III) that readily precipitates as colloid-size Fe oxyhydroxide phases. Arsenate ions released from scorodite dissolution can subsequently be sorbed onto the surface of the iron phases. Since congruent or incongruent scorodite dissolution depends on pH, the main objective of this work was to study scorodite dissolution at different pH values and leaching time conditions in order to characterize the dissolution products and thus assess the potential role of the resulting iron phases as As scavengers in natural systems. It is necessary to know the molecular-scale nature and the stability of the As-Fe interactions to predict the environmental impact of these As-colloid associations.

Because of the high reactivity of natural nanoparticles attributed to their large surface area, high mobility and electrochemical stability, the mobilization of contaminants associated to nanoparticles present in weathering-dominated acid mine locations has been emphasized as an important spreading mechanism. Colloidal fraction from mine waste rocks, sediments and soil samples impacted by mine activities can be isolated through centrifugation and subsequently characterized using three complementary techniques: Single nanoparticle detection, extended X-ray absorption fine structure (EXAFS) and transmission electron microscopy (TEM). In single particle detection, the atoms of the analyte (i.e. a nanoparticle) produce a flash of gaseous ions when it is introduced into the ICP. This phenomenon is measured as a single pulse by the detector. The number of counts of this single pulse is related to the quantity of analyte atoms in the nanoparticle, and the frequency of the pulses is proportional to the number concentration of nanoparticles [1]. Due to the different behaviours of dissolved species, single particle detection using ICP-MS allows for the selective determination of dissolved arsenic and scorodite nanoparticles. The X-ray absorption near edge structure (XANES) is sensitive to the valence state of the atom, whereas the extended X-ray absorption fine structure (EXAFS) provides quantitative information on the distances between absorbing and surrounding atoms, and their relative disorder. Lastly, transmission electron microscopy is useful to validate the results from single detection in addition to provide complementary information about the physical and chemical characteristics of the samples.

The coordination of these powerful analytical techniques has proved effective for studying the interaction of contaminant elements in the media.

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References

[1] F. Laborda, J. Jimenez-Lamana, E. Bolea, J.R. Castillo. Selective identification, characterization and determination of dissolved silver(I) and silver nanoparticles based on single particle detection by inductively coupled plasma mass spectrometry. *J. Anal. At. Spectrom.* (2011), 26, 1362-1371.

Evaluation of a simple and fast method for on-line preconcentration of trace elements by ICP-MS

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A method for the determination of essential (Fe, Cu, Zn, Co, Mn, Mo, Ni, V) and toxic (Al, As, Pb, Cd, Cr) trace elements in seawater has been developed using the SeaFAST2 (Perkin Elmer, Norwalk, USA) preconcentration system coupled to ICP-MS. Samples were desalinated, and most of the elements were preconcentrated using the iminodiacetate column, except for Al, As y Cr. Hiperpur or Hiperpur-Plus reagents were used to avoid the contamination problems.

A study was performed to evaluate the influence of the sample matrix during the calibration. The slopes of the calibrations graphs using different matrixes (ultrapure water, acidified ultrapure water, 3% NaCl, acidified 3% NaCl, seawater and acidified seawater) were compared. Significant differences were found (test t, 95% confidence level) among the slopes, and therefore acidified seawater was selected to perform the calibrations. The introduction of several internal standards (Y, Rh, In) did not improve the results or the linearity of the calibration graphs. Mn was analyzed using the direct mode and the preconcentration mode. The preconcentration factor was 92 (slope ratio between the calibration obtained in preconcentration and direct mode).

The limits of detection were: $1,70 \mu\text{g l}^{-1}$ (Al^{27}), $0,12 \mu\text{g l}^{-1}$ (Cr^{52}), $0,14 \mu\text{g l}^{-1}$ (Mn^{55}), $0,26 \mu\text{g l}^{-1}$ (As^{75}), $0,015 \mu\text{g l}^{-1}$ (Mo^{95}), $0,022 \mu\text{g l}^{-1}$ (V^{51}), $0,26 \mu\text{g l}^{-1}$ (Fe^{54}), $0,09 \mu\text{g l}^{-1}$ (Fe^{56}), $0,012 \mu\text{g l}^{-1}$ (preconcentrated Mn^{55}), $0,079 \mu\text{g l}^{-1}$ (Ni^{58}), $0,074 \mu\text{g l}^{-1}$ (Ni^{60}), $0,0009 \mu\text{g l}^{-1}$ (Co^{59}), $0,21 \mu\text{g l}^{-1}$ (Cu^{63}), $0,25 \mu\text{g l}^{-1}$ (Cu^{65}), $5,75 \mu\text{g l}^{-1}$ (Zn^{64}), $4,09 \mu\text{g l}^{-1}$ (Zn^{66}), $0,005 \mu\text{g l}^{-1}$ (Cd^{111}) and $0,075 \mu\text{g l}^{-1}$ (Pb^{208}). The limit of detection for Mn decreased 12 times using the preconcentration system.

The method showed a good precision with relative standard deviations lower than 5% ($n=10$). The accuracy was evaluated using the certified reference materials NASS-4 (ocean water), SLEW-3 (estuarine water) and TM 23.3 (lake water). The analytical recovery was also calculated with average levels of approximately 100% for all the elements studied.

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

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Identification of harmful compounds present in steel slag used in forest tracks through spectroscopic techniques

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The use of recycled material is currently booming because it is a good alternative to reduce wastes and the natural resources exploitation, and thus, the environmental impact. A material that is often reused is the steel slag, which is a by-product comes from the steel-making process. In the steel manufacture through Electric Arc Furnace (EAF) are firstly generated black slag and secondly white slag. White slag is mainly used as constituent of the cement, and the black one is generally employed as filler in different layers of roads [1]. In spite of these uses, slag has compounds that could be harmful to the environment where it has been used; and it also has characteristics not very suitable to the construction field, such as its volumetric instability due to its content of expansive compounds like free lime, free MgO, sulphates, iron oxides, etc., which depending on their concentration, in presence of water suffer a change of volume. This could result in loss of efficacy and durability [2, 3].

In this work it has been analysed two types of steel slag (black and white). They were collected from two different forest tracks of the Basque Country (Northern Spain), where they were used as filler approximately 15 and 30 years ago respectively, with the purpose of improving the access to that area. The aim of this study was to determine their elemental and molecular composition to know the possible impact of the slag towards the environment (rivers, soil, etc.) in a real location. For this purpose, it was used Raman Spectroscopy, X- Ray Diffraction and Scanning Electron Microscope coupled to Energy-Dispersive X-Ray Spectroscopy (SEM-EDS) to analyse the slag samples.

Black slag was mainly characterized by iron oxides, such as magnetite (Fe_3O_4), hematite ($\alpha\text{-Fe}_2\text{O}_3$), goethite ($\alpha\text{-FeOOH}$), etc. Also, it was identified calcite (CaCO_3), magnesioferrite (MgFe_2O_4), portlandite ($\text{Ca}(\text{OH})_2$), quartz (SiO_2), larnite ($\beta\text{-Ca}_2\text{SiO}_4$), hashemite (BaCrO_4), etc. However, white slag presented a composition less heterogeneous, it was recognized fewer compounds: calcite (CaCO_3), quartz (SiO_2) and mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$). Hence, it could be observed the evolution of some compounds with hydration processes. For instance, $\text{Ca}(\text{OH})_2$ was formed in the slag because of the transition of CaO (compound that is present in the slag when it leaves the furnace [1]) by hydration. This would be indicating the change of volume in this type of material, and it might affect the structure of the forest track road. On the other hand, it was also recognized compounds such as BaCrO_4 , which could be harmful to the environment. In addition, all this information could be supported by SEM images and EDS analysis, that allowed us to observe the correlations between elements.

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References

- [1] IHOBE, S. A. Libro Blanco para la minimización de residuos y emisiones, Servicio Central de Publicaciones del Gobierno Vasco, Vitoria-Gasteiz, 1999.
- [2] M. Frías Rojas, M.I. Sánchez de Rojas. Chemical assessment of the electric arc furnace slag as construction material: Expansive compounds. Cement Concrete Res. 34 (2004) 1881.
- [3] E. Vázquez Ramonich, M.barra. Reactivity and expansion of electric arc furnace slag in their application in construction. Mater Construcc. 51 (2001) 137.

Application of a molecularly imprinted polymer for mercury preconcentration in water samples

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The proliferation of industrial activity in recent decades has led to a significant increase in the presence of mercury in natural environments. This is particularly problematic, because Hg can be accumulated in the food chain, and once assimilated by the body, is highly toxic at very low concentrations, acting as a potent neurotoxin, and also affecting the cardiovascular and immune systems [1]. Of all the methods for extraction and determination of mercury, the solid phase extraction using molecularly imprinted polymers (MIP- SPE) as highly selective sorbents, allows us to analyze low concentrations of the species of interest and the interference removal [2-3].

In this work a molecularly imprinted polymer (MIP) for the preconcentration of mercury in water samples was used. The MIP was previously developed for the determination of mercury and methylmercury in seafood samples. For the polymer synthesis, a methylmercury chloride template was employed, in addition to phenobarbital as ligand, methacrylic acid as monomer and ethylene glycol dimethacrylate as crosslinker. The influence of some parameters (pH of the sample, composition of the eluent, load and elution flow rates) was studied to optimize mercury extraction. Aqueous samples buffered at pH 8 were preconcentrated using solid phase extraction cartridges with 300 mg of packaged MIP. Working at a load flow of $0.5 \text{ mL} \cdot \text{min}^{-1}$ and eluting with thiourea 1M in 1M HCl at the same flow, we were able to determine $50 \text{ ng} \cdot \text{L}^{-1}$ concentrations using cold vapor generation coupled to optical emission spectroscopy - inductively coupled plasma (CV-CP-OES).

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References

- [1] A. Sigel, H. Sigel, Metal ions in biological systems, vol. 34: Mercury and its effects on environment and biology, 1st ed., Marcel Dekker, New York, 1997.
- [2] S. Xu, L. Chen, J. Li, Y. Guan, H. Lu. Novel Hg^{2+} -imprinted polymers based on thymine- Hg^{2+} -thymine interaction for highly selective preconcentration of Hg^{2+} in water samples. J. Hazard. Mater. 237-238 (2012) 347.
- [3] M. Firouzzare, Q. Wang. Synthesis and characterization of a high selective mercury(II)-imprinted polymer using novel aminothiols monomer. Talanta 101 (2012) 261.

Analysis of pollutants in water by combining ICP-AES and UV-visible spectroscopy

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The quantification of liquid solutions with arsenic and chrome can be obtained by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), although it is necessary the setup method based on certain parameters. One of the most important parameters is the wavelength for analysing. The wavelengths most commonly used for arsenic are 189.042 nm, 193.759 nm, 197.206 nm and 228.810 nm and for chrome are 206.150 nm, 205.550 nm and 267.720 nm. In the measures of water samples polluted with As and Cr firstly, it is necessary to eliminate the wavelengths that have high interference with items that are easily found in the matrix as Al, Fe and Si. Due to this elements present high solubility in water from the sediments that make up the stream bed where the water flows. Some of the wavelengths that have interferences are 193.759 nm and 197.206 nm for arsenic and 205.550 nm for chrome [1].

Also, the stabilization and delayed sampling times are required parameters. Thus, it has been proved that arsenic is entrained for lows times, while for higher readout times than 40 seconds between replicas, the drag is inexistent. This delay and stabilization time in the case of chrome is not necessary because it does not remain in the system, so it is plausible to measure a blank directly after a concentrated sample with a normal cleaning, about 20 seconds.

The radiofrequency power is necessarily around 1.35-1.40 kW for As, because it requires high power to overcome the ionization potential of As ions. In contrast, if this power was lower, around 1.00 kW, the problem would be that the measure would not be real because not all the arsenic ions would be measured completely. Yet, for elements with lower ionization potential such as Cr, the plasma power does not need to be high; due to the Cr measurements can be carried out with 1.20 kW.

In addition, it is important to perform the measurements with two different methods to verify that the results are reliable and also, because with ICP-AES just is possible to measure total arsenic and chrome but not the concentration of the species with different oxidation states. Not to mention that it is essential to discern between the oxidation states of arsenic and chromium in water, due to both As(III) and Cr(VI) are even more toxics than As(V) and Cr(III). UV-Visible Spectroscopy is used for analysing As(V) and Cr(VI).

So, to quantify As(V) in water, the technique of UV-Visible Spectroscopy is used by the combination of two methods described by Murphy and Riley [2] and by Lenoble et al. [3]. The sample preparation for the analysis of As(V) was performed with the use of a mixture of reagents added to each sample. The UV-Visible Spectroscopy could also measure total arsenic thereof. For that, it is required a KMnO_4 solution intended to oxidize all species of arsenic. As(V) forms a blue solution and its concentration was calculated from absorbance at 884 nm.

In the case of Cr(VI) its concentration was detected by diphenyl carbazide method [4], because it forms a pink complex in the presence of Cr(VI) ions in acidic solutions. The concentration of Cr(VI) was calculated at 540 nm.

The results obtained in the determination of total arsenic by both techniques were reproducible, so is plausible performing the measures for total arsenic using ICP-AES and UV-Visible Spectroscopy. Also, the results of total chromium concentration obtained by ICP-AES were comparable with those by Atomic Absorption Spectrometry.

References

- [1] R.K. Winge, V.A. Fassel, V.J. Peterson, M.A. Floyd. Inductively Coupled Plasma-Atomic Emission Spectroscopy, 6th ed., Elsevier, Amsterdam, 1993.
- [2] J. Murphy, J.P. Riley. A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta*, 27 (1962) 31.
- [3] V. Lenoble, V. Deluchat, B. Serpaud, J.C. Bollinger. Arsenite oxidation and arsenate determination by the molybdene blue method. *Talanta*, 61 (2003) 267.
- [4] L. Chabaane, S. Tahiri, A. Albizane, M. El Krati, M.L. Cervera, M. de la Guardia. *Chem. Eng. J.*, 174 (2011) 310.

Analysis of ceramics decoration and coverings from the *oppidum* of Puente Tablas (Jaén, Spain) by MRS, XRD and XRF

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This paper is about ceramic materials and coverings recovered during the excavations carried out since 2011 in the Iberian *oppidum* of Puente Tablas (Jaén) and dated between the sixth and third centuries b. C. In particular, we have analyzed the white and red wall coverings in several rooms of the sanctuary area, and the black and red ceramic decorations from the palatial structure, the sanctuary and the main gate of the site

The analyzes performed have focused on the study of the mineral and elemental composition of the materials selected using instrumental techniques such as micro Raman spectroscopy (MRS), X-ray diffraction (XRD) and X-ray fluorescence (XRF). These techniques have proven their effectiveness in the analysis of materials Iberian period [1,2,3]. The results obtained allowed the identification of hematite as responsible for the red color, gypsum for the manufacture of white coverings, and various manganese oxides as the origin of black color in ceramic vessels.

Beyond the specific results, information obtained leads to a better understanding of the work processes involved in the development of the decorations, on the selection of raw materials and contributes to the historical reconstruction of the archaeological site.

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References

- [1] Parras D, Montejo M, Ramos N, Sánchez A. Analysis of pigments and coverings by X-Ray Diffraction (XRD) and Micro Raman Spectroscopy (MRS) in the cemetery of Tútugi (Galera, Granada, Spain) and the settlement Convento 2 (Montemayor, Córdoba, Spain). *Spect. Acta Part A*, 64, (2006): 1133.
- [2] D, Parras. P, Vandenabeele. A, Sánchez. M, Montejo, L, Moens. N, Ramos. Micro-raman spectroscopy of decorated pottery from the iberian archaeological site of Puente Tablas (Jaén, Spain, 7th-4th century B.C.). *Journal of Raman Spectroscopy* 41, (2010): 68.
- [3] A. Sánchez, J. Tuñón, M. Montejo, D. Parras, Micro raman spectroscopy (MRS) and energy dispersive x-ray microfluorescence (μ EDXRF) analysis of pigments in the Iberian cemetery of *Tutugi* (from the fourth to the third century B.C., Galera, Granada, Spain. *Journal of Raman Spectroscopy*; 43 (11), (2012): 1788.

The palette of the Pompeian artists: In situ spectroscopic analysis of raw pigments from the Naples National Archaeological Museum (MANN)

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It is widely accepted that, in the field of art and archaeology, the material analysis requires usually the use of portable instrumentation. In this way, the valuable objects will not have to be moved from their place of storage/exhibition, achieving a minimum intervention on them. Furthermore, the transport of objects/materials from museums involves the emission of licences and bureaucracy. The Naples National Archaeological Museum (MANN) possesses a wide collection of bowls containing pigments used for the creation of Pompeian wall paintings (Figure 1). The opportunity to analyze, by portable spectroscopic instrumentation, the raw material used for the paintings was unique, since pure pigments and not mixtures would be easier identified and the artist's palette could be straightforward reconstructed.

These pigments were analyzed by three portable spectrometers: two Raman spectrometers (B&WTEK_{INC.}, USA), one using the 785 nm and the other the 532nm excitation laser, and an Energy Dispersive X-ray Fluorescence (ED-XRF) spectrometer (Innov-X, Alpha SeriesR, Innov-X Systems Inc., USA). In this way, the molecular and elemental characterization was achieved.



Figure 1: Bowls with various pigments (MANN).

The presence of typical Pompeian pigments was confirmed by Raman, such as Pompeian blue, goethite and hematite [1, 2]. Moreover, the ED-XRF analysis was focused in the detection of the minor and trace elements. This information could be proven essential, since the impurities of the raw material could give significant information about the nature and origin of the pigments.

These data could be used from archaeologists, art historians, etc. in order to understand better the Romans cultural level, trades and commercial relations with other people, etc.

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References

- [1] I. Aliatis, D. Bersani, E. Campani, A. Casoli, P. P. Lottici, S. Mantovana and I.-G. Marino. Pigments used in Roman wall paintings in the Vesuvian area. *J Raman Spec* (2009) 1537.
- [2] R. Piovesan, R. Siddall, C. Mazzoli, L. Nodari, The Temple of Venus (Pompeii): a study of the pigments and painting techniques, *J Archaeol Sci* (2011) 2633.

The solution to the unanswered questions in cultural heritage analysis around the Raman spectroscopy spectra of $\text{CaSO}_4\text{-H}_2\text{O}$ system compounds

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Anhydrite (CaSO_4), commonly found in the Cultural Heritage bibliography, is identified by its main Raman band at 1017 cm^{-1} [1] and it is one of the most important compound related to the building material decaying by the action of the atmospheric acid gases. However, there exist incongruences around this compound because it could be also related to the main Raman band at 1025 cm^{-1} [2]. This contradiction goes beyond to the natural evolution of the research as it prevalence in the latest works leading difficulties for new researches [3]. Moreover, this band is share with other compounds usually found in this field and the identification of one of other is crucial for the correct evaluation of the state of Built Heritage [4].

For that reason, this works claims to clarify once and for all, the Raman spectra of the different phases of $\text{CaSO}_4\text{-H}_2\text{O}$ system, which are based on different rehydration-hydration states, through an analysis of the bibliography and Raman spectroscopy thermodynamic studies.

In this sense, the main responsible for the incongruence problems found in the literature is associated with an incomplete or incorrect definition of the system. Due to this fact, the studies are not well focused and the correct conclusion could not be achieved. Based on an accurate definition of the whole system, which is composed by at least five different compounds ($\text{CaSO}_4\cdot 2\text{H}_2\text{O}/\text{CaSO}_4\cdot 0.5\text{H}_2\text{O}/\gamma\text{-CaSO}_4/\beta\text{-CaSO}_4/\alpha\text{-CaSO}_4$), thermodynamic and spectroscopic studies of gypsum were carried out by the use of a Renishaw InVia confocal microRaman spectrometer (514 nm) coupled to a high temperature stage TS1500 Linkam Scientific Instrument. Thanks to the development of different tests under variable temperatures and the simultaneous measurement of the Raman spectra, the different spectrum of each compound were obtained. It is need to mention that, the key of the incongruences found were the consequence of the existence of three different anhydrites with different structure each one and therefore, with a different Raman spectra. In this way, the main Raman band at 1017 cm^{-1} it was always related to $\beta\text{-CaSO}_4$ or insoluble anhydrite, which is the phase of the anhydrite mineral. In contrast, the Raman band at 1025 cm^{-1} it is a metastable compound called soluble anhydrite or $\gamma\text{-CaSO}_4$. It must be highlighted that these phases are sensitive to phase transformation by laser power, depending on the studied matrix. Finally, the main Raman bands of $\text{CaSO}_4\text{-H}_2\text{O}$ system were identified at 1008-1015-1025-1017-1017 cm^{-1} respectively, ending this work with the contradictions found in literature.

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References

- [1] R.T. Downs. The RRUFF Project: an integrated study of the chemistry, crystallography, Raman and infrared spectroscopy of minerals. Program and Abstracts of the 19th General Meeting of the International Mineralogical Association in Kobe (2006) Japan. 003-13.
- [2] L.P. Sarma, P.S.R. Prasad. N. Ravikumar, Raman spectroscopic study of phase transitions in natural gypsum. *J. Raman Spectrosc.* 29 (1998) 851.
- [3] A. Tournié, L.C. Prinsloo, C. Paris, P. Colomban. B. Smith, The first in situ Raman spectroscopic study of San rock art in South Africa: procedures and preliminary results. *J. Raman Spectrosc.* 42 (2011) 399.
- [4] N. Prieto-Taboada, M. Maguregui, I. Martinez-Arkarazo, M. Olazabal, G. Arana. J.M. Madariaga, Spectroscopic evaluation of the environmental impact on black crusted modern mortars in urban-industrial areas. *Anal. Bioanal. Chem.* 399 (2010) 2949.

Structural modification of cultural heritage materials produced by CW CO₂ laser. Micro-Raman and Raman imaging studies

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Glazing, vaporization and spalling, process can produce over an irradiated surface with a high power laser beam. When power density of the irradiating laser beam is high enough to raise surface temperature beyond the glass transition temperature, a glassy surface layer is formed. However, if surface temperatures are below those (melting point), vaporization of water can produce on the material surface. Due to small diffusivity of water vapour, its transport is hindered and an over-pressure is attained producing its decay (spalling) [1].

Hydraulic building materials used as modern Cultural Heritage, i.e mortar, concrete, etc, have about 4-10% bounded water. After irradiation with the CW CO₂ laser, water vapour spread out in a vaporization front reacting with the CaO present in the sample and producing Ca(OH)₂, besides a glassy surface [2].

This present work describes the distribution of the portlandite over the surface of the sample and the mineralogical composition of the glassy material. Both Micro-Raman and Raman mapping have been used for structural studies.

The irradiation was carried out with a CW (Synrad Firestar t80, Mukilteo, WA) CO₂ laser operating at a wavelength of 10.591 μm , 10P(20) CO₂ laser line. The laser output was kept at 8, W as measured with a Synrad PW-250 (Mukilteo, WA) power meter. The laser beam was focused by means of a NaCl lens of 10 cm focal length. Irradiation time was 5 seconds.

Raman spectra were collected with a Renishaw Raman Invia Spectrometer, equipped with a CCD camera, using 532 nm (Nd:YAG) excitation line. The laser on the sample was 5 mW and the integration time was 10 seconds. For mapping measurements, an area of 80 μm x 80 μm was chosen in the internal part of the glass. The step size was 5 μm with an individual grid size of 25 μm^2 .

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References

- [1] J. Lawrence, L. Li. High power diode laser surface glazing of concrete. J. Laser Appl 12 (2000) 116.
- [2] S. Martínez-Ramírez, L. Díaz, J.J. Camacho. CW CO₂-Laser-Induced Formation of Fulgurite on Lime-Pozzolan Mortar. J. Am. Ceram. Soc. 96 (2013) 2824.

Study of the efficacy of the desalination treatment applied to an archaeological artifact affected by chorine

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In the present work the outcome of the desalination treatment applied on a medieval gilded spur (XIII century) recovered from the excavations in Ereñozar castle ruins (Basque Country, Spain) are investigated. This artifact was characterized by a high concentration of chlorine which is generally very harmful to the iron made archaeological findings causing the formation of akaganeite (β -FeOOH).[1] The tubular structure of this compound compromises the compactness of the corrosion layer leading to the formation of fractures and loss of material. In this sense, the cross section of some corrosion fragments detached after the desalination process in which the spur was subjected were analyzed with the aim of studying the penetration as well as the efficiency of the treatment.

To achieve this aim an energy dispersive spectrometer (EDS) on a EVO40 scanning electron microscope (SEM) was used in order to characterize the elemental composition. Furthermore the Raman imaging realized with an inVia Renishaw confocal microRaman spectrometer (785 cm^{-1} excitation laser) helped to understand the distribution of the iron corrosion phases.

The analysis showed that the samples presented a stratification characterized by the superimposition of several corrosion phases. The most internal layer was composed of magnetite (Fe_3O_4) which presence was favored by the limited presence of oxygen. On the other hand, the external layer, more in contact with the external environment, allowed the formation of goethite (α -FeOOH). Raman imaging also made possible the identification of three akaganeite layers at different depths. Among them, the most superficial one was the only layer highlighting the absence of chlorine and the joint presence of lepidocrocite (γ -FeOOH).

This information suggests that the treatment used for this spur was able to extract the Cl only superficially. Furthermore, the presence of lepidocrocite suggests that the absence of chlorine caused the partial phase transformation of akaganeite into a more stable compound.[2]

To conclude, this investigation project shows that in some cases one of the most used desalination treatment ensures positive effects only superficially. For this reason, even though outwardly the objects appears to be well preserved, the lack of stabilization of the innermost corrosion leaves the way open to a further degradations of the artifacts, which can lead to new fractures and detachments.

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References

- [1] S. Réguer, P. Dillmann, F. Mirabet. Buried iron archaeological artefacts: Corrosion mechanisms related to the presence of Cl-containing phases. *Corros.Sci.* (2007) 2726.
- [2] K. Stahl, K. Nielsen, J. Jiang, B. Lebech, J.C. Hanson, P. Norby, J. van Lanschot. On the akaganéite crystal structure, phase transformations and possible role in the post-excavational corrosion of iron artifact. *Corros.Sci.* (2003) 2563.

Rapid screening of terpenes in fragrance-free cosmetics by combining headspace single-drop microextraction and micro-fluorospectrometry

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Terpenes are a large class of organic compounds that are widely used as fragrance in cosmetics. Usually, terpenes are related to allergenic reactions [1], so the commercialization of free-fragrance cosmetics has increased notably in the last years in order to diminish possible allergies. Nevertheless, some of them contain fragrance chemicals in low amounts (<0.001% (w/w) in leave-on cosmetics or 0.01% (w/w) if these are rinsed off) [2] and it is not required to indicate these concentrations in the labels. For this reason, the analytical control of terpenes even in fragrance-free cosmetics in a simple and rapid way is desirable on a routine basis. In this sense, screening methods, which provides a binary yes/no response, are suitable for this purpose.

In this work, a fast screening of terpenes based on the combination of a liquid-liquid microextraction approach and micro-fluorospectrometry is developed [3]. The use of headspace single-drop microextraction (HS-SDME) allows obtaining a miniaturized, rapid and simple assay with a minimum consumption of sample and reagents [4].

A drop containing bovine serum albumin with fluorescein is used as optical probe. The fluorescence is quenched by the presence of terpenes. Under optimal conditions, similar slopes of calibration curves were obtained for all of the terpenes tested, and procedural detection limits were in the range of 0.49-0.87 µg/g. Among terpenes usually present in cosmetics, citronellol was selected as representative conventional standard for calibration purposes. Repeatability, expressed as relative standard deviation, was 4% (N=6), whereas the reproducibility was 6% (N=3). Moreover, a large enrichment factor (408) was achieved using citronellol as representative compound. The unreliability region of the proposed method was 0.0006–0.0012% (w/w) as citronellol concentration, by using a cut-off value of 0.001% (w/w) to avoid having false negatives.

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References

- [1] A. Chisvert, A. Salvador, in: A. Salvador, A. Chisvert (Eds.), *Analysis of Cosmetic Products*, Elsevier, Netherlands, 2007, pp. 243-256.
- [2] Regulation (EC) No. 1223/2009 of the European Parliament and of the Council of 30 November 2009 on cosmetic products.
- [3] N. Cabaleiro, I. de la Calle, C. Bendicho, I. Lavilla. Fast screening of terpenes in fragrance-free cosmetics by fluorescence quenching on a fluorescein-bovine serum albumin probe confined in a drop. *Anal. Chim. Acta* 719 (2012) 61
- [4] F. Pena-Pereira, I. Lavilla, C. Bendicho, Liquid-phase microextraction techniques within the framework of green chemistry, *TrAC, Trends Anal. Chem.* 29 (2010) 617.

Ultrasound-assisted cytosol preparation for the determination of Cd and Cu bound to metallothioneins in mussel tissue by ICP-MS

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Determination of metals in biomarkers is an efficient approach for environmental assessment of metal pollution. Metallothioneins (MTs) in aquatic organisms are considered to be attractive biomarkers for the assessment of metal pollution in the marine environment. [1]

In general, determination of metals bound to MTs entails three stages: cytosol preparation, MTs separation and measurement of metal contents in the corresponding fraction. Cytosol preparation is generally tedious and lengthy. [2] Usually, preparation of cytosol includes cutting/homogenization, centrifugation, thermal treatment and further centrifugation in order to eliminate proteins with high molecular weight. Apart from being tedious and time consuming, the main problems of conventional procedures for cytosol preparation arise from the cutting/homogenization step, because the contact with air during the process can increase tissue oxidation as well as contamination risks.

In order to overcome these disadvantages and simplify the process, a new cytosol preparation based on indirect sonication by means of a cup-horn sonoreactor for the determination of Cd and Cu bound to MTs in mussel tissue is developed. [3] The cavitation phenomenon promotes cellular disruption and thus, cytosols can be easily obtained. In addition, indirect sonication diminishes the risk of contamination.

Variables influencing the procedure of ultrasound-assisted cytosol preparation are studied: Tris-HCl buffer concentration, pH, sample mass, sonication time and sonication amplitude. Under optimal experimental conditions, only 20 mg of tissue are necessary for cytosol preparation. The heating step used in conventional procedures for cytosol preparation can be removed, because propagation of ultrasound energy through the liquid medium causes heating of the sample, thus reaching a temperature up to 65°C following sonication.

An acid ultrasound-assisted extraction procedure with diluted acid is also used for determining total Cd and Cu in mussel tissues.

The new proposed approach for cytosol preparation is combined with liquid chromatography for MTs separation followed by determination by inductively coupled plasma-mass spectrometry (ICP-MS). With this methodology, the limits of detection (LODs) for metal bound to MTs are 0,17 ng g⁻¹ and 4,93 ng g⁻¹ for Cd and Cu, respectively. LODs for total metal determination are 0,10 ng g⁻¹ and 2,74 ng g⁻¹ for Cd and Cu respectively.

The proposed methodology for determining Cu and Cd bound to MTs allows simplifying and shortening the sample pretreatment procedure. It also entails the elimination of the heating treatment and some centrifugation steps included in conventional procedures. In addition, six samples can be simultaneously processed, thereby enhancing sample throughput. The novel methodology could encourage many environmental studies for assessment of metal pollution.

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Financial support from the Spanish Ministry of Science and Innovation (projects CTQ2012-32788 and CTQ2009-06956/BQU) is gratefully acknowledged.

References

- [1] S. N. Frank, B. Singer, B. Sures. Metallothionein (MT) response after chronic palladium exposure in the zebra mussel, *Dreissena polymorpha*. Environ. Res. 108 (2008) 309.
- [2] K. T. Suzuki, M. Sato. Preparation of biological samples for quantification of metallothionein with care against oxidation. Biomed. Res. Trace Elem. 6 (1995) 51.
- [3] I. Lavilla, M. Costas, S. Gil, S. Corderí, G. Sánchez, C. Bendicho. Simplified and miniaturized procedure based on ultrasound-assisted cytosol preparation for the determination of Cd and Cu bound to Metallothioneins in mussel tissue by ICP-MS. Talanta 93 (2012) 111.

Optical sensors for detection and continuous monitoring of VOCs during the cooking process

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During the cooking process there are several chemical reactions than produce a complex mixture of compounds. These compounds are able to generate an autoignition process, to present high toxicity and carcinogens, and most of them have unpleasant odours. For these reasons, during the last decades several authors have studied these processes with the purpose of improving the knowledge and to contribute with new and different solutions.

In these sense, our research group has developed [1] new methodologies for continuous monitoring the UV-VIS or IR spectroscopic signal of the volatile organic compounds (VOCs) generated when heating edible oils.

Thanks to these methodologies, it has been carried out different studies at lab scale in order to obtain the release profile of VOCs in ideal conditions. Besides lab scale studies, it has been carried out different studies with a lab prototype (Fig.1) in order to reproduce real conditions during cooking process and validate previous results.

After VOC characterization, it has been developed and optimized several optical sensors able to detect and monitor VOCs. These sensors are based on scattering effect (Fig. 2), UV-Vis and M-IR molecular absorption.

Finally, these sensors have been tested at real scale conditions in a Pyrolysis room (Fig. 3). During these studies, it has been proved that the sensors are able to solve one of the problems generated during the cooking process (i.e. autoignition of edible oils), apart from to characterize the point at which edible oils starts to decompose.



Figure 1. Lab prototype



Figure 2. Example of developed sensor.
Multi-wave scattering sensor



Figure 3. Testing sensor at real scale conditions

Acknowledgements

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References

[1] J. Sanz, I. Ontañón, S. de Marcos, A. Escudero, J. Galbán. Caracterización de volátiles generados durante el calentamiento de aceite mediante UV-VIS e IR. Contribución en XXIII RNE–VII CIE (2012).

Reagentless fluorescent biosensor based on chemically modified glucose oxidase and Tm^{3+} , Yb^{3+} doped fluorohafnate glasses

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In a previous work [1], our research group has designed a fluorometric sensor for glucose using glucose oxidase chemically modified with a fluorescein derivative (GOx-FS). The methodology of the determination is based on the alteration of the fluorescence intensity of the FS during the enzymatic reaction with glucose, which is related to the concentration of this analyte. Taking this in mind and with the purpose of developing a sensor for glucose determination in biological samples, lanthanides-doped fluorohafnate glasses [2] have been employed.

In this work, we present an alternative approach for glucose sensing, which minimizes the autofluorescence background of the biological matrix of samples. The biosensor combines the fluorescence of GOx-FS and the upconversion luminescence of Tm^{3+} , Yb^{3+} doped fluorohafnate glasses (UC glasses), which are capable of emitting light in the visible range upon near-infrared laser excitation (980 nm). The upconversion emission can be used for the excitation of the GOx-FS immobilized in a polyacrylamide film.

The GOx-FS film together with the UC glass was placed in a homemade flow cell, which was incorporated in a FIA system (flow injection analysis), for the fluorescence measurements. Figure 1 shows how the fluorescence intensity changes at FS emission wavelength for 1 mL of different concentration of glucose. Area and height values of the peaks can be used as calibration parameters. A linear relationship was observed from 5.7 to 14 mM of glucose.

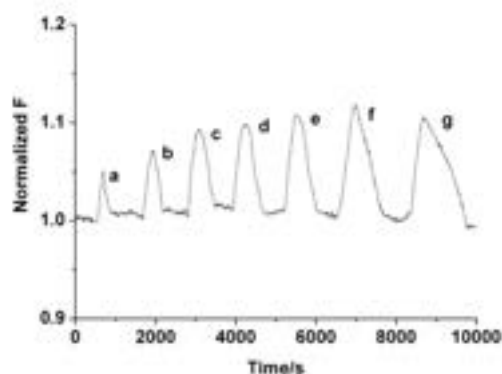


Fig.1: Variation in fluorescence intensity of the sensor with glucose concentration (mM): (a) 4.6, (b) 5.7, (c) 6.8, (d) 8.0, (e) 9.1, (f) 11, (g) 14.

The results obtained demonstrate that the combination of the upconverting luminescence of doped glasses and the optical properties of GOx-FS allow the determination of glucose using near-infrared laser excitation. Moreover, the methodology could be easily extended to other biochemical analytes (cholesterol, choline...) by the use of the corresponding enzymes.

Acknowledgements

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References

- [1] J. Galbán, I. Sanz-Vicente, E. Ortega, M. del Barrio, S. de Marcos. Reagentless fluorescent biosensors based on proteins for continuous monitoring systems. *Anal Bioanal Chem* (2012) 402 3039.
- [2] M.A. Chamarro, R. Cases. Energy up-conversion in (Yb, Ho) and (Yb, Tm) doped fluorohafnate glasses. *J Lumin* (1988) 42 267.

Development of a magnetic ELISA spectrophotometric immunosensor for the determination of cocaine in biological samples

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Cocaine is an alkaloid derived from coca leaves (*erythroxylum coca*, *erythroxylum novogranatense*), being one of the most worldwide used illicit drugs. After cannabis, it is the most popular drug of abuse in Europe. It has local anesthetic action, but above all, it is a potent central nervous system stimulant that elicits a state of increased alertness and euphoria, being its action similar to those of amphetamine but of shorter duration [1].

Diagnosis of cocaine consumption has interest in rehabilitation, overdose and judicial processes, epidemiological studies and sports.

Drug of abuse tests for cocaine are usually based on benzoilecgonine (BZE) determination, which is the major cocaine metabolite in the human body, but has no effect on person ¿humans? [2]. This metabolite can remain and can be detected up to 36 hours after cocaine consumption. Thus, a positive result indicates that the individual has consumed cocaine but does not give us information about whether he is or not under its effects.

Cocaine quantification can also be useful in pharmacokinetic studies and in the analysis of very recent intake, a positive result in this spectrophotometric immunosensor for the determination of cocaine indicates that the individual is under the influence of the drug.

All processes involving immunosensor have been optimized: antibody immobilization on magnetic beads (MBs), competition, signal transduction and sample treatments.

The developed immunosensor has the following analytical properties:

- good sensitivity with low detection limit: $(\text{Inh}_{10})_{\text{immunosensor}} 1.42 \text{ ng mL}^{-1}$ in urine, 1.00 ng mL^{-1} in saliva and 0.09 ng mL^{-1} in human serum samples;
- good reproducibility: 5-6% DSR in four measurements;
- high selectivity: cross-reactivity with BZE lower than 1.6%;
- rapid analysis: it allows the determination of more than six samples in approximately 3 hours.

This analytical method has been validated with recovery assays, obtaining recovery values of 88.7-92.4% for urine samples, 86.3-117.3% for saliva samples and 86.9-92.5% for human serum samples.

References

[1] F. Bortolotti; R. Gottardo; J. Pascali; F. Tagliaro. Toxicokinetics of Cocaine and Metabolites: The Forensic Toxicological Approach, Curr. Med. Chem. (2012), 19, 5658-5663

[2] H.H Maurer; C. Sauer; D.S. Theobald. Toxicokinetics of drugs of abuse: Current knowledge of the isoenzymes involved in the human metabolism of tetrahydrocannabinol, cocaine, heroin, morphine, and codeine. Therapeutic drug monitoring, (2006) 28, 447-453.

Development of a magnetic ELISA spectrophotometric immunosensor for the determination of ochratoxin A (OTA) in wheat and wine

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Ochratoxin A (OTA) is a mycotoxin produced by *Aspergillus* y *Penicillium* fungi with nephrotoxic, teratogenic, carcinogenic, and immunotoxic activity in human and animals.

OTA frequently occurs in foodstuffs like cereals, coffee beans, nuts, licorice, raisins, cocoa, wine and there is a very strictly control and mycotoxin regulations at the EU [1] and over the world. The maximum allowed contents of OTA are at low ng/g levels.

We have developed a sensitive, rapid and cheap spectrophotometric immunosensor.

This immunosensor is based on magnetic beads (MBs) which are used as monoclonal antibody biorecognition surface. The use of MBs greatly improves the performance of the immunological reaction increasing the biorecognition surface and a faster immunoassay kinetics because MBs are in suspension.

All steps are performed on an ELISA plate except the antibody immobilization on the MBs.

Different parameters as quantity of monoclonal antibody, type and quantity of MBs, conjugate dilution (OTA-HRP), incubation and competition temperature and incubation and competition time have been optimized.

The developed immunosensor has the following analytical properties:

- good sensitivity with low detection limit: $(\text{Inh}_{10})_{\text{immunosensor}} 1.14 \text{ ng mL}^{-1}$ (0.35 ng g⁻¹ in wheat and 0.17 ng mL⁻¹ in wine samples);
- good reproducibility: 6-7% DSR in four measurements;
- high selectivity: cross-reactivity with other mycotoxins (DON or FB1) is lower than 1.7%;
- rapid analysis: it allows the determination of more than four samples in approximately 2 hours.

This analytical method has been validated through: (i) the interpolation of certified reference materials like TR-O100 and MYC-0880 (wheat flour), obtaining errors of -9.4% and 3% respectively; (ii) analysis of real samples and comparison with official analysis methodology, high-performance liquid chromatography with fluorescent detection (HPLC-FLD) and commercial spectrophotometric ELISA kit; (iii) recovery assays, obtaining recovery values of 90.1% for wheat flour and 85.7-88.2 for samples of different wines.

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This work has been sponsored by Ministry of Science and Innovation with the contract PTQ-10-03580 (Torres Quevedo 2010), and the project IPT-2011-1766-010000 (INNPACTO 2011).

References

[1] COMMISSION REGULATION (EC) No 1881/2006 of 19 December 2006 amending Regulation (EC) No 1881/2006 setting maximum levels for certain contaminants in foodstuffs.

Development of a magnetic ELISA spectrophotometric immunosensor for the determination of fumonisin B1 in cereals

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The fumonisin B1 (FB1) is a mycotoxin present in different types of food, mainly in cereals and cereal derivatives. This mycotoxin is considered as a carcinogen by the International Agency for Research on Cancer (IARC) classified in group 2B. FB1 levels in food are legislated by European Union [1], the permitted levels ranging from 200 to 4000 ng.g⁻¹ depending on the type of food. Due to the great importance of mycotoxins in food contamination, the Spanish and European legislation are demanding in recent years an exhaustive control.

"Rapid tests" for food analysis have been increasingly demanded by analytical community, especially during the last decade. The term "rapid" is usually assigned to a method after comparison with the respective reference method. For example, if the reference method needs one working week to yield a result, an alternative method may be called rapid even if it requires three working days. For mycotoxin analysis, there are other features commonly attributed to rapid tests: these methods should also be more simple (easy to perform) and cheaper than, for example, chromatographic methods.

Since we started to research for the determination of FB1 about 2 years ago, we have used a variety of specific antibodies (monoclonal and polyclonal) to develop spectrophotometric immunosensors. The best selectivity and sensitivity were obtained with a monoclonal antibody highly specific and selective to FB1, which has low cross reactivity with other mycotoxins such as ochratoxin A (OTA) or deoxynivalenol (DON) that can be present in the same samples and produce a synergistic effect.

A very sensitive competitive magnetic spectrophotometric immunosensor was developed using magnetic microparticles (MBs) as solid surface to carry out the immobilization of biorecognition element and competition-incubation steps. After competition and washings, enzymatic reaction takes place between the substrate and the enzyme HRP-peroxidase. The best analytical properties were obtained working with TMB substrate.

The developed immunosensor allows a quick and sensitive determination of FB1 in food samples in validated applications comparing with high-performance liquid chromatography with fluorescence detection official methods, under the concentrations allowed by the very restrictive European Union legislation. The best analytical properties and the fastest protocol of analysis were obtained working with a time for the overall FB1 determination about 30 min.

In this case a limit of detection of 6 µg.kg⁻¹ was obtained, an EC₅₀ value near to 1.20 ng.ml⁻¹, and a relative error of 6.4% when the results obtained were compared when the concentration in a certified reference material of FB1 (TR-FC-433).

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References

[1] COMMISSION REGULATION (EC) No 1126/2007 of 28 September 2007 amending Regulation (EC) No 1881/2006 setting maximum levels for certain contaminants in foodstuffs as regards Fusarium toxins in maize and maize products.

Development of a magnetic ELISA spectrophotometric immunosensor for the determination of deoxynivalenol in cereals

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Deoxynivalenol (DON) is a frequent and very toxic mycotoxin that commonly contaminates cereal-based foods worldwide. DON is produced by certain *Fusarium* species that frequently contaminate corn, wheat, oats, barley, rice, and other grains in the field or during storage. The exposure risk to human is directly through foods of plant origin (cereal grains) or indirectly through foods of animal origin (kidney, liver, milk, eggs).

Due to the great importance of mycotoxins in food contamination, the Spanish and European legislation are demanding in recent years an exhaustive control. Maximum permissible concentrations of DON for different foods are between 200 and 1750 $\mu\text{g.Kg}^{-1}$ and the tolerable daily intake is 1 $\mu\text{g.Kg}^{-1}$ body weight [1].

Analytical procedures for trichothecene mycotoxins usually differ in extraction procedures, clean-up, and final analytical steps, depending on which trichothecene is actually determined. A variety of extraction procedures have been reported in bibliography depending on the analytical techniques used in DON determination, such as gas-chromatography (GC), high-performance liquid chromatography (HPLC) or immunoassays.

In this report, a method for DON determination with a spectrophotometric immunosensor was evaluated and improved. This work proposes a direct competitive immunosensor where we immobilize the biorecognition element and then the competitive reaction takes place between DON and DON-HRP. Enzymatic reaction takes place between the substrate and the enzyme HRP-peroxidase. We have optimized the different parameters and variables with the technique ELISA.

The best analytical properties and the fastest protocol of analysis were obtained working with a time for the overall DON determination is about 60 min. In this case a limit of detection of 5.3 $\mu\text{g.kg}^{-1}$ was obtained, an EC_{50} value near to 10 ng.mL^{-1} and a relative error of 3.6 % when the results obtained were compared when the concentration in a certified reference material of DON (TR-D100).

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References

[1] COMMISSION REGULATION (EC) No 1126/2007 of 28 September 2007 amending Regulation (EC) No 1881/2006 setting maximum levels for certain contaminants in foodstuffs as regards *Fusarium* toxins in maize and maize products

Analytical possibilities using flavoenzymes fluorescence: Towards to a multicomponent sensor based on ChOx fluorescence

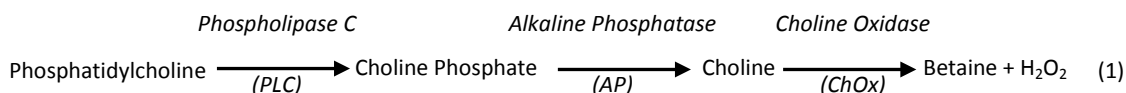
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The research group where this study takes place has extensive experience in the use of fluorescence of flavoenzymes, both intrinsic (tryptophan and flavin wavelengths) as extrinsic in the visible area (fluorophore with the enzyme), for the determination of different analytes (choline, cholesterol, glucose...)^[1].

A further step in the development of this methodology is to couple several enzymatic reactions increasing the number of substances to determine. Our study is based on the sequence of reactions shown below (1).



For all cases, the fluorescence variation of the choline oxidase (ChOx) enzyme is measured when it reacts with choline (Cho) released in previous reactions of hydrolysis:

a.- choline phosphate (ChoP) with the alkaline phosphatase (AP) enzyme^[2].

b.- phosphatidylcholine (PC) with the action of the Phospholipase C (PLC) and AP enzymes.

All of them, analytes with biological interest (as part of plasma cell membranes in our body).

Kinetic measurements have been developed in a plate reader, using a minimum volume of sample and finding the optimal working conditions. Also ChoP and Cho have been determined in a real sample, such as infant formula. In order to overcome matrix effects, the method has been designed using FAD fluorescence. To quantify both substrates present in the sample, a sequential addition of enzymes will take place.

In this way, this methodology is implemented in optical sensors, to determine biological substances that contain Cho, in particular ChoP. ChOx enzyme has to be labeled with a fluorophore in order to measure in visible region so an exhaustive study was made to choose the label. Likewise, studies of enzyme immobilization, ChOx and AP, both of them together, have been conducted on support in polyacrylamide gel, forming a sensor film, with the main advantage of not having to use new enzyme for each test, regenerating in each reaction which is already immobilized. The best reaction conditions for the analytes determination have been studied (enzyme concentration, measurement wavelength, sample injection time and flow).

This methodology has been applied to the determination of Cho and ChoP in real samples.

Acknowledgements

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References

- [1] J. Galbán, I. Sanz-Vicente, M.E. Ortega-Castell, M. Del Barrio, S. de Marcos, Anal. Bioanal. Chem. 402, (2012) 3039
- [2] M.P. Lapieza-Remón, A. Domínguez, M.E. Ortega-Castell, I. Sanz-Vicente, J. Galbán. Luminescence. 27, No. 6, (2012) 565.

Chemical sensors based on new hydrazone derivatives

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A chemical sensor is a device which responds to a particular analyte in a selective way through a chemical reaction and can be used for the qualitative or quantitative determination of the analyte.[1] For a specific example, a sensor is concerned with detecting and measuring a certain chemical substance or a set of related chemicals. Among the plethora of sensors reported in literature, devices based on optical properties have received considerable attention due to their simplicity, high sensitivity and spatial and temporal resolution.[2] Different techniques such as absorption spectroscopy, fluorescence spectroscopy, luminescence spectroscopy, internal reflection spectroscopy, surface plasmon spectroscopy and light scattering have been used to determine analytes of interest. For instance, visible absorption spectroscopy has been used in the measurement of pH with different dyes and fluorescent reagents are useful in the detection of halides and cations.[3]

In this contribution we present the variation of the optical properties on new hydrazone derivatives (Figure 1) in response to different modifications in the medium. Specifically, the effect of solvent, polarity, concentration and pH will be considered. In addition, the capabilities of these compounds as metal sensors will be explored.

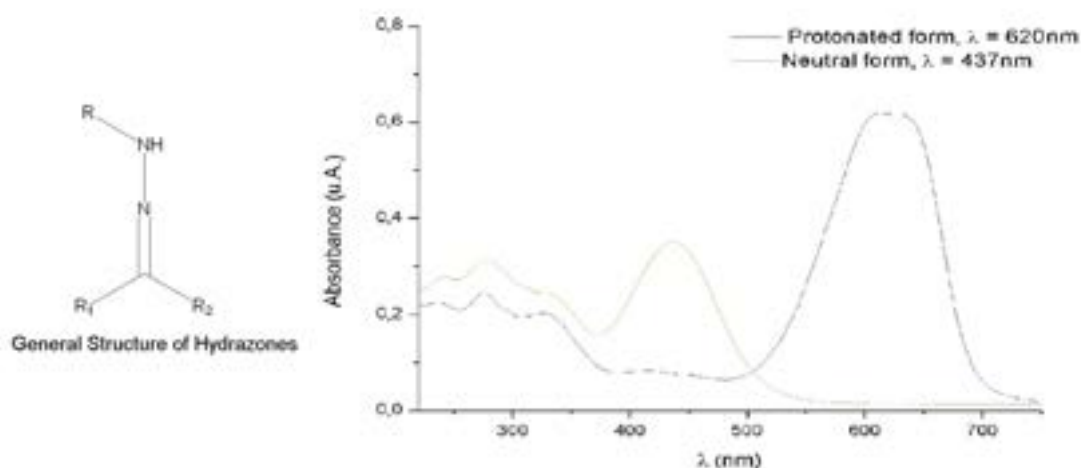


Figure 1. General structure of hydrazones and variation in optical properties with acid presence.

Acknowledgements

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References

- [1] B. Eggins. Chemical Sensors and Biosensors; Analytical Techniques in the Sciences, John Wiley & Sons: Chichester, UK, 2002.
- [2] X.Chen; T. Pradhan; F. Wang; J. S. Kim, J. Yoon. Chem. Rev. 112 (2012) 1910.
- [3] R. Pérez-Ruiz, A. G. Griesbeck, D. Sampedro. Tetrahedron 68 (2012) 5724.

Antibiotic sensing with electrochemiluminescent sensors

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In the last decade, there has been an increasing public interest to detect the presence of antimicrobials in the environment as uncontrolled antibiotic levels may lead to bacterial resistance in ecosystems. In particular, pharmaceutical waste containing fluoroquinolones (FQs), a group of antibiotics widely used in treatments for human and veterinary use, has been detected in aquatic systems.

Analytical methods based on electrochemiluminescence (ECL) measurements are particularly attractive for environmental analysis due to its high sensitivity, wide range of linearity and the relatively simple instrumentation required.

In this work, different luminescent complexes of Ru(II) such as tris(1,10-phenanthroline)ruthenium(II), among others, have been used to determine FQs. The presence of co-reactants with electron-donating groups tends to increase the ECL, which makes the tertiary amines present in some FQs, such as enrofloxacin (ENRO), more effective than other reductants. Formation of the (triplet) excited state of the Ru(II) complex, responsible for the ECL emission, occurs by electron transfer from the reductive group present in the FQs to the ground state Ru(III) species.

We have described previously an ECL method in solution for the analysis of ENRO in natural waters using a solution of $[\text{Ru}(\text{phen})_3]^{2+}$ as luminescent reagent [1]. This presentation will report on the development of ECL sensors based on immobilized Ru(II) complexes. This approach allows a significant decrease in reagent consumption, allows signal amplification, simplifies the required instrumentation, and facilitates miniaturization.

The Ru(II) complex has been immobilized by covalent or non-covalent interactions onto screen-printed electrodes based on gold or carbon nanotubes. Several immobilization strategies have been explored including the formation of self-assembled monolayers (SAM), *via* thiol or amino groups, or using functionalized silica nanoparticles (NPs) doped with the luminescent dye. Modifications of the electrode surface after functionalization have been characterized by transmission electron microscopy (TEM) and confocal fluorescence microscopy.

Different variables affecting the sensor performance for ENRO monitoring have been optimized, namely, the immobilization time of NPs on electrode surface, the oxidation potential, the solution pH and the reagents concentration using cyclic voltamperometry and luminescence emission.

The different sensing surfaces have been compared in terms of ECL signal amplification, stability, reusability and response time to achieving the best analytical performance.

Acknowledgements

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References

[1] L. Carranza; B. Diez-Buitrago; M. Luaces; C. Valdés; C. Pérez-Conde; A. M. Gutiérrez; M.C. Moreno-Bondi. Determination of enrofloxacin in natural water by EQL of ruthenium complexes. XVIII Meeting of the Spanish Society of Analytical Chemistry, Jaen (Spain), June, 2013, page 251, Book of Abstracts

Ion mobility spectrometry as a vanguard technology to assess the quality of heat transfer fluid

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Heat Transfer fluid (HTF) is commonly used in thermosolar plants. Despite the fact that this HTF is thermically stable, it is necessary to assess and control if there is any possibility that this HTF exposed at high temperatures (around 400 °C) and overheated in continuous cycles in the thermosolar plant could change its initial composition. These possible variations in the initial formulation of the product and the probable generation of other compounds (benzene and phenol among others) require of quick and portable instruments such as Ion Mobility Spectrometry (IMS) for quality control. In this work, different ionisation sources (UV or tritium) were used to study which one is more suitable to monitor the lifecycle of HTF. Once the most appropriate ionisation source was chosen, two different chromatographic columns: multicapilar column (MCC) or gas chromatography column (GC) were tested to assess if it is possible to identify the degradation products present in used HTF sample. A method was optimized and proposed to measure the HTF after certain time of using it in a thermosolar plant.

IMS is a reliable, rapid, portable and inexpensive technique that can be useful for process control. The potential capabilities of this powerful tool in workplace monitoring make it attractive to be considered in environmental field. The results obtained by analysing HTF with IMS were compared with the one obtained with Gas Chromatography (GC) and Near Infrared Spectroscopy (NIR). Not so much differences in the raw and used HTF fingerprint were appreciated with GC or NIR but different profiles were obtained when both types of HTF samples were analysis by IMS. Therefore, it seems that IMS is a promising technique for quality control of HTF in a thermosolar plant.

Digital image-base methods as novel tools of high efficiency in quantitative analytical determinations

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Digital Image-based methods, in particular Digital Image Colorimetry –DIC- [1] could be considered as a new type of analytical methodology . It uses easily captured digital images, with cameras, web-cams, hand scanners, or also by the very expanded smart telephones [2], to produce, in a ready procedure, feasible analytical results at low cost. The equipment is based in Complementary Metal-Oxide Semiconductors (CMOS) or Charge Coupled Detectors (CCD) that could provide fast Red Green Blue basic colors of direct or indirect chromogenic systems.

With this type of systems, analytical results could be implemented for rapid surveillance in fields with high demand of analysis in semi-quantitative determinations but also in critical and currently needs in quantitative control of bio-clinical test [3]. The strategic function of these methods has been recognized by the most important chemical manufacturers. ISO has also recognized the importance of the ready-to use named methods, in particular in environmental analysis, and has issued an important guide.

A principal and open point, regarding the analytical applicability of digital image –based methods is the selection of the instrumental variable. Individual RGB basic colors but also others alternatives could be proposed.

In this work, the analytical meaning of different chromatic parameters was studied by multivariable statistical procedures. Principal component analysis and Fourier Transform evidenced the influence of different factors. Thus, variance of a digital image could be interpreted in terms of analytical variables of high potential, while other side- parasite effects could be detected but tailored to a minimum. Therefore, more than 95% of the total variance of a digital image could be analytically employed while the influence of other parasite effects could be drastically reduced

It could be demonstrated that the influence of different conditions were of high relevance. Thus, selection of illumination conditions and color detection could provide significant improvement in both selectivity and sensitivity of analytical determinations. Also, the image capture conditions could be relevant in the color variance. Two chromogenic system based in colored reaction between Ca(II) and common dyes were elected as representative case for the evaluation purpose.

Finally they were applied in practical Ca determinations in real sample food, milk, and environmental samples: water calcium hardness . Results were compared and validated by alternative techniques of atomic spectroscopy: flame absorption and ICP-emission.

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References

- [1] A. Lopez-Molinero, V. Tejedor, R. Domingo, D. Sipiera, *Talanta* 103 (2013) 236.
- [2] Z. Iqbal, M. Eriksson, *Sensors and Actuators B: Chemical* 185 (2013) 354.
- [3] A.K. Yetisen, J.L. Martinez-Hurtado, A. Garcia-Melendrez, F. da Cruz Vasconcellos, C. R. Lowe, , *Sensors and Actuators B: Chemical* 196 (2014) 156

Bonding properties in $\text{HNO}_3\cdot\text{HOCl}\cdot(\text{H}_2\text{O})_n$ clusters

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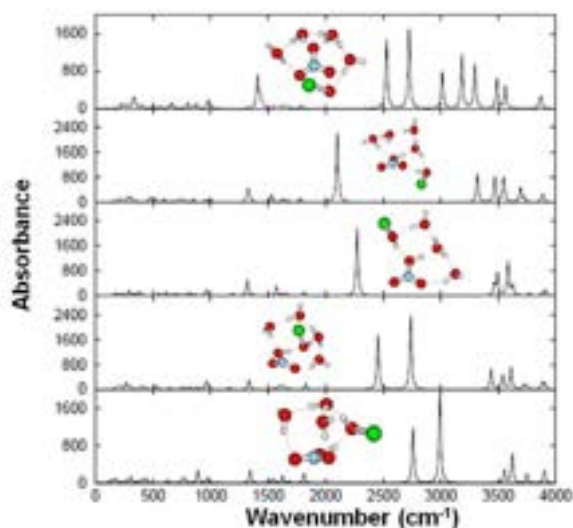
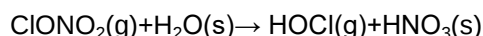
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Nitric acid and hypochlorous acid are species of atmospheric relevance [1,2]:



Molecular clusters containing water and these two acidic species are studied using several theoretical techniques, with especial emphasis on their bonding characteristics. Stable structures are found with a minimum in their potential energy surface for aggregates with three and four H_2O molecules. In the most stable configurations the H atom of HNO_3 is partly donated to the O atom of HOCl . Proton transfer parameters, electron density at the bond critical point, atomic charges and spectroscopic properties are studied for all these species, revealing direct relationships among several of these properties. The proton transfer parameter gives a straightforward indication of the degree of ionization of the aggregates, with negative or positive values for molecular or ionic (i.e. with fully ionized nitric acid) clusters, respectively. The calculated electron densities yield values typical of hydrogen bonded

species. Atomic charges are calculated using three different methods, namely Mulliken, Natural Bond Order, and Bader. The predicted spectra present large variations in wavenumber and intensity of the main bands, which could be used to identify specific aggregates among complex spectra (see Figure). Finally, the HOCl clusters studied here are compared with similar aggregates containing HCl [3]. The weaker acid favors a higher degree of proton sharing in HNO_3 .

Acknowledgements

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References

- [1] J.P.D. Abbatt; M.J. Molina, The heterogeneous reaction of $\text{HOCl} + \text{HCl} - \text{Cl}_2 + \text{H}_2\text{O}$ on ice and nitric acid trihydrate - Reaction probabilities and stratospheric implications. *Geophys. Res. Lett.* 19, (1992), 461.
- [2] J.H. Seinfeld, S.N. Padis, *Atmospheric Chemistry and Physics*. Ed Wiley: New York, 1998.
- [3] F.M. Balci; N. Uras-Aytemiz; P.C. Gómez; R. Escribano, Proton transfer and autoionization in $\text{HNO}_3\cdot\text{HCl}\cdot(\text{H}_2\text{O})_n$ particles. *Phys. Chem. Chem. Phys.* 13 (2011), 18145.

Optical properties of two isomers of the heteronuclear complex $[\{\text{Au}(\text{C}_6\text{Cl}_5)_2\}\text{Ag}([\text{9}] \text{aneS}_3)]_2$

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The chemistry of heteropolynuclear extended supramolecular systems built by secondary interactions has attracted physicists' and chemists' interest in recent years. This is mainly due to the particular characteristics of the chemical bonding in these systems and to the physical and chemical properties associated with them [1]. In particular, the luminescence observed in these compounds seems to be closely related to the presence of metal...metal interactions, which have in many cases been implicated in these optical properties [2].

On the other hand, it is well known that S-donor polydentate ligands with different numbers of donor atoms can be employed for their coordination to closed-shell metal centers. This leads to the synthesis of metallic derivatives with different coordination environments, nuclearity and dimensionality [3].

Taking into account this precedents, we decided to study the reactivity of the basic gold(I) species $[\text{Au}(\text{C}_6\text{Cl}_5)_2]^+$ against the acid salt $\text{Ag}(\text{OCIO}_3)$ in presence of S-donor polydentate ligand $[\text{9}] \text{aneS}_3$ in different solvents. Thus, we obtained two different isomers of stoichiometry $[\{\text{Au}(\text{C}_6\text{Cl}_5)_2\}\text{Ag}([\text{9}] \text{aneS}_3)]_2$ depending on the solvent, dichloromethane or tetrahydrofuran, which show different luminescence.

In summary, this work includes a study of the optical properties of both isomers, as well as TD-DFT theoretical calculations that were carried out to determine the origin of the luminescence.



Acknowledgements

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References

- [1] See for example: R. Hoffmann. How Chemistry and Physics Meet in the Solid State. *Angew. Chem., Int. Ed. Engl.*, 26 (1987) 846.
- [2] See for example: E.J. Fernández, A. Grau, A. Laguna, T. Lasanta, V. Lippolis, J.M. López-de-Luzuriaga, M. Montiel, M.E. Olmos. Long-Chain Ketimine Synthesis in a Gold-Thallium Polymer. *Organometallics*, 29 (2010) 2951.
- [3] See for example: a) A.J. Blake, R. Donamaria, E.J. Fernández, T. Lasanta, V. Lippolis, J.M. López-de-Luzuriaga, E. Manso, M. Monge, M.E. Olmos. Heterometallic gold(I)-thallium(I) compounds with crown thioethers. *Dalton Trans.* 42 (2013) 11559. b) A.J. Blake, W.S. Li, V. Lippolis, M. Schröder. Mercury(II), silver(I) and gold(I) thioether crown chemistry: Synthesis, electrochemistry and structures of $[(\text{HgBr}_2)_2[\text{24}] \text{aneS}_8]$, $[\text{Ag}_2([\text{24}] \text{aneS}_8)(\text{CF}_3\text{SO}_3)_2(\text{MeCN})_2]^-$, $[\text{Ag}_2([\text{28}] \text{aneS}_8)]^-$ $[\text{NO}_3]_2$. *J. Chem. Soc. Dalton Trans.* (1998) 2931.

Stability of interstellar carbonaceous dust analogues and the aminoacid glycine under UV irradiation and electron bombardment

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The formation and survival of molecules in extraterrestrial environments is a subject of considerable interest to the astronomical community [1]. In particular, to know how organic molecules withstand the conditions of high radiation flux and low temperature found in the surface layers of many solar system objects is very valuable in astrobiology. In this contribution we will discuss our results on the stability of glycine in various analogues of interstellar grains made of carbonaceous materials with and without ice mantels. In particular we investigate the effect of bombardment with UV photons (120-200 nm) or with 2 keV electrons, pretending to simulate the effects of cosmic rays present in different regions of the interstellar media. The evolution of the samples is monitored with infrared spectroscopy.

We use radiofrequency discharges of CH₄ mixed with other gases for the generation of different types of hydrogenated amorphous carbon (HAC), taken as dust analogues in this work. Glycine layers were grown by vapour deposition on an infrared transparent substrate [2].

Films of HAC were found to be stable under UV photon and electron bombardment. High fluences of photons and electrons, of the order of 10^{19} cm^{-2} , were needed for a film depletion of a few per cent. UV photons were energetically more effective than electrons for depletion and led to a certain dehydrogenation of the HAC samples, whereas electrons, with a smaller penetration depth, led seemingly to a gradual erosion with no appreciable changes in the hydrocarbon structure. The rates of change observed may be relevant over the lifetime of a diffuse cloud, but cannot account for the rapid changes in hydrocarbon IR bands during the evolution of some proto-planetary nebulae.

Glycine samples under the same photon and electron fluxes decay at a much faster rate, but tend usually to an equilibrium value different from zero, especially at low temperatures. Reversible reactions re-forming glycine, or the build-up of less transparent products, could explain this behaviour. CO₂ and methylamine were identified as UV photoproducts. Electron irradiation led to a gradual disappearance of the glycine layers, also with formation of CO₂. No other reaction products were clearly identified. From an energetic point of view, 2 keV electrons are less efficient than UV photons and, according to literature data, much less efficient than MeV protons for the destruction of glycine. The use of keV electrons to simulate effects of cosmic rays on analogues of interstellar grains should be taken with care, due to the low penetration depths of electrons in many samples of interest.

Acknowledgements

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References

- [1] P. A. Gerakines, and R. L. Hudson, Glycine's radiolytic destruction in ices: first in situ laboratory measurements for Mars. *Astrobiology* 13 (2013) 647
- [2] B. Maté, Y. Rodríguez-Lazcano, O. Gálvez, I. Tanarro and R. Escribano. An infrared study of solid glycine in environments of astrophysical relevance. *Phys. Chem. Chem. Phys.* 13 (2011) 12268L.

Electrochemical SERS spectra of isonicotic acid analyzed under a photoinduced charge-transfer mechanism

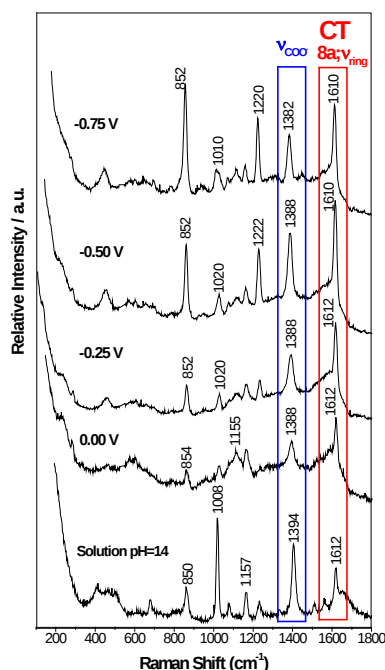
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Isonicotinic (IN) acid is one of the three monocarboxylic derivatives of pyridine in which the acid group is located in para-position of the heterocyclic ring. It is a weak acid ($pK_2=4.86$) and therefore, it is not completely ionized in neutral aqueous solutions, being the zwitterion and the anion the majority chemical species at neutral pH. In acidic solutions ($pK_1=1.84$) the pyridinic nitrogen atom can be protonated yielding a third chemical species with positive charge [1].

In addition, IN acid shows two functional centres that can interact with the silver metallic surface such as the carboxylate group and the aromatic nitrogen atom. Therefore, the analysis of the SERS spectra of IN has been focused on identifying the chemical species adsorbed on the silver surface and its centre of interaction by considering the participation of a photoinduced charge-transfer (CT) mechanism in each particular SERS record as we have previously detected in the SERS of pyridine derivatives [2].

SERS spectra of the IN acid (5×10^{-3} M) have been recorded on silver at electrode potentials ranging from 0.00 up to -1.00 V and at different pH by using 0.1 M Na_2SO_4 aqueous solution as electrolyte. The figure shows the SERS recorded at basic pH. The experimental set up is described elsewhere and the excitation line of 514.5 nm wavelength was used. [2]. The detection of the presence of CT processes, which are similar to resonance Raman, requires to carry out quantum mechanical calculations [2].



A simple Ag_2 -IN model for the surface complex involving two silver atoms with the IN linked through two possible groups to the metal, $\text{Ag}_2\text{-N(IN)}$ and $\text{Ag}_2\text{-O}_2(\text{IN})$, has been taken into account.

Time-dependent density functional theory (TDDFT) has been employed in order to identify the CT states of the studied $[\text{Ag}_2\text{-IN}]$ systems at the M06HF/LanL2DZ level of calculation. After that, the intensities of the theoretical SERS-CT spectra have been calculated by independent mode displaced harmonic oscillator (IMDHO) method.

The results yield that the isonicotinate ion adsorbs on silver at any pH with an almost perpendicular orientation with respect to the metallic surface, given that the carboxylate band is observed in all SERS spectra and only bands assigned to totally symmetric modes are enhanced. The vibrational frequency does not shift in the whole electrode potential range and therefore, a reorientation of the isonicotinate with the electrode potential is discarded.

The calculated SERS-CT spectra predict the enhancement of the 8a:ring stretching band recorded at 1600 cm^{-1} in agreement with the experimental results what demonstrates once again the participation of resonant CT processes in SERS of pyridine derivatives.

Acknowledgements

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References

- [1] S.M. Park, K. Kim, M.S. Kim. "Raman Spectroscopy of Isonicotinic Acid Adsorbed onto Silver Aol Surface" J. Mol. Struct. 328 (1994) 169.
- [2] S.P. Centeno, I. López-Tocón, J. Roman-Perez, J.F. Arenas, J. Soto, J.C. Otero. "Franck-Condon Dominates the Surface-Enhanced Raman Scattering of 3-Methylpyridine: Propensity Rules of the Charge-Transfer Mechanism under Reduced Symmetry" J. Phys. Chem. C 116 (2012) 23639.

Comparison of the luminescent properties of tetrahedral Au(I)-Sn(II) and Au(I)-Ge(II) complexes

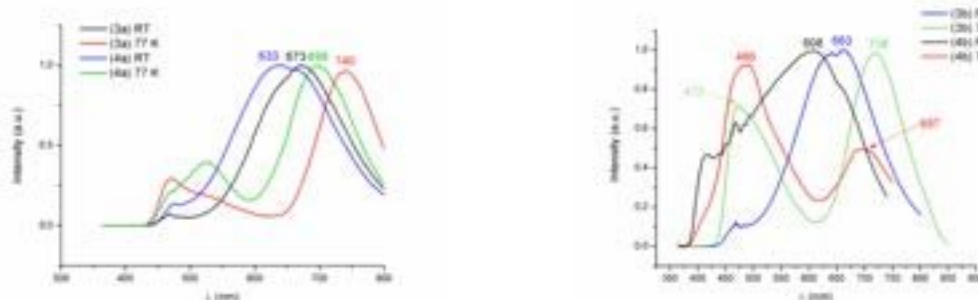
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Compounds with well-defined gold-germanium and gold-tin bonds and their photophysical properties have remained scarcely explored. In fact, there are only a few gold-germanium [1a–b] or gold-tin compounds [2] and only the absorption spectra of $[(PPh_3)_3Au-SnCl_3]$ has been reported [3].

With the main goal of luminescence studies, we have carried out the synthesis of compounds with Au-M (M = Ge (a), Sn (b)) bonds of the general formula $[L_3Au-MCl_3]$ (L = Me_3P (1), Me_2PhP (2), $MePh_2P$ (3) and Ph_3P (4)). While complexes 3a,b and 4a,b show luminescence, 1a,b and 2a,b do not.

This study allows us to compare the influence of both Au(I) and Sn(II) or Ge (II) in their luminescent properties. The combination of the tricoordinated $[Au(PR_3)_3]^+$ fragment and the anionic $[MCl_3]^-$ moiety, both intense phosphors in the 509–535 nm range, produces a new type of phosphorescent red emitters, whose lifetimes are in the microseconds range. In the case of tin a emission band is observed owing to the combination of a first-order excited state Jahn–Teller effect at Au(I) and a second-order Jahn–Teller effect at the $[SnCl_3]^-$ unit [4]. This combination produces a large distortion of the molecule in the T1 state, as observed through correlated ab initio calculations. However, with the germanium two emission bands are observed corresponding to two different triplet excited states leading to a different structural distortion in these excited states.



We have used the theoretical predictions as a guide to examine experimentally whether the luminescence energy can be tuned by varying the steric bulk of phosphines and metals.

For this, we have also carried out with DFT calculations to study the structural distortion for these complexes in the triplet excited state from which the luminescent emission occurs. The study of the electronic structure of the frontier orbitals of the ground state and the first triplet state provides information about the type of electronic transition origin of the optical behavior.

References

- [1] a) A. Bauer, A. Schier, H. Schmidbaur, The Gold-Germanium Bond in Co-ordination Compounds of Type $[(Ph_3P)_nAu-GeCl_3]$ with $n = 1, 2$ or 3 . J. Chem. Soc. Dalton Trans. (1995), 2919; b) J. A. Cabeza, J. M. Fernandez-Colinas, P. Garcia-Alvarez, D. Polo, Diaminogermylene and Diaminostannylene Derivatives of Gold(I): Novel AuM and AuM_2 (M = Ge, Sn) Complexes. Inorg. Chem. 51 (2012), 3896.
- [2] W. Clegg; Bis(dimethylphenylphosphine)trichlorostannio-gold. Acta Cryst. B34 (1978) 278.
- [3] V. Pawlowski, H. Kunkely, A. Vogler, Photoredox decomposition of $[(PR_3)_3Au-SnCl_3]$ induced by metal-to metal charge transfer excitation. J. Inf. Rec. Mats. 21 (1994) 673.
- [4] R. V. Bojan, J. M. Lopez-de-Luzuriaga, M. Monge, M. E. Olmos, R. Echeverria, O. Lehtonen, D. Sundholm, Double Photoinduced Jahn-Teller Distorsion of Tetrahedral Au^I-Sn^{II} Complexes. ChemPlusChem, 79 (2014) 67.

Terpyridine Au(I) and Au(III) organometallic compounds: Redox and photophysical properties.

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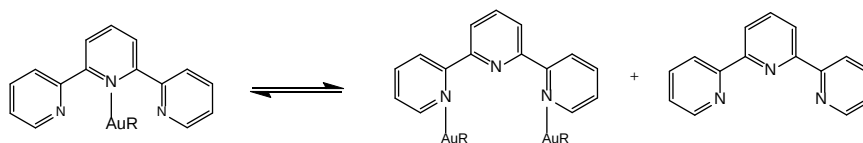
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Aromatic N-donor ligands have been used as one of the more versatile ligands in coordination chemistry. Lately, apart from the intrinsic interest in the structural characteristics of complexes bearing these ligands, recent studies have shown a rich photophysical behaviour in Au(I) and Au(III) complexes containing them.[1] [2]

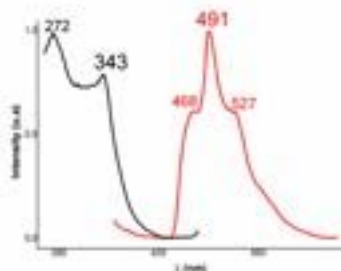
Among the N-donor substrates that can act as ligands towards Au(I) and Au(III) centers without the presence of additional functional groups, terpyridine constitutes a very interesting molecule since it could be used to induce both photophysical and redox properties in both oxidation states for gold and, from a structural point of view examples of mono-, bi- or tridentate terpyridine coordination are known.[3]

In this communication we report the synthesis, spectroscopic characterization and study of the photophysical properties of gold(I) and gold(III) organometallic compounds. The behaviour in solution of these species and the redox interconversion between Au(I) and Au(III) oxidation states has been spectroscopically studied. The interpretation of the photoluminescent properties of this type of complexes is also discussed (see Figure).

Dissociation on solution of complex $[\text{Au}(\text{C}_6\text{F}_5)(\text{terpy})]$ characterized through ^{19}F and ^1H NMR



Excitation and emission spectra of complex $[\text{Au}(\text{C}_6\text{F}_5)(\text{terpy})]$ in solid state at 77K



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References

- [1] E. J. Fernández, A. Laguna, J. M. López-de-Luzuriaga, M. Monge, M. Montiel, M. E. Olmos, J. Pérez, M. Rodríguez-Castillo. Pyridine gold complexes. An emerging class of luminescent materials. *Gold Bulletin*, 40 (2007) 172.
- [2] V. R. Bojan, J. M. López-de-Luzuriaga, E. Manso, M. Monge, M. E. Olmos. Metal-Induced Phosphorescence in (Pentafluorophenyl)gold(III) Complexes. *Organometallics*, 30 (2011) 4486.
- [3] J. E. Aguado, M. J. Calhorda, M. C. Gimeno, A. Laguna. Unprecedented $\eta^3\text{-M}_3$ coordination mode in a terpyridine ligand. *Chemical Communications* (2005) 3355 and references therein.

Self-assembly structures of 2-propil-1H-benzimidazol in solution and solid phases: A vibrational (IR, farIR, Raman and VCD) and computational study

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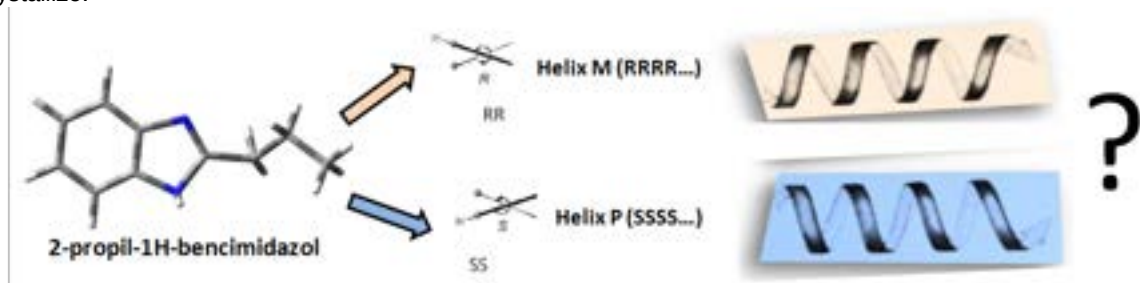
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1H-indazoles are good candidates to study phenomena of molecular association and spontaneous resolution of chiral compounds [1]. Thus, because the 1H-indazoles can crystallize forming dimers, trimers or catemers [2,3], depending on their structure and the phase where they are, the difficulty of the experimental analysis of the structure of the family of 1H-indazoles is clear. This lead to contemplate several questions: How can we determine the presence of different structures of a given molecular species if they change according to the phase? Could these different structures be present in the same phase simultaneously? How can they be determined? In order to shed light on these questions, we outline a very complete strategy by using different techniques of vibrational spectroscopy sensitive (VCD) and not sensitive (IR, FarIR and Raman) to the chirality together with quantum chemical calculations. In particular, in this communication we study the 2-propil-1H-benzimidazol compound (see figure 1) with the use of the methodology explained.

Figure 1. Molecular structure of 2-propil-1H-benzimidazol and the two types of helixes in which its catemers can crystallize.



References

- [1] A. G. Cairns-Smith. Seven Clues to the Origin of Life, Cambridge University Press, Cambridge, UK, 1985.
- [2] J. R. Avilés Moreno, M. M. Quesada Moreno, J. J. López González, R. M. Claramunt, C. López, I. Alkorta, J. Elguero. ChemPhysChem 14 (2013) 3355.
- [3] J. J. López González, F. Partal Ureña, J. R. Avilés Moreno, I. Mata, E. Molins, R. M. Claramunt, C. López, I. Alkorta, J. Elguero. New J Chem 36 (2012) 749.

When sugars do not seem sugars, where is the carbonyl?

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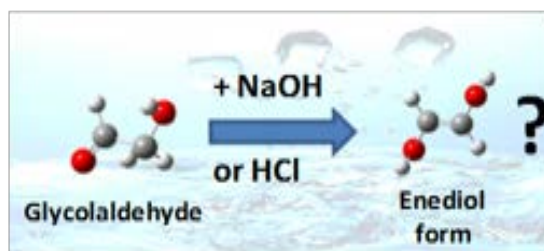
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Carbohydrates of general formula $C_nH_{2n}O_n$ with $n \geq 2$ are the most abundant organic compounds on earth by mass, with a string of relevant functions as energy storage, metabolic intermediates and structural building blocks [1].

The biochemically important interconversion of aldoses and ketoses is presumed to take place via 1,2-enediol or 1,2-enediolate intermediates, but such intermediates have never been isolated as stable entities [2]. In particular, glycolaldehyde (hydroxyacetaldehyde) exists in equilibrium with its enediol form in acid and alkaline media (see figure 1) [3]. The current work was undertaken in an attempt to detect the presence of the 1,2-enediol structure of the glycolaldehyde molecule. To reach this goal, we added different amounts of NaOH and HCl to fresh prepared water solutions of glycolaldehyde. The Raman spectra of these solutions were recorded according to the time for four days. Surprisingly, the bands that could be associated with the presence of the enediol species were changing, namely, the bands associated with the C=O str., C=C str., CH₂ sciss. and HCO bend. vibrational modes.

In addition, all the experimental spectra were analyzed with the help of quantum chemical calculations. Explicit molecules of water were taken into account to study the behaviour of the glycolaldehyde in water solution. Besides, theoretical studies using NaOH and HCl as catalysts were carried out. DFT and *ab initio* calculations were performed to simulate the catalysis and to get accurate structures and relative energies.

Figure 1. Molecular structures of the glycolaldehyde and its enediol form.



References

- [1] M. M. Quesada-Moreno, L. M. Azofra, J. R. Avilés-Moreno, I. Alkorta, J. Elguero, J. J. López-González. Conformational preference and chiroptical response of Carbohydrates D-Ribose and 2-Deoxy-D-ribose in aqueous and solid phases. *J Chem Phys B* 117 (2013) 14599.
- [2] S. J. Eitelman, D. Horton. Studies on enolization of aldehydo-aldose derivatives. *Carbohydr Res* 341 (2006) 2658.
- [3] M. Fedoroňko, P. Temkovic, J. Königstein, V. Kováčik, I. Tvaroška. Study of the kinetics and mechanism of the acid-base-catalyzed enolization of hydroxyacetaldehyde and methoxyacetaldehyde. *Carbohydr Res* 87 (1980) 35.

Molecular properties of zwitterionic, protonated and deprotonated forms of L-valine by vibrational spectroscopy (IR, Raman, VCD) and quantum chemical calculations

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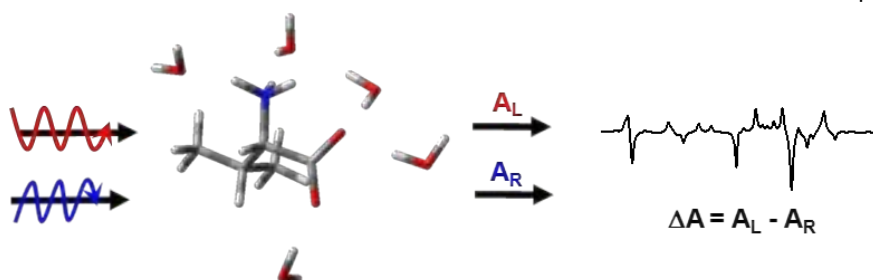
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The structure of the aliphatic amino acids, the building blocks of the proteins, has caused a growing interest since some years ago [1]. They have been analysed by means of many different techniques in order to get relevant information about their structures and their biological functions. The study of their behaviour in water is of major interest, because it is the natural medium for biological molecules [2,3].

In this work, the behaviour in water at different pH of *L*-valine has been analysed both experimentally and theoretically. The studied pH values were: 6.00 (zwitterionic species, see figure 1), 1.00 (protonated species) and 13.00 (deprotonated species). We carried out a vibrational study using non-chiroptical techniques (IR-Raman) and chiroptical techniques (VCD) complemented with quantum chemical calculations. Our strategy was dual: i) The performance of hybrid density functionals, B3LYP and M062X, and the *ab initio* MP2 method, with the same 6-311++G(d,p) basis set, in order to characterize the relative energies and structures of an extensive set of conformers of *L*-valine. On the one hand, the presence of water was included with the IEF-PCM implicit solvation model at the levels of theory mentioned previously. On the other hand, explicit and implicit solvation models were performed at the same time at the M062X/6-311++G(d,p) level of theory. ii) The analysis of vibrational spectroscopy experiments has been accomplished with both sensitive techniques to chirality (VCD) and non sensitive ones (IR, including MIR and FIR, and Raman), especially in aqueous solution. The comparison between theory and experiment is reasonable, which allows us to conclude the presence of the most stable set of conformers according to the pH. Moreover, for the first time, the chiroptical response of *L*-valine has been studied in aqueous solution. Finally, the analysis of low frequency region with the IR and Raman techniques has been very important in order to understand the conformational preference of zwitterionic species.

Figure 1. Molecular structure of the most stable zwitterion of *L*-valine and its theoretical VCD spectra.



References

- [1] J. Sadlej, J. Cz. Dobrowolski, J. E. Rode, M. H. Jamróz. Density Functional Theory Study on Vibrational Circular Dichroism as a Tool for Analysis of Intermolecular Systems: (1:1) Cysteine–Water Complex Conformations. *J Phys Chem A* 111 (2007) 10703.
- [2] L. Stryer, J. M. Berg, J. L. Tymoczko. *Bioquímica*, 5th ed., Reverté, 2003.
- [3] G. E. Schulz, R. H. Schirmer. *Principles of Protein Structure*, Springer-Verlag, New York, 1990.

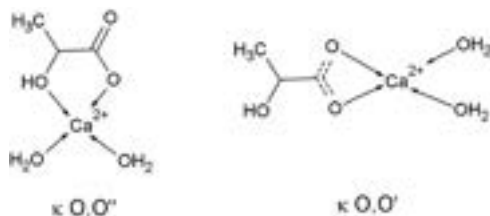
Insights into the structure / vibrational spectra relationship of the system $[\text{Ca}(\text{I-Lac})(\text{H}_2\text{O})_2]^+$ from DFT, NBO and QTAIM

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α -Hydroxycarboxylic acids are ubiquitous in nature, playing a key role in many biological processes, as Krebs (citrate, isocitrate and malate) and Cori (lactate) cycles and in the active transport of metals across cell membranes. For example, Ca^{2+} cation is transported complexed with citrate anion by *Bacillus subtilis*, *Enterococcus faecalis*, *Streptomyces coelicolor*, *Pseudomonas fluorescens* and *Corynebacterium glutamicum*. On the other hand, they and their derivatives are widely used in pharmacy, cosmetics, production of food and other general chemical fields. In addition, small anions of them are able to behave as more complex natural ligands [1]. However, the coordination chemistry of such complexes are relatively poorly understood [2,3].

In the present work, we study as a model the $[\text{Ca}(\text{I-Lac})(\text{H}_2\text{O})_2]^+$ complex (with coordination number fixed at 4 [4,5] and two coordination patterns, see figure).



A thorough analysis of the conformational landscape is carried out at DFT level [6]. A previous conformational analysis is done at the MM level. In order to test the influence of the functional in the number and molecular structure of predicted conformers, all the obtained conformers were optimized using two well-known global-hybrid GGA (B3LYP and B3PW91), two global-hybrid

meta-GGA (M06 and M06-2X) and three long-range corrected hybrid (ω B97, ω B97X and ω B97X-D) ones. In all cases, the basis set chosen was the LACVP+** (LANL2DZ ECP for Ca plus 6-31+G(d,p) for the rest of elements) [7]. Those calculations were carried out using Spartan08 [8].

In order to test the influence of taking into account solvent effects in predicted structures and vibrational spectra, conformers from B3LYP, M06-2X and ω B97X-D were newly optimized with the 6-311++G(2d,2p) basis set and IEF-PCM, C-PCM and SMD solvent continuum models. Gaussian09 software [10] was used for this task. The characterization of the different bonding types in the complexes is carried out applying NBO analysis [10] and QTAIM [11]. NPA charges are used to study the metal-ligand charge transfer.

Acknowledgements

University of Jaén for financial and technical supports. Junta de Andalucía for financial support.

References

- [1] E. Bermejo, R. Carballo, A. Castiñeiras, A. B. Lago, Coord. Chem. Rev. 257 (19-20) (2013) 2639.
- [2] J. J. Lensbouer, R. P. Doyle, Critical Rev. Biochem. Mol. Biol., 45 (5) (2010) 453.
- [3] B. Huta, J. J. Lensbouer, A. J. Lowe, J. Zubieta, R. P. Doyle, Inorg. Chim. Acta 393 (2012) 125.
- [4] L. Rulíšek, J. Vondrášek, J. Inorg. Biochem. 71 (1998) 115.
- [5] M. Dudev, J. Wang, T. Dudev, C. Lim, J. Phys. Chem. B 110 (2006) 1889.
- [6] C. J. Cramer, D. G. Truhlar, Phys. Chem. Chem. Phys. 11 (2009) 10757.
- [7] Y. Yang, M. N. Weaver, K. M. Merz, Jr., J. Phys. Chem. A 113 (2009) 9843.
- [8] Spartan08 for Windows, Macintosh and Linux. Wavefunction, Inc., Irvine, CA USA.
- [9] Gaussian 09, Frisch M. J. et al., Gaussian, Inc., Wallingford CT, 2009.
- [10] F. Weinhold, C. L. Landis Discovering Chemistry with Natural Bond Orbitals, Wiley, Hoboken, New Jersey, 2012.
- [11] R. W. Bader Atoms in Molecules. A Quantum Theory, Oxford University Press, Oxford UK, 1990 (Reprinted 2003).

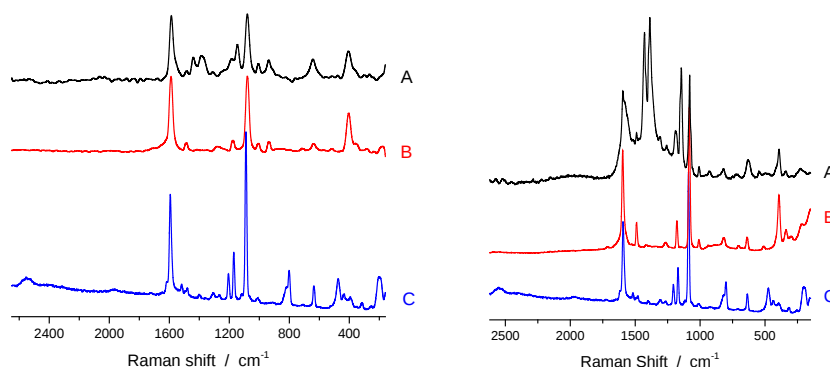
SERS of 4-aminothiophenol (4-ATP) adsorbed on Ag and Pt nanoparticles: Photochemical transformation or chemical enhancement?

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SAMs based on aromatic thiols have been vastly studied. Amino thiophenols (ATPs) are frequently studied as SERS probe molecules and particularly the 4-ATP (is often used as molecular junction and building block in SAMs). The formation of organic monolayers by self-assembly is directed by a specific interaction between a terminal functional group and the surface, in this case the bond formed between the thiol sulphur and the metal. A huge amount of work has been reported about the 4-ATP adsorbed on Ag and Au due to same specific behaviour under certain experimental circumstances. The SERS spectra from the self-assembled monolayer of 4-ATP on Ag and Au are significantly different from the normal Raman spectrum of the molecule in the solid state. In normal Raman spectrum only bands that correspond to completely symmetric a_1 vibrations are observed, but in its SERS spectrum, non- a_1 -type bands are also present (1142, 1390 and 1432 cm^{-1}). However, The SERS from thiophenol on these metals are substantially the same as the normal Raman spectrum. It was first speculated [1, 2] that the alteration of the spectrum of 4-ATP can be due to the contribution of the CT mechanism of enhancement, as a consequence of the alteration of electronic states of thiophenol by the introduction of an NH_2 group on the benzene ring. Alternatively, it is shown, based on the spectral similarity of 4-ATP and 4,4'-DMAB (4,4'-Dimercaptoazobenzene), that the non- a_1 -type bands correspond to N=N stretching vibrations of 4,4'-DMAB produced from 4-ATP via a catalytic coupling reaction [3]. In our knowledge no studies have been done with Pt-group metals that are generally accepted to be weak electromagnetic enhancing metals under conditions of visible wavelength excitation unlike silver, so we report in this work a comparative SERS spectroscopy study using silver and platinum nanoparticles.



SERS spectra of a self-assembled monolayer of 4-ATP on Pt and Ag nanoparticles at (A) -0.5 V and (B) -0.9 V vs AgCl/Ag (test solution 0.1 M NaClO_4 + 10^{-3} M 4-ATP) and (C) normal Raman spectrum of the solid 4-ATP.

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References

- [1] M. Osawa, N. Matsuda, K. Yoshii, I. Uchida, J. Phys. Chem. 98 (1994) 12702
- [2] K. Kim, K.L. Kim, K.S. Shin, J. Phys. Chem. C 117 (2013) 5975
- [3] Y.F. Huang, H.P. Zhu, G.K. Liu, D.Y. Wu, B. Ren, Z.Q. Tian, J. Am. Chem. Soc. 132 (2010) 9244

Detailed laboratory and DFT calculated far and mid-IR spectroscopy of phyllosilicates

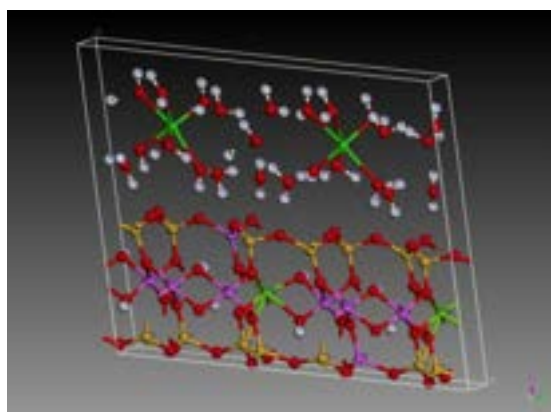
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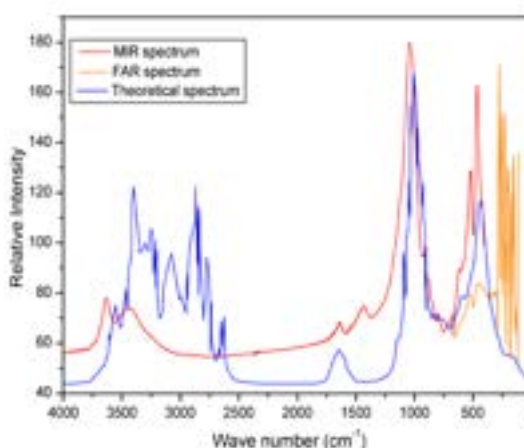
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The spectra of hydrated and non-hydrated common phyllosilicates is studied in the mid- and far-IR regions, and by quantum-chemical calculations based on density-functional theory (DFT). Most of the natural phyllosilicate samples were obtained from the Iberian Peninsula. Samples were prepared as KBr pellets for the mid-IR and deposited on an Al substrate for the far-IR. Spectra were recorded at room temperature with a Vertex70 Bruker FTIR with MCT detector with spectral resolution of 4.0 cm^{-1} . DFT calculations for bulk geometry optimization and infrared spectra were carried out using the CASTEP code [1] implemented in Materials Studio 7.1. The Fig. 1a) shows the theoretical model for bentonite (Ca/Na montmorillonite) that fits the experimental lattice parameters and atomic arrangement taken from XRD data [2]. Similar agreement is found for the other phyllosilicates under study, namely Biotite, Bentonite, Talc, Kaolinite, Smectite and Palygorskite.

The theoretically calculated IR spectra at 0 GPa of pressure clarify the wide peaks and uncertainties of the experimental spectra of the different phyllosilicates with special emphasis in the far-IR region. The comparison between theoretical and experimental spectra for bentonite is shown in Fig1.b. The calculated frequencies agree reasonably well with the measurements. The calculation results show the animation of the displacement of every atom for each vibrational mode in the unit cell.



a) Optimized unit cell



b) Mid and Far-IR Spectrum

Fig 1. Double hydrated Bentonite (Ca/Na montmorillonite) atomic optimized structure (left) and IR (experimental and theoretical) IR spectrum (right) of a bentonite from Colorado (USA).

Acknowledgements

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References

- [1] S. J., Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M.J. Probert, K. Refson, M.C. Payne, First principles methods using CASTEP. *Zeitschrift für Kristallographie* 220, 567-570.
- [2] Viani A , Gualtieri A , Artioli G , 2002, The nature of disorder in montmorillonite by simulation of X-ray powder patterns, *Note: Structural simulation model, American Mineralogist* , 87, 966-975.

Combining FTIR, Raman and INS for a full vibrational assignment of $[\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3]^{2+}$

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Although polyamine crystals were found in human seminal liquid by Leeuwenhoek about 300 hundred years ago, only very recently has the biological importance of these compounds been acknowledged. In fact, 1,2-diaminoethane ($\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_2$) and 1,3-diaminopropane ($\text{H}_2\text{N}(\text{CH}_2)_3\text{NH}_2$), as well as 1,4-diaminobutane (putrescine, $\text{H}_2\text{N}(\text{CH}_2)_4\text{NH}_2$), are precursors of the biogenic tri- and tetramines: spermidine ($\text{H}_2\text{N}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_4\text{NH}_2$) and spermine ($\text{H}_2\text{N}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_4\text{NH}(\text{CH}_2)_3\text{NH}_2$), that play key physiological functions. Changes in their biological levels produce modifications in cellular proliferation and differentiation, in DNA replication and also in the proliferation of healthy and neoplastic cells [1]. Up to this date, several studies have reported different biological functions for 1,3-diaminopropane, namely: regulator of ornithine decarboxylase (ODC) activity [2], protein aggregation suppressor [3], and carcinogen biomarker [4]. However, the exact nature of the mechanisms involved, at a molecular level, is still unknown, which highlights the relevance of gathering detailed structural information on this compound, in order to understand its paramount biochemical role. Actually, few structural and spectroscopic studies have been performed for this system and even these are limited to narrow regions of the vibrational spectra [5-7]. Moreover, at physiological conditions biogenic amines exist as polycations, i.e., in their full protonated form, which renders the study of their ammonium salts of the utmost importance.

This communication reports a combined experimental and theoretical study of $[\text{H}_3\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}_3]^{2+}$, in the solid state. A complete assignment was carried out, using all the vibrational spectroscopy techniques: FTIR, Raman and Inelastic Neutron Scattering (INS), for both the hydrogenated and the N-deuterated samples.

DFT simulations of the corresponding vibrational pattern, using the mPW1PW functional and the 6-31G* basis set functions, were performed and compared with the experimental data.

Acknowledgements

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References

- [1] H.M. Wallace, A.V. Fraser, A. Hughes, *Biochem. J.* 376 (2003) 1-14.
- [2] E.I. Salim, H. Wanibuchi, K. Morimura, S. Kim, Y. Yano, S. Yamamoto, S. Fukushima, *Carcinogenesis* 21 (2000) 195-203.
- [3] M. Okanojo, K. Shiraki, M. Kudou, S. Nishikori, M. Takagi, *J. Biosc. Bioeng.* 100 (2005), 556-561
- [4] M. Y. Khuhawar, G. A. Qureshi, *J. Chromatogr. B* 764 (2001) 385-407.
- [5] M.P.M. Marques, L.A.E. Batista de Carvalho, and J. Tomkinson, *J.Phys.Chem.* 106 (2002) 2473.
- [6] A.M. Amorim da Costa, M.P.M. Marques, L.A.E. Batista de Carvalho, *Vib.Spectrosc.* 35 (2004) 165.
- [7] L.A.E. Batista de Carvalho, M.P.M. Marques, J. Tomkinson, *J.Phys.Chem.* 110 (2006) 12947.

Conformational preference and spectroscopic properties of tobacco alkaloids: (-)-S-nicotine, (-)-S-cotinine and (+)-R-anabasine. Theoretical calculations and experimental insights

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(-)-S-nicotine is the main alkaloid present in tobacco leaves (~90%), and it is its main psychoactive ingredient responsible for producing strong tobacco smoking addiction (one of the most widespread causes of premature death, among other diseases). [1] Moreover, nicotine has been proved to act as a potent agonist of the nicotinic acetylcholine receptor (nAChR) and have been identified as therapeutic target for the treatment of numerous illnesses including Parkinson, Tourette's syndrome, anxiety, cognitive and attention deficits and smoke addiction. [2] One of the lesser alkaloid in tobacco leaves: anabasine (~0.5%), is also relevant due to the fact that N-H compounds are generally rather more active than N-methyl ones (e.g. anabasine is ten times more active than nicotine). [3] Furthermore, the minor alkaloidal tobacco constituent: (-)-S-cotinine, has been shown to be the most abundant (-)-S-nicotine metabolite after administration of nicotine and has a much longer half-life. [4] For these reasons, we thought that a deep understanding of molecular, electronic structure, and conformational preference of these systems and related compounds, is undoubtedly essential to elucidate the structure and function of receptors and for the subsequent design of new drugs.

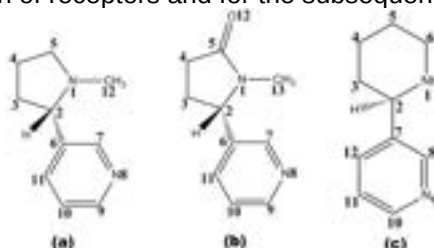


Figure 1. Molecular structure of (a) (-)-S-nicotine, (b) (-)-S-cotinine and (c) (+)-R-anabasine molecules.

Here we present a thorough analysis of the conformational landscape (using MM and DFT calculations) of the mentioned chiral tobacco alkaloids and a comprehensive study of their molecular structure in gas-phase and in solution. For the theoretical modeling of the systems studied, two hybrid DFT functionals have been used, namely the widespread B3LYP and the so-called B3PW91, in conjunction with the 6-311++G** and aug-cc-pVTZ basis sets. The conformational preference of energetically reachable conformers has been justified by means of the analysis of their electronic structures according to the NBO methodology.

Experimental data from vibrational spectroscopy techniques, both sensitive (i.e. vibrational circular dichroism, VCD) and non-sensitive to chirality (IR and Raman) have been used to validate the theoretical models.

References

- [1] M. Saponi, Neuronal Nicotinic Receptors, in: S. P. Arneric, J. D. Brionic, (Eds) Pharmacology and Therapeutic Opportunities, Wiley-Liss, New York, 1998.
- [2] a) A. W. Bannon *et al.* Broad-spectrum, non-opioid analgesic activity by selective modulation of neuronal nicotinic acetylcholine receptors. *Science*, 279 (1998) 77; b) R. M. Elgen, J. C. Hunter, A. Dray. Ions in the fire: recent ion-channel research and approaches to pain therapy. *Trends. Pharm. Sci.* 20 (1999) 337.
- [3] S. B. Soloway. Naturally occurring insecticides. *Env. Health Perspect.* 14 (1976) 109.
- [4] a) P. A. Crooks, L. P. Dwoskin. Contribution of CNS nicotine metabolites to the neuropharmacological effects of nicotine and tobacco smoking *Biochem Pharmacol* 54 (1997) 743; b) P. A. Crooks, M. Li, L. P. Dwoskin. Metabolites of nicotine in rat brain after peripheral nicotine administration. Cotinine, norcotinine, and norcotinine. *Drug Metab Dispos* 25 (1997) 47.

Assessment of the occurrence of anomeric effect and its associated VCD spectroscopic features: A case of study

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One of the main principles of the conformational analysis states that the substituents in a cyclohexane ring tend to adopt equatorial rather than axial positions, mainly due to steric reasons. [1] Nevertheless, it has been observed that polar groups with lone electron pairs (such as -OMe, -OAc, -Cl, etc.) in six-membered heterocycles show a preference to adopt the axial position, being this phenomenon known as anomeric effect. According to the electrostatic theory, this tendency is the result of destabilizing interactions between the dipole moments of the bonds adjacent to the endocyclic heteroatom (or anomeric center, atom Y in the figure below). This dipole-dipole interaction is attenuated when the polar substituents adopt axial disposition. On the other hand, the hyperconjugative model propose that the stabilization of the axial conformers is due to the stabilizing electronic delocalization established between the antiperiplanar lone pair orbital on the endocyclic heteroatom (Y) and the σ^* antibonding orbital of the C-X bond.



Figure 1. Schematic representation of dipole-dipole interactions of polar bonds in a hypothetical substituted heterocyclic compound. *Axial/equatorial* conformational preference.

The molecule (2R,3R,5R,6R)-5,6-dimethoxy-5,6-dimethyl-1,4-dioxane-2,3-dicarboxylate is an excellent paradigm to study the mentioned effect, since the carbon atoms adjacent to the endocyclic oxygen atoms are substituted by -OMe groups. All the possible molecular conformations for this system can be distributed in four general groups, depending on the orientation of the ring side groups, namely: all axial, all equatorial, MeO axial/ COOMe equatorial, and MeO equatorial/ COOMe axial, whose stability order (hence their populations) will be controlled mainly by the anomeric effect (among other steric or electrostatic effects).

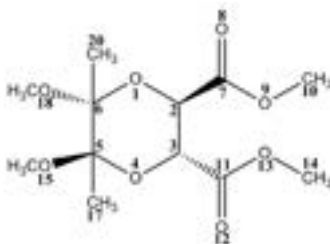


Figure2. Molecular structure (2R,3R,5R,6R)-5,6-dimethoxy-5,6-dimethyl-1,4-dioxane-2,3-dicarboxylate molecule.

In this work a thorough conformational analysis of the system has been performed by means of MM (MMFF and SYBYL force fields) and DFT calculations (B3LYP and M062X). The relative stabilities of the energetically accessible conformers have been justified in terms of their electronic structure using the NBO methodology, which explain the stability of axial structures instead of equatorial in gas phase. The effect of increasing solvent polarity over the conformational mixture composition in solution has also been assessed using IEF-PCM calculations. IR, Raman and Vibrational Circular Dichroism (VCD) spectral features observed confirmed the theoretical results, i.e., the so-called anomeric-favored conformers are more populated in few polar or non-polar media.

References

[1] D. G. Gorenstein. Stereoelectronic effects in biomolecules. Chem. Rev. 87 (1987) 1047.

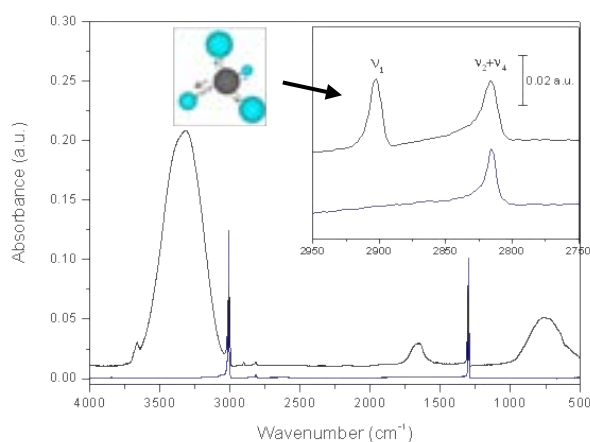
Infrared activation of the breathing mode of methane

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The so-called breathing mode of methane consists in an in-phase stretching and shrinking of all four C-H bonds of this molecule. Because of its tetrahedral structure, the C atom and the charge distribution remain undisturbed during the vibration, and no net dipole moment is generated. Thus, as is well known, this vibrational mode is inactive in the infrared spectrum, although it is a very strong feature in the Raman. In gas-phase methane or in a pure methane solid, this vibration is not seen in the IR spectra. However, in low-temperature methane/water mixtures, like those generated to model astrophysical ices, a small but distinguishable feature has been observed in IR spectra, at the expected frequency of this vibration. Hodyss et al [1] were the first to report this observation, which was subsequently confirmed by Gálvez et al [2] (see figure). Although weak in general terms, the strength of this anomalous band could be large enough to allow detection in astrophysical or atmospheric field observations, thus providing a direct evidence of the presence of a form of methane in direct interaction with water.

The IR inactivity of the breathing mode of methane is one of the firm foundations of vibrational spectroscopy. The striking breakdown of this postulation justifies the study of this effect. A possible way to tackle this problem is to construct theoretical models that mimic experimental samples and find out if, and when, this activation is predicted. We will present in this communication our results for a number of quantum chemical models for methane/water mixtures. The results turn out to be diverse, ranging from no activation at all to the prediction of some very strong features in specific cases.



We have carried out theoretical calculations using several modules of the Materials Studio package, namely Amorphous Cell, Adsorption Locator, and CASTEP. These allow building models for amorphous solids for specific values of density and temperature, and performing geometry optimization and prediction of vibrational spectra of these systems. We have considered two amorphous water (ASW) models, of densities 0.7 g cm⁻³, to simulate low-density ASW, and of 0.94 g cm⁻³, for more compact water solids. Methane molecules were introduced into these amorphous structures looking for stable samples at 30 K. The CH₄/H₂O ratio varied between 1/20 and 1/8. Density Functional Theory (DFT) was applied

with GGA-RPBE functionals.

Acknowledgements

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References

- [1] R. Hodyss et al. Photochemistry of methane-water ices, *Icarus*, 200 (2009) 338.
- [2] O. Gálvez et al. Spectroscopic effects in CH₄/H₂O ices, *Astrophys. J.*, (2009) 703:2101.

Excited state proton transfer reactions of anti-tumor agents in cyclodextrin nanocavities

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In the search of new therapeutic agents for treatment of cancer, proteins involved in the cell growth and division cycle are increasingly important [1]. Camptothecin (CPT) is a potent anti-tumour agent due to its ability to inhibit topoisomerase I, but it presents the handicap of its chemical stability. Luotonin A (LA) behaves as a selective topoisomerase inhibitor, however it shows better chemical and toxicological features than camptothecin. CPT and LA present a notable native fluorescence and exhibit peculiar acid-base properties in excited state [2]. Natural and chemically modified cyclodextrins (CDs), are valuable nanocarriers for controlling the release rate of drugs and thus enhance their bioavailability and therapeutic efficiency [3]. With the aim to enhance their bioavailability, the complexes of CPT and LA with beta-CD and HP-beta-CD were synthesized and characterized.

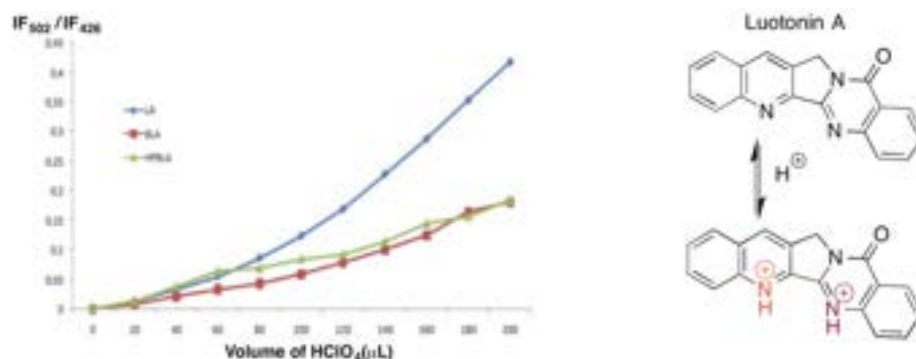


Figure 1: Titration curves obtained for free luotonin A and their inclusion complexes. Protonation reaction of luotonin A

Proton transfer reactions of free drug and their inclusion complexes were used initially as models to study the protection of CPT LA in CD cavities. The titration of aqueous solutions of free drugs with HClO_4 causes the protonation of the basic nitrogens on CPT and LA, but in the case of the inclusion complexes, the volume of HClO_4 required for the protonation of both molecules was significantly higher, and it is not possible to shift the acid-base equilibria to the protonated forms. These observations show that the complexation not only increases the hydro-solubility of LA and CPT, but also protects the guest molecules. In the case of CPT this result is particularly relevant because the formation of the inclusion complexes increases its stability. Thus in the case of aqueous alkaline solutions of CPT, the lactone moiety is easily opened to the corresponding carboxylate form, while in the case of the inclusion complexes, this undesirable reaction is diminished. The behaviour is discussed in connection with the nature of the CD and the geometry of the complexes.

Acknowledgements

Financial Support from Universidad Complutense de Madrid for GR35/10-A-920234.

References

- [1] C. Avendaño, J.C. Menéndez, Medicinal Chemistry of Anticancer Drugs, 1st ed., Elsevier, Amsterdam, 2008.
- [2] V. González-Ruiz, Y. González-Cuevas, S. Arunachalam, M. A. Martín, A. I. Olives, P. Ribelles, M. T. Ramos, J. C. Menéndez, Fluorescence Properties of the Anti-tumour Alkaloid Luotonin A and New Synthetic Analogues: pH Modulation as an Approach to their Fluorimetric Quantitation in Biological Samples, J. Lumines. 132 (2012) 2468.
- [3] K. Uekama, F. Hirayama, Improvement of Drug Properties by Cyclodextrins, in C. G. Wermuth (Ed.), The Practice of Medicinal Chemistry. Academic Press, New York, 2011, pp. 813-840.

Different solvent-induced luminescent responses in Pt₂Pb clusters

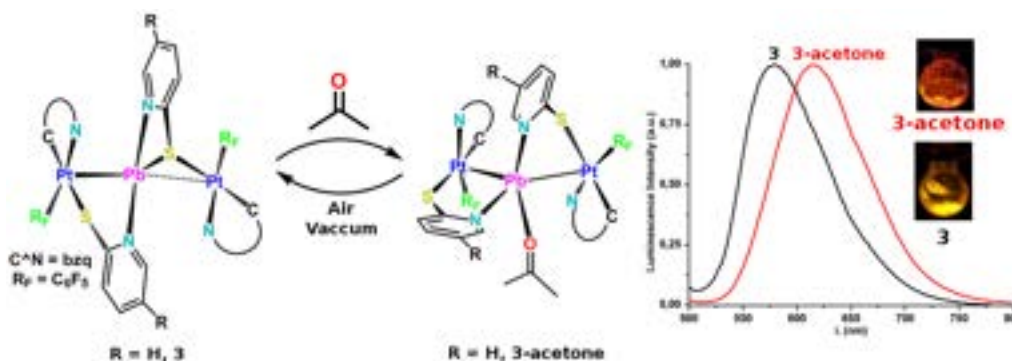
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Controlling the photoluminescence properties of luminescent materials based on transition-metal complexes by external stimuli is currently attracting widespread interest due to their possibilities to obtain photofunctional materials. Among various luminescence and colour changes in response to external stimuli, vapochromism, vapoluminescence, mechanochromism and thermochromism occur in some solid-state materials based on various metal coordination compounds [1,2]. External stimuli cause variations in metallophilic contacts, $\pi\cdots\pi$ stacking or H-bonding interactions, although for some polymetallic systems, metal-ligand coordination/decoordination has also demonstrated.

Following our interest on luminescent materials based on different attractive interactions between Pt^{II} fragments and the borderline closed-shell Pb²⁺ ion [3,4], we report here a series of new luminescent trinuclear Pt₂Pb clusters $[\{Pt(C_6F_5)(C^N)\}_2Pb(SpyR-5)_2]$ [C^N = benzoquinolyl (bzq), phenylpyridyl (ppy); R = H **3**, **5**; CF₃ **4**, **6**] and different solvate forms obtained under different crystallization conditions. These clusters and their solvates have been characterized by spectroscopic, X-ray crystallography and luminescence studies. Benzoquinolyl complexes **3** and **4** display selective vapoluminescent properties (and also vapochromic properties in **4**) to vapours of several donor solvents (see Figure). Phenylpyridinyl derivatives **5** and **6** do not show vapoluminescent response, but **6** shows different emissions after treatment with different solvents. Interestingly, complex **6** exhibits reversible and naked-eye perceivable mechanical stimuli-responsive colour and luminescence changes. In these clusters, vapour- and mechanical grinding-triggered colour and luminescence switches are most likely correlated to the versatility of the coordination of the Pb^{II} centre, modified by $\pi\cdots\pi$ stacking interactions.



Acknowledgements

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References

- [1] X. Zhang, B. Li, Z. H. Chen, Z. N. Chen. Luminescence vapochromism in solid materials based on metal complexes for detection of volatile organic compounds (VOCs). *J. Mater. Chem.* 22 (2012) 11427. Initial.
- [2] X. Zhang, Z. Chi, Y. Zhang, S. Liu, J. Xu, Recent avances in mechanochromic luminescent metal complexes. *J. Mater. Chem. C* 1 (2013) 3376.
- [3] J. R. Berenguer, J. Fernández, B. Gil, E. Lalinde, S. Sánchez. Reversible binding of solvent to naked Pb^{II} centers in unusual homoleptic alkynyl-based Pt₂Pb₂ clusters. *Chem. Eur. J.* 20 (2014) 2574.

Characterization of supramolecular complexes formed between non-steroidal anti-inflammatory drugs and cucurbit[n]urils in solution and adsorbed on silver nanoparticles

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Design of new drug delivery systems is, nowadays, one of the most important topics in research fields. It is necessary that medicine molecules arrive to disease tissues like "magic bullets" without interacting with healthy cells thus optimizing their effectiveness and avoiding secondary effects that are to a large extent undesirable. Nanomedicine has revealed a very useful tool to achieve these goals. In this sense formation of drug complexes with host molecules can serve as vehicle to transport molecules directly or to include in multi-step drug delivery systems.

Cyclodextrins and calixarenes are synthetic receptors able to form inclusion complexes but they present several disadvantages associated to their low solubility except on strongly acid water solutions and the difficulty to introduce any functional group. As an alternative in supramolecular chemistry, cucurbiturils constitutes a new family of molecules with important characteristics to develop [1]. They have a highly symmetrical and rigid structure with two identical openings and possess a hydrophobic defined internal cavity hindered by carbonyl groups which line two rims able to host cationic forms.

In this work we present the characterization of several complexes formed by cucurbiturils and the non-steroidal anti-inflammatory drugs (NSAIDs) piroxicam (PX), indomethacin (IM) and ketorolac (KT). All the three molecules present an acid-base equilibrium and while PX and IM are poorly soluble in water KT exhibit high solubility. None of these extremes are desirable for the release of the drug. In the case of PX and IM complexation increases the solubility and in the case of KT transportation into the host molecule avoids the loss of effectiveness caused by its binding to other molecules found in their way to disease tissues. Our results show that PX and IM form complexes with cucurbit[8]uril while KT does it with cucurbit[7]uril. We have used the corresponding adequate spectroscopic techniques for every case: UV to obtain the Job's plot; ¹H NMR, and fluorescence lifetime to detect the presence of complexes and steady-state fluorescence to obtain the binding constant.

Complexes have been studied also in silver colloids, using our previous experience on pure drugs [2], with the purpose of design more complicate systems able to include recognition molecules and to use the properties of localized surface plasmon resonances obtaining enhanced spectroscopies, SERS and SEF.

These studies provide preliminary results necessary to use these complexes in biotechnology and biomedicine.

Acknowledgements

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References

- [1] J. Lee, S. Samal, N. Selvapalam, H.-J. Kim, AND K. Kim, Acc. Chem. Res. Cucurbituril Homologues and Derivatives: New Opportunities in Supramolecular Chemistry, 36 (2003) 621.
- [2] P. Sevilla, M. Hernández, E. Corda, J.V. Garcia-Ramos, C. Domingo, Opt. Pura Apl., Molecular characterization of drug's nanocarriers based on Plasmon-Enhanced spectroscopy: Fluorescence (SEF) and Raman (SERS), 46 (2013) 111.

Determination of silver content in polymeric and inorganic nanomaterials by microwave-assisted digestion followed by flame atomic absorption spectroscopy

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Silver nanoparticles (Ag NPs) constitute one of the most important inorganic materials in the quest for antimicrobial agents used against multi-drug resistant bacteria. An increasing number of studies in this field has been reported in the last years, specially focused on the synthetic design of new forms of silver nanomaterials and the study of their antimicrobial activity. These include *hybrid inorganic* silver nanomaterials in which the nanoparticles are supported or embedded in inorganic substrates such as TiO_2 , hydroxyapatite, SiO_2 , ZnO , Fe_3O_4 , etc. or *hybrid organic* substrates such as hydrogels, organic polymers or copolymers, etc.[1]

One of the key factors in the design of the new nanomaterials is the control of the silver content in the substrate of choice. Thus, the development of new methods for the determination of silver content and, therefore, its direct relationship with the bacteriostatic or bactericidal effect exerted by the nanomaterial, is a field of research of increasing interest.

In this communication, a method based on microwave-assisted digestion and flame atomic absorption spectroscopy to determine the total silver content in nanomaterials is presented. We have chosen several types of nanomaterials synthesized in our group for the determination of their silver content including polymer coated silver nanoparticles or aluminosilicate-based silver nanomaterials (see Figure) [2,3]

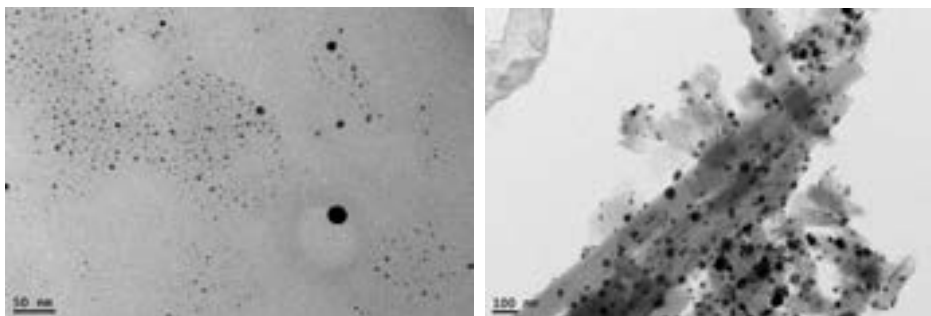


Figure 1. Transmission Electron Microscopy micrographs of polyvinylpyrrolidone-coated Ag NPs (left) and Ag NPs grafted at the surface of aluminosilicate nanotubes (right).

The variables affecting the microwave-assisted digestion process, such as, solvent mixture, temperature and time were studied for the different types of substrates bonding AgNPs, by both univariate and experimental design approaches. Once the digestion conditions were optimised, the method was characterised in terms of sensitivity, accuracy and precision. Finally, the content of silver in different nanomaterials was determined.

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References

- [1] J. García-Barrasa, J. M. López-de-Luzuriaga, M. Monge. Silver nanoparticles: synthesis through chemical methods in solution and biomedical applications. *Cent. Eur. J. Chem.* 9 (2011) 7.
- [2] J. Crespo, J. García-Barrasa, J. M. López-de-Luzuriaga, M. Monge, M. E. Olmos, Y. Sáenz, C. Torres. Organometallic approach to polymer-protected antibacterial silver nanoparticles: optimal nanoparticle size-selection for bacteria interaction. *J. Nanopart. Res.* 14 (2012) 1281
- [3] J. Villanueva. Trabajo fin de Máster. Universidad de La Rioja (2012).

AsFIFFF-UV-Vis-ICP-MS applied to cellular toxicity studies of silver nanoparticles: characterization of silver forms in culture media and cells

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The study of the hazards of engineered nanoparticles (ENPs) is mainly done by applying standard toxicology tests used for bulk forms of the same materials. However, ENPs possess new properties, mainly linked to their size, but also to other physical and chemical parameters. Furthermore, these properties can be altered by the medium used to suspend or disperse the ENPs. The correct interpretation of the toxicological results requires then, a proper characterization of the ENPs. The physical and chemical parameters for characterizing nanomaterials in toxicological studies should include at least the particle size/size distribution, agglomeration state/aggregation, overall composition, and surface-related parameters. In addition, some overarching considerations should be taken into account, such as its stability, including the material release through dissolution and the context/media.

In vitro cell-based assay systems are an important tool in the field of toxicology. The considerations mentioned above with respect to how the nanomaterial behaves in the test system are especially important for *in vitro* systems given the strong interactions that ENPs may suffer with culture media. As speciation strongly affects the bioavailability of nanoparticles, it is important to develop proper methods to characterize the transformation of these nanoparticles.

In this work, a methodology based on Asymmetric Flow Field-Flow Fractionation (AsFIFFF) coupled with UV-Vis absorption spectrometry and ICP mass spectrometry (ICPMS) has been developed and applied to the study of silver nanoparticles (AgNPs) and dissolved species of silver in culture media and cells used in cytotoxicity tests. The effect of a nano-silver based product (protein stabilized silver nanoparticles ca. 15 nm average diameter) on human hepatoma (HepG2) cell viability has been studied. UV-Vis absorption spectrometry provided information about the nature (organic vs. nanoparticle) of the eluted species, whereas the silver was monitored by ICPMS.

AgNPs associated with the cultured HepG2 cells were also identified by AsFIFFF, after applying a solubilisation process based on the use of tetramethylammonium hydroxide (TMAH) and Triton X-100. These results have been confirmed by transmission electronic microscopy (TEM) analysis of the fractions collected from the AsFIFFF. The effect of AgNPs on HepG2 cells has been compared to that caused by silver(I) as AgNO₃ under the same conditions.

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Bioavailability of silver nanoparticles and silver speciation in biological systems through separation techniques and ICPMS detection

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Due to their biocidal properties, silver nanoparticles have been used in number of several applications, such as paints, food storage containers, water treatments and environmental remediation [1]. This widespread use can result, directly or indirectly, in the incorporation of silver nanoparticles to human being and other living organisms, as well as aquatic systems, which, together with the lack of knowledge about their fate, behaviour and toxic effect, has led to a growing concern in the scientific community about the environmental impact of silver nanoparticles.

The precise mechanisms for silver, and in particular silver released from nanoparticles, bioaccumulation and biotransformation processes are still not fully understood. The studies reported in the literature have not explored so far silver transformation in living organisms at the molecular level. It must be also pointed out that many studies were carried out using poorly characterized nanoparticles which makes their results difficult to interpret.

Therefore, research focused on silver containing bio-molecules resulting from the silver nanoparticle oxidation is of high interest for the assessment of the bioaccumulation and biotransformation mechanisms and thus the toxicological impact of silver. Currently, the study of bioavailability and toxicity of silver nanoparticles in model mammals, are becoming one of the hot research topics in the field of analytical science [2].

In this work, the distribution of silver in rat organs from *in vivo* assays with rats treated orally with a commercial silver-based nanomaterial has been studied through a methodology based on acid digestion followed by ICPMS analysis.

Moreover, silver containing bio-molecules in cytosols from liver and kidney tissues from *in vivo* rats and *in vitro* human hepatome cells, treated with the commercial silver-based nanomaterial have been identified by using separation techniques and ICPMS detection.

Acknowledgements

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References

- [1] Woodrow Wilson International Centre for Scholars. Project on Emerging Nanotechnologies. Consumer products inventory of Nanotechnology Products. <http://www.nanotechproject.org/inventories/consumer/>
- [2] Ahamed, M. Alsalihi, M. S. Siddiqui, M. K. J. *Clin. Chim. Acta.* 411 (2010), 1841.

Multi-analytical characterization of engineered cerium oxide nanoparticles by spectroscopic techniques

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Nanotechnology has rapidly grown in the last decades, with a number of engineered nanomaterials (ENMs) being increasingly developed and commercialized. As new ENMs are more and more used in daily life, concerns about their widespread release to the environment are being raised by regulators, workers and consumers [1]. Once in the environment, ENMs and resulting nanoparticles interact with living beings in diverse ways. Nanotoxicology deals with the study of the ENMs hazards, while little is known about the role played by their particular physical-chemical properties in determining their toxic effect. Due to their nano size, ENMs possess new properties that may result into different toxicity patterns relative to their bulk counterparts. Full characterization of ENMs is crucial to identify the properties responsible for the ENMs toxic effects.

CeO₂ nanoparticles (NPs) are commercialized as fuel additive for diesel engines to improve burning efficiency of engine carbon deposits. The strong oxidising capacity of CeO₂ makes it an excellent product for reducing the emission of greenhouse gases and particulate number, as well as for diminishing fuel consumption [2]. While the use of CeO₂ NPs contributes to a reduction of soot nanoparticles especially rich in diesel engine exhaust, there is a lack of understanding of the intrinsic toxicity of the CeO₂ NPs emitted in the exhaust.

Here, we propose to apply a series of analytical techniques to physical-chemically characterize CeO₂ NPs in relation to key properties such as particle size/size distribution, shape, agglomeration/aggregation state, oxidation state or surface chemistry. The analytical platform will combine size fractionation (Field Flow Fractionation) with spectroscopic (Inductively Coupled Plasma – Mass Spectrometry, and UV-VIS Spectroscopy) and microscopic (Transmission Electron Microscopy) techniques to exhaustively characterize the size and stability of CeO₂ NPs [3]. Electrochemical techniques (Voltammetry of Immobilized Particles) [4] will also be employed for detection and quantification purposes, as well as for determining oxidation state of cerium in the CeO₂ NPs, which affects its reactivity and toxicity. A comparative study of bulk CeO₂ NPs and those emitted from the combustion of CeO₂-doped diesel is envisioned to assess the effect of physical-chemical changes during combustion on the NPs toxicity.

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References

- [1] F. Gottschalk, B. Nowack. The release of engineered nanomaterials to the environment. *J. Environ. Monit.* 13 (2011), 1145.
- [2] S. Logothetidis, P. Patsalas, C. Charitidis. Enhanced catalytic activity of nanostructured cerium oxide films. *Mater. Sci. Eng. C* 23 (2003), 803.
- [3] E. Bolea, J. Jiménez-Lamana, F. Laborda, I. Abad-Álvarez, C. Bladé, L. Arola J. R. Castillo. Detection and characterization of silver nanoparticles and dissolved species of silver in culture medium and cells by AsFIFFF-UV-Vis-ICPMS: application to nanotoxicity tests. *Analyst* 139 (2014), 914.
- [4] G. Cepriá, W.R. Córdova, J. Jiménez-Lamana, F. Laborda, J.R. Castillo. Silver nanoparticles detection and characterization in silver colloidal products using screen printed electrodes. *Anal. Methods*, accepted (Feb. 2014).

Silver nanoparticle-proteins interaction: Evaluation of protein corona formation

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Nanomaterials are at the foremost periphery of the swiftly developing field of commercial exploration of nanotechnology. The advent of nanotechnology has accelerated the evolution of materials with many exceptional size-dependent properties for use in several biological and medical applications. Owing to the high surface to volume ratio, nanoparticles (NPs) are highly reactive. However, the knowledge about the effects of Nps on biological systems and their potential toxicity is very limited yet. Exposure to nanomaterials for humans may be accidental, for example occupational exposure, or intentional, for example in the use of nano-enabled consumer products. Hence, there is an urgent need to understand the mechanisms of NPs on biological system interaction.

When NPs reach a biological fluid, immediately interact with and are covered by fluid proteins. These proteins form a so-called "protein corona" which is considered to consist of two different components: the "hard" corona (the fraction of proteins which are bound to the surface) and the "soft corona" (the proteins which are in exchange with surrounding proteins). There are many factors influencing the detailed nature of the NP biomolecule corona, with NP size, shape, surface charge, and solubility all playing a role in the interaction of the NPs with proteins. It is necessary to know the properties and composition of the protein corona in order to predict possible immunological and toxicologically relevant reactions or to elucidate the mechanisms which determine uptake and mediate accumulation in organs.

Silver nanoparticles (Ag NPs) have been incorporated as antibacterial/antifungal agents in medical devices, textile engineering, water treatment, and have been integrated into the surfaces of many household appliances and food storage container.

In this study the influence of different parameters concerning AgNP-protein corona formation and evolution has been evaluated. Some of these parameters are: time evolution of the protein corona, NP concentration, NP size, NP coating, protein concentration and formation of hard and soft corona. Different AgNPs standards, a commercial sample (Collargol) and two proteins, albumin and transferrin (major proteins in blood serum), were used for the study. Based on our previous research [1], different electrophoretic methods have been applied for AgNP-proteins corona characterization. Investigations for successful detection of Ag forms by LA-ICP-MS have been carried out. The formation of AgNP-proteins corona formation was also investigated by UV-VIS Molecular Absorption Spectroscopy.

Acknowledgements

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References

[1] M. S. Jiménez, L. Rodríguez L, Juan R. Bertolin, M.T. Gomez MT, J.R. Castillo JR, *Anal. Bioanal. Chem.* 405 (2013) 359-368.

Control of the bioconjugation of functionalized luminescent nanoparticles to antibodies by asymmetrical flow field-flow fractionation coupled to elemental and molecular spectrometry detection

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Bioanalysis often require labeling of biochemical compounds for detection. Although mass spectrometry techniques offer a label-less method of detection, however, they are expensive and cannot be easily applied for fast screening tests or in-live studies. Alternatively, other widely used bioanalytical techniques, such as those based on detection of isotopes, enzyme-linked chromophore/fluorophores, chemiluminescence and bioluminescence are among the methods that could require appropriate analyte labelling.

In this context, functional luminescent quantum dots (QDs), as a new generation of high-value optical labels, have been also applied for molecular detection [1]. The great potential of such novel optical labels has paved the way to the development of new biomolecule assays with unprecedented analytical performance characteristics, related to sensitivity, multiplexing capability, sample throughput, cost effectiveness and ease of use.

It should be considered that the success or failure in the use of the QDs in these applications is largely determined by the ability to bioconjugate such nanoparticles to specific recognition elements, such as aptamers or antibodies, a mandatory previous step for the successful development of new bioassay and bioanalytical applications based on biolabeling and bioimaging. Actually, despite recent progress in the use of QDs for bioanalytical applications, there is still an urgent need for effective procedures for QDs bioconjugates purification and characterization, in order to further facilitate reliable quantitative bioassays.

In this communication, a novel concept based on the combination of asymmetric field flow fractionation nanoparticles separation coupled on-line with molecular spectroscopy (fluorescence) and elemental (inductively coupled plasma-mass spectroscopy, ICP-MS) detection is proposed as a diagnostic tool to control the quality of water-solubilized CdSe/ZnS QDs bioconjugated to antibodies.

Acknowledgements

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References

[1]Coto-García A.M., Sotelo-González E., Teresa Fernández-Argüelles M.T., Pereiro R., Costa-Fernández J.M., Sanz-Medel A. 2011. *Anal. Bioanal. Chem.*, 399: 29-42.

In vitro evaluation of cellular uptake and toxicity of engineered L-cysteine capped phosphorescent Mn²⁺-doped ZnS quantum dots

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The intentional introduction of transition metal impurities in semiconductor nanocrystals (doped quantum dots, d-dots) is an attractive approach for tuning quantum dot photoluminescence emission. Particularly, doping ZnS quantum dots with Mn²⁺ (Mn:ZnS QDs) results in a phosphorescence-type emission, attributed to the incorporation of manganese ions within the nanocrystal structure. Mn:ZnS QDs photoluminescence properties offer both, large Stokes shifts and longer lifetimes (as compared to more traditional fluorescent QDs) [1]. In this way, general problems in biological and biomedical luminescence applications related to high autofluorescence backgrounds (affecting significantly to the analytical sensitivity and selectivity) could be minimised or perhaps avoided. Metal-doped ZnS nanoparticles, exhibiting a phosphorescence-like emission, have a great potential for biochemical applications, although no conclusive information on their eventual cytotoxicity is available.

Herein, a systematic study on the interaction of water-soluble Mn²⁺-doped ZnS quantum dots (Mn:ZnS QDs), surface stabilized with cysteine molecules, using as in vitro model mouse embryonic fibroblast, NIH3T3, cells has been carried out.

After incubating cells with different amounts of Mn:ZnS QDs at different exposure times, cellular uptake and quantum dots localization were assessed. In all cases, quantitative values for the nanoparticle uptake by the cells were given.

Different complementary analytical techniques have been employed and values obtained were correlated with microscope images in which the uptake of the particles by the cells has been also investigated. Data obtained suggest intracellular localization of the QDs but outside of the cell nucleus.

Moreover, the morphology of the NIH3T3 cells has not been affected by the presence of high levels of QDs in the culture media. However, after rather long exposure times cellular damage has been observed for high concentrations of the Mn:ZnS QDs.

Acknowledgements

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References

[1] E. Sotelo-Gonzalez, M.T. Fernandez-Argüelles, J.M. Costa-Fernandez, A. Sanz-Medel, *Anal. Chim. Acta*, 2012, 712, 120-126.

Optical spectroscopy of metal-semiconductor nanowires: Transparent nanocontacts

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In recent years, plasmonic cloaking has received considerable attention as a mechanism to dramatically reduce the electromagnetic scattering cross section of an object [1]. Considering available technologies, the use of metallic nanowires (NW) is suited for many optics and optoelectronics applications [2,3]. In this work [4] NWs coated with a high permittivity dielectric are proposed as means to strongly reduce the light scattering of the conducting NW (Fig. 1), rendering them transparent at infrared wavelengths of interest in optical spectroscopy. We find appropriate parameters to reduce the scattering efficiency of hybrid metal dielectric NW by up to three orders of magnitude as compared with the scattering efficiency of the homogeneous metallic NW. The bandwidth of the transparent region entirely covers the near IR telecommunications range. Although this effect is optimum at normal incidence and for a given polarization, rigorous theoretical and numerical calculations reveal that transparency is robust against changes in polarization and angle of incidence. A wealth of applications based on metal-NWs may benefit from such invisibility.

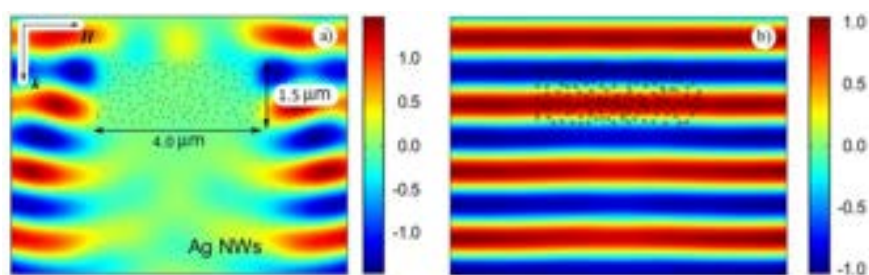


Fig. 1. (a) Map of the electric field along the cylinder axis direction at a wavelength of $\lambda = 1550$ nm for TM polarized waves for an ensemble of bare Ag Nws ($R = 13.6$ nm) distributed randomly within a slab of $4 \mu\text{m}$ by $1.5 \mu\text{m}$. (b) Electric field map corresponding to the same arrangement of (a). The scattering units in this case are Ag@Si core-shell NWs ($R_{\text{core}} = 13.6$ nm, $R_{\text{shell}} = 45$ nm), the filling fraction of the arrangement is 16%.

Acknowledgements

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References

- [1] P.-Y. Chen, J. Soric, A. Alù, Invisibility and cloaking based on scattering cancellation, *Adv. Mater.* **24**, (2012), OP281.
- [2] Y. Li, F. Qian, J. Xiang, C. M. Lieber, Nanowire electronic and optoelectronic devices, *Mater. Today* **9**, (2006), 18.
- [3] R. Paniagua-Domínguez, D. R. Abujetas, J. A. Sánchez-Gil, Ultra low-loss, isotropic optical negative-index metamaterial based on hybrid metal-semiconductor nanowires, *Sci. Rep.* **3**, (2013), 1507.
- [4] R. Paniagua-Domínguez, D. R. Abujetas, L.S. Froufe-Pérez, J. J. Sáenz, and J. A. Broadband telecom transparency of semiconductor-coated metal nanowires: more transparent than glass, *Opt. Express.* **21**, (2013), 22076.

Highly effective SERS nanopattern substrate. The enhancement is demonstrated using thiophenol as a molecular probe

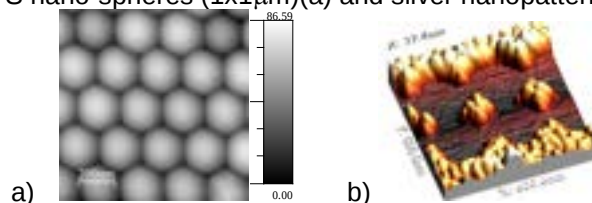
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The number of different types of Surface-enhanced Raman Scattering (SERS) substrates available for experimentation is increasing at high speed. New alternatives are introduced and explored every year in the literature including both novel nano-particles in solution as well as self-assembled or engineered structures with different levels of control over their optical properties. In this work silver nanopattern obtained by the nano-sphere lithography approach was prepared and characterized by AFM. This method basically exploits the regular patterns formed by self-assembly of dielectric (polystyrene, PS) nano-spheres on a surface upon drying. The evaporation of a silver film on top of the array can be followed by the lift-off of the nano-spheres themselves in which case an array of interstitial sites is left on the surface [1-2] (Fig. 1). We have observed in the AFM images that the shape of the nanopatterns is regular but the surface is rough and they are homogeneously distributed with dimensions in the sub-wavelength range.

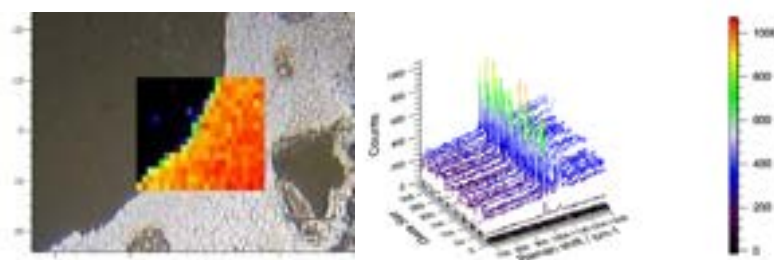
Figure 1. AFM images of PS nano-spheres (1x1 μ m)(a) and silver nanopatterns (0.6x0.6 μ m) (b).



SERS properties of this substrate were examined by using thiophenol (TP) as molecular probe through the preparation of self-assembled monolayer (SAM) by dipping the substrates for 1h in 0.1mM solution of TP in CH₂Cl₂ at the temperature of 25°C. Samples were subsequently rinsed with solutions solvents and dried before scanning.

The surface interaction of this molecule has been studied by several groups and the most significant Raman change after the adsorption is the disappearance of the S-H stretching mode at about 2566 cm⁻¹ in the SERS spectrum and indicating that an Ag-S bond has been formed [3]. The reproducibility on different areas of this substrate has been analyzed by using this molecular probe concluding that a fairly homogeneous distribution of the SERS intensity is observed (Fig. 2) which is a prerequisite for applications as ultrasensitive sensing assemblies.

Figure 2. Raman mapping of TP on silver nanopatterns and related Raman spectra.



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References

- [1] W. Ruan, Z. Lu, T. Zhou, B. Zhao, L. Niu. Surface micropatterning technique for surface-enhanced Raman scattering analysis. *Anal. Methods* 2 (2010) 684.
- [2] J.A. Dieringer, A.D. McFarland, N.C. Shah, D.A. Stuart, A.V. Whitney, C.R. Yonzon, M.A. Young, X. Zhang, R.P. Van Duyne. Surface enhanced Raman spectroscopy: new materials, concepts, characterization tools, and applications. *Faraday Discuss.* 132 (2006) 9.
- [3] R. Aroca, *Surface-enhanced Vibrational Spectroscopy*. Ed. John Wiley & Sons, Chichester, 2006.

Study in nanoscale of bivalve mollusk scallop for application as raw material in the industry

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In the field of science, the study of marine molluscs is currently a field of great importance because it has been found that these compounds in nanoscale may exhibit some very interesting mechanical properties for application in the field of industry in their possible applications in the design of protective armor for human, or for automotive cars safer chassis industry. Understand the fundamentals of the design of natural armor systems like shells, can help engineers to develop similar systems for men and women who work in dangerous situations, like soldiers or policemen. We have the previous notions that the military research center at MIT nanotechnology scientists are working to define the structures and mechanisms characteristic of shells and molluscs in nanoscale. In this paper, nanoscale morphology Bivalve mollusk from the Peruvian Sea Scallop is studied. The sample was collected at Vegueta beach, located in the province of Huaura, department of Lima. Because the position of its rings, the shellfish is commonly known as scallops or "conchas de abanico". For chemical analysis, the technique of X-ray fluorescence (XRF) was used, while for the mineralogical analysis was performed using X-ray Diffraction (XRD). FRX analysis detected the presence of calcium as the major chemical element in the sample composition. XRD analysis revealed the presence of calcium carbonate as the main mineralogical phase in the sample. The average crystallite size of the calcium carbonate obtained by the Scherrer formula is 200 nm. Morphological analysis and grain shape was performed using Scanning Electron Microscopy (SEM), it was observed in the same structures a grain size approximate of 150 nm thickness 400 nm. Although calcium carbonate is very fragile and brittle structure, that forms in the shells of shellfish increases your strength, and research shows how much harder could be built and protective materials, made with synthetic compounds that mimic biology. These compounds could be used both in armor or vests for people like car bodies or wings of airplanes as mentioned above. The results obtained in this work are compared with those of other molluscs reported by other authors. Also in a later paper aims study from these seashells the estimation for the temperature of the sea. This study is made possible by Mass Spectroscopy.

References

Bruet, B. J. F.; Qi, H. J.; Boyce, M. C.; Panas, R.; Tai, K.; Frick, L.; Ortiz, C "Nanoscale morphology and indentation of individual nacre tablets from the gastropod mollusc *Trochus niloticus*", Journal of Materials Research, vol. 20, issue 9, pp.2400-2419

Assessing the uniformity of API distribution in low dosage pharmaceuticals using Raman spectroscopy

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Raman spectroscopy has found its place in pharmaceutical analysis because it is non-destructive, requires minimal sample preparation and gives clear, easily interpretable, spectra. These spectra can be used subsequently for different objectives, the most common being the quantitation of the active principal ingredient (API) in a pharmaceutical dosage form. The intensity of Raman is proportional to the amount of the Raman scatterer present in the sample. Even though its sensitivity is not very high, several works have reported the quantitative determination of API in low dosage pharmaceuticals (≤ 2 % w/w) [1].

The assessment of the uniformity of content is a key indicator for the evaluation of how the manufacturing process has evolved. Even though the current European Pharmacopoeia only considers necessary the uniformity test in the context of differences between single doses (intact tablets), it is clear that the uniformity of API distribution in a tablet is critical in case of tablets that can be split in fractions.

Sintrom[®] is the most used anticoagulant in Spain. It is commercialized in two different dosage units containing 1 mg and 4 mg acenocoumarol per tablet. Sintrom 4 mg[®] is bear marked with a cross suggesting its division in quarters. Since this kind of anticoagulant has a very narrow therapeutic window, the therapeutic dose has to be fixed for each patient, doing analytical controls with frequency, every week at the beginning, and every month afterwards. One of the strategies to fix the dose for each patient consists in dividing the tablets, as the prescribed dose should be taken only once a day [2].

In this communication we report a study about the quantification and homogeneity of acenocoumarol distribution for the two presentations of Sintrom[®] using Raman backscattering spectroscopy. First, a multivariate calibration procedure has been developed using a mixed calibration sample set. This method has proved to be a competitive procedure for the determination of the uniformity content of single doses. Later, it has been applied to the quantification of API distribution in the quarters of the intact tablets. Also, a semi-quantitative procedure, based on the measurement of the area of an acenocoumarol peak, has been developed. Performances of both procedures are compared and discussed in terms of precision and robustness .

References

- [1] N. Townshend, A. Nordon, D. Littlejohn, M. Myrick, J. Andrews, P. Dallin. Comparison of the determination of a low-concentration active ingredient in pharmaceutical tablets by backscatter and transmission Raman Spectrometry. *Anal. Chem.* 84 (2012) 4671.
- [2] A. Bonet, V. Gosalbes, M. Ridao-López, J. Navarro, B. Navarro, S. Peiró. Dabigatran versus acenocoumarol para la prevención del ictus en la fibrilación atrial. Análisis de impacto presupuestario en un departamento sanitario. *Rev. Esp. Salud Pública* 83 (2013) 331.

Determination of additives from plastic polymers by focused ultrasonic solid-liquid extraction

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Additives such as stabilizers, antioxidants, UV-protectors, slip agents, etc. are added to polyethylene films and other polymers in order to preserve and improve their properties. Likewise the amount of these additives must be determined for quality and regulatory reasons.

In this communication a fast and simple method to determine several additives in plastic polymers based on focused ultrasonic solid-liquid extraction (FUSLE) and ultra high performance liquid chromatography (UHPLC) coupled to an UV detector and quadrupole-time of flight mass spectrometry (QTOF-MS/MS) detector is presented.

The selected analytes were separated in a C18 column and detected at a wavelength of 280 nm and by mass spectrometry in positive ESI ion mode. Several mobile phases, such as water:methanol and water:ACN were tested. The use of formic acid and buffers like ammonium formate and sodium formate were also tested.

This is the first time that FUSLE is used to determine additives in polymers. The optimum solvent extraction was selected by univariate analysis. After that, the main FUSLE factors affecting the extraction efficiency (solvent volume, extraction time and ultrasonic irradiation power) were studied by means of a central composite design. Finally, the number of extraction cycles necessary for complete extraction was established.

The FUSLE-UHPLC-UV-(Q-TOF)MS/MS method was validated in terms of sensibility, intermediate precision and accuracy. In addition, FUSLE results were compared to those of PLE in terms of extraction efficiency, rate and cost. Finally, the whole method was applied to the analysis of different polymeric samples.

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Formation of ABTS radical cation in the presence of silver nanoparticles as revealed by surface-enhanced Raman scattering

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ABTS (2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonic acid) is extensively employed to evaluate the free radical trapping capacity of antioxidant compounds and complex mixtures such as biological fluids or foods [1], when it is incubated in presence of a free radical source in the so-called Trolox equivalent antioxidant capacity (TEAC) assay. This assay is performed by using a colorimetric experiment, where ABTS is previously oxidized by sodium persulfate to get the radical cation $ABTS^{*+}$ [2], giving rise to an intense absorbance at 734 nm. In this work we report the formation of the radical cation in the presence of star-shaped silver nanoparticles (AgNS) [3]. $ABTS^{*+}$ was characterized by surface-enhanced Raman scattering (SERS) and detected at trace concentrations (2 μ M). The $ABTS^{*+}$ /AgNS system is proposed here as a reliable substrate to test the antioxidant activity of various compounds. This approach is based on the high sensitivity of plasmonic nanostars for SERS detection of trace amount of studied molecules and can serve as an alternative method to the TEAC test.

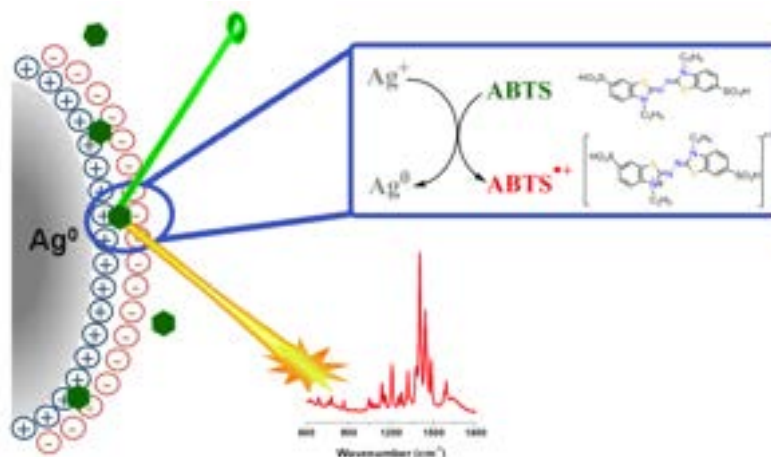


Figure 1: Scheme of a redox process occurring on the silver nanoparticle surface when a neutral ABTS molecule is localized in the electrical double layer surrounding silver surface.

Figure 1 shows the proposed scheme of a redox process that occurs in the vicinity of nanoparticle surface. When $ABTS^{*+}$ is close to the NP surface it is possible to detect the $ABTS^{*+}$ by fingerprint SERS bands of this molecule.

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References

- [1] C. Aliaga, E.A. Lissi, Reactions of the radical cation derived from 2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonic acid) ($ABTS^{*+}$) with amino acids. Kinetics and mechanism. *Can. J. Chem.* 78 (2000) 1052.
- [2] R.B. Walker, J.D. Everette, Comparative Reaction Rates of Various Antioxidants with $ABTS$ Radical Cation, *J. Agric. Food Chem.* 57 (2009) 1156–1161.
- [3] A. Garcia-Leis, J.V. García-Ramos and S. Sanchez-Cortes, Silver Nanostars with High SERS Performance. *J. Phys. Chem. C*, 117 (2013) 7791.

Monitoring vineyard parameters through at-field hyperspectral indices

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Field radiometry based on high spectral capacity of spectroradiometers is an alternative to the high-cost direct or destructive measurements for monitoring agricultural vegetation. This technique has not scale restrictions (i.e., remote sensing) and, unlike the laboratory experiments, it reflects the actual conditions of the plants and their environment. Parameters related with phenology, status and physiognomy either at leaf, plant or canopy level can potentially be estimated and monitored using measurements of the reflected energy in the visible and near infrared spectrum range. In this work, hyperspectral indices derived from combination of reflectance measurements were proposed for estimating biophysical parameters of vines plants. A vineyard of 100 has of *Vitis vinifera* L. cv. Tempranillo was studied in the Castilla y León region of Spain (41.18° N, 5.21° W, 717 m a.s.l.). The vines are trellised to a vertical shoot position and equispaced 1.5 m. Seventeen sampling points were selected within the vineyard. Two vines at each side of these sampling points were monitored during the complete growing season of 2013. The biophysical parameters that have been controlled in these 34 vines were Leaf Area Index (LAI), chlorophyll relative content, and vegetation water content (VWC), all of them estimated at leaf and plant level. LAI and VWC were directly estimated through destructive measurements, and chlorophyll was measured by means of a Minolta SPAD-502. The spectral measurements were taken with a spectroradiometer Ocean Optics USB4000, with a spectral range of 500-1100 nm and spectral resolution of 0.21 nm. Both direct and indirect measurements were acquired approximately every 20-30 days at noon (5 measurements in total) along the vineyard growing season.

Several hyperspectral indices have been used in this work, related with canopy structure and vigour (Normalized Difference Vegetation Index, NDVI; Soil-Adjusted Vegetation Index, SAVI), pigments (Photochemical Reflectance Index, PRI; Transformed Chlorophyll Absorption in Reflectance Index, TCARI; Chlorophyll Normalized Difference Index, CNDI; Greenness index; and two Carotenoids indices, CAR), and water status (Water Index, WI).

Correlation among LAI, VWC and chlorophyll measurements with hyperspectral indices was established and evaluated. Soil moisture observations were also included in the comparisons. Regarding the coefficient of correlation (R) between vine parameters and hyperspectral indices, non significant correlations were obtained with the NDVI as well as poor results in terms of R from the carotenoids and the Greenness indices. Even though, good results were found for SAVI, TCARI, PRI and CNDI indices for LAI, VWC and chlorophyll characterization, with a high number of significant correlations ($R > 0.60$), specially for the SAVI. Detailed results will be presented at the conference.

The results suggested that field radiometry might provide valuable information to predict growing vine attributes. Hyperspectral indices SAVI, TCARI, PRI and CNDI provided reliable estimates of vine canopy vigour parameters such as LAI, VWC and chlorophyll.

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Luminescent cyclometalated Pt(II) and Pt(IV) complexes

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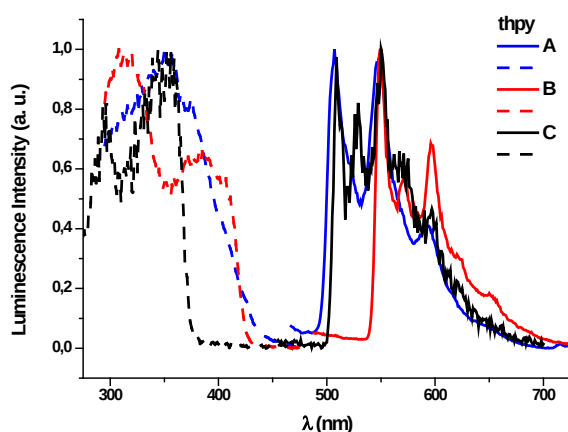
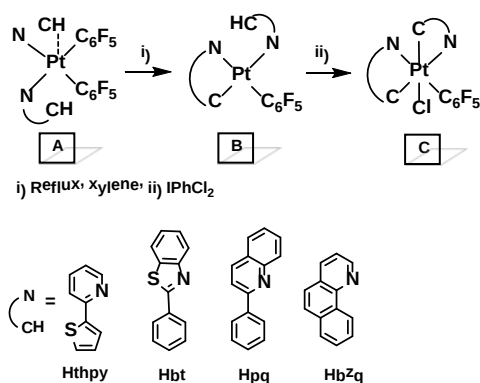
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Luminescent Pt(II) cyclometalated complexes have attracted great interest in recent years because they have shown extraordinary potential in highly efficient organic light-emitting diodes (OLED) devices, as molecular sensors, in biological labeling and photocatalysis. However, the photoluminescence properties of Pt(IV) complexes have received a very limited attention, which contrasts with the extensive luminescence studies carried out on complexes of other d^6 ions, such as Re(I), Ru(II), Os(III) and Ir(III).

In the last years, our research group has published several articles related to luminescent mono and polymetallic Pt(II) materials, studying the influence of the cyclometalated ligands and coligands [1,2]. Recently, we have described some Pt(IV) derivatives obtained from oxidative reactions to Pt(II) compounds, but they have resulted to be non-emissive [3].

Following our interest in Pt(IV) chemistry and in luminescent materials, in this communication we present new cyclometalated compounds of Pt(II) and Pt(IV) with C_6F_5 as coligand. The derivatives containing two *N*-heterocyclic ligands [*cis*-Pt(C_6F_5)₂(HC^N-κ*N*)₂] (type **A**) (HC^N = 2-(2'-thienyl)pyridine (Hthpy), 2-phenylbenzo[d]thiazole (Hbt), 2-phenylquinoline (Hpq) and 7,8-benzo[h]quinoline (Hbzq)) involve in drastic conditions to the monocyclometalated complexes [Pt(C^N-κ*C,N*)(HC^N-κ*N*)(C_6F_5)] (type **B**). The bis-cyclometalated Pt(IV) derivatives (type **C**) are obtained by oxidation from the species type **B**.

Spectroscopic studies have showed that the emissive properties depends on the type of cyclometalated ligand, the coordination mode and the Pt oxidation state. The emitting states in complexes type **A** and **C** have metal-perturbed intraligand character, whereas in the type **B**, the emission is mainly assigned to mixed intraligand/metal-to-ligand charge transfer (³IL/³MLCT) transitions.



References

- [1] A. Díez, E. Lalinde, M. T. Moreno, Heteropolynuclear cycloplatinated complexes: Structural and photophysical properties. *Coord. Chem. Rev.* 255 (2011) 2426.
- [2] J. R. Berenguer, A. Díez, E. Lalinde, M. T. Moreno, S. Ruiz, S. Sánchez, luminescent Cycloplatinated Complexes containing poly(pyrazolyl)-borate and methane ligands. *Organometallics* 30 (2011) 5776.
- [3] J. R. Berenguer, J. Fernández, N. Giménez, E. Lalinde, M.T. Moreno, S. Sánchez. Unexpected Formation of Ferrocenyl(vinyl)benzoquinoline Ligands by Oxidation of an Alkyne Benzoquinolate Platinum(II) Complex. *Organometallics* 32 (2013) 3943.

Phosphors and chemiluminiscent reactions for the experimental assessment of uncertainty in fluorescence detectors

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The experimental uncertainty generated when fluorescent measurements are being acquired (spectrofluorometers and CCDs) include three different sources [1]: (a) *background* current, including *dark current* and *non-uniformity* [2]; (b) *shot noise*, a consequence of the variability in the number of photons arriving at detector per unit of time, and (c) *flicker noise*, mainly due to fluctuations generated in the radiation source. The (a) effect depends upon the detector temperature, but not upon the signal extent; the (b) and (c) effects do not depend upon the temperature but they do depend upon the number of photons arriving at the detector (the signal, I_s). The signal/noise ratio (S/N) is related to uncertainty in a way that can be expressed as:

$$S/N = \frac{I_s}{\sqrt{k_1^2 + k_2^2 I_s + k_3 I_s^2}} \quad (1)$$

Where the terms in the denominator correspond to (a), (b) and (c) effects respectively. The values of k_1 , k_2 and k_3 can be used as parameters to assess the performance of the analytical instrument used for measurements. To calculate k_1 , k_2 and k_3 a number of consecutive measurements (say 20-30) on a luminescent species can, for instance, be obtained and then mean (I_s) and standard deviation (uncertainty, N) can be evaluated. The procedure can be repeated for solutions containing different concentrations of the luminescent species and a plot of S/N vs I_s can be made; from it a non-linear regression of S/N on I_s according to equation (1) may allow the values of k_1 , k_2 and k_3 ; however, the precision of these values can be improved if regression lines with a lower number of parameters can be obtained. When chemical systems that do not need excitation source are used no flicker noise is involved. Equation (1) will then have just two terms ($k_1^2 + k_2^2 I_s$) because $k_3 I_s^2$ has no sense and only k_1 and k_2 will have to be adjusted.

Phosphors (once they are activated) and chemiluminiscent reactions meet these conditions, but they are approaching equilibrium and transient signals are generated, so measurements (20-30) must be taken in a very short period of time. Only in these conditions any change in the signal can only be charged to uncertainty and not to the absolute value of the signal, which does not change significantly. The present communication deals with this kind of measurements. A green phosphor from www.inteligentes.org and a chemiluminiscent reaction with luminol have been used in both a Shimadzu RF-540 Spectrofluorometer and charge-coupled devices (from Ocean Optics) with a configuration for fluorescence measurements. The data calculated are compared with those obtained with fluorescent solutions when equation (1) is applied.

Acknowledgements

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References

- [1] J.D. Ingle Jr., S.R. Crouch, Spectrochemical Analysis, 1988, Prentice Hall, Chapter 5.
- [2] J. Galbán, S. de Marcos, I. Sanz, C. Ubide, J. Zuriarrain, Analyst 135 (2010) 564.

Characterization of linear alcohol ethoxylates by ion mobility spectrometry

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Ion mobility spectrometry (IMS) is a technique that separates gas phase ions at ambient pressure, when those ions pass through a drift tube under the influence of an electric field. The ions are separated according to their mobility constant (K). The mobility constant depends on their mass/charge relation, shape and size. The main advantages of IMS are the high sensitivity and fast data-acquisition. [1] In addition, the minimal solvent consumption and the low waste generation convert IMS into a low cost analytical technique.

Linear alcohol ethoxylates (AE) are the most common non-ionic surfactants used for the manufacturing of detergents and industrial cleaning products. AE molecules present a hydrophobic part (hydrocarbon chain) and a hydrophilic part (ethylene oxide groups). Usually, AE samples contain mixtures of several products (different hydrocarbon length chain and number of ethylene oxide groups). The development of analytical methods is not easy, because of the complex mixture of the samples and the lack of reference standards for all the AE. It is important to determine the number of hydrophobic carbons and the number of ethylene oxide units since the product properties depend on them. Typically, chromatographic techniques coupled with mass spectrometry are used for the characterization of AE. [2]

The aim of this work is to fully characterize the linear alcohol ethoxylates mixtures using ion mobility spectrometry (IMS). We want to determine the number of hydrophobic carbons and ethylene oxide units for every individual AE under study, and, evaluate the relationship between the mobility constant (K_0) and the molecular weight of the AE among the homologous series. Therewith, it is possible to classify the different molecules according to the number of carbons and ethylene oxide units. Moreover, a multiple linear regression (MLR) is calculated where an empirical relationship is obtained between the inverse of mobility constant ($1/K_0$) and the number of carbons in the alkyl chain and the number of ethylene oxide units.

References

[1] J.I. Baumbach. Process analysis using ion mobility spectrometry. *Anal. Bioanal. Chem.* 384 (2006) 1059.

[2] K. A. Evan, S. T. Dubey, L. Kravetz, I. Dzidil, J. Gumulk, R. Mueller, J. R. Stork. Quantitative determination of Linear Primary Alcohol Ethoxylate Surfactants in Environmental Samples by Thermospray LC/MS. *Anal. Chem.* 66 (1994) 699

Fluorescence study of GFP-chromophore analogs and their application as cell markers

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Since its discovery, the green fluorescent protein (GFP) has shown an impressive potential in many different scientific fields from organic chemistry to biological imaging.[1] In this contribution we present the photophysical behaviour of several compounds based on the GFP chromophore structure (Figure 1).

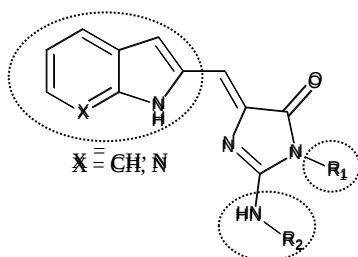


Figure 1. Synthesized family of fluorescent GFP-chromophore analogs.

The fluorescence properties of these compounds depend directly on their structure, so we have tested the fluorescence emission of different GFP derivatives changing the three moieties showed in Figure 1 getting different emission wavelengths.[2]

Also we have tested these compounds as fluorescent probes in PC-3 human prostate cancer cell lines with image techniques (Figure 2).



Figure 2. A) Bright-field images of PC-3 human prostate cancer cells stained with a GFP-chromophore analogue; B) fluorescence image; C) merged image.

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References

- [1] D. Martínez-López, D. Sampedro, "Targets in heterocyclic systems-Chemistry and Properties", Vol. 17, **2013**, in press.
- [2] A. Follenius-Wund, A. Bourotte, M. Schmitt, F. Iyice, H. Lami, J.-J. Bourguignon, J. Haiech, C. Pigault, *Biophys. J.*, **2003**, 85, 1839.

Nanotubes of carbon (CNTs) applications in medicine and engeneering

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Abstract. the 1:1 CH₃CN:BCl₃ complex was prepared by reacting equimolecular quantities of CH₃CN and BCl₃ and was characterized by UV, IR, ¹H-NMR, ¹³C-NMR, mass spectroscopy and elemental analysis.

Pyrolysis of CH₃CN:BCl₃ at ca 900-1000°C over C powder generates novel graphitic B_xC_yN_z nanotubes and nanofibres. In these experiments the metal particles play an important role in the growth since nanotube formation appears to occur at the metal surface. High resolution electron microscopy (HRTEM) and electron energy loss spectroscopy (EELS) studies suggest that the stoichiometry of the filaments ca. [BC₂N₂]_n.

The pyrolysis was carried out in a two-stage furnace system fitted with temperature controllers CH₃CN:BCl₃ (ca.100-200 mg) was placed in one end of a quartz tube (6 mm O.D and 60 cm in length) located in the first furnace.

Cobalt powder (Al drich 99.9 µmm particle size) in a quartz boat (6 cm length) was placed in the second furnace.

Residues (CNTs) scraped from the tube wall in the second furnace were analysed by HRTEM and EELS [1].

Applications:

a) With engeneering aeronautics



Figure 1. Scheme of the parts of the Space elevator



Figure 2. E-skin in the left and how is supposed to be used in the right

b) With medicine: Artificial Muscles

A new type of artificial muscle made from carbon nanotubes has been developed by reasearchers in the US. The muscles flex when electrically charged and can expand to 220% of their original lenhgt in a matter of miliseconds

References

- [1] M. Terrones, A. M. Benito, C. Manteca-Diego, H.W. Kroto. D.R. M. Walton. *Chem, Phys. Lett.*, 1996, 257, 576.
- [2] L. Yuan. et al, *Nano Lett*, 2008, 8, 2576.

Spectroscopy analysis of different types of impact melts: Libyan desert glass and Darwin glass

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Impact glasses are natural silica-rich melts produced by impact events of a meteorite or comet on any geographically area on the earth. These impact products are thrown away from the impact site and usually named with their location of their origin. Impact melt composition depends on target lithology, so target rock composition plays an important role on the characteristics of the impact product. Different types of impact melts such as Darwin glass, moldavite, Libyan Desert glass, etc. have been found around the world.

Libian Desert Glass (LDG) fragments are scattered in the Western Desert of Egypt, near Libyan border. LDGs are irregular yellow pieces with brownish inclusions that are estimated to be 28.5 million years old [1]. Another interesting type of impact melt is Darwin glass located on the West coast of Tasmania (Australia) and was formed at 800ka [2].

In the present work, two different types of glasses (LDGs and Darwin glass) from the Meteorites Collection of the Basque Country University (UPV/EHU) were analyzed combining different techniques as Raman Spectroscopy and image, Scanning Electron Microscopy/Energy Dispersive X-Ray Spectroscopy (SEM-EDS) and micro-Energy Dispersive X-Ray Fluorescence (μ -EDXRF) in order to identify the elemental and molecular composition of the matrix, inclusions and bubbles of both enigmatic materials.

The LDG external matrix is composed by mainly Si, and little amounts of K, Ti, Ca, V, Mn, Fe and Sr. Regarding to the molecular composition of the superficial matrix, by means of Raman spectroscopy it was recognized three distinct Raman spectra according to the different crystallization of silica. The outer inclusions are defined by the high concentration of Al, Ca and Si. According to mineral phases, it was noticed that corundum and natrite only appeared in the outer inclusions. The inner inclusions as well as the inner matrix were able to be analyzed after slicing the samples. In the inner matrix, Fe, Sr and Ti presented higher signal than in the surface. In the inner inclusions, calcite, anhydrite, hematite, limonite, anatase and gypsum were encountered by Raman spectroscopy, as well as in the superficial inclusions. Rutile was only found in the inner inclusions. Finally, it could be observed cavities as bubbles in most of the LDGs analyzed. Over these bubbles were realized an analysis by image Raman with the 532 and 785 nm excitation laser and it was observed a different composition between matrix and bubbles. In the case of the Darwin glass different elemental content were observed due to the flux texture but they were silica rich. It was characteristic the occurrence of vesicular textures filled with sedimentary materials.

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References

- [1] Aramendia, J., Gomez-Nubla, L., Fdez-Ortiz de Vallejuelo, S., Castro, K., Murelaga, X., Madariaga, J.M. New findings by Raman micro spectroscopy in the bulk and inclusions trapped in Libyan Desert Glass. *Spectrosc. Lett.* (2011), 44, 7-8, 521-525.
- [2] Lo, C., Howard K., Chungi S. , Meffre S. Laser fusion argon-40/argon-39 ages of Darwin impact glass *Meteoritics & Planet. Sci.* (2004), 37, 1555-1562.

Laser induced breakdown spectroscopy as a geochemical tool to determine paleoclimatic changes using speleothem

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Speleothems (mineral deposits formed in caves such as stalagmites and stalactites) are being investigated for the reconstruction of past climate change. Most speleothems consist of calcium carbonate, with variable amounts of trace elements such as Mn, Mg, Fe and Sr. Changes in these elements through the stratigraphy of the speleothem can be used to reconstruct past climate, as they are controlled by environmental factors occurring outside the cave, such as temperature and rainfall [1-2]. As some speleothems can be precisely dated by radiometric methods and because they show an internal microstratigraphy [3] consisting in most favourable cases of micrometre-scale annual growth bands [4] these deposits allow the construction of high-resolution series of climate variability. *Laser Inducted Breakdown Spectroscopy* (LIBS) provides enough analytical sensitivity to the most abundant trace elements from micro and macro samples of CaCO₃, and is remarkably fast and affordable in front of other techniques.

A longitudinal section of a stalagmite from Kaite cave (N Spain) has been analyzed by LIBS at a resolution of 500 µm (getting more than 2300 analyses) with minimal sample preparation. The Mg/Ca and Sr/Ca ratios in the calcite, usually considered as good climate proxies, were chosen for this study. Both ratios show significant changes, which can be interpreted in terms of paleoclimate. Mg/Ca ratio is sensible to temperature [1], whereas the changes in Sr/Ca could be related to rainfall [1]. Lateral continuity, replicability and repeatability tests were done in order to validate the methodology.

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References

- [1] I. J. Fairchild, A. Borsato, A. F. Tooth, S. Frisia, C. J. Hawkesworth, Y. Huang, F. McDermott, y B. Spiro, «Controls on trace element (Sr–Mg) compositions of carbonate cave waters: implications for speleothem climatic records», *Chem. Geol.*, vol. 166, n.º 3-4, pp. 255-269, may 2000.
- [2] I. J. Fairchild, C. L. Smith, A. Baker, L. Fuller, C. Spötl, D. Matthey, F. McDermott, y E.I.M.F., «Modification and preservation of environmental signals in speleothems», *Earth-Sci. Rev.*, vol. 75, n.º 1-4, pp. 105-153, mar. 2006.
- [3] J. Martín-Chivelet, M. B. Muñoz-García, A. I. Ortega, J. Cruz-Martínez, A. Garralón, y M. J. Turrero, «Speleothem microstratigraphy: some clues for paleoclimate series reconstruction at centennial to decadal scales», *Ciênc. Terra*, vol. 18, n.º 0, jul. 2013.
- [4] A. Baker, C. Smith, C. Jex, I. Fairchild, D. Genty, y L. Fuller, «Annually laminated speleothems: a review», *Int. J. Speleol.*, vol. 37, n.º 3, ene. 2008.

Time evolution of the infrared laser ablation plasma plume of SiO

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The optical emission spectroscopy of the ablation plume from a material is a useful tool to study the dynamics of species formed in this process [1]. Ablation of silicon monoxide targets permits the synthesis of films with different properties and structures. After CO₂ laser ablation of SiO targets, formation of Si nanocrystals takes place on the SiO surface [2]. A better understanding of the mechanisms of the SiO laser ablation plume, can provide control on the properties of the final deposition products. In this work the Laser Induced Breakdown Spectroscopy (LIBS) was applied to study the time dependence of different parameters that define the plasma plume. This plume was rich in atomic, strongly ionized and molecular excited species as SiI, SiII, SiIII, SiIV, OI, OII, OIII, OIV or SiO. Stark-broadened profiles of some lines of SiII were used for calculate the electronic density, n_e , the ionization degree was also estimated. Time of Flight (TOF) measurement of some plasma species allowed to calculate the time evolution of such species as well as the time dependence on their velocity distribution. Plasma plume image and 2D spectral image were taken to understand the temporal behaviour.

Acknowledgements

We gratefully acknowledge t

he support received by the MICINN (Spain, Ministerio de Ciencia e Innovación), Project: CTQ2010-15680 for this research.

References

[1] L. Díaz, L. Rubio, J.J. Camacho, *Appl Phys* . 110:847–851 (2013)

[2] L. Díaz, M. Santos, J.A. Torresano, M. Castillejo, M. Jadraque, M. Martín, M. Oujja, E. Rebollar, *Appl Phys A* 85, 33-37 (2006)

Spectral characterization and temporal evolution of the induced plasma emission in the ablation of aluminium alloy

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Laser-induced breakdown spectroscopy (LIBS) is a powerful optical emission analytical tool capable of sampling solids, liquids and gases for research and industrial applications[1]. A pulsed high-power laser is used to ablate a piece of the sample and excite it till plasma state. The optical emission from the relaxation of excited species within the plasma yields information regarding the composition of the material under test. Moreover, LIBS enables the study of some parameters regarding the fundamental point of view: electron temperature T_e and number density N_e . This is feasible since some assumptions can be made, such as the existence of local thermodynamic equilibrium (LTE) conditions and optically thin plasma. Even though the plasma parameters rapidly change during the measurement time due to its expansion, the plasmas fulfil LTE conditions.

In this communication we report some results on wavelength and time resolved measurements of the optical emissions in a plasma induced by both, Nd-Yag and CO₂ pulsed-laser on the target surface of an aluminium 2024 alloy. The composition of this alloy allows the analysis of emission lines from atomic and ionic species of Al, Mg, Cu and Mn. This study was made in both medium vacuum conditions and atmospheric pressure of air. In these conditions, vibrational bands sequence of AlO is observed. The time dependence and velocity distributions of space-integrated emission of some excited species are registered thanks to time-resolved optical emission spectroscopy and imaging techniques. Intensities of some species were used for determining electron temperature and their Stark-broadened profiles were employed to calculate electron density as described in previous papers[2-3]. Some important differences in the obtained spectra are observed because of different characteristics between Nd-Yag and CO₂ pulsed laser. The plasma spectrum obtained using CO₂ laser shows more lines, due to ionic species, than the plasma spectrum obtained using Nd-Yag laser. On the other hand, the imaging and time-resolved combined techniques allow the identification of some low-intensity lines, which are hidden in the integrated spectrum.

References

- [1] DA. Cremers, LJ. Radziemski "Handbook of Laser-Induced Breakdown Spectroscopy", Wiley, Chichester 2006.
- [2] JJ. Camacho, JML. Poyato, L. Díaz, M. Santos, "Spectroscopic analysis of chemical species in carbon plasmas induced by high-power IR CO₂ laser" in Applied Physics in the 21st century. Chapter 2, Nova Science Publishers Inc., New York, 2009.
- [3] JJ. Camacho, L. Diaz, M. Santos, LJ. Juan, JML. Poyato, "Optical Breakdown in Gases Induced by High-Power IR CO₂ Laser Pulses", in: Laser Beams: Theory and Applications. Chapter 13, Nova Science Publishers Inc., New York, 2009.

Time characterization of the laser ablation plasma plume of CaO produced by a pulsed infrared TEA-CO₂ laser

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The underlying physics of laser ablation remains incompletely understood due to complex laser-target and laser-plasma interactions, plasma expansion and confinement, plasma condensation interaction processes.

The experimental setup and equipment used has been described elsewhere [1]. The laser beam from a transversely excited atmospheric (TEA) CO₂ pulsed-laser was focused onto a CaO target. The laser induced plasma was imaged 1:1 onto the entrance slit of different spectrometers. For time-resolved measurements, the detectors are synchronized with the trigger of the laser pulse. A Dove prism was inserted between to lenses into the observation optical path for rotating $\pi/2$ rad the plasma image for recording 2D spectral images.

The spatio-temporal evolution of the calcium oxide plasma produced by a high-power pulsed TEA-CO₂ laser has been investigated using optical emission spectroscopy (OES) and imaging methods. The emission observed in the plasma region is mainly due to electronic relaxation of excited Ca, Ca⁺, Ca²⁺, O, O⁺ and CaOH fragments. Time-integrated and time-resolved two-dimensional OES plasma profiles were recorded as function of emitted wavelength and distance from the target. The temperature measurements have been performed by Boltzmann diagram method. The temporal behaviour of specific emission lines of the species was characterized. The results show faster decays for continuum and Ca²⁺ species than for Ca⁺ and Ca. The Stark broadening of isolated calcium emission lines was employed for deducing the electron densities.

Acknowledgements

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References

[1] J.J. Camacho, M. Santos, L. Díaz, L.J. Juan, J.M.L. Poyato. Spectroscopy study of air plasma induced by IR CO₂ laser pulses. *Appl. Phys.* 99 (2010) 159.

Pulse tuneable SLM laser in the 205 nm UV region tailor-made for laser aided plasma diagnostic

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Some highly sensitive spectroscopic techniques demand tunable Single Longitudinal Mode (SLM) laser radiation not provided by standard commercial products. In particular some laser aided plasma diagnostics techniques, like those based on two-photon excitation of the 1S-3S/D transition of hydrogen isotopes, require nanosecond UV-laser radiation (200 nm – 300 nm) with some megawatt power in a spectral bandwidth down to 0.5 GHz, frequency tuning with pulse-to-pulse fluctuations below 0.1 GHz and absolute frequency stabilization. As a result of our experience in sensitive spectroscopic techniques and lasers suitable for plasma diagnostics, our group had developed a pulsed UV laser spectrometer fulfilling those requirements. The laser system is based on a similar modular concept as the laser at 243 nm working in our laboratory for the 1S-2S hydrogen transition [1].

Pumped by the second harmonic of a commercial SLM Q-switched Nd:YAG laser, the solid state UV laser spectrometer consists of a seeded KTP (KTiOPO₄) OPO (Optical Parametric Oscillator), Titanium Sapphire (Ti:Sa) amplifiers and UV conversion via stepwise sum frequency generation (SFG) using BBO (β -BaB₂O₄) crystals. The following description explains the details of the UV laser spectrometer.

The seeded KTP-OPO is pumped with a small fraction of the second harmonic of the Nd:YAG laser and the seed beam is provided by a commercial tunable SLM CW diode laser. SLM operation of the OPO is achieved, when the frequencies of the seed beam and the created opto-parametric radiation are identical and well centered on a resonance mode frequency of the cavity. The cavity length control is provided by mounting the out-coupling mirror on a translator stage that allows the variation of the cavity length with nanometer precision. Excellent frequency control is achieved when the OPO is tuned by moving the out-coupling mirror and the seed laser is kept locked on the central cavity mode. The pulse energy of the OPO output at 820 nm is about 1 mJ with 4 ns pulse duration, and the nanometer translation stage provides a tuning range of about 50 GHz.

The OPO pulse is amplified in two Ti:Sa crystals pumped with the main fraction of the second harmonic of the Nd:YAG laser. The first Ti:Sa crystal provides six pass amplification while the second crystal serves as two pass amplifier, generating pulse energies of about 60 mJ.

Finally, in order to obtain the best conversion efficiency, the 820 nm radiation is converted into the deep UV by stepwise SFG via Second (SHG), Third (THG) and Fourth Harmonic Generation (FHG) using three BBO crystals. The resulting radiation at 205 nm has up to 5 mJ pulse energy in about 4 ns and a spectral bandwidth around 300 MHz.

The excellent scan linearity and spectral bandwidth of the laser radiation at 205 nm, as demanded for plasma diagnostic, has been demonstrated by measuring Doppler free the hyperfine structure of the 1S-3S/3D transition of atomic hydrogen in an optogalvanic cell.

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References

[1] K. Grützmacher, M.I. de la Rosa, A.B. Gonzalo, M. Steiger, A. Steiger. Two-photon polarization spectroscopy applied for quantitative measurements of atomic hydrogen in atmospheric pressure flames. *Appl. Phys. B* 76 (2003) 775.

Ultrafast elemental mapping via pulsed radiofrequency glow discharge optical emission spectroscopy

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Glow discharges (GD) are being used as atomization/excitation/ionization sources for different techniques in the area of analytical spectrochemistry. First, glow discharge optical emission spectroscopy (GD-OES) gained interest for direct bulk solid analysis, and later on, as surface analysis technique, especially due to the high depth resolution (in ranges of nm) and multi-elemental quantitative information within a very short time (sputtering rates are of $\mu\text{m min}^{-1}$) that can be obtained. However, its lateral resolution of elemental information is really poor due to the sputtering process of the solid sample surface to produce sample atomization, depends on the inner diameter of the anode used in Grimm-type glow discharge sources (typically 4 mm).

However, more than once it has been demonstrated that useful laterally resolved information can be obtained within the sputtered area of the sample while operating the GD under pulsed conditions. As an example, Webb et al. [1] demonstrated through the analysis of a nickel - chromium alloy substrate with a solid copper inclusion by pulsed powered GD, the spatial resolution was greatly improved compared to when using direct-current powering. Running the discharge in continuous mode gives time to the sputtered analytes to diffuse throughout the whole plasma resulting in emission far from the original position and, thus, causing a loss in surface spatial information. Also, it was found that the lateral resolution is strongly affected by gas pressure and both the pulse width and frequency.

This means that in principle it would be possible for the GD lamp to accommodate very large samples making it possible to carry out ultra-fast 3D elemental mapping, opening the way for a whole new range of possibilities and applications. The real-life impact of this technique has already been shown by Gamez et al. through the elemental mapping of separated protein mixtures of blotting membranes and photographic film sample targets [2,3], as well as the coupling of the GD to a push-broom hyperspectral imaging system using a pulsed dc source [4]. The aim of the present study is to perform two dimensional surface elemental mapping of thin films employing pulsed radiofrequency. The effects of operating parameters of the glow discharge and detection system on the achievable spatial resolution are also investigated.

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References

- [1] M. R. Webb, V. Hoffmann, G. M. Hieftje. Surface elemental mapping using glow discharge – optical emission spectrometry. *Spectrochim. Acta Part B* 61 (2006) 1279.
- [2] G. Gamez, S. J. Ray, F. J. Andrade, M. R. Webb, G. M. Hieftje. Development of a pulsed radiofrequency glow discharge for three-dimensional elemental surface imaging. 1. Application to biopolymer analysis. *Anal. Chem.* 79 (2007) 1317.
- [3] G. Gamez, M. Voronov, S. J. Ray, V. Hoffmann, G. M. Hieftje, J. Michler. Surface elemental mapping via glow discharge optical emission spectroscopy. *Spectrochim. Acta Part B* 70 (2012) 1.
- [4] G. Gamez, G. Mohanty, J. Michler. Ultrafast elemental mapping of materials combinatorial libraries and high-throughput screening samples via pulsed glow discharge optical emission spectroscopy. *J. Anal. At. Spectrom.* 28 (2013) 1016.

Development and analytical characterization of a laser ablation glow discharge optical emission spectroscopy prototype (LA-GD-OES)

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Laser induced breakdown spectroscopy (LIBS) is widely employed for solid elemental analysis due to their important advantages such as little or no sample preparation, high sample throughput, applicability to almost all materials, and high spatial resolution ($\sim \mu\text{m}$), allowing analysis of small selected areas; As drawbacks it can be pointed out the low depth resolution, currently limited to a few hundred nanometers and the matrix effects to carry out quantitative analysis. To overcome this matrix effects it is possible to de-couple the excitation/ionization processes from the atomization by using a secondary source.

On the other hand, glow discharge (GD) devices are typically used as primary spectrochemical sources for direct solid elemental analysis with very interesting properties, such as high depth resolution ($\sim \text{nm}$), fast sputtering rate (in the order of $\mu\text{m}/\text{min}$), multi-element capabilities or low matrix effects although the lateral resolution achievable is rather low (1-4 mm). However it has been scarcely used as a secondary source with laser ablation techniques. In this approach, the laser would transform solid samples into gas phase that could be efficiently excited by the glow discharge.

In this line, Tarik and Günter have explored the combination LA-GD [1] coupled to mass spectrometry, showing its capability as a molecular analytical technique by analyzing organic compounds. On the other hand Wagatsuma [2] and Tereszuschuk et. al. [3] have shown the capability of improving the analytical signals when a LA-GD-OES system is employed.

In this work, a comparison between LIBS and LA-GD-OES is carried out using He and Ar as plasma gases and a Si wafer as sample. For this purpose, an ablation chamber which includes two faced electrodes to generate the discharge has been designed and built; the distance between the sample surface and the electrodes can be modified to achieve the highest boost of the LA plasma and the gas flow path has been optimized to carry the ablated material towards the electrodes. The resulting enhancements when the discharge is on as well as the images of the whole plasma region under the different conditions studied will be shown.

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References

- [1] M. Tarik, D. Günter. A laser ablation millisecond-pulsed glow discharge time-of-flight mass spectrometer (LA-GD-TOFMS) for quasi-simultaneous elemental and molecular analysis. *J. Anal. At. Spectrom.* 25 (2010) 1416.
- [2] T. M. Naeem, H. Matsuta, K. Wagatsuma. Development of a laser ablation-hollow cathode glow discharge emission source and the application to the analysis of steel samples. *Analytical Sciences* 20 (2004) 1717.
- [3] K. A. Tereszchuk, J. M. Vadillo, J. J. Laserna. Energy assistance in laser induced plasma spectrometry (LIPS) by a synchronized microsecond-pulsed glow discharge secondary excitation. *J. Anal. At. Spectrom.* 22 (2007) 183.

Simultaneous ion-photon measurements in laser-induced plasmas of organic compounds

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Coincident detection is of interest to get as much information as possible about transient events occurring in laser induced plasmas. The present work is focused on coincident ion-photon detection of laser plasmas of high-energy organic compounds (TNT and DNT) in condensed phase irradiated with UV laser pulses using an advanced instrument for simultaneous monitoring of both type of chemical species generated. These compounds presented a similar fragmentation pattern in time-of-flight mass spectra in the low-mass region and analogous features in emission LIBS spectra. The optical emission spectrum is acquired from atoms, atomic ions and diatomic molecules, whereas the mass spectrum derives from fragment ions of the molecule. These fragments result from direct ionization or may be formed through indirect pathways. Fluence-resolved experiments showed the evolution of the main optical-mass signals in the acquired spectra for a limited energetic range, showing the different stages of lifetime of plasma: the rising thresholds and extinction of the different atomic and molecular studied species, besides the breakage of the aromatic ring and the later excitation of ionic species at higher fluence level. A good agreement between the trends of the emission and mass atomic species (H, C, N and O) was found out, indicating a high correlation between both processes in the time and energetic scales. As for molecular species, the observed trends were different for diatomic ion signals ($^{24}\text{C}_2^+$ and $^{26}\text{CN}^+/\text{C}_2\text{H}_2^+$) and emission of molecular bands C_2 and CN mainly due to differences in the energetic regime of excitation and ionization processes.

Differential laser-matter interaction in the ablation of solid samples with laser pulses in the interval between 35 fs – 4 ps.

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Our communication is focused on the influence of the pulse width in the laser-matter interaction during laser ablation of solid materials. The experiments were performed with an 80 MHz, 100 nJ, 400 fs Ti-Sapphire oscillator, amplified to produce an output of 3,5 mJ at 35 fs and a maximum repetition rate of 1 KHz. Modifications in the stretcher-compressor have allowed the continuous selection of amplified pulses in the range between 35 fs to 4 ps. The pulses are subjected to measurements in the autocorrelation, spectral bandwidth and energy per pulse. A 0.5 m focal-length spectrograph fitted with an intensified CCD or fast single-channel detectors is used to determine the time constants, to establish the fluence threshold, and to record multi-channel spectra from the generated plasmas. Additionally, morphological characterization making use of optical and electron microscopy were performed.

The effect of the longer laser pulses in the laser-matter interaction - particularly in the extension of the heat-affected zone - and its implication in depth-profiling studies was also checked. For such purpose, a layered sample with a defined structure was analyzed by laser-induced breakdown spectroscopy under different pulse widths conditions. The effect on the averaged ablation rate, depth resolution and layer mixing will be commented.

Time and space resolved optical emission diagnostics of laser induced breakdown muscle tissue samples

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The recent progress made in developing laser-induced breakdown spectroscopy (LIBS) has transformed this technique from an elemental analysis method to one that can be applied for the analysis of complex biological material or clinical specimens. The LIBS method has gained a reputation as a flexible and convenient technique for rapid identification of unknown materials (chemical, biological or explosive). The plasma generated by LIBS technique on muscle tissue samples [1] was investigated using two high-power pulsed lasers (transverse excitation atmospheric CO₂ and Nd:YAG lasers). A remarkable fact is the no influence of the laser wavelength on the observed spectral lines and molecular bands. The emission of the plasma shows excited neutral Na, K, Ca, Mg, H, N and O atoms, ionized C⁺, C²⁺, Mg⁺, N⁺ and O⁺ species and molecular band systems of CN(B²Σ⁺ – X²Σ⁺), C₂(d³Π_g – a³Π_u), CH(A²Δ – X²Π), NH(A³Π – X³Σ) and OH(A²Δ – X²Π). For the assignment of the atomic/ionic lines we used the information tabulated in NIST [2]. The molecular bands were compared with the LIBS experiments obtained in our laboratory on different samples [3-6]. We focus our attention on the dynamics of the muscle tissue laser induced plasma species expanding into air (atmospheric pressure) or into vacuum (air pressures of 0.8 and 0.01 Pa). In conventional one dimensional optical emission spectroscopy (OES) studies, various plasma-plume segments were selected along the plume expansion axis and averaged over line-of-sight. This setup was easily transformed to a two-dimensional (2D) OES setup [7] by inserting a Dove prism between the focusing and collimating lenses. Time-integrated and time-resolved 2D OES plasma profiles were recorded as a function of emitted wavelength and distance from the target. Different plasma parameters such as velocities, temperatures and electron densities were evaluated using OES. The temporal behaviour of specific lines of atomic/ionic lines was characterized.

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References

- [1] A. Marin-Roldan, S. Manzoor, S. Moncayo, F. Navarro-Villoslada, R.C. Izquierdo-Hornillos, J.O. Caceres, Spectrochim. Acta B, published online at <http://dx.doi.org/10.1016/j.sab.2013.07.008>.
- [2] NIST Atomic Spectra Database (version 3.1.5), USA. Available at: <http://physics.nist.gov>
- [3] J.J. Camacho, L. Diaz, M. Santos, D. Reyman, J.M.L. Poyato, J. Phys. D: Appl. Phys. 41 (2008) 105201.
- [4] J.J. Camacho, L. Diaz, M. Santos, L.J. Juan, J.M.L. Poyato, J. Appl. Phys. 106 (2009) 0333306.
- [5] J.J. Camacho, L. Diaz, J.P. Cid, J.M.L. Poyato, Spectrochim. Acta B 88 (2013) 203.
- [6] L. Diaz, L. Rubio, J.J. Camacho, Appl. Phys. A 110 (2013) 847.
- [7] L. Diaz, J.J. Camacho, J.P. Cid, M. Martin, J.M.L. Poyato, Appl. Phys. A, published online at DOI 10.1007/s00339-014-8287-5.

LIPS spectroscopy for chlorine detection in cement samples

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Laser Induced Plasma Spectroscopy (LIPS), or Laser-induced breakdown spectroscopy (LIBS), has been used for elemental analysis of a wide variety of materials since its introduction in the 1960s. LIPS uses a high-power laser pulses focused on a target to obtain a plasma which emits light. Collection of the plasmas light, followed by spectral dispersion and detection permits identification and quantification of the elements present in the sample using their spectral lines. This technique has been successfully tested for the on-line evaluation of P, Mg, Fe, Al, and Si in phosphate ores and of ash content in coal.

The detection of chlorine is interesting for process analysis, environmental or geological exploration (including Mars missions). Process analytical applications are found e.g. in the pharmaceutical, steel, polymer, recycling, mining industry and recently in the material of civil engineering [1-3]. Determination of Cl in concrete and other construction materials is important for knowing the erosion state of these materials [4].

Our group have demonstrated the utilities of LIP spectroscopy for the Cl detection in minerals sample: pure Cl, KCl and NaCl. The main objective of this preliminary work is the study of the applicability of these results for chlorine detection mixed in cement samples.

Different cement samples were prepared with various NaCl concentrations from no-salt to saturated salt sample. In the high NaCl concentrated different atomic lines have been detected that correspond to the Cl-I spectrum and that can be used to the determination of this element in the cement: 725'7 nm, 771'8 nm, 808'7 nm, 837'6 nm, etc. By its isolate character the 837,594 nm seems to be an appropriated choice for this detection.

The oxygen of the air reacts with the excited states of Cl and in consequence the intensity of spectral lines of these elements decreases. In order to avoid this problem, the measurements were made with a controlled atmosphere. The spectrum of air atmosphere was compared on on controlled atmosphere of He.

An important parameter for the Cl detection with LIPS is the pressure of this atmosphere. Using a vacuum pump on-line with the reactor, the pressure is varied from 0.1 to 1000 mb. The optima pressure, corresponding a highest intensity of 837.6 nm Cl-I line, is obtained for a value lower than atmospheric one, about 100 mbar.

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References

- [1] B.Sallé, J.L. Lacour, E. Vors, P. Fichet, S. Maurice, D.A. Cremers, R. Wiens. Laser-induced breakdown spectroscopy for Mars surface analysis: capabilities at stand-off distances and detection of chlorine and sulfur elements. *Spectrochimica Acta Part B* 59 (2004) 1413-1422
- [2] F. Weritz, D. Schaurich, G. Wilsch. Detector comparison for sulfur and chlorine detection with laser induced breakdown spectroscopy in the near-infrared-region. *Spectrochimica Acta Part B* 62 (2007) 1504-1511
- [3] L.St Onge, E. Kwong, E.B. Vadas, Quantitative analysis of pharmaceuticals products by laser-induced breakdown spectroscopy, *Spectrochim. Acta, Part B: Atom. Spectrosc.* 57 (2002) 1131-1140.
- [4] G. Wilsch *, F. Weritz, D. Schaurich, H. Wiggenhauser. Determination of chloride content in concrete structures with laser-induced breakdown spectroscopy. *Construction and Building Materials* 19 (2005) 724-730

SIA optosensor for the simultaneous spectrofluorimetric determination of mixtures of pesticides

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A versatile flow-through multi-optosensor system is proposed for the separation and spectrofluorimetric determination of mixtures of four widely used pesticides, carbendazim, thiabendazole, carbaryl and o-phenilphenol at $\mu\text{g l}^{-1}$ levels in fruits. The flow system is based on the on-line preconcentration and separation of the pesticides on a solid sensing microzone, followed by the sequential measurement of their native fluorescence, monitored the multi-wavelength detection at 279/335, 304/380, 270/324 and 245/337 nm/nm for carbendazim, thiabendazole, carbaryl and o-phenilphenol, respectively; and later desorption of them from the flow-cell using aqueous acetonitrile mixtures as carrier and eluent solutions.

The separation of the pesticides is based on the temporary immobilization of the analytes on a solid support located in the same flow-cell, just above the irradiation area, due to the different retention/desorption kinetics of the analytes when they interact with the C₁₈ silica gel microbeads in the cell. Therefore, both separation and determination are integrated in the flow-cell of a spectrofluorimetric detector that allows a multi-wavelength detection, so considerably simplifying the manifold and the procedure. In addition, the use of Sequential Injection Analysis provides a high degree of automation and minimum wastes generation.

Implementation of flow-through solid phase spectroscopic transduction with photochemically induced fluorescence detection: Determination of clothianidin

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A flow-through optosensor based on the integration of solid-phase spectroscopic detection implemented with photochemically-induced fluorescence (PIF) is described for the determination of clothianidin (a non-fluorescent neonicotinoid insecticide) through multicommutated method. The pesticide is injected in the carrier/eluting stream ($0.0075 \text{ mol l}^{-1} \text{ CH}_3\text{COOH/CH}_3\text{COONa}$, pH=4.8) and flows to a home-made photoreactor, which consists of a PTFE tubing loosely coiled around a low pressure mercury lamp (8W, 254 nm) without any cooling device, because no significant heating is observed. There, the photochemical reaction takes place in slightly acid medium (pH 4.0-4.8) and after this, the fluorescent photoproduct flows to a Hellma 176.752-QS flow cell (internal volume 25 μl , optical length 1.5 mm) which is packed with Sephadex SP C-25 and where it is continuously monitored ($\lambda_{\text{ex}} = 357 \text{ nm}$ and $\lambda_{\text{em}} = 418 \text{ nm}$).

The effect of different physicochemical and Multicommutated Flow Injection Analysis (MCFIA) parameters were optimised, including the irradiation time, flow rate, photoreactor length, solid support, nature and pH of the carrier/eluting solution and sample, and ionic strength. The described sensor will be applied to the determination of the pesticide in real samples of the food industry.

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