X IBERIAN SPECTROSCOPY CONFERENCE
XXVI NATIONAL SPECTROSCOPY MEETING

9 – 11 JULY 2018

LISBOA | PORTUGAL

BOOK OF ABSTRACTS

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Edited by: Maria José Calhorda e Ana Mourato

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12:20 - 12:30		**Closing**
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WELCOME

It is a pleasure to invite you to attend the X Iberian Spectroscopy Conference (X CIE) and the XXVI National Spectroscopy Meeting (RNE), which will take place at Faculdade de Ciências (building C6), Universidade de Lisboa, from 9 to 11 July 2018 in Lisboa, Portugal. This conference has been organized by SPQ (Sociedade Portuguesa de Química) in collaboration with SEQA (Sociedad Española de Química Analítica), SEDOPTICA (Comité de Espectroscopia de la Sociedad Española de Óptica) and SEA (Sociedad de Espectroscopia Aplicada).

The program of the conference includes plenary and invited lectures delivered by well-known international speakers, as well as oral, flash, and panel presentations from participants, addressing a broad range of topics within the field of Molecular and Atomic Spectroscopy, including applications. They will contribute to spread the latest developments in the relevant fields, to promote the exchange of ideas, and to give an opportunity for young researchers and students to present their results. There will be one prize for the best oral presentation (sponsored by SPQ) and another for the best panel presentation (sponsored by Springer - Analytical & Bioanalytical Chemistry).

Maria José Calhorda

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CONFERENCE VENUE

Faculdade de Ciências, Universidade de Lisboa, building C6, room 6.2.56

HOW TO GET TO THE CONFERENCE VENUE

By Metro (Underground)

The "Airport (Aeroporto)" metro station is now available. Exit station- **Campo Grande**.

By Bus

Bus 732. Direction: Hospital Santa Maria. Leave the bus at the stop "Hosp. St^{a}. Maria / Av. Prof. Gama Pinto" before the bus turns left to the final stop in front of the Hospital St^{a}. Maria. Walk down the avenue for about 50 m. The route of bus 732 provides an alternative transportation for participants staying at hotels in the city centre along the Avenida da Liberdade and the area of the Saldanha Square.

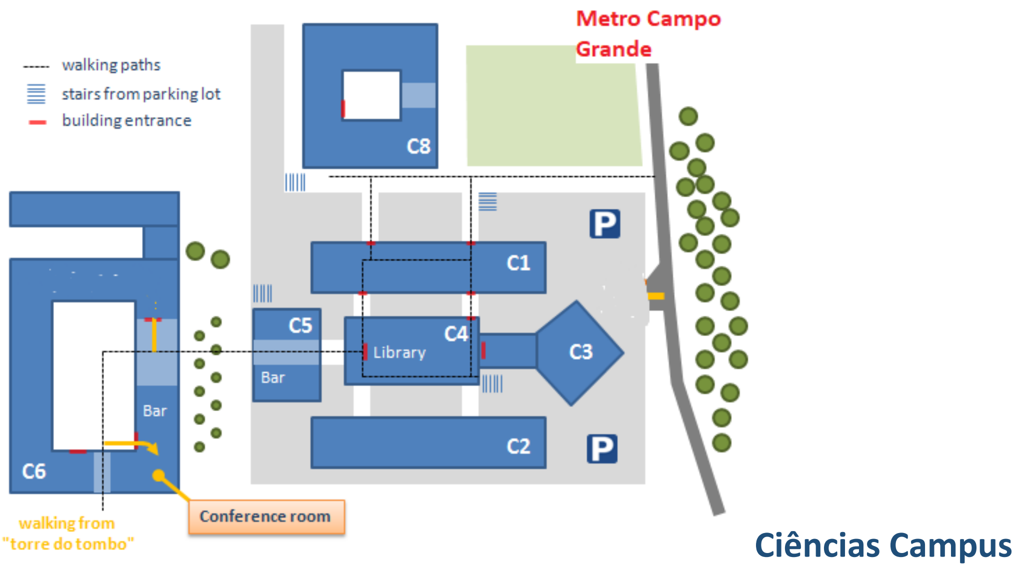
Bus 735. Direction: Hospital Santa Maria. Leave the bus at the stops Cidade Universitaria or Cantina Universidade located in front of the Lisbon University Rectory. The route of bus 735 provides an alternative transportation for participants staying at hotels at Avenida de Roma.

Bus 736. Direction: Odivelas (B. Dr. Lima Pimentel). Leave the bus at the stop Campo Grande / Av. Brasil. Walk along the Avenida de Brasil towards the Alameda da Universidade. The route of bus 36 provides an alternative transportation for participants staying at hotels in the city centre, along the Avenida da Liberdade and the area of the Saldanha Square.

By Taxi

A taxi ride from the airport to the conference venue and the city centre should cost between 8€ and 15€. Taxis are widely used by the locals, and in comparison to the taxi fares in other countries, the Lisboa taxis are still considered a rather inexpensive means of transportation.

Taxi telephone numbers: Autocoope 217 932 756 | Radiotaxis de Lisboa 218 119 000



GENERAL INFORMATION

Registration / Reception Desk

It is located in the Atrium of the C6 building near the conference room. You will collect your delegate badge and conference documentation at the registration desk and check in. Please note that meeting, visit and exhibition areas are accessible only with your delegate badge.

Information on site

During the conference, participants should refer to the reception desk for any changes in the program or need of information

Working language

The working language of the conference is English.

Certificate of Attendance

All registered participants will receive a certificate of attendance inside their personal bag.

Internet

Wireless internet access is available in the hall, amphitheater and room poster.
The password will be provided on site.

Poster sessions

There will be one poster session on Monday from 18:05 to 20:00, but the posters should be exhibited until the end of the conference.

Lunches

Participants who have booked lunchs will receive their ticket meals in their personal bag.
Midday lunches will be taken in the Building C7 on the first floor.

SOCIAL PROGRAM

WELCOME COCKTAIL 9TH JULY

The Welcome cocktail provides an excellent opportunity to network, meet old friends and colleagues, as well as meet new people. It will take place in the Faculty of Sciences at the same time as the poster session.

TOURS 10TH JULY

WALKING THROUGH LISBON

Participants are invited to join a free guided walking tour through the city of Lisbon with Anísio Franco, author of "Caminhar por Lisboa na companhia de Anísio Franco" and "Lisboa Desconhecida e Insólita". Only participants registered for the event in our online platform will be granted access to the tour (40 max).

CITY TOUR BY BUS

Participants may alternatively join a Guided City tour by bus for free. However, only participants registered for the event in our online platform will be granted access to the tour (48 max)

CONFERENCE DINNER 10TH JULY

The Conference Dinner will take place in the The Zambeze Restaurant. Located in the historic centre of Lisbon, between the "Largo do Caldas" and the "S. Jorge Castle", the Zambeze enjoys a superb view over the Downtown Lisbon and the Tagus River. Enhancing the magnificent surrounding, the 300m^2 outdoor terrace offers a modern and relaxed ambiance, ideal for late afternoon moments.

PLENARY COMMUNICATIONS

PL1 Recent Advances in Infra-Red Spectroelectrochemistry

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Information regarding the structural nature of species in solution, and the explication of detailed mechanistic features remain outside the scope of the routine cyclic voltammetric experiment. Instead, experimental methodology which allows for the combination of voltammetric and spectroscopic techniques may permit the in situ elucidation of involved species that form and react under the controlled potential conditions. Furthermore, the stability and chemical reversibility of electrogenerated species can be confirmed. Such experiments, dubbed spectroelectrochemical (SEC) techniques, usually incorporate common molecular spectroscopic techniques, including IR spectroscopic monitoring focused on a range of key reporting groups and their IR-active modes (e.g., in coordination and organometallic chemistry, M-CO, M-NCS, M-NCR, M-H, M-CO-R, M-COOH, M-C=C, M-C≡C, etc.). The design of the IR-SEC experiment warrants the use of a purpose-built optically transparent thin-layer electrochemical (OTTLE) cell. The thin-layer design of the airtight electrochemical cell is necessary in to ensure complete conversion of species in the optical path upon electrochemical reduction, and eliminate the phenomenon of diffusion from the experiment.

The lecture material will tackle two major lines for further expansion of IR spectroelectrochemistry. In the first part, the conventional application will be shown to encompass new facets – variation of electrode material (including a carbon based working electrode), solvent / electrolyte (including ionic liquids), window materials (including HDPE for SEC in the far-IR region), temperature (LT IR SEC) and time-resolution (rapid-scan IR SEC, stopped-flow, pulse-radiolysis). In the second part, emerging less common in situ IR SEC techniques and their application will be presented. The selected topics include vibrational circular dichroism (VCD) SEC, two-dimensional infrared (2D-IR) SEC, and IR-visible sum-frequency generation (IR-vis SFG) SEC, the latter providing great mechanistic insight into redox reactions at diverse electrode surfaces.

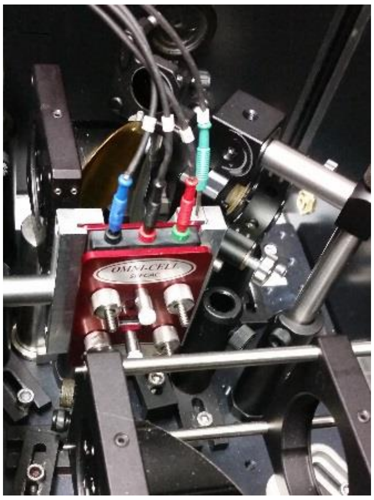

Figure 1. IR OTTLE cell adapted for laser 2D-IR spectroelectrochemistry.

Acknowledgements
The spin-out Reading Spectroelectrochemistry project.

PL2 Spectroscopy of astrophysical ice analogs in the IR and vacuum-UV

Guillermo M. Muñoz Caro[a] , Cristóbal González[a] , Héctor Carrascosa[a]

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Interstellar and circumstellar ices covering dust grains toward cold regions are observed mainly in the midinfrared and occasionally in the far-infrared, along with the silicate grain cores. Bare silicate and carbon dust grains are also seen in the UV, in particular a UV-absorption bump is detected at 217 nm. A detailed spectroscopic characterization of dust and ice analogs in the laboratory is therefore essential to interpret the observations. Meanwhile, some findings are also of interest for physical chemistry. Spectroscopy allowed to unveil that ice mantles are made of H2O and lower amounts of CO, CO2, CH3OH, and NH3, while other species like OCS or OCNare below 1% in abundance compared to H2O. Polar molecules like H2O should accrete first on the dust surface, while less polar ones like CO will accrete on top. This presentation will focus on second-order effects inferred by means of mid- and far-IR, and vacuum-UV spectroscopy. We will provide examples where the interactions between different molecules in ice mixtures can be traced as variations in the band profiles, frequency shifts, or the appearance of new bands. Structural transitions between amorphous and crystalline ice are also known to infer spectral changes. But spectral variations can also be associated to may be less familiar effects in the ice, such as porosity, segregation of molecules in ice mixtures during warm-up of the ice, ice growth, molecular disorder, or even the spontaneous generation of an electric field in the ice.

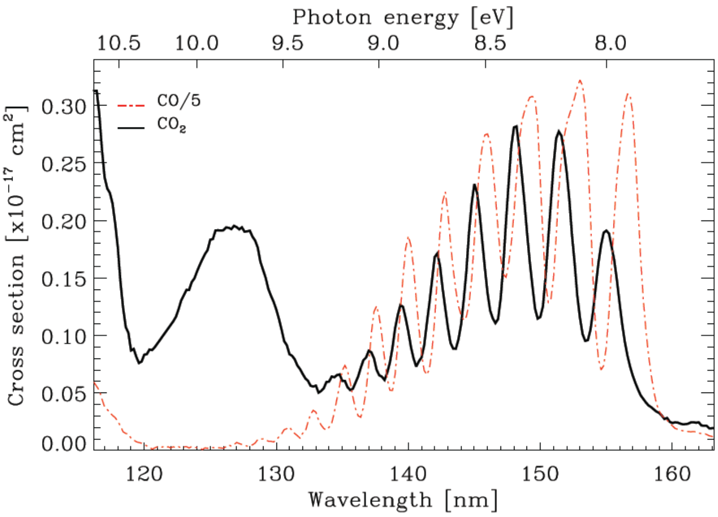

Figure 1. The UV-absorption bands of CO mixed with CO_2 (black solid trace) are shifted to shorter wavelengths with respect to the pure CO ice transitions (red dashed-dotted trace)[1].

Acknowledgements

Support for this work was provided by Spanish MINECO under projects AYA2014-60585-P and AYA2017-85322-R. H. Carrascosa acknowledges financial support from an INTA scholarship.

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PL3 Analytical Nanometrology: Looking for solutions to the challenge

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As in many other areas, Nanoscience and Nanotechnology (N&N) have had a deep impact in Analytical Chemistry [1]. On the one hand, analytical chemists welcome the challenge and opportunities that N&N offer in this area because of both the powerful nanotools to improve analytical properties of results of analytical processes and analysis of the nanoworld. On the other hand, the basic (Nanoscience) and applied (Nanotechnology) developments and achievements need information from the nanoworld to fulfil their respective objectives and to make founded and timely decisions. Just in this last way, the determination of nanomaterials (nanoparticles in many cases), in specific types of samples is a recognized challenge in today analytical science.

Analytical nanometrology (ANM) merges as the metrology applied to nanomaterials for analytical purposes. In this field nanomaterials are considered as analytes, and the analytical goal is the development of analytical strategies for the analysis of specific samples in which they are present. Hence, the validation of the corresponding analytical methods, assuring traceability and expressing the associated uncertainty. This approach is different than the proper characterization of nanomaterials, and it can be seen as full analytical processes, or screening methods for a rapid information about the presence of nanomaterials in particular samples. For this last objective direct spectroscopic and electrochemical techniques can be very useful, whereas for full analytical processes commonly instrumental separation techniques must be involved [2,3]. In any case, some bottle-necks appear when these methodologies can be used to solve true analytical problem in control laboratories. All this aspects will be pointed out in this presentation.

Acknowledgements

Support for this work was provided by the project MINECO CTQ-2016-78793-P.

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PL4 Optical capillary-based microfluidic devices

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The development of new outside-the-lab analytical methods and their corresponding technologies to gather in situ and real time chemical information using low-cost, compact devices is one of the most challenging issues facing the analytical sciences.

One type of analytical system that has the potential to provide fast, laboratory-quality results is the lab-on-a-chip device. These simple, low-cost and robust diagnostic tests are especially interesting in developing regions that lack infrastructure and have shortages in trained personnel, where they can improve healthcare, environmental safety, animal health and food quality.

Typically, these devices consist of silica, glass or polymer chips incorporating enclosed flow channels fabricated using different procedures in which solutions are transported by different propulsion principles providing a set of fluidic unit operations performing the analytical process. As an alternative to glass or polymer microfluidic chips, capillary-based analytical devices use paper, thread or cloth as the support.

The design of capillary-based devices plays an important role in the performance of the device. It must include a sampling area, an analytical operations area for preconcentration, derivatization, metering, mixing, separation, filtration and the like, and a detection area, with colorimetric and electrochemical measurement techniques being the most common.

The widespread use of imaging devices for the colour measurement of capillary-based devices based on the change, appearance or disappearance of colour or any property measured through a colour change, such as luminescence, has paved the way for the development of innovative, complete analytical systems for outside-the-lab applications.

In this presentation, we will discuss some recent developments in the use of capillary-based devices along with computer vision in analytical chemistry [1], looking at the strategies developed for analyte recognition, the imaging devices used –paying special attention to the use of mobile phones, the colour spaces used and the analytical system architecture for colorimetric determination.

Acknowledgements

Support for this work was provided by projects from the Spanish MINECO (CTQ2016-78754-C2-1-R).

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INVITED Lectures

IL1 Modeling the effect of the electrode potential in SERS by electronic structure calculations

Francisco J. Avila Ferrer[a], Daniel Aranda[a], Jéssica Román-Pérez[a], María Rosa López-Ramírez[a], Isabel López-Tocón[a], Juan Francisco Arenas[a], Juan Carlos Otero[a], Juan Soto[a]

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Surface Enhanced Raman Spectroscopy (SERS), due to the ability of greatly intensify the weak Raman signal of molecules adsorbed to metal surfaces, has proven to be a very useful tool to investigate changes in the electronic structure of metal-molecule surface complex.[1] A deep knowledge of the electronic structure of these metal-molecule hybrid systems is key in electrochemistry, catalysis,[2] plasmonics, molecular electronics,[3] and in the development of selective and ultra-sensitive analytical sensors. The origin of this huge enhancement in SERS is due to two contributions: the electromagnetic (EM), related to surface plasmons, and the chemical mechanism, due to resonant charge transfer (CT) process between the adsorbate and the metal (CT-SERS)[4,5] and/or important changes in the electronic structure of the metal-molecule hybrid system.[1] Moreover, electrochemical SERS has proven to be a useful tool to identify resonant CT process and to investigate the effect of the electrode potential in the electronic structure of the surface complex.[4-8] Unfortunately, the SERS implies very complex phenomena where the molecule and the metal nanoparticle are involved. This fact makes challenging to build realistic theoretical models that take into account both the metal and the molecule at quantum level. We propose a methodology, based on Density Functional Theory and ab initio electronic calculations, to simulate the effect of the electrode potential on the absorption, on the charge transfer states energies, and on the electronic excitations in metal-molecule hybrid systems from a microscopic point of view, with special emphasis on their impact on the CT-SERS mechanism. This methodology consists on the prediction of Raman intensities from ab initio calculations of the geometries or the energy gradients at the excited states Franck-Condon point, bringing the possibility to predict the intensities in CT-SERS as well as in resonance Raman without the need to know the excited state geometries, not always feasible to compute. The microscopic model adopted to mimic the effect of the interphase electric potential consist in a molecule adsorbed to a linear silver cluster $[Ag_n\text{-Adsorbate}]^q$, were n is the number of silver atoms, and the total charge of the system (q) is zero for n=2 and q=±1 for n=1, 3 and 7. The combination of the charge and the metal size permits to tune the energy of the CT electronic states though the microscopic parameter $q_{eff}=q/n$, the microscopic analogue of the surface excess of charge.[4-8] q_{eff} can be correlated with the applied potential in electrode SERS experiments, opening the possibility to plot the CT states energies vs q_{eff}, to predict the conditions for CT processes and to reproduce the effect of the electrode potential in the SERS-CT intensities and, as a consequence, in the selection rules.

Acknowledgements

Support for this work was provided by Spanish Ministerio de Economía y Competitividad (Project: CTQ2015-65816-R). FJAF acknowledges financial support from E-29-2018-0016654 from University of Malaga.

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IL2 Quest for a novel preparation method of carbon materials in routine chemical analysis

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Ever since the fullerene molecule was first reported, there has been a continuous stream of investment in research and innovation on the so-called Nanocarbon materials. Amongst these, graphene and carbon nanotubes gathered much attention, as demonstrated by the >150,000 articles published over the last decades. With Nanocarbons soon entering a stage when the know-how accumulated by laboratories worldwide initiates its translation to product development in Industry, one of the most pressing matters is to implement (or strengthen) relevant quality control procedures [1].

Considering that most production methods of graphene and nanotubes originate by-products containing other elements than carbon, quantifying the elemental concentration in sample batches is a key issue. However, the chemical analysis of Nanocarbons is often performed with very localised methods (e.g. energy dispersive X-ray spectroscopy) while more informative techniques such as inductively coupled plasma optical emission spectroscopy (ICP-OES) are overlooked. The main reason for this is known: the challenge of dissolving or disintegrate the graphitic carbon and bring it into solution (i.e. the sample preparation step for ICP-OES analysis). Dry ashing, acid digestion or a combination of these can be used but the protocols are material-specific and involve multiple stages or lengthy procedures, none of which is desirable in routine analysis.

Recently, and upon verifying that considerably expensive Nanocarbons that we procured often had a chemical composition that did not correspond to the technical specifications provided, we re-visited the ICP-OES pre-treatment procedures available for these materials. To our surprise, a commonly used approach for refractories and minerals, the alkaline oxidation (a.k.a. fusion), had been ignored by the research community. Here, I will communicate how we have been developing fusion as an alternative sample pre-treatment step for ICP-OES analysis of Nanocarbons [2-4].

Acknowledgements

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IL3 Luminescent techniques as analytical tools for environmental analysis

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Luminescence has been known as a natural phenomenon since ancient times, with writings dating from 1500-1000 BC. in China, which describe phenomena such as the northern lights or refer to the light emitted by fireflies. The first observations made on solids or solutions capable of emitting light date from the late 16th or early 17th century, but it was not until the 19th century that the physicist Stokes carried out the first scientific experiments that set the foundation of luminescent methods. And it was in the 20th century, with the development of quantum mechanics, that the "*modern era of luminescence*" began, defining itself as a phenomenon of spontaneous radiation emission by deactivation of electronically excited species. Obviously, for the emission of radiation to occur, previously the molecules must be electronically excited, which gives rise to different types of luminescence, depending on whether the excitation is by photons (photoluminescence), thermal (thermoluminescence), by application of an electrical potential (electroluminescence) or, by means of a chemical or biochemical reaction ((bio)chemiluminescence), among others.

The two manifestations of photoluminescence, fluorescence and phosphorescence, differ in that while in the first the excited molecule has the same spin multiplicity as the initial molecule, in phosphorescence the new molecule exhibits a change in the spin multiplicity, which makes the lifetime of the excited state longer and therefore the emission is delayed with respect to the excitation. Luminescent techniques are widely applied in analytical chemistry due mainly to their high sensitivity, which can be up to six orders of magnitude higher than that of techniques based on the measurement of absorbance, and of course to their high selectivity, inherent to the technique itself, which implies that only a few electronically excited molecules emit light.

Nowadays, luminescent techniques are applied to the development of sensors, particularly in the area of biosensing. The (bio)sensor-luminescence binomial is one of the most attractive approaches to develop devices that allow a rapid response to the presence of a given analyte. Some of the advantages of (bio)sensors include that they can measure remotely, *in situ*, in real time, in most cases without analyte consumption, can be easily miniaturized and automated, being portable. The use of a luminescent transducer also provides improved sensitivity, selectivity, reliability, lack of electrical interferences and multiplexing capability. These advantages in combination with the introduction of fiber optics, integrated optics and nanotechnology, broadened the field of application of luminescent (bio)sensors.

These devices have been applied to the determination of a wide range of analytes including, gasses, cations and anions, organic compounds such as hydrocarbons, molecules of clinical interest, etc., being able to work measuring the intrinsic luminescence of a given analyte or that of a luminescent indicator whose emission changes depending on the concentration of the target compound.

This presentation will describe representative examples of luminescent (bio)sensors developed in our group for the determination of gasses, biological oxygen demand (BOD), pesticides, natural toxins or antibiotics using biological or biomimetic recognition elements [1-3]. Finally, the development of (electro)chemiluminescent devices and their application to the analysis of toxic metals in contaminated environmental waters will be reported as well [4,5].

Acknowledgements

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IL4 Photopatterning molecularly imprinted polymers

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In the context of chemical microsensors or microbiosensors, Molecularly Imprinted Polymers (MIPs) are particularly well adapted as synthetic biomimetic recognition materials. Recent examples of MIP have demonstrated their interest for chemical sensors associated to a wide range of chemicals for which these materials exhibit both specificity and sensitivity. However, their development in devices has been confronted to the difficulty to interface the functional material with the transducer or with a microchip. The photochemical route that we proposed significantly simplifies the integration of the functional material into the sensor device. Specific MIP precursors formulations were prepared to fulfil the requirements for micropatterning and molecular imprinting.

Photoinduced polymerization can be used to achieve the preparation of the MIP and at the same time spatially controlled irradiation allows shaping the material. Such route significantly simplifies the integration of MIP in sensors[1]. Advanced methods of photopatterning were used including interference (holography)[2], optical near-field[3], lithography on optical fibers[4] and two-photon stereolithography[5]. Photopatterning appears thereby as one of the most suitable methods for patterning MIP at the micro and nanoscale, directly on the transducer surface. Demonstration of use of these strategies for sensor application is presented. Such route opens new opportunities for low cost, highly sensitive and highly specific sensors.

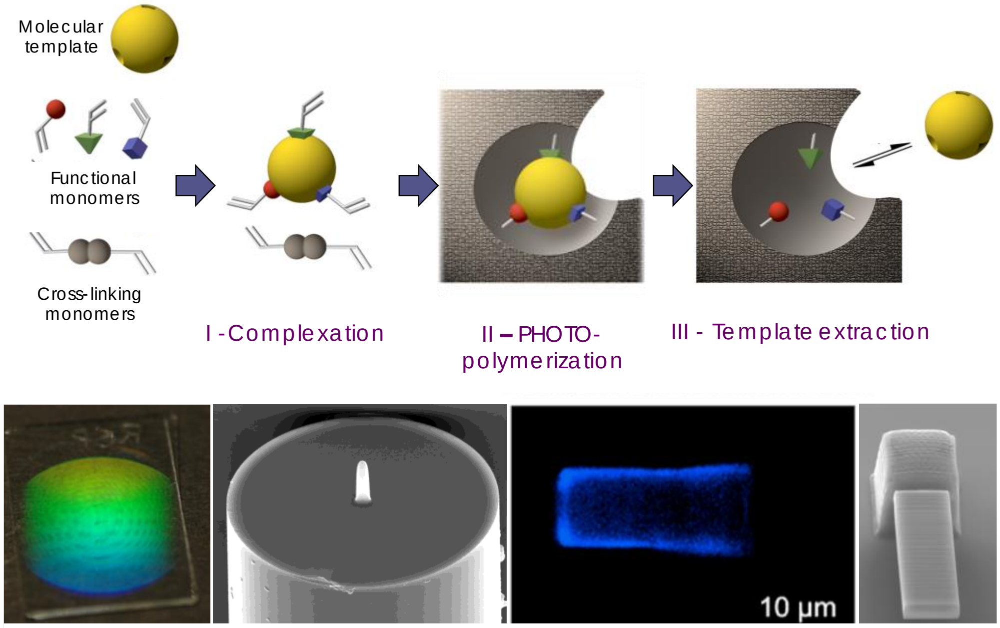

Figure 1. Schematic of the Molecularly Imprinted Polymer (MIP) material preparation by photopolymerization and examples of microstructures

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ORAL COMMUNICATIONS

O1 Adaptation of fungal plasma membrane to a drug challenge

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For a thorough biophysical characterization, one that enable us to answer how the several types of domains may differ in abundance and organization in the presence of a drug agent, the fungal plasma membrane was labeled with fluorescent probes and several photophysical approaches, including steady-state and time-resolved fluorescence spectroscopy, were exploited.

Plasma membrane of *Neurospora crassa*, an orange mold found in old bread that can be used as a model for pathogenic fungi, was characterized by us using *t*-PnA, DPH and di-4-ANEPPS [1]. In this work, we have taken advantage of this recently established strategy, to monitor, *in vivo*, *N. crassa* biophysical changes upon a drug challenge. After 1 h treatment with staurosporine, an alkaloid with antifungal and anticancer properties, an increase in the rigidity of the more ordered membrane domains was observed, possibly associated with the increment on the levels of sphingolipids with smaller headgroups, allowing a tighter packing of the lipid acyl chains [4]. This stronger segregation of sphingolipids contributes to a decreased order in the remainder membrane regions, thus globally the membrane order remains essentially unchanged.

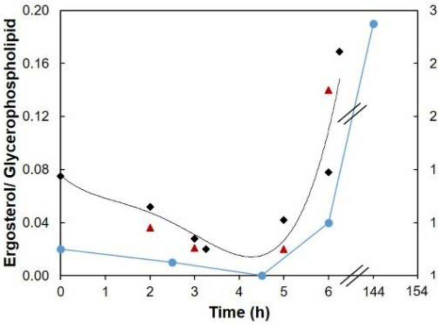

Fig.1 - Ergosterol/ Glycerophospholipid ratio [2, 3] (blue), and amplitude-weighted mean fluorescence lifetime of di-4-ANEPPS in WT at 30 °C, in the absence (CTRL, black) or in the presence of STS (red) *versus* time of growth. The last blue data point corresponds to the composition of mycelium (6 days growth). The lines are merely to guide the eye.

In the conidial stage of growth, *N. crassa* presents vestigial amounts of ergosterol [2]. However, this essential membrane component is a major target for antifungals. To understand to what extent the amplitude-weighted (τ_{av}) mean fluorescence lifetime of di-4-ANEPPS, is related to ergosterol levels, the controls and the ergosterol/glycerophospholipid ratios taken from the literature were plotted *versus* time of growth (**Fig.1**). The overall trend of di-4-ANEPPS τ_{av} correlates remarkably with that of ergosterol/glycerophospholipid ratios. Both departure from a small value that further decreases and then increase exponentially upon starting the *log* phase. In this figure it can be observed how staurosporine e.g. at 5 h growth prevents the marked increase of di-4-ANEPPS τ_{av} observed upon transition to the *log* phase, i.e., the drug inhibits mycelium formation. In conclusion, it was possible to establish clear relations between plasma membrane biophysical properties involving sphingolipids and differences in drug response in vivo. Moreover, we developed a highly sensitive and specific spectroscopic method to follow ergosterol/glycerophospholipid ratio, a paramount biochemical parameter in biomembrane analysis, with crucial relevance in antifungal therapy.

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O2 XPS studies on the in situ synthesis of nanostructures on polysaccharide surfaces

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The chemical modification of fabrics surfaces with metal and/or metal oxides nanoparticles aiming the development of textiles with enhanced surface properties has been the focus of our work in the last few years [1]. Several hybrid (organic/inorganic) systems were synthesized and tested regarding their photocatalytic ability, under visible light, to degrade pollutant organic compounds and, ultimately, chemical warfare agents. X-ray Photoelectron Spectroscopy (XPS) is our main tool used to tune the more efficient experimental protocols to obtain nanostructures chemically adsorbed on the cellulose-based fabrics, like cotton, or on chitosan, providing, all at once, the suitable photoactivity. XPS had helped to characterize the oxidation state of the adsorbed species, their distribution on the surface, giving insights on the syntheses mechanisms. Figure 1 is a chemical state plot (also known as Wagner plot) for silver, which summarises a small calibration study that has been very useful to attest the oxidation state of silver nanoparticles synthesized in situ, i.e. in heterogeneous phase and in mild conditions (low temperature, friendly solvents) directly at the surface of different polysaccharides.

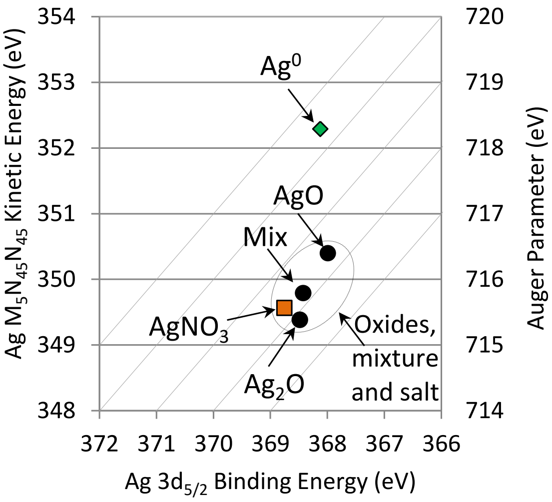

Figure 1. Chemical state plot for silver [2].

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O3 FT-Raman, SERS and DFT studies of the main alkaloids of Syrian Rue

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Syrian Rue, obtained from the seeds of the *Peganum Harmala* plant, is a reddish dye traditionally used as an alternative source for Turkey Red and employed for dyeing carpets and wool fabrics in Western Asia. The main components of the Syrian Rue dye are harmalol, harmaline, harmane, and harmine, which belong to a group of substances called harmala alkaloids [1]. They are also known as β-carboline alkaloids, as their molecular structures are very similar and consist of a pyridine ring that is fused to an indole skeleton.

In a previous work, the extract of *Peganum Harmala* seeds was characterized by surface-enhanced Raman spectroscopy (SERS) upon separation of the individual components by thin-layer chromatography (TLC). In addition, the main alkaloid constituents of Syrian Rue, purchased commercially, were analyzed by normal Raman spectroscopy and SERS, providing valuable reference data to be used for identification purposes [2].

In the present study, Density Functional Theory (DFT) methods were used to perform a vibrational analysis of structurally related molecules, i.e. harmalol, harmaline, harmane, and harmine, by means of the Gaussian Package [3]. The molecular geometry of each alkaloid was optimized and the Raman spectrum was then calculated using B3LYP/6-31G** as a basis set. Subsequently, each Raman band was assigned to each vibrational normal mode of the corresponding molecule. This procedure had been applied successfully to the study of the adsorption mechanism of several molecules on Ag nanoparticles used as SERS substrates [4].

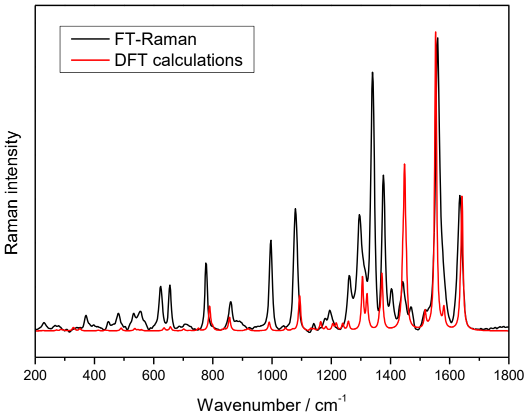

Figure 1. FT-Raman and DFT calculated spectra of harmalol.

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O4 Spectroscopic characterization of amphorae from the 8th to the 7th c. B.C. found at the Phoenician site of Almaraz, Almada, Portugal

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The archaeological site of Almaraz is located in the old part of the city of Almada, in the south shore of Tagus River, region of Lisbon. The excavated findings and the radiocarbon dating of the contexts where these were found show an occupation that can in fact be dated from the 8th to the 7th c. B.C. period, thus a very early stage of the Phoenician occupation in the Iberian Peninsula. Numerous amphorae sherds were found at Almaraz. A spectroscopic characterization of those ceramics was made and is presented here, to help us understand if they were produced locally, in Lisbon workshops, or imported.

Sixteen sherds representative of the thousands found at Almaraz were studied with the use of non-invasive spectroscopies, namely by crossing information from micro-Raman and X-Ray Fluorescence Emission data. X-Ray Diffraction experiments were also performed. Raw materials from several clay sources were collected North and South of the Tagus river, as much as possible from the same clay sources as were used in the initial workshops in this region, and XRD patterns were compared with the ceramics' pastes.

In spite of the fact that no ceramic kilns were found at Almaraz until now, the results point to two major groups of amphorae of local origin: one which used clays of Miocene origin, found on the southern shores of the Tagus river, very close to the Almaraz site, at Palença (with Quartz, Anorthite, Diopside and Hematite). Another group, remarkably different, made use of clays of Pliocene origin also from the Tagus estuary, the Fontaínhas clay source (where Quartz, Anorthite, Muscovite and Hematite were found).

The analysis made in this study thus confirm that the majority of the amphorae found at Almaraz in the Early Iron age was in fact of local/regional production with very few imports, confirming a suspicion that archaeologies shared for some years.

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O5 Gold nanoparticles characterization in cell culture medium using single particle-inductively coupled plasma-mass spectrometry (SP-ICP-MS)

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The application of nanomaterials, such as nanoparticles (NPs), have risen in the last decades in various pharmaceutical and biomedical domains due to their interesting physical and chemical properties. However, there are some evidences showing that NPs could be potentially harmful depending on their concentration, size and characteristics and toxicological studies are required [1]. In this context, it is crucial to develop accurate, robust and fast methods enabling the identification and characterization of metallic NPs in samples from clinical and biological assays.

An emerging powerful technique for the detection and characterization of metallic NPs is single particle-inductively coupled plasma-mass spectrometry (SP-ICP-MS). This technique combined to data evaluation tools allows to obtain information relative to NP size, NP number concentration and the presence of ionized and particle elements in a short period of time at low concentrations [2]. However, there are still some limitations and lack of information concerning its application for the determination of NPs in complex biological matrices and further studies are necessary.

In this work, a new analytical methodology based on the use of SP-ICP-MS has been applied for the identification and characterization of gold nanoparticles (AuNPs) in cell culture medium (Dulbecco's Modified Eagle Medium, DMEM) supplemented with 10% of fetal bovine serum (FBS). AuNPs of different sizes and its ion have been chosen as model analytes. Several performance characteristics influencing data acquisition have been carefully studied. The developed method allows to detect transformations in the biological medium and this information will be very relevant to have a correct interpretation of toxicological test and human health studies in the future.

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O6 The stuccos of the archaeological site of Cástulo (Linares, Spain): archaeometric approach by MRS, EDXRF and GC-MS

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The Project *Cástulo: archaeometric research and social transfer* proposes an archaeometric research carried out jointly by the Universities of Jaén (Spain) and Ghent (Belgium). Cástulo is one of the most outstanding archaeological sites of the Iberian Peninsula, with a long chronological sequence (8th BC-4th AD, Late Bronze, Iberian, Punic and Roman phases). The Project *Cástulo* wants to be a support for the general plan of intervention in the site in order to generate a first level tourist resource that contributes to the social and economic recovery of the city of Linares (Spain).

Within the framework of this project, the physical-chemical analyzes of some of the most interesting Roman stuccos of Building D (dated to the end of the 1st century AD), also known as the building for the imperial cult of Roman emperor Domitian, have been carried out. In total, 7 stuccos from five rooms have been studied, analysing both figurative and schematic motifs in order to obtain the repertoire of raw materials, colourants and organic products used in the elaboration of the decorations.

The samples have been analyzed using a multi-analytical approach, which includes Micro-Raman spectroscopy (MRS) (employing portable and laboratory equipment [2]), Energy Dispersive X-ray Fluorescence (EDXRF) and Gas Chromatography-Mass Spectrometry (GC-MS).

The first results obtained allow identifying and establishing a group of raw materials used in the elaboration of the decoration: cinnabar, hematite and lead compounds for the red colour, goethite for the yellow colour, and Egyptian blue and copper compounds for the elaboration of the blue and green colours. It has also been identified in the main room the use of beeswax and animal fat in the preparation and completion of stucco, which leads to raise questions about the pictorial techniques used in Cástulo: fresh, temper or encaustic.

Figure 1. Stuccos from Cástulo (Linares, Spain)

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O7 Application of SERS technique for characterization of the drug- metal nanocarriers interaction

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The World Health Organization reports the lung cancer as the most common cancer disease, which leads to the highest mortality rate. About 85% of lung cancers are non - small cell lung cancers (NSCLC) [1]. Two small - molecule tyrosine kinase inhibitors gefitinib and erlotinib have been already used to treat NSCLC [2]. Although, gefitinib and erlotinib indicate good results in cancer therapy, not for all patients response to this therapy, has been achieved [3,4]. One of the possibilities of the cancer therapy enhancement is finding appropriate carriers which may improve drug delivery to the target tissues. The effectiveness of the applied carriers is affected by their size and surface features [5]. Therefore the detailed characterization of the carrier coupled with information about how the drug interacts with it, is essential.

In this study, the surface - enhanced Raman spectroscopy (SERS) was applied to characterize the drug - metal nanocarrier interaction and changes in this interaction upon different conditions (applied metal nanoparticles, drug concentration, presence of stabilizers). Fig. 1 presents the SERS spectra for the interaction between erlotinib and silver nanoparticles covered by different stabilizers (SBTC - trisodium citrate; ASC - ascorbic acid; GALL - gallic acid). The observed spectral changes, especially for the band due to the C≡C stretching vibrations [1983 cm^{-1}; ν(C≡C)], indicates that the stabilizer has a significant influence on the investigated interaction.

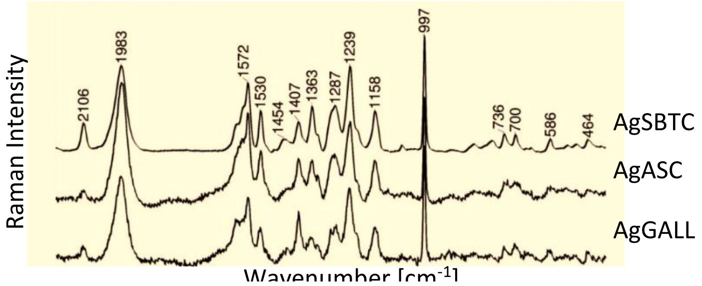

Figure 1. SERS spectra for erlotinib immobilized onto silver nanoparticles covered by different stabilizers.

Acknowledgements

This project has been supported by the National Science Centre Poland under decision no UMO-2016/21/D/ST4/02178. This research was performed using equipment purchased in the frame of the project co-funded by the Małopolska Regional Operational Program Measure 5.1 Krakow Metropolitan Area as an important hub of the European Research Area for 2007-2013, project No. MRPO.05.01.00-12-013/15.

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O8 Frequency shift on the potential-dependent surface-enhanced Raman scattering of pyridine: simplified models for metal and solvent effects

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The electronic structure of adsorbates is altered when it interacts with a surface, modifying the properties of both entities and giving rise to interesting phenomena related to heterogeneous catalysis or molecular electronics. If such surface is a metallic substrate, the electrode potential can be used to tune this interaction. Potential-dependent Surface-Enhanced Raman Scattering (SERS) is a particularly useful technique to study the induced effects on the molecule when the metal-adsorbate surface complex is formed, as the observed frequency shifts of the vibrational modes can provide information about it. However, from the computational point of view, these systems are difficult to model, because the macroscopic metal cannot be modelled easily using quantum mechanics. As an approach, we propose a simple model using silver atomic wires with different size and charge bonded to the molecule (Ag_nPy^q, n = 2,3,5,7 and q = 0 and ±1 for n even and odd, respectively) which has been developed by the group and provides a good description of the effect of the electrode potential on the chemical enhancement mechanism of SERS.[1-3] Electronic calculations were performed using Density Functional Theory (DFT). In order to study the frequency shifts, solvent effects have been taken into account by using the Polarizable Continuum Model (PCM). We have used three different functionals (B3LYP, PW91 and M06HF) and two basis sets (LANL2DZ for all atoms and LANL2DZ for Ag and 6-31G(d) for C,N,H) and, in all cases, a good agreement is achieved in terms of amplitude and trend of the frequency shift for most of the vibrational modes, especially when solvent interactions are included (Figure 1). The method was extended to other metals and solvents giving results in agreement with the available experimental data.

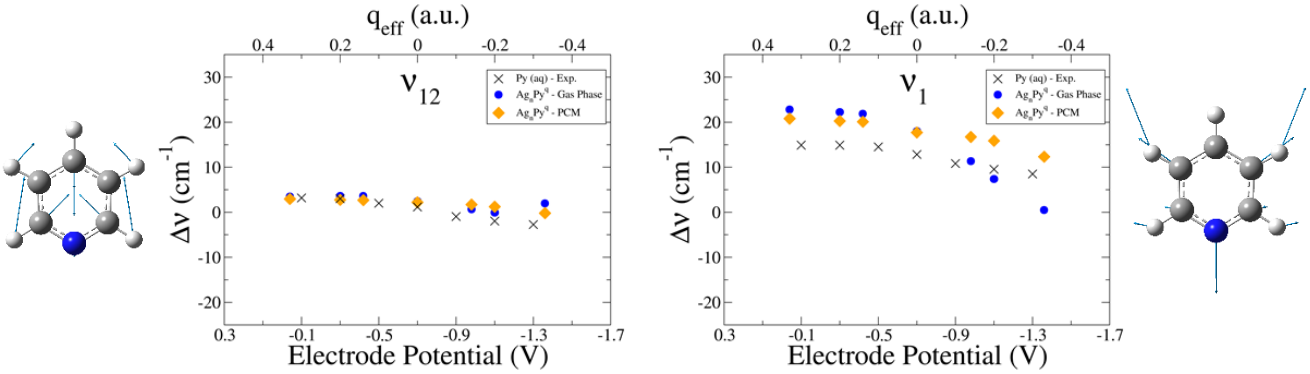

Figure 1. Frequency shifts comparison between experimental (black x) SERS of aqueous pyridine solution and calculated Ag_nPy^q in gas phase (blue circles) and in solution (orange diamonds) for trigonal deformation (ν_{12}) and the breathing (ν_1) vibrational modes.

Acknowledgements

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O9 Unveiling elusive phenolic acid-membrane interactions with fluorescence spectroscopy techniques

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Phenolic acids are widespread phytochemicals that can modulate oxidative stress and chronic inflammation, which have been implicated in the onset/progression of a multitude of degenerative and ageing related diseases [1]. Interaction of polyphenols with the membrane lipid bilayer of various cell types may link antioxidant and anti-inflammatory activities, and therefore underlie their protective effects against diseases. Hence, changes in membrane structure and dynamics upon interaction with polyphenols may be at the core of the mechanism of action of these compounds [2]. Previous study of membrane surface hydration and order did not suggest phenolic acid interaction with lipid bilayers. However, those experiments could not rule-out changes in more subtle properties such as membrane dipole potential and organization of lateral lipid nanodomains such as lipid rafts, i.e. membrane regions enriched in cholesterol and sphingomyelin, involved in cellular processes with broad implications in stress responses.

In this work, using different membrane models, we studied the impact of phenolic acids: caffeic acid (CA), rosmarinic acid (RA) and chlorogenic acid (CGA) on: (a) lipid raft organization in (45:25:30) POPC/PSM/Chol Large Unilamellar Vesicles (LUV), using Forster Resonance Energy Transfer (FRET) and self-quenching phenomena involving membrane probes NBD-DPPE and Rhod-DOPE, measuring changes in fluorescence lifetime and anisotropy of both probes. (b) membrane dipole potential in POPC and (1:1) POPC/Chol LUV, by measuring changes in the excitation spectra of di-8-ANEPPS.

RA and CGA decreased dipole potential in both lipid systems, CGA decreasing by ~10% in both cases and RA inducing the largest decrease, around 30% for both systems. An increased FRET efficiency, consistent with a decrease in raft size, further proved phenolic acid interactions with membrane lipids, with RA showing, once again, the largest impact. A more detailed analysis of probe photophysical properties allowed differentiating the mechanisms of interaction for each phenolic acid.

These results demonstrate the use of advanced fluorescence spectroscopy to quantitively and qualitatively characterize, refined, but impacting, interactions between molecules and biomembranes, that might be undetected by other methods. Indeed, the nanoscale reorganization of sphingolipid/cholesterol-enriched domains by phenolic acids justifies, at least in part, their diverse biological activities.

Acknowledgements

This work was financed by F.C.T., I.P. Portugal: CQB strategic project UID/MULTI/00612/2013 and associated C. S. and H. A. L. F. post-doc fellowships (CC6222-BPD2 and CC6222-BPD4); grants IF/00317/2012 to R.F.A (POPH, Fundo Social Europeu).

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O10 Surface-enhanced infrared absorption spectroscopy in molecule-metal conjugate study

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Surface-enhanced infrared absorption (SEIRA) spectroscopy was first noted by Hartstein and co-workers in the attenuated total reflection (ATR) mode [1]. Later studies have shown that the signal enhancement can also be reached in a transmission, diffuse-reflection, and external-reflection modes [2]. Furthermore, Osawa et al. have also proved that there is a significant dependence between the spectral signal intensities and the incidence angles or polarization modulation [3]. Thus, the application of SEIRA technique together with the tracking the influence of various incidence angles and two orthogonal polarizations on the adsorption geometry provides the possibility of a more detailed characteristics of the solid/liquid interface with a monolayer sensitivity. This study reports a multi-analytical approach to the SEIRA investigation of an indolic molecule geometry on a gold nanoparticle substrate (GNPs) (Figure 1 shows the exemplary FTIR and SEIRA spectra of α-methyl–DL–tryptophan registered in the transmission mode with the suggested way of adsorption onto GNPs). The general aim of this work was to compare the spectra registered in the transmission, ATR and reflection modes to predict the way of adsorption. Additionally, the effect of different incidence angles and two orthogonal polarization modulations (p and s) was discussed to better describe the molecule/metal interaction.

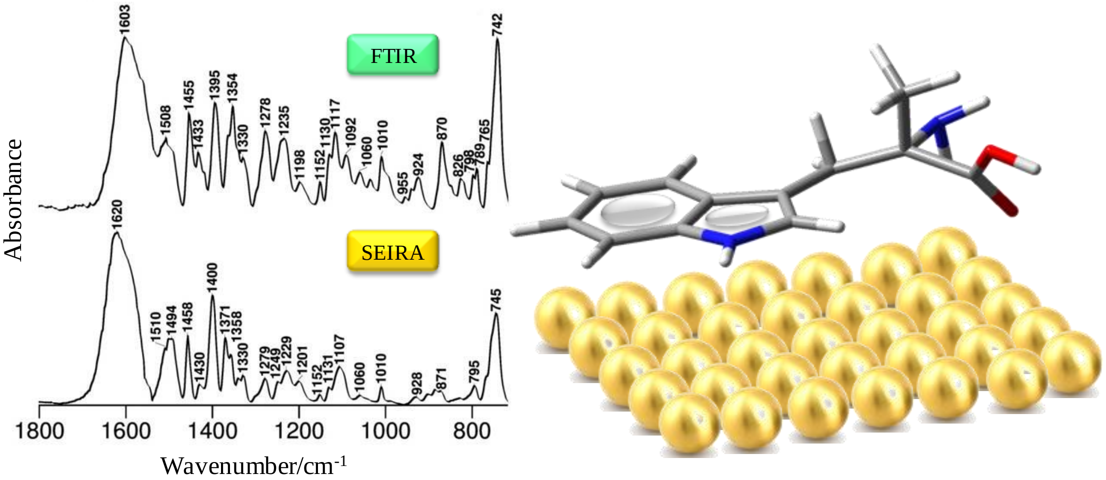

Figure 1. FTIR and SEIRA spectra of α-methyl–DL–tryptophan collected in the transmission mode together with the suggested adsorption geometry onto studied GNPs [unpublished data].

The research was performed by the use of the equipment purchased in the frame of the project co-funded by the Małopolska Regional Operational Program Measure 5.1 Krakow Metropolitan Area as an important hub of the European Research Area for 2007–2013 (No. MRPO.05.01.00–12–013/15). This study was also supported by the National Science Centre Poland (No. 2017/01/X/ST4/00428 to E. P.). The authors acknowledge Dr. M. Oćwieja, J. Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, for nanoparticles synthesis.

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O11 Improving vibrational mode interpretation using Bayesian regression

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Making the assignment of signals found in the vibrational spectra to the atomic motions involved in each vibrational mode can be a cumbersome task. In general, this involves matching between experimentally recorded signals and those gathered from predictions made using first principles calculations. In a subsequent step, the atomic motions generated by the theoretical calculations must be interpreted, which is usually done either by visual inspection, or recurring to Potential Energy Distribution (PED) analysis. While the former technique is simple, it is highly prone to human error[1]. On the other hand, PED usually requires specialized human intervention in order to generate accurate description of the atomic motions[2]. However, such assignments provide valuable physical insights onto the structure and reactivity of matter at the molecular level.

In this work, we explore the viability of using Bayesian Linear Regression with Automatic Relevance Determination (ARD) in order to automate the process of describing the molecular motions associated to a given vibrational mode. For this purpose we developed a software application[3] which inner workings are detailed in Figure 1. The results from example applications[4] show that the VMARD is able to achieve assignments comparable to those of well-established implementations of PED, without the need of prior human intervention (selection of internal coordinates).

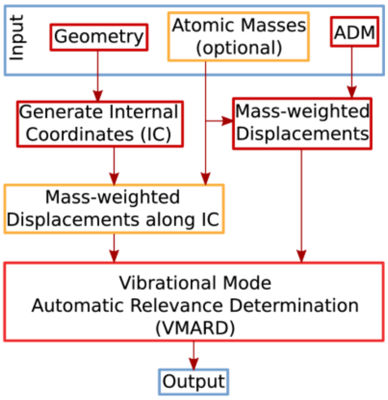

Figure 1. Flow diagram of the VibAnalysis software.

Acknowledgements

This work had the financial support of Fundação para a Ciência e a Tecnologia (FCT/MEC) through national funds and co-financed by FEDER (PT2020 projects UID/QUI/50006/2013 and POCI/01/0145/FEDER/007265).

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O12 DFT and experimental IR spectra of adsorbed and UV processed glycine on bentonite: a Martian study

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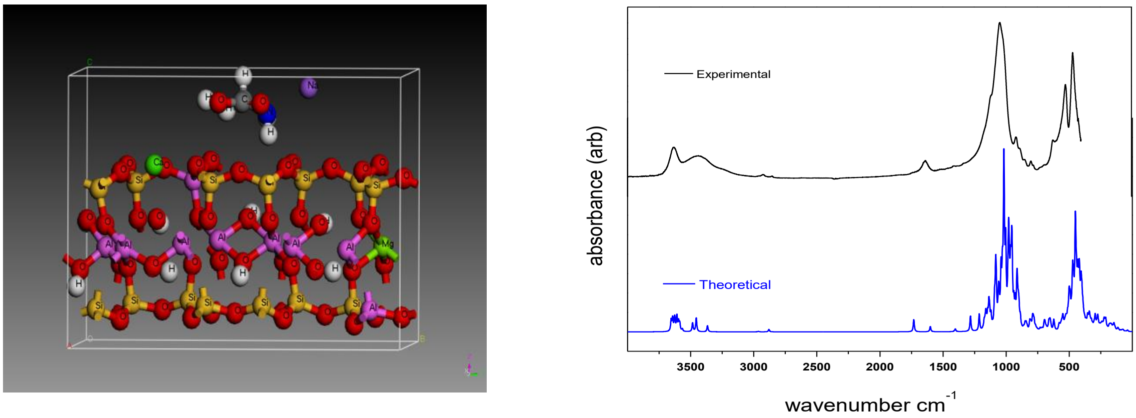
The presence of clay minerals in the solar system extends beyond the planet Earth as they are found on other planets such as Mars [1] and other minor bodies. On the other hand, glycine, the smallest and the only non-chiral amino acid is a fundamental component of peptides and proteins, described as one of the possible life precursors, along with the rest of amino acids. Glycine has been found beyond Earth on comet 67/p[2] and meteorites.

To understand the survival on Martian environment of life building blocks such us amino acids, a spectroscopic research has been done adsorbing glycine on a sample of bentonite (Wyoming), registering its spectra with a Bruker Vertex70 FTIR spectrometer, and following the effects of processing with ultraviolet radiation. Besides, a theoretical structural and spectroscopic DFT study using the CASTEP code [3] has been carried out to understand the adsorption and to achieve an accurate assignment of the vibrational modes before and after the irradiation of the sample with UV.

As shown in Figure 1, a) glycine is adsorbed in a lay-down configuration between the sheets of the bentonite. The corresponding IR spectrum is shown in b), displaying a good agreement between the predicted and the experimental spectra. Features form the UV resulting products of the processed glycine are also found.



a) b)

Figure 1. a) DFT atomistic model and b) IR (experimental and theoretical) IR spectra of adsorbed glycine on bentonite

Support for this work was provided with funding from the Spanish Ministry of Education, Project FIS2016-77726-C3-1-P and Prof Rafael Escribano for his help. Supercomputer time by CSIC-Trueno and CESGA centers are also acknowledged.

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O13 Theoretical assessment of new excited state pathways in a photochromic chromene: The 2,2-Dimethyl-2H-1-benzopyran-6-carbonitrile

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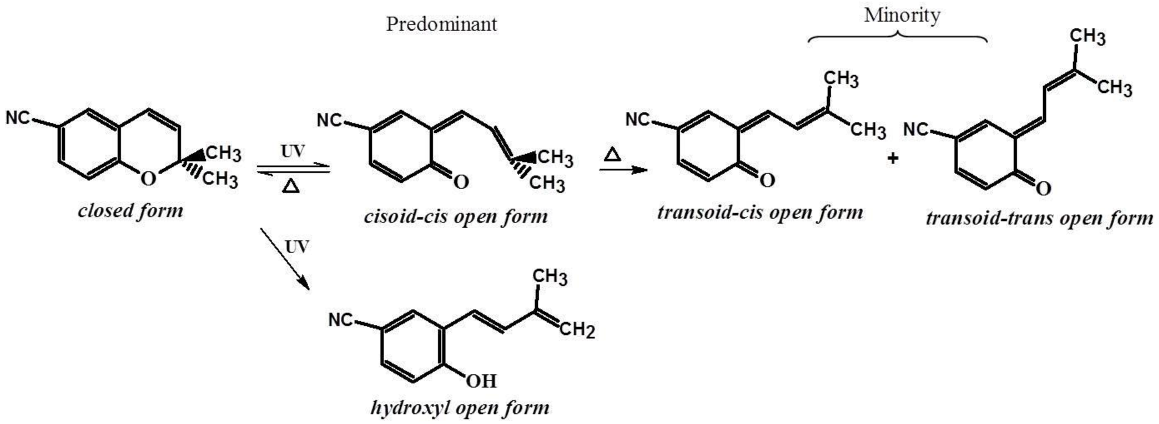
Photochromic applications, such as optical switches or photochromic lenses,[1,2] require fast reversible photoreaction rates. The design of new or improved photochromic compounds require a full understanding of the photochemical and photophysical processes that can occur in the excited state Potential Energy Surface (PES).

The 2,2-Dimethyl-2H-1-benzopyran-6-carbonitrile (DMBPCN) ring-opening reaction was found to consist of two ultrafast competing photochemical processes leading to different photo-products (Scheme 1). Computational methods, coupled to femtosecond pump-probe spectroscopy results, were used to probe the PES aiming at fully understanding the topological features that condition the photochemical pathways.



Two reaction coordinates were involved in the photoreaction processes of DMBPCN. One is a three-step reaction coordinate, called the photochromic reaction coordinate to produce the traditional thermally reversible open forms in the ground state with *cis*- and minor *trans*- geometries, via an intermediate species with a *cisoid* structure. The other one is a one-step reaction coordinate which refers to the ultrafast formation of a strongly emissive and thermally stable hydroxyl open form in the excited state within hundreds of femtoseconds.

Acknowledgements

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O14 Characterization of gold nanoparticles and dissolved gold species in in vitro toxicological studies by AF4-ICPMS

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The use of gold nanoparticles (AuNPs) in biomedical applications has rapidly grown due to recent innovation in the emerging field of nanotechnology [1]. However, their impacts on human health and the environment are not fully known and *in vitro* toxicological assays are necessary. In biological systems used in these studies the nanoparticles can suffer different transformations, such as agglomeration/aggregation, adsorption of proteins (or other biomolecules) onto their surface or metal ions release [2]. Therefore, special attention must be paid to the behaviour and transformations of AuNPs in samples from *in vitro* assays in order to obtain a correct interpretation of the toxicity results and to assess the human and environmental risks of this material. For this purpose, the coupling of hydrodynamic separation techniques with sufficiently sensitive and selective detectors begin to play a decisive role but they are still under development and need to be tested in complex samples [2].

An analytical strategy based on asymmetric flow filed flow fractionation (AF4) hyphenated to inductively coupled plasma mass spectrometry (ICP-MS) has been developed. An *in vitro* toxicological study with HeLa cells (a human cervical adenocarcinoma cell line) in cell culture medium (Dulbecco's Modified Eagle Medium, DMEM, containing 10 % fetal bovine serum, FBS) have been carried out with different AuNPs characteristics (size and stabilizing medium) and incubation conditions. Cells and culture medium from these studies were characterized by the developed AF4-ICP-MS method. The AuNPs can undergo an oxidation process, because Au^{3+} coated by biomolecules present in the cell culture medium has been detected. Also, slight shift towards larger hydrodynamic diameters was observed in the NPs after the incubation time both in the cell culture medium and in the cells. These results suggest that AuNPs could form protein corona, although the formation of aggregates/agglomerates cannot be discarded. The cellular uptake of NPs has also been examined by confocal microscopy, and it is greater at 72 h than 24 h of incubation, even if the difference is very small. Moreover, the biological impact of AuNPs was tested by a classical viability assay onto HeLa cells using cellular media DMEM in the presence of increasing dosage of 10 and 30 nm AuNPs.

Acknowledgements

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O15 Doped-photoluminescent nanoparticles in bioanalytical applications

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Recent advances in nanotechnology have led to a new generation of high-quality nanomaterials with outstanding properties that can be exploited in bioanalytical applications. Among them, the use of nanoparticles (NPs) as imaging probes provides important advantages over traditional molecular-scale contrast agents, including tailored surface functionality with ligands that allow specific targeting and improved circulation time, high loading capacity, or multimodal capabilities that combine two or more different contrast properties to be monitored simultaneously through different imaging techniques [1]. Colloidal semiconductor quantum dots (QDs) constitute an attractive new class of optical contrast agents, exhibiting excellent properties, such as broad absorption bands, narrow and tunable emission colors, high resistance against photobleaching and large surface area for further functionalization [2]. However, tissue auto-fluorescence imposes a limitation to the application of fluorescent QDs like these for in vivo imaging, as it leads to low signal-to-noise ratios that complicate their detection in biological environments, reducing contrast and the clarity of the resulting image.

In order to overcome this limitation, one possibility consists in the development of metal nanoparticles whose excitation/emission wavelengths are in the NIR region. Such type of novel fluorescent labels is very promising in bioanalysis since combine the advantages of both QDs and NIR light. Another approach consists in the development of NPs that join several functionalities (e.g. photoluminescence and magnetic resonance), which is an attractive research area due to their great potential for the advance of biomedical imaging technologies. In this sense, doping a semiconductor nanocrystal host with metal impurities constitutes one of the active research topics in this area. The introduction of transition metals (e.g. Mn) in nanocrystals provides new energy levels that allow that the deactivation process takes place through the dopant energy levels, giving rise to emission characteristics typical of phosphorescent emitters, exhibiting long Stokes shifts, and long luminescent lifetimes. As consequence, the resulting phosphorescent emission allows simple discrimination between the luminescent emission from Mn doped QDs from the background fluorescence of the sample using time-resolved photoluminescence (PL) measurements [3]. Moreover, some of the possible doping ions can be paramagnetic, and therefore act as excellent MRI contrast agents. Therefore, doping with such elements the photoluminescent nanocrystals confers additional MRI contrast capabilities to the QDs.

Results obtained in our laboratory using NIR Ag_2S QDs, and Mn:doped ZnS QDs will be presented as novel probes for bioanalytical applications. Deep characterization in order to estimate key parameters such as nanoparticle concentration, or surface ligand density, as well as imaging applications will be shown.

Acknowledgements

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O16 Which distinctive organizational features in mammals and fungi plasma membrane rely on their main sterol component?

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To understand why sterols evolved towards cholesterol in mammalians and ergosterol in fungi was the main purpose of this work. Here, living mammalian and *Saccharomyces Cerevisiae* cells were used concomitantly with membrane model systems, using a transversal fluorescence spectroscopy approach allowing direct comparison of sterol-dependent properties in all these biosystems. The results strongly suggest that liquid ordered domains in the plasma membrane of mammalian cells arise from the interaction of cholesterol with sphingomyelin or other saturated lipids, whereas in yeast they arise in consequence to the interaction of ergosterol with monounsaturated phospholipids. Zymosterol is a common metabolic precursor to both cholesterol and ergosterol. The integrated analysis of all biophysical data allowed to infer that zymosterol in unable to induce the formation of the liquid ordered phase. In conclusion, sterols in mammals and fungi evolved to sustain in vivo two distinct types of liquid ordered-like phase.

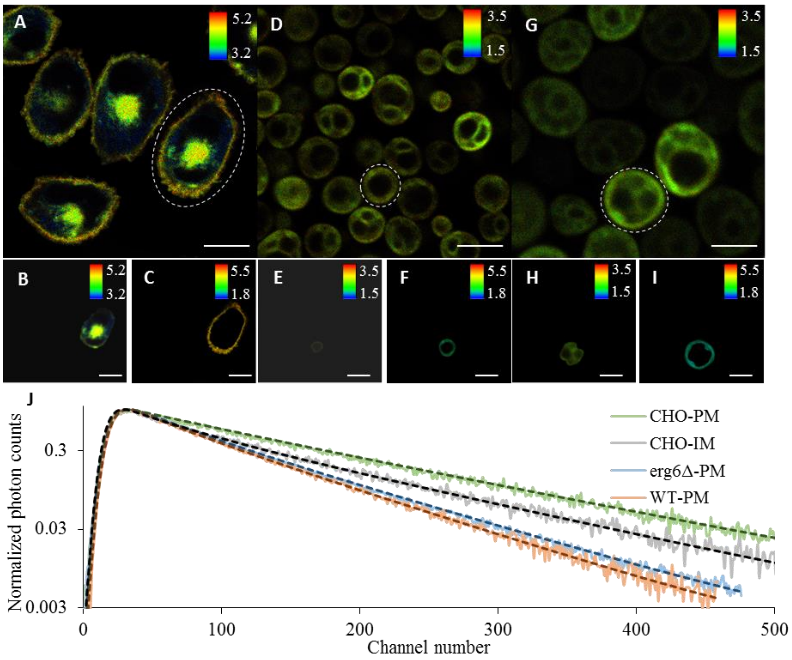

Figure 1. Fluorescence-lifetime imaging microscopy (FLIM) of (CHO-K1) (A-C), wt (D-F) and *erg*6Δ (G-I) *S. cerevisiae* cells labelled with di-4-ANEPPS, a membrane probe which reports preferentially sterol-enriched domains composition and properties. Whole cells are shown in A, D and G, and selected regions corresponding to inner membranes (IM) in B, E, and H and plasma membrane (PM) in C, F and I. Scale bar = 10 µm. In panel J, the fluorescence intensity decays of di-4-ANEPPS in the PM (green) and IM (grey) of mammalian cells, and in the PM of both *erg*6Δ (blue) and wt (orange) yeast cells are shown.

Acknowledgements

Fundação para a Ciência e a Tecnologia (FCT), Portugal is acknowledged for the research grant PTDC/BBB-BQB/6071/2014, which includes a post-doc fellowship to J.T.M., UID/Multi/00612/2013, IF/00317/2012 (POPH, Fundo Social Europeu).

O17 Alkynone-Based Synthesis of Heterocycles

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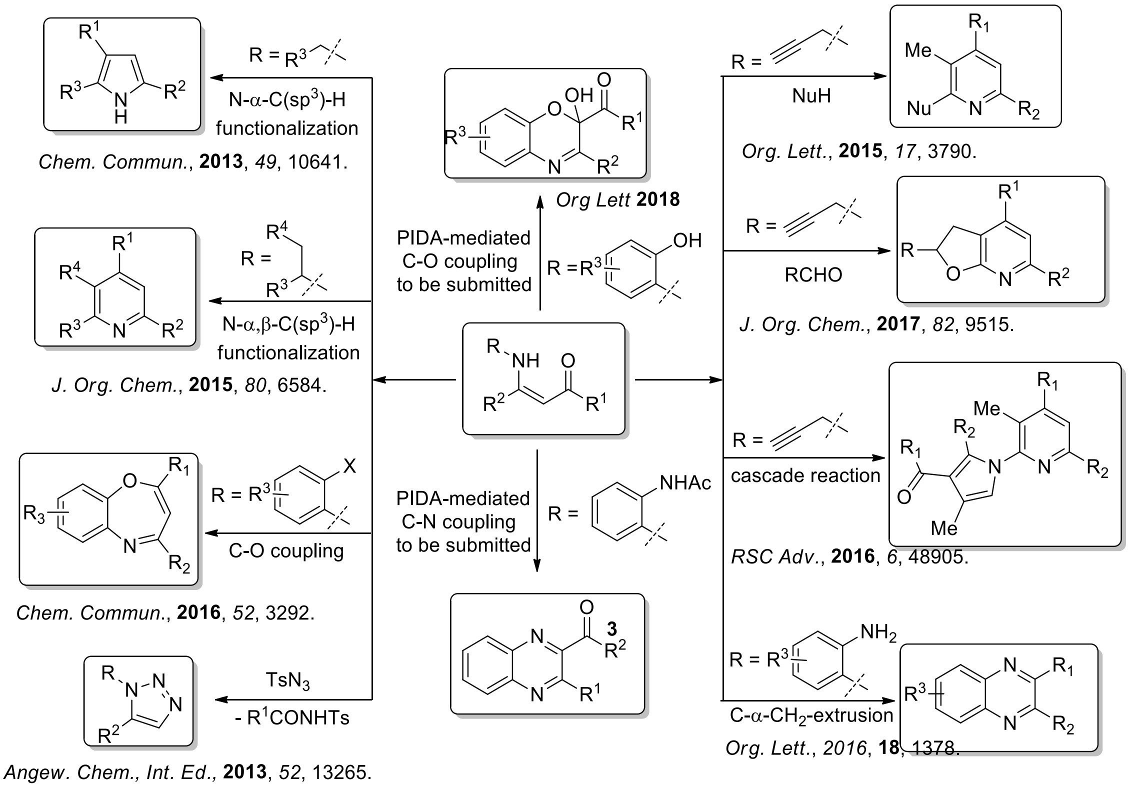
Alkynones are versatile intermediates in organic synthesis. Enaminoes and enolones, result from the conjugate addition of alkynones with amines and alcohols, have emerged as versatile synthetic intermediates that combine the ambident nucleophilicity of enamines (enols) with the ambident electrophilicity of enones. During the course of our studies on the chemistry and application of alkynone derivatives, we developed series of metal-free approaches for the construction of the skeletons of heterocycles, including fuctionalized pyrroles, pyridiens, 1,2,3-triazoles, chromones, and 4(3H)-quinazolinones. In addition, a metal-free synthesis of diaryl-1,2-diketones by C–C triple bond cleavage of alkynones also has been developed in our laboratory.



O18 Single Cell Cisplatin Measurements by ICP-MS

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Cisplatin, carboplatin, and oxaliplatin are the most widely used class of cancer chemotherapy drugs in the Western world treating a variety of cancers.
Many cancers are initially sensitive to platinum-based treatment but patients frequently relapse with tumors displaying resistance to further cisplatin treatment (1)

Cisplatin drug resistance is due to 3 major molecular mechanisms:

- Increased DNA repair
- Increased cytosolic inactivation
- Altered cellular accumulation: decreased uptake or increased export

Cellular uptake of cisplatin is related to tumor burden, thus lower intracellular cisplatin levels are associated with a decreased tumor response Traditional methods involve digesting a cell population and measuring the total platinum content. These methods do not reflect distribution or individual cellular variation of cisplatin uptake.

Objective

Develop the method, Single Cell-Inductively Coupled Plasma Mass Spectrometry (SC-ICP-MS), to quantitate the platinum concentration within individual cells. Ultimate Goal: Increase the uptake of cellular cisplatin resulting in increased DNA damage.

Method

Cisplatin time course experiments were performed using the A2780 cisplatin-sensitive and the corresponding cisplatin-resistant A2780/CP70 ovarian cancer cell lines.

Conclusions

SC-ICP-MS analysis allows for the quantitation of cisplatin within individual cells and is a better method for analyzing cisplatin uptake in a population of cells.

- The distribution of cisplatin uptake is heterogeneous in cells, which more closely reflects what occurs within tumors.
- SC-ICP-MS allows for the development of strategies to increase cisplatin uptake, translating to a better clinical response.
- Cisplatin resistant cells display differences in other metals as well. Further method development is needed to measure other metals.

Acknowledgements

Support for this work was provided by Perkin Elmer Corp.

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O19 Nonlinear absorption spectroscopy of carbon dots reveals selective targeting of carbon clusters

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Molecular materials with efficient nonlinear absorption have found application in optical imaging and sensing in biological media, microfabrication, data storage, photodynamic therapy and power limiting. Recent progress in nanoscience has enabled new kinds of nanostructured materials with improve nonlinear response that can have a real impact in society, among them lanthanide nanoparticle, metal nanoclusters and carbon dots.[1] Due to their optical properties, water solubility and ease of functionalization carbon dots (C-dots) became especially attractive as a platform for biomedical applications (imaging, sensing, drug-delivery).[2] Nevertheless, the largely ignored origin of their emission has precluded an insightful approach to their practical applications, which remains mostly driven by empirical evidence and curiosity.

In this presentation, emphasis will be laid upon our recent study on the nonlinear emission spectroscopy of nitrogen doped carbon dots (Figure 1). We found that both linear and nonlinear emission can be understood based on the existence of isolated sp^2 clusters involved in π–π stacking interactions with clusters in adjacent layers, with the biphotonic interaction being selective towards sp^2 clusters bearing electron donor and acceptor groups on the edge. Our comprehensive study provides an extra piece of the puzzle of the origin of photoluminescence emission in carbon dots.

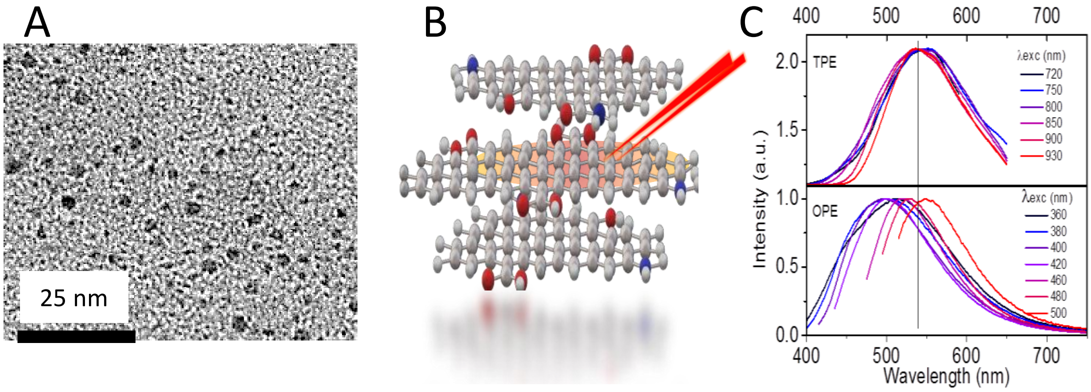

Figure 1. Carbon dots structure and emission spectroscopy: A, TEM image, B, representation of the selectivity of two-photon absorption in C-dots , two-photon and one-photon induced emission.

Acknowledgements
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O20 Development of direct analysis methodologies for dolerite prehistoric objects

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Nowadays, the use of direct analysis are increasing in front of traditional analysis that requires handle sample [1]. The advantages of direct analyses are related to the facts that are faster, cheaper, easier and more ecological than the traditional methods. However, the use of these analytical methods need to be developed and optimize to obtain reliable results.

This study aims to develop a direct analysis approach to measure dolerite prehistory objects to determine their mineralogical profile and the origin of polished axes. Direct analyses are very important for the objects preservation giving also access to useful information. In this case, a methodology is developed based on the use of portable X-ray fluorescence (pXRF) for major elements analysis and Raman microscope to obtain a mineralogical profile of samples [2].

The aforementioned methodologies were applied to dolerite samples from different archaeological fields or natural outcrops located in the Mediterranean area of Spain, between Valencia and Alicante. The use of statistical methodologies as principal component analysis and partial least square (PLS) allow to stablish differences and similarities between the studied stones, therefore these preliminary results show that statistical analysis can discriminate stone samples from different origins as for example stones from the north of Valencia (Spain) than those collected in the province of Alicante (Spain).

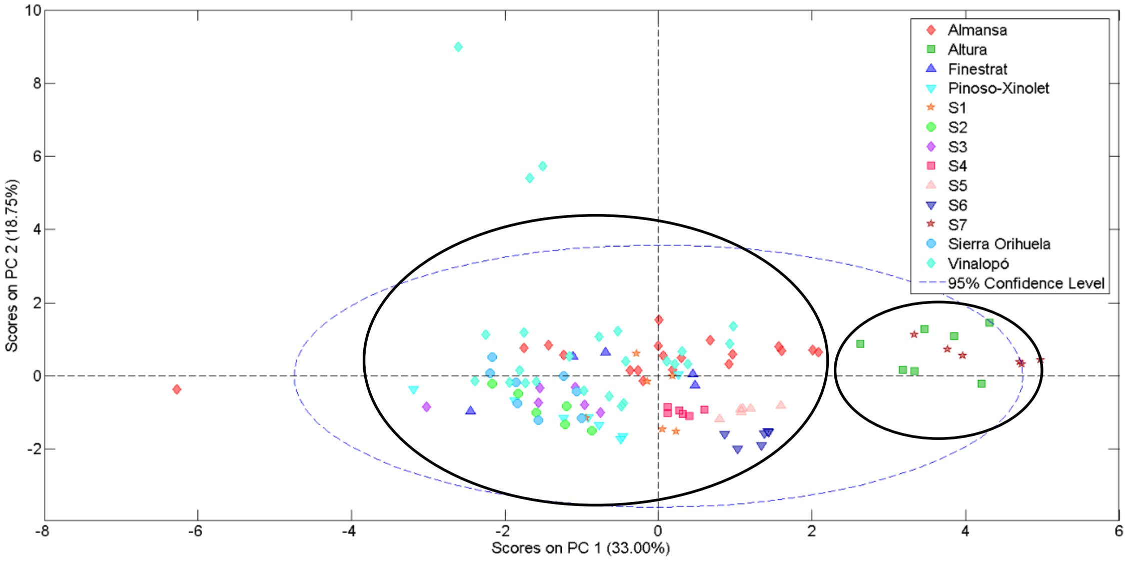

Figure 1. PCA model for natural and archaeological dolerite

Acknowledgements

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O21 Spectroscopic characterization of foods and drinks obtained by addition of new natural colorants

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Colorants are additives widely used in industrial sectors such as food, drinks and cosmetics. Currently a high percentage of these molecules are synthetic and many of them can produce toxic reactions in susceptible organisms [1]. Thus, there is a growing interest in searching new molecules with good coloring capacity to expand the catalogue of natural colorants available in the market. Our research group has patents describing methodologies to obtain two new colorants from microalgae [2]. In this work, we study the potential use of these colorants in different foods and drinks. The aim is to compare the news molecules with the synthetic ones which are being usually used. In this sense, commercial yogurts, milkshakes, isotonic drinks, etc. have been utilized trying to reproduce their color using our new colorants.

Spectroscopic characterization, following color parameters (CIELAB Space: L, a, b), has been utilized to study different samples, obtaining coloring factors and measuring stability against degradation variables such as: time, light exposure and temperature. Figure 1 shows two examples of color variation (ΔE) versus colorant extract added (volume), in order to reproduce the commercial brands color (Table 1). The samples obtained using new colorants have colors very close to the commercial ones and they show an acceptable stability.

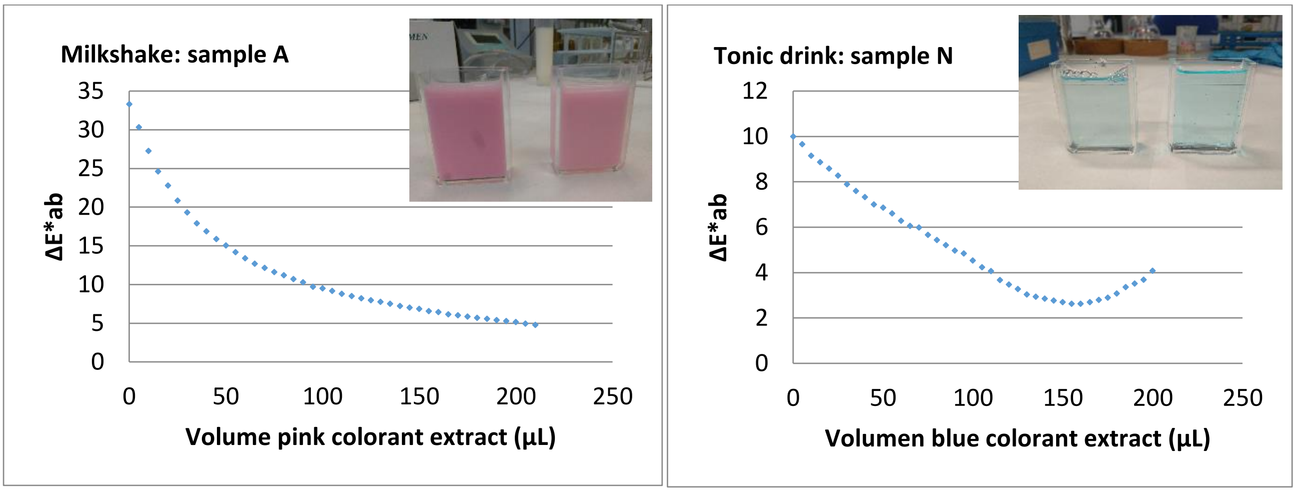

Figure 1. Color differences among commercial samples and samples obtained with new natural colorants.

Table 1. Foods and drinks utilized in the study. Letters represent commercial brands that currently are being sold in the market involving pink and blue colors.

	Milkshakes	Yoghurts	Liquid yoghurts	Isotonics	Tonics
Pink colorant (BPE)	A,B,C,D,E,F	B,C,G,I	B,G,G,H,I		
Blue colorant (PC)				J,K,L	M,N

Acknowledgements

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O22 Fast determination of Cd in wastewater using Solution Cathode Glow Discharge (SCGD) Optical Emission Spectroscopy

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Glow Discharges operating at atmospheric pressure have shown a strong analytical potential for the fast analysis of liquids using optical emission spectroscopy. In particular, Solution Cathode Glow Discharge (SCGD) or Electrolyte-Cathode Atmospheric Glow Discharge (ELCAD), is an alternative source for a fast elemental analysis of liquids. In essence, SCGD is a GD microplasma with 3-4 mm base diameter and several mm height, operating between an electrolytic solution cathode and a metal (e.g. tungsten) rod anode under ~1 kV plasma voltage and ~50 mA discharge current.[1]

SCGD has important advantages over conventional, nebulization-based analytical techniques (e.g. ICP-OES), which are extensively used as reference techniques for inorganic analysis. ICP-OES requires high power (>1 kW) and gas (>15 L min-1 Ar) consumption. These operating conditions effectively tie ICP-OES to the laboratory. As an alternative, SCGD has a small footprint, low power consumption (75 W), and operates in atmospheric pressure air [2]–[5].

The aim of the study is the development of a fast and sensitive method for the determination of cadmium in wastewater using SCGD-OES. The experimental set-up consists of an in-house SCGD coupled to an optical spectrometer with an ICCD (charge coupled device) as the detector. The prototype has been optimized and the influence of key parameters, including cathode-anode distance, the composition of the conductive solution, etc., are investigated. Moreover, different methods are evaluated to enhance the atomic and ionic emission signals, while decreasing the potential interferences due to the emission of the molecular species. The results show that limits of detection of Cd in the range of ppbs can be achieved.

Acknowledgements

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O23 Quantification of low-levels of cyanide in contaminated waters using water-soluble Nir-emitting quantum dots

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Photoluminescent semiconductor nanoparticles, known as Quantum Dots (QDs) have been of increasing interest for luminescent applications in recent times, as they present several important advantages such as long luminescence lifetimes, improved photostability and high sensitivity. However, the most common QDs synthesized emit fluorescence in UV-Vis spectral range, reducing their applicability for biological applications due to self-fluorescence of biological media, which increases the luminescence background and affects the sensitivity.

In this work, Ag_2S Near-Infrared Emitting Quantum Dots (NIR QDs) were synthesized using a one-pot approach in aqueous solution and extensively characterized using a wide variety of complementary techniques, including Transmission Electron Microscopy (TEM), X-Ray Diffraction (XRD), Asymmetric Flow Field Flow Fractionation (AF4) and Inductively-Coupled Plasma Mass Spectrometry (ICP-MS). The effect of different purification techniques on the quality of the NPs was also studied.

Of note are the great luminescent properties of these nanoparticles. Ag_2S QDs present an emission maximum at $\lambda_{em}\approx800$ nm but can be optimally excited at two different excitation wavelengths, $\lambda_{ex}\approx530$ nm and $\lambda_{ex}\approx750$ nm. The second excitation wavelength is of special interest as it allows Ag_2S QDs to be excited in the infrared region, with all the advantages for bioanalysis that implies.

Due to their simple synthesis, long lifetime, appropriate photoluminescent properties and high cytocompatibility, Ag_2S QDs show a promising future for the development of immunosensing approaches. Using the NIR window (700-900 nm) allows us to bypass the quenching effect that water, and therefore biological samples, presents in the visible region (400–700 nm). Ag_2S NIR QDs are also reported to have enormous potential for cytocompatibility. Applicability of the synthesized photoluminescent nanomaterials has been investigated for control of traces of dissolved cyanide in contaminated natural waters, obtaining very good analytical performance based on direct-interaction of the reactive compound with the surface of the NP and quenching of the IR.

O24 PQMS capabilities for calcium isotopes tracer in human nutrition studies

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The use of stable isotope tracers in human studies is a rapidly growing research field that benefits from the many new developments in inorganic mass spectrometric instrumentation and from the better availability of mass spectrometric techniques to nutritional scientists during the last three decades. PlasmaQuant® MS with iCRC technology and cool plasma mode were used to minimized polyatomic ions such as $^{12}C^{16}O_2^+$ and $^{40}ArH_2^+$ at the calcium masses and to develop a method for calcium isotopes ratios in different types of milks.

O25 Low fragmentation by Pulsed Glow Discharge-TOFMS: the analysis of volatile organic compounds samples

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The accurate identification of gaseous compounds, such as Volatile Organic Compounds (VOC), is a key issue in analytical chemistry. Gas Chromatography Mass Spectrometry is one of the most used techniques to separate and identify these compounds without degradation. In this case, the ionization method is based on electron impact. Complementarily, modulated ion sources might be used to provide comprehensive elemental/fragmental/molecular information. Therefore, the analytical potential of a low pressure Pulsed Radiofrequency Glow Discharge (PGD) is here investigated.

GD ionization source is temporally pulsed in order to obtain a dynamic plasma, providing three temporal regimes: the prepeak (at the onset of the GD pulse), where the information about the elemental composition is obtained; the plateau, where structural information might be observed; and afterpeak (just after the end of the GD pulse), related to soft ionization and production of non-degrade molecular ions.

Analytes need to be introduced into the spatial afterglow region of the GD (several mm away from the negative glow region). Therefore, the main goal of this investigation is the coupling of a new sampling interface to enter VOC at the appropriate spatial region of a PGD-Time of flight mass spectrometer (TOFMS). Sample introduction and operating conditions of the PGD-TOFMS are investigated to optimise sensitivity and reduce fragmentation of the selected compounds.

Acknowledgements

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O26 Smartphone-based spectrometry: new portable system for food and pharmaceutical analysis

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Here we present a new smartphone-based spectrometer for vitamin C quantification in real-world quality control applications. When combined with some simple optical components, the rear-facing CMOS camera in a smartphone can provide spectrometric data that rivals that of laboratory instruments, but at a fraction of the cost [1]. The use of a smartphone-based platform poses significant advantages based upon the rise of smartphone apps, which provides a user interface that facilitates adjustment of experimental conditions, data processing, display, cloud storage and/or remote expert analysis.

Our approach utilizes an oxidation-reduction reaction between vitamin C and methylene blue, followed by a dispersive liquid-liquid microextraction (DLLME) to extract the aqueous-phase methylene blue into organic media. Then, a back-extraction procedure is employed to transfer the methylene blue to aqueous media, followed by analysis of the sample's absorption spectrum using the smartphone-based system. The DLLME and back-extraction procedures are optimized by use of a two-step multivariate optimization strategy, using Plackett–Burman and circumscribed central composite designs. Vitamin C supplements and orange juice are used as real-world samples to assess the applicability of the smartphone-based method, which is successfully compared with the standard laboratory-based approach.

In short, the promising analytical methodology proposed here presents a new advance in the development of portable and economical systems available to any laboratory.

Acknowledgements
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O27 Vibrational portrait of a deep eutectic solvent: shape and hydrogen bonds

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The solids choline chloride and urea, mixed in a 1:2 molar proportion, form the iconic deep eutectic solvent "Reline". A combination of computational and vibrational spectroscopy tools, including inelastic neutron scattering (INS), have been used to probe intermolecular interactions in the eutectic mixture. Reline's experimental spectra were estimated using discrete and periodic ab initio calculations of a molecular aggregate with two choline chloride and four urea units. The INS spectrum of reline, compared with that of pure choline chloride, reveals a displacement of chloride anions away from their preferred positions on top of choline's methyl groups, whose torsional movement becomes less hindered in the mixture. Urea, which adopts a planar (sp^2) shape in the crystal, becomes non-planar (sp^3) in reline, a feature herein discussed for the first time. In reline, urea molecules form a wide range of hydrogen bonds, from soft contacts to stronger associations, the latter being responsible for the deviation from ideality. The chloride's interactions with choline are largely conserved at the hydroxyl end while becoming weaker at the cationic headgroup. The interplay of soft and strong interactions confers flexibility to the newly formed hydrogen-bond network and allows the ensemble to remain liquid at room temperature.

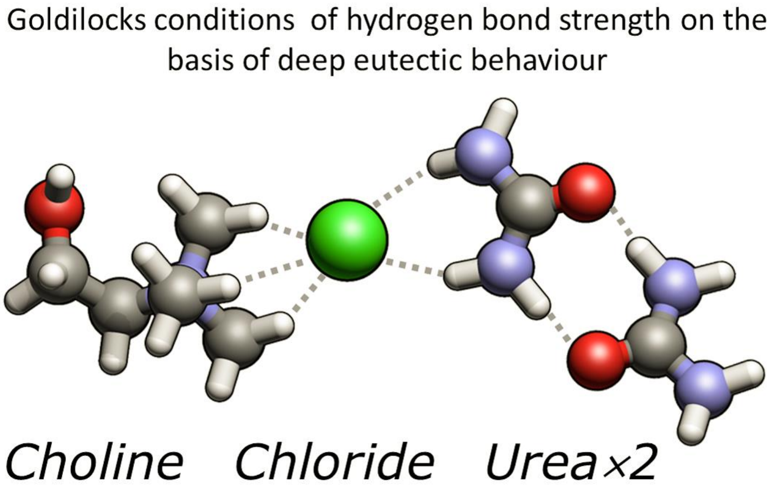

Figure 1. Ball and stick representation of choline chloride and urea. Dotted lines highlight important intermolecular contacts in the deep eutectic mixture.

Acknowledgements

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O28 Sensitive rapid fluorescence polarization immunoassay for free immunosuppressants determination in human serum

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Immunosuppressive drugs (ISDs) are administered to avoid graft rejection in patients receiving solid organ transplants. The free fraction of this drugs in plasma, responsible for its pharmacological activity, is only 1-5% of the administered dose. Higher concentrations can be toxic therefore, considering its narrow therapeutic window, (semi)continuous monitoring in transplanted patients is of great interest to improve the therapeutic efficacy of this drugs. Liquid chromatography analysis of ISDs is the standard analytical tool on clinical laboratories although the development of screening methods based on antibodies has received much attention from both clinical laboratories and diagnostics companies, as they can be better integrated into point-of-care testing (POCT) devices [1].

Fluorescence polarization immunoassays (FPIA) are homogeneous fluorescence-based immunoassays that have been applied to the determination of immunosuppressant drugs (e.g., everolimus and cyclosporin A). In most cases, a competitive immunoassay is performed where either the antibody-bound or antibody-free fractions of a fluorescently labeled antigen (Ag*) are indirectly proportional to the amount of target drug in the sample. One disadvantage associated with this type of immunoassays is the relatively high detection limits obtained for some targets, ascribed in some cases to the use of fluorescein as a label. On this basis, one of the biggest challenges is replacing fluorescein with more photostable labels, absorbing and emitting in the red-near infrared region (650 – 900 nm) [2,3].

The present contribution describes the synthesis of tacrolimus (FK506), mycophenolic acid (MPA), and cyclosporin A (CsA) fluorescent analogs using a ω-amino derivative of a benzo[a]phenoxazine dye. The near-infrared fluorescent dye, which exhibits emission at 662 nm (λ_{em}^{max}) upon excitation at 629 nm ((λ_{exc}^{max}), shows higher photochemical stability than other luminescent tracers [4] and displays significant emission quantum yield in PBS buffer (0.16 ± 0.02). We evaluated the FPIA performance for the three immunosuppressive drugs however only mycophenolic acid provided enough sensitivity. A limit of detection of 0.8 ng mL^{-1} (10% binding inhibition) and a dynamic range of 1.7–39 ng mL^{-1} (20–80% binding inhibition) were obtained for the analysis of free MPA in blood serum and plasma, confirming and excellent sensitivity, that fits the therapeutic requirements. No cross-reactivity was observed to other immunosuppressive drugs administered in combination with MPA (typically CsA and FK506), as well as for the metabolite MPA glucuronide, confirming the suitability of these fluorescent analog for the implementation of immunoassays. Moreover, the assay did succeed in the analysis of free MPA in blood samples of a heart transplanted patient after oral administration of the MPA/FK506 combination, and the results were validated by HPLC-DAD [5].

Acknowledgements

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O29 Cement microstructural changes via continuous CO_2 laser irradiation

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At the present time, cement is the construction material with the highest production and consumption rate worldwide, because of its significant mechanical properties. These properties are modified when the material is subjected to extreme conditions due to several physical and chemical changes which occur in it. [1] One of the most usual extreme conditions is fire, which causes not only a considerable decrease in the mechanical properties of cement, but also chemical changes associated with structural modifications.

In order to study these changes, fire conditions are recreated via continuous CO_2 laser irradiation, which produces a rapid and precise heating. [4]

Portland cement specimens were exposed to these “laser-recreated” extreme conditions, and after irradiation, it is possible to observe areas with different colours determined by the temperature reached, which depends on the radial direction (Figure 1). [5] These specimens were irradiated at different powers, and the reaction products were studied through micro-Raman spectroscopy. In this way, different types of calcium silicates (tricalcium silicate and bicalcium silicate) were characterized according to the temperature reached. Additionally, the formation of calcium sulphate dihydrate (gypsum) and calcium hydroxide (portlandite), both hydrated compounds and unstable at high temperatures, was observed. This means that their formation has been produced by hydration with ambient water.

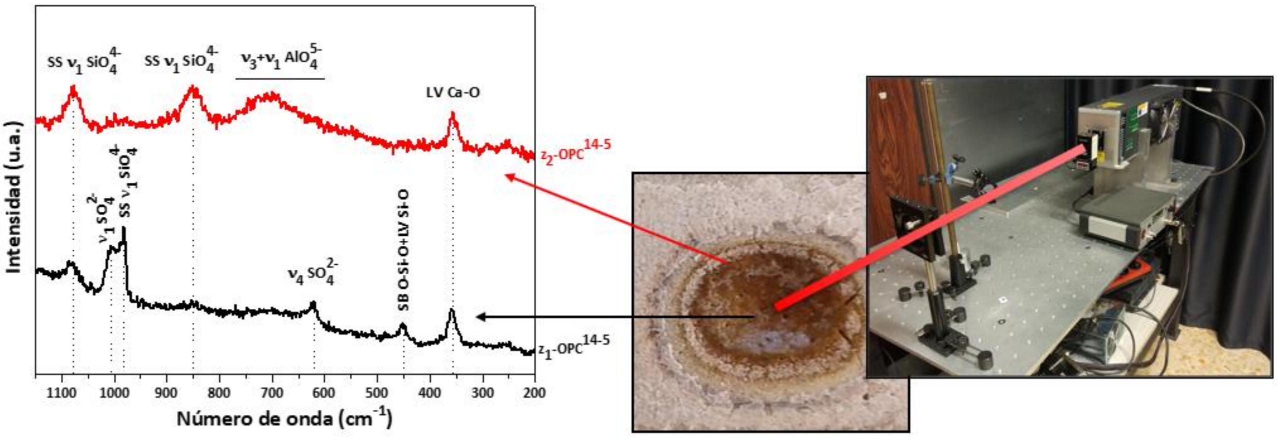

Figure 1. Micro-Raman spectra (λ=785 nm) of different zones after irradiation of Portland cement specimens.

Acknowledgements
This research was supported by the Comunidad de Madrid and the European Social Fund (Program Geomateriales 2-S2013/MIT-2914).

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O30 Time and space resolved study of a modified LIBS plasma by on-line nebulization of Ca-containing solution

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Spectroscopic detection of fluorine in solid samples and, in particular, using Laser-Induced Breakdown Spectroscopy (LIBS), is a challenging task due to the low excitation efficiency of this element. A strategy to increase the sensitivity of fluorine detection is the productionof the LIBS plasma in a helium atmosphere. Therefore, the signal-to-background ratio of fluorine atomic emission lines in the infrared spectral region (680 - 710 nm) increases, improving its detection limits [1]. Alternatively, it has been demonstrated that the determination of fluorine in Ca-containing solid samples can be improved using the emission signal from molecular CaF bands [2].

A novel approach to quantify fluorine in Ca-free samples has been recently developed. This procedure is based on the on-line nebulization of Ca-containing solution in the region where the plasma LIBS is being produced by the laser ablation of the sample [3]. Nebulization parameters were optimized in order to maximize the molecular emission and a linear relationship between the CaF molecular emission signal and the amount of F in the solid samples was achieved with a limit of detection in the order of several µg/g. However, the nebulization process can noticeably modify the plasma properties. Therefore, further studies of the laser-induced plasma dynamics in presence of nebulization are required to fully comprehend the behaviour of the subsequent emission spectra.

To this effect, an imaging system has been developed and coupled to a standard LIBS experimental system. The LIBS system consists of a ns Nd:YAG laser to produce sample ablation and a half-meter Czerny-Turner spectrometer with an intensified charge coupled device (ICCD) as a detector. One of the spectrometer entrances is used for spectroscopic measurements while the other one allows to guide the emission from the plasma directly to the detector; therefore, both types of measurements (spectroscopic and imaging) can be carried out without any modification of the experimental set-up. In this work, a comparative study of the characteristics of the plasma produced with and without Ca solution nebulization when a Cu sample is being ablated is carried out. In this way, properties such as plasma size, temperatures, emission intensities, emission spatial distribution and emission time evolution are obtained and compared.

Acknowledgements

The authors would like to acknowledge the financial support from the Government of the Principality of Asturias through FC-15-GRUPIN14-040 and from the Ministry of Economy (Spain), through the national project MINECO-17-CTQ2016-77887-C2-1-R.

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FLASH COMMUNICATIONS

F1 Ligand substituent effects in Group-6 CO_2 reduction catalysts, $[Mo(CO)_4(x,x'\text{-dimethyl-}2,2'\text{-bipyridine}]$ (x = 4- 6)

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A series of molybdenum tetracarbonyl complexes have been synthesized and their electrochemical properties investigated by cyclic voltammetry and in situ IR-spectroelectrochemistry in THF/NMP using Au/Pt electrodes. The Au electrode allows access to a secondary pathway, red-highlighted in Figure 1, which is producing the 2-reduced five-coordinate catalyst at a less negative overpotential. Particular attention is paid to the catalyst efficiency, with the dimethyl substitution at the 6,6'-position on the 2,2'-bipyridine ligand having the largest positive impact in the studied series, indicating that the methyl groups are involved in the interaction with the surface of the working electrode. In THF, the substitution at both the 4,4' and 5,5' positions disclose the alternative low-overpotential pathway, reported originally for unsubstituted 2,2-bipyridine [1]. Switching to NMP turns this route back on, implying that while being a general feature of this family of Group-6 tetracarbonyls, it is extremely sensitive to not only surface but solvent interactions as well. The trends in NMP are more difficult to resolve as in this solvent the catalysis is strongly enhanced in all cases; with the increased lability of the CO ligands playing a key role.

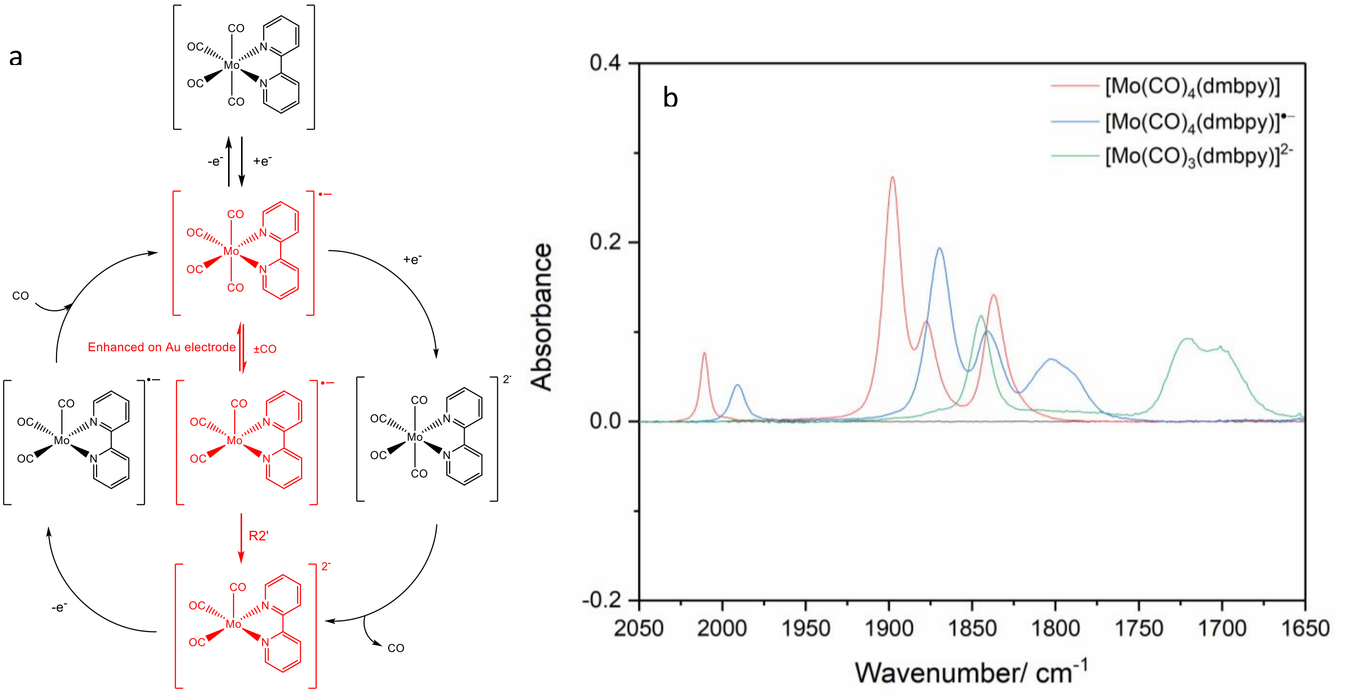

Figure 1. [a] Electrochemical reduction pathway of $[M(CO)_4(bipyridine)]$ complexes (M = Mo, W, Cr).[1] Highlighted in red is an alternative pathway at an Au cathode, producing the catalytic species, $[M(CO)_3(bipyridine)]^{2-}$, ca 600 mV less negatively compared to the Pt electrode surface. [b] IR-SEC of carbonyl ligands charting the conversion of parent to catalyst in THF/Bu_4NPF_6.

Acknowledgements

Financial support for this work was provided by the spin-out Reading Spectroelectrochemistry project and the EPSRC.

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F2 Insights on the acting role of Martian atmosphere in the fragmentation pathways of organic and C-containing inorganic compounds using LIBS

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In the present work, a preliminary fundamental study about the influence of background gas in Martian surface conditions (CO_2, P=7 mbar) on the formation of emitting species in laser-induced plasmas of ablated C-containing compounds was performed. Results were compared with those obtained using ambient air as surrounding gas of irradiated samples.

Energy thresholds were evaluated for excited atomic and molecular species of interest resulting in the plasma using a home-made LIBS system coupled to a pressure chamber for simulating Martian environment during the analysis of samples. Inorganic salts as calcium carbonate and magnesium carbonate besides pyrene as organic reference compound were analyzed in order to discern the origin of C-containing species coexisting in the plasma plume (C, C_2 and CN, mainly).

Results from acquired emission spectra shed light on the different carbon sources of emitting species as a function of energetic and pressure conditions.

F3 Rapid and simple detection of miRNA based on gold nanoparticles

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Micro RNAs (miRNA) are an emerging class of short RNA biomarkers, between 19 and 25 nucleotides, that are involved in different biological processes related to gene expression and regulation, the immune system, cell proliferation, differentiation, apoptosis, etc.

The public available database of confirmed and suspected miRNAs contains information on nearly 36,000 mature miRNA products from 223 species. Many miRNAs have been grouped into families based on shared seed sequences, compounding the difficulty of teasing apart biological effects of a specific miRNA. One of those families is the miR-146, for which a growing number of studies reports correlation of the miR-146 family members with certain pathological conditions. The studies that focus on these miRNAs fall mainly into two broad categories: cancer and inflammation related diseases.

The bovine miR-146 family contains two similar members: bta-miR-146a and bta-miR-146b, which are present in cases of Bovine mastitis, an inflammation of the mammary gland caused by bacterial infection, which is a highly prevalent and costly disease of dairy cattle. Therefore, there is very important to develop a simple, specific and sensitive method to carry out the detection of miRNAs.

The present work aims to show the firs results obtained to perform the detection of miR-146 taking advantage of the excellent optoelectronic features that offer nanomaterials. Specifically, the use of gold nanoparticles is here proposed due to the high sensitivity that can be achieved, the reduction of synthesis cost, and the possible detection by means of colorimetric measurements (or even visual measurements without the need for instrumentation) through the formation of gold nanoparticle aggregates when they are modified with short DNA sequences.

Acknowledgements

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F4 Synthesis of planar chiral ferrocene derivatives via palladium-catalyzed C-H bond activation

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Planar chiral ferrocene derivatives have received great attention in view of their increasing importance in the fields of asymmetric catalysis, enantioselective synthesis, and materials science. They have been widely used as privileged scaffolds for the synthesis of efficient ligands and catalysts. A widely used method is diastereoselective directed *ortho*-metalation reactions of ferrocenes with central chirality. Enantioselective directed ortho-metalation reactions have also been disclosed to introduce planar chirality into non-chiral ferrocenes. Both of these methods need stoichiometric chiral auxiliaries or chiral ligands to control the selectivity, and organolithium reagents are required as a strong base in these reactions. We have developed efficient routes towards synthesis of planar chiral ferrocenes through a palladium-catalyzed C-H bond activation of N,N-dimethylaminomethylferrocene with alkyne, alkene, and diketone via desymmetrization of cyclopentadiene rings in ferrocene by enantioselective C-H activation.

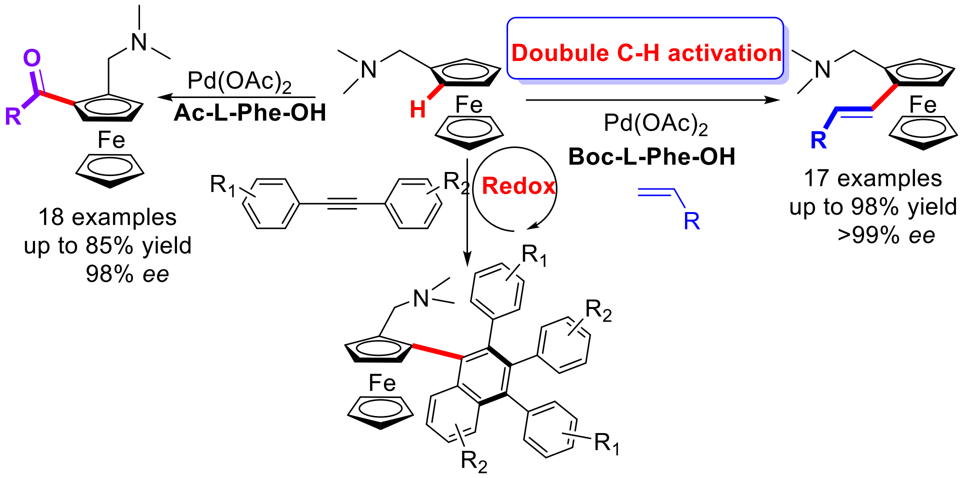

Figure - Strategy to Planar Chiral Ferrocene Derivatives

F5 In situ synthesis model of flavoprotein gold nanoparticles with fluorescent and plasmonic properties for nanobiosensors development

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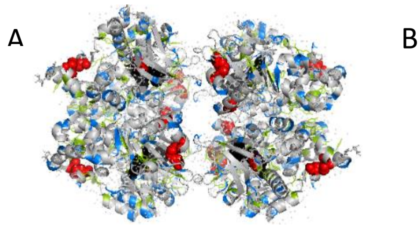
The flavoprotein family possess, in most cases, a flavin adenine dinucleotide (FAD) group as a redox cofactor. FAD presents absorption and fluorescence properties in the visible region, which are different to that of its reduced form ($FAD.H_2$) so changes in these properties during the enzymatic reaction with the substrate can be used as the basis of optical biosensors. [1] However, very often the conformational structure of the enzyme surrounding the FAD, makes the fluorescence cofactor to be highly quenched by the environment and these spectroscopic properties cannot be used as a method of determination.

To improve these intrinsic properties, we propose linking flavoenzymes to nanostructures with appropriate optical properties, such as gold nanoclusters (AuNCs) (nanostructures smaller than gold nanoparticles, biocompatible and that presented fluorescence in the near infrared (NIR)). The idea is promoting fluorescence energy transfer phenomena (FRET) between the FAD and the AuNCs; moreover, these nanomaterials could also modify the structure of the enzyme, leading to an improvement of the intrinsic fluorescence of FAD.

In this work, we present the first steps towards the *in-situ* synthesis of enzyme-encapsulated gold nanoclusters. This "botton up" methodology consists in the use of the amino acid residues of the enzymes to carry out the chemical reduction of a gold salt ($AuCl_4Na \cdot 2H_2O$). Cysteines (cys) stabilize the formation of AuNCs due to the thiol-gold interaction; the reducing residues tyramine (tyr) and tryptophan (trp) reduce the Au ions; and the positively charged amino acids arginine (arg), lysine (lys) and histamine (his) are responsible for the coordination of the $AuCl^-$ ions and determine the amount of Au incorporated in the enzyme. [2]

The flavoenzyme L-amino acid oxidase (LAAO) of *crotalus adamanteus*, has been chosen as a model. Its structure and available amino acid residues have been studied and the synthesis methodology has been optimized. (Fig.1A) The spectroscopic properties of the obtained nanostructures, AuNPs and AuNCs, have been studied (absorption and fluorescence) and have been assigned to the two sizes found by optical transmission microscopy (Fig. 1B). The monitoring of these new optical properties during the enzymatic reaction of LAAO with its analyte L-phenilalanine, ensures the possibilities of this methodology to be used for the development of optical nanobiosensors for bioanalytical applications, based on flavoprotein gold nanoparticles.



Protein data banck LAAO: 2iid.pdb					
Thiol-gold interaction	Reducing residues		Positively charged residues		
cys	try	trp	Arg	Lys	His
24	100	20	118	128	44

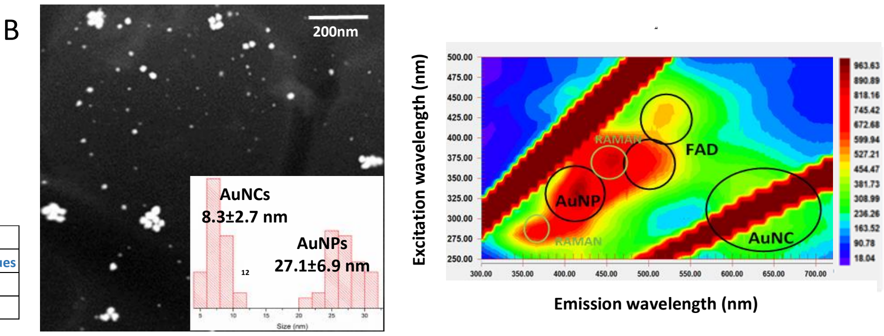


Figure 1. A) LAAO structure and available amino acid residues B) TEM image and size distribution of flavoprotein gold nanoparticles and its fluorescence properties.

Acknowledgements

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POSTER Communications

P1 Validated spectrophotometric methods for the simultaneous determination of chlorpheniramine maleate, pseudoephedrine hydrochloride and propyphenazone

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Green analytical chemistry is embraced now across many pharmaceutical companies and research labs. In this context, two sensitive and eco-friendly UV spectrophotometric methods have been developed for the simultaneous determination of chlorpheniramine maleate (CPM), pseudoephedrine hydrochloride (PSE) and propyphenazone (PRO) in their synthetic mixture and combined dosage form. The proposed spectrophotometric methods namely; derivative ratio spectra-zero crossing method and dual wavelength in ratio spectra method. Linearity was observed in the concentration ranges of 3-50 µg/mL for CPM, 3-35 µg/mL for PSE and 5-40 µg/mL for PRO for the two spectrophotometric methods. No preliminary separation steps are needed for the proposed procedures. The suggested methods were validated with regard to linearity, accuracy and precision according to the International Conference on Harmonization guidelines with good results. It could be used for routine analysis of the mentioned drugs in quality control laboratories without having a bad impact on the environment.

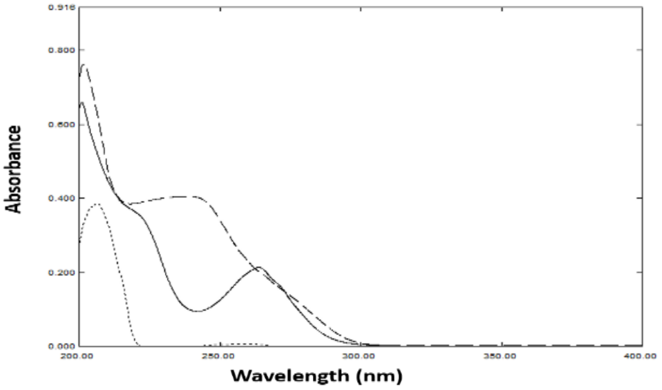

Figure 1. Zero-order absorption spectra of 10 µg/mL Chlorpheniramine maleate (——), 10 µg/mL Pseudoephedrine hydrochloride (…..) and 10 µg/mL Propyphenazone (_ _ _) using 0.1 N HCl as a blank.

Acknowledgements
The authors express their sincere thanks and gratitude EIPICO-Egypt for supplying pure samples of propyphenazone.

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P2 Lighting as active factor in Multi-Calibration of Digital Image Based Methods: expanding the potential of the technique

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Illumination has been principally considered an effect of variability and inconsistency between images. However, this work addresses the lighting as an active factor for boosting the color amplitude in Digital Image Colorimetry, DIC [1]. That is, as a variable that might affect the apparent chromaticity with potential to favor or inhibit analytical sensitivity. This is a change of paradigm, illumination from a re-active to a pro-active consideration. Then, it provides a new factor with capacity to differentiate analytes and to correct interferences when illumination changes.

In this report, the analytical performance of the digital chromaticity produced by sulphites with sodium nitroprusside, SNP, in the Boedecker reaction, was characterized. The reaction is known to form a red precipitate which in our procedure could be boosted by previous precipitation of nanoparticles of Zn(II)- SNP. The method was developed in a simplified assembly with spot test plates, and white D65 lighting. Colours were measured by digital cameras, in jpg and raw formats.

The chromogenic behaviour of sulphites was evaluated by Factorial Analysis in RGB space. The chromatic variance could be justified up to 95% by the analyte influence, while the effects of the method and camera presented lower effects. Linear calibrations with single R or G reflected colours were obtained. R exhibited linear response up to 150 µg L^{-1} sulphite while G showed shorter linear range. However, G response exhibited twice sensitivity. In the best conditions, and G colour, a 3.0 µg L^{-1} Limit of Detection was obtained.

The illumination change, from multi-chrome lamp to a monochrome red, green or blue LEDs demonstrated that reflected RGB single colours increased the linear sensitivity of linear calibrations. The lighting colour favoured the sensitivity of the same reflected colour and inhibited the variance of complementary colours. This was very pronounced with red and blue lighting whereas green illumination acted with amplification of the chromatic variance of all colours.

More, the results evidenced that multi-calibration, with RGB reflected colours obtained with red, green and blue lightings produced sulphite prediction with maximum linear calibration, 150 µg/ml, and lowest prediction error. Statistical comparison between single and multi-colour calibrations evidenced that the prediction error decrease in MLR procedures.

Sulphite determination in commercial white wine could be carried out by MLR with a very simplified procedure of sample dilution. Results of the MLR-DIC new method could be statistically compared to the total sulphite content determined by a reference method.

Acknowledgements

Support for this work was provided by Project CTQ2016-76846-R(MINECO). And Funding for Research groups DGA-FEDER (E25 17R).

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P3 Infrared band strengths and optical constants of solid methanol

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Ices mantles on dust grains in dense clouds in the interstellar medium are formed mainly by H_2O, CO and CO_2. Methanol is the fourth most abundant species in those mantles with an abundance of 6% with respect to water [1]. Solid methanol has also been detected on the surface of minor bodies of the Solar System like some TNOs and Centarus [2]. The information about the composition and structure of astrophysical ices, and in particular confirmation of the presence of solid methanol, is based on the comparison of infrared absorption spectra retrieved by spatial missions or ground based observatories with laboratory data [3].

The goal of this work is to provide new spectroscopic data of solid methanol in the near and mid IR spectral range, that could help to identify and quantify this species in astrophysical ices. Densities and visible refractive index for methanol ices at eight temperatures, from 20 K to 130 K, have been measured. The infrared band strengths and optical constants of those ices from 650 cm^{-1} to 5000 cm^{-1} (15.4 μm to 2.0 μm) were also determined, following the procedure described previously [4]. Comparison with other literature data, when available, will be commented.

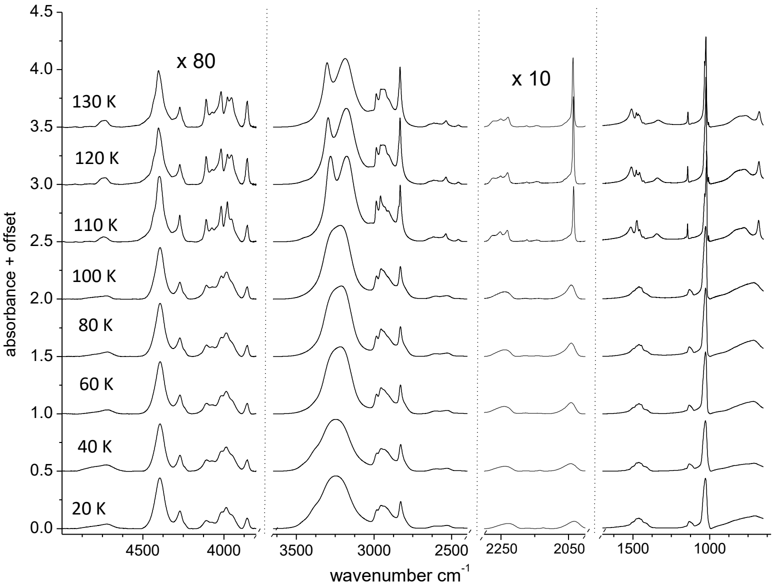

Figure 1. Infrared spectra of methanol ice layers, about 990 nm thick, grown at the indicated temperatures

Acknowledgements

Support for this work was provided by MINECO FIS2016-77726-C3-1-P, and FIS2016-77726-C3-3-P

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P4 Molecular dynamics prediction of near-IR spectra of astrophysical interest

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Many observations in the solar system are carried out in the near-IR region, 1.25-2.5 µm, or 8000-4000 cm^{-1}, where ices of simple molecules and mixtures of them present relatively strong absorption or reflexion spectra, corresponding to their overtone or combination bands. However, whereas theoretical methods to predict and analyze the fundamental vibrations of molecules and solids, appearing usually in the mid-IR, are well-established and straightforward to apply, there are no similar procedures available to deal with the vibrational modes leading to higher excited states.

We propose the use of ab initio Molecular Dynamics to predict the spectra of solid samples containing mixtures of molecules such as those found in different bodies of the Solar system. In particular, we are focused on the exciting recent data obtained by the New Horizons mission on Pluto and Charon [1], where spectra of ices with strikingly different content of methane, water, nitrogen and other gases were recorded.

We have carried out an initial study of these systems using the CASTEP program [2], as contained in the Materials Studio software [3], which uses a first-principles description of the electrons based on density functional theory with plane waves as basis sets. We are currently working on similar systems with a different theoretical approach, using numerical atomic orbitals as basis functions, implemented in the Siesta code [4]. We will present the current state of results at the meeting.

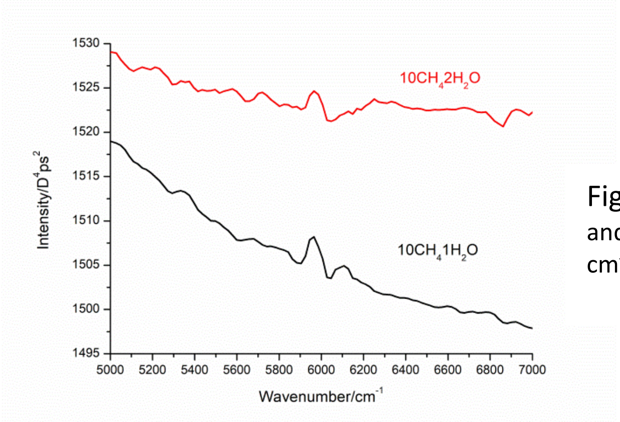

Figure 1. Example of calculations for samples with $10CH_4$ and $1H_2O$ or $2H_2O$ molecules. The spectra in the 5000-7000 cm^{-1} region are reproduced.

Acknowledgements

The calculations have been performed at Trueno (CSIC), CESGA (CSIC-Xunta de Galicia) and Cambridge Computing Centre. Funding has been provided by MINECO FIS2016-C3-1P and MINECO/FEDER CTQ2015-65033-P, and MECD PRX17/00126.

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P5 Semi-quantitative study of the distribution of the active ingredient in divisible tablets

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The divisible tablets are an important product of the pharmaceutical industry since they make it easier to adjust the dose necessary for each patient. For this reason, it is important to ensure that the active pharmaceutical ingredient (API) is distributed homogeneously in each potential fraction of the tablet. Furthermore, in the compaction process there may be a partial segregation of content, so it is also important to verify the homogeneity of content between the two surfaces and the tablet core. Raman spectroscopy has been proposed as analytical tool for this purpose [1]. Because of the low diameter of the laser spot, it is possible to record the spectra in different positions and, after a proper multivariate calibration, to get a map of the API concentration in the tablet. However, the need of this prior calibration is precisely the bottleneck that reduces the practical applications of this methodology in a routine industrial control. In this communication, the intensity of an aromatic peak of the API is used to evaluate its distribution on both surfaces of the tablet and in its core. The drug studied is Lisinopril, which is used to control hypertension and that is break-scored, suggesting the possibility of splitting it into two halves. A *MultiRAM Bruker spectrophotometer,* with a laser of 1064 nm and a spot diameter of 500 µm has been used.

The first step was to perform an experimental design to choose the experimental conditions (spectral resolution, number of scans averaged) to get a good signal-to-noise ratio in a short acquisition time. Once selected the operational parameters, 10 tablets of 4 different production batches were analyzed. 16 spectra (8 in each half) were acquired following a prefixed grid on the break scored tablet surface. Also 16 spectra were recorded on the back surface of some tablets. To get the spectra of the tablet core, three tablets of each batch were randomly selected, split, polished using a cutter and its spectra recorded.

Results were graphically and statistically (ANOVA) analyzed, showing that the API content on both halves is in the limits of dosage uniformity content prescribed by pharmacopoeias. Also no significant differences were found between surfaces and core. Surprisingly, a change in one of the excipients has been found in one of the batches, without affecting the distribution of the API. Also, the minimum number of spectra that must be recorded in each half to get a representative value has been studied.

Acknowledgements

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P6 Portable multispectral imaging system based on colour detector

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Multispectral imaging is an analysis technique based on the acquisition of the same image in different wavelength [1]. Spectral imaging combines two methodologies: spectroscopy and imaging. A spectral image provides a spectrum at each pixel; this additional resolution can be used to detect changes in the surface, structure or composition of the sample [2]. The objective of this work is to create a portable low-cost multispectral imaging system where the camera is substituted by a colour detector. This detector provides an averaged measurement of the colour of a small surface, therefore reducing the size of image to be processed to 1 pixel.

The developed instrument is presented in Figure 1(a). The imaging system consists on a colour detector model S11059-02DT (Hamamatsu Photonics, Japan) which is an I2C interface-compatible digital detector sensitive to red (λ_{peak} =615 nm), green (λ_{peak} = 530 nm), blue (λ_{peak} = 460 nm), and infrared (λ_{peak} = 855 nm) radiation. The measured incident radiation is codified in four words of 16 bits, one for each colour. The wavelength selection is carried out using an array of light emitting diodes (LEDs) with 10 different wavelengths in the range 360-890 nm. A microcontroller model PIC18F2550 (Microchip, USA) receives the output data from the colour detector and sends them to an external computer through an USB connection where they are processed.

The presented system has been applied in three different scenarios. In the first one a material classification has been carried out where several kinds of white paper have been analyzed. In the second experience, a package of fresh pork meat has been monitored along 8 days. In the third experiment the instrument has been applied as a colorimeter to measure the concentration of potassium in water solutions at pH 9. In the Figure 1(b)-(d) low-dimensional 2D representations of the data using principal component analysis are presented. It can be observed that is possible to find a wavelength for which the data are perfectly separable. This means that the system is able to classify materials as well as to determine the freshness of packaged meat and the concentration of potassium in water solutions, as example of applications.

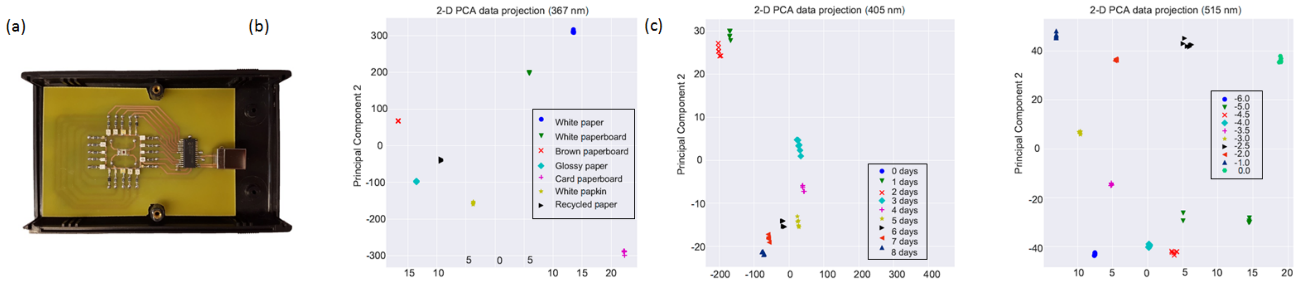

Figure 1. Developed instrument (a) and PC plot for the paper classification (b), freshness of the meat (b) and potassium determination (c).

Acknowledgements

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P7 Excitation-Emission fluorescence as a tool to assess a fraud and counterfeit issue related to aging in the wine vinegar industry

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High quality wine vinegars, as those with a Protected Designation of Origin (PDO), have high prices in the market due to their high quality and their long and high cost of production, making them vulnerable to frequent frauds [1]. These fraudulent activities range from incorrect labelling to the addition of substances not allowed or a production that differs from those regulated by the PDO. Prevention of frauds in the wine vinegar industry has become a key challenge that requires finding better systems and reliable and cost-effective analytical process. One of the unfair practices carried out in the Spanish wine vinegar industry is related to changes of color during aging. Although the addition of grape-must caramel is allowed by the current legislation to correct and unify the final color of the different batches, sometimes it is added to simulate the effect of a greater aging in wood. Thereby, less aged wine vinegars ("Crianza" category) could be sold as more aged wine vinegar categories ("Reserva" or "Gran Reserva") simply because their color resemble the dark color of these old samples. For detecting this unfair practice, excitation-emission fluorescence spectroscopy (EEF), which has previously demonstrated its usefulness in the characterization and authentication of these PDO wine vinegars [2], has been applied. Hence, 6 different amounts of grape-must caramel were added to "Crianza" PDO wine vinegars without caramel. They were compared to "Reserva" PDO wine vinegars without any caramel. Finally, PDO wine vinegars from the market were also analyzed to test the models and to determine their real aging and amount of caramel. Differences due to the addition of grape-must caramel could be observed with an only visual assessment of fluorescence landscapes (Figure 1). Parallel Factor analysis (PARAFAC) was applied for preprocessing the three dimensional array, and multivariate data analysis was carried out to observe if it was possible to fully differentiate real aged wine vinegars from those less aged vinegars modified with the addition of caramel. EEF allows the detection of samples whose color was modified in order to resemble the aged ones. This preliminary study could be furtherer applied to perform a rapid and easily determination of the amount of grape-must caramel added to wine vinegar as well as to detect and defend brands and correct category labelling.

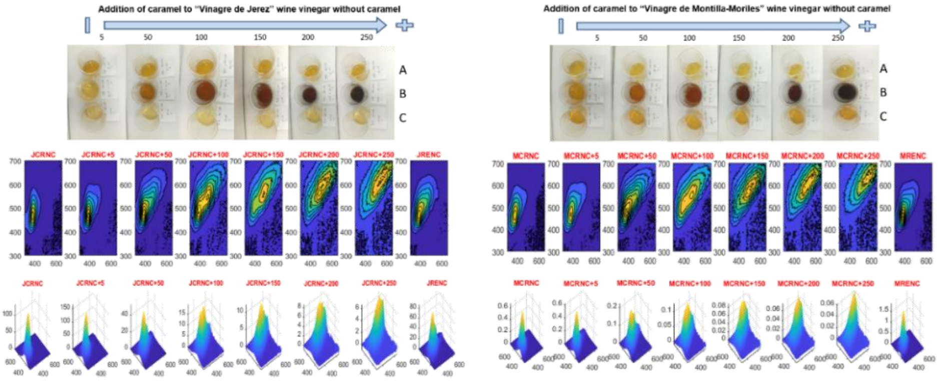

Fig 1. Changes in the color of wine vinegar related to the addition of grape-must caramel: Photos and fluorescence landscapes.

Acknowledgements

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P8 Effect of different excitation wavelength on SERS spectra of pyridine

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The analysis of electrochemical SERS experiences of aromatic acids like benzoic[1] and isonicotinic[2] acid and heterocyclic aromatic molecules such as, pyridine, pyrazine, pyrimidine[3], etc. has allowed us to shed light on the nature of SERS phenomena and, above all, to recognize and identify the contribution of the charge transfer (CT) mechanism on a SERS record. In few words, the CT mechanism is similar to a resonance Raman process in which a certain charge transfers from the Fermi level of the metal (M) to vacant orbitals of the adsorbate (A), resulting a charge redistribution between the ground electronic state of the superficial M-A complex and other excited states ($M\text{-}A + h\nu \rightarrow M^{+}\text{-}A^{-}$). In any resonance process, the resonance condition is fulfilled when the photon of the excitation wavelength matches with the energy of the electronic transition. In a SERS-CT process there is another more variable to take into account in achiving the resonance conditions and that is the electrode potential, because of the CT electronic state of the M-A complex can be tune by the electric potential of the interphase[4], which is macroscopically controlated by a potenciostat in the electrochemical experiences.

SERS spectra of pyridine has been already recorded on a silver electrode in a potential range from 0.0 to -1.40 V with a saline solution, pyridine / KCl (0.1M / 0.1M), by using the 514.5 nm exciting line[5]. Under these experimental conditions, the maximum intensity of the enhanced 8a and 9a bands is reached at -0.75 V and -1.20 V, respectively, being the 9a band what dominates the spectrum at negative electrode potential. We intend now to record pyridine SERS spectra under the same experimental conditions but varying only the excitation wavelength, 488 nm and 785 nm, in order to check how it affects to the relative intensities and to vibrational wavenumbers of the bands. The analysis of the relative intensities of the bands vs the electrode potential at different excitation wavelength allows to detect the resonance condition. From the analysis of SERS spectra, it can be concluded that no significant wavenumbers shifts have been detected, while the relative intensities of the bands and the electrode potential to which the maximum intensity is reached are slightly different at 785 nm, as expected for an incident radiation at low energy.

Acknowledgements

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P9 Combination of ^{1}H NMR profiling and chemometrics to characterize and classify Spanish PDO wine vinegars

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Nowadays, there is a growing consumer's demand for food products with a high quality. Protected Designation of Origin (PDO) is one of the label adopted by the European Community as recognition of some specific food quality attributes. Among the PDO products with high demand there are the high-quality vinegars. Three important Spanish wine vinegars have been protected by three different PDOs because of their unique characteristics and traditional production: "Vinagre de Jerez" (also known as "Sherry wine vinegar"), "Vinagre de Condado de Huelva" and the most recently "Vinagre de Montilla-Moriles". These wine vinegars are very complex multi-component mixtures of chemical compounds due to the traditional making procedure, the raw material used and the aging. Hence, different analytical techniques have been applied for extensive characterization and authentication [1,2]. Among them, rapid, non-destructive and direct methodologies based on non-targeted techniques are becoming more interesting for an authentication approach. In this context, ^{1}H-NMR has been applied in many food authenticity studies [3] but scarce research could be found in the literature regarding wine vinegars. For this reason, the aim of this work was to characterize and classify the different Spanish wine vinegar PDOs by using the ^{1}H-NMR profile. Sixty-five wine vinegar samples including the three PDOs were analyzed by ^{1}H-NMR. Prior to data analysis, several preprocessing steps were applied on the spectra such as the alignment by means of Icoshift [4]. Then, Multiple Curve Resolution (MCR) was applied in order to obtain the most information possible from the spectra, obtaining sixty-two resolved components. The data set comprising the integrated areas of the resolved compounds was preprocessed by autoscaling and was used to build a PCA and a classification model based on PLS-DA. Seven principal components and latent variables were used, respectively. The classification results were promising enough for ^{1}H-NMR PLS-DA models (around 90% of correct classification rates) (Table 1). The proposed methodology takes the advantage of being an objective analysis, based on simplicity and reproducibility. The classification approach proposed confirmed NMR to be a good tool for qualitative determination and classification of PDO wine vinegars.

Table 1. PLS-DA classification results for each individual data block.

DATA	PRETREATMENT	LVs	%CORRECTED CLASSIFIED								
			TRAIN			CV[a]			TEST[b]		
			C	J	M	C	J	M	C	J	M
^{1}H-NMR	MCR+autoscale	7	96.6	92.5	91.6	93.3	90.0	83.3	100	75.0	75.0

[a]Venetian blind cross validation (7 splits, 2 samples per split). [b]Independent test set, average correct classification rate for 5 random training/ test splitting is reported.

Acknowledgements

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P10 Study of phenolic extractability in cooperage byproduct using vibrational spectroscopy and scanning electron microscopy features

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In the oenology field, oak wood plays a significant role. Wood is an important source of phenolic compounds which are transferred to wine during the ageing process, improving the properties of the wine from an organoleptic point of view [1]. Extractability of phenolic compounds depends on the quantity of compounds that are potentially extractable [2, 3], but can also be affected by the ease/difficulty of extraction, and hence by the cellular structure of the wood.

Near infrared spectroscopy was employed to select a representative subset of wood samples according to their spectral features (900–1700 nm). Subsequently, the selected samples have been classified according to their total phenol extractability (low, medium and high extractability), as determined by chemical analysis.

Mid-infrared and Raman spectra are characteristic for the chemical composition of the samples and their peaks can be easily assigned to specific molecular bonds or functional groups. In the present study, the structural composition of oak wood samples has been evaluated using Raman and attenuated total reflectance Fourier transform infrared (ATR-FTIR) and their main spectral features have been linked to phenolic compound extractabilities. To support the analysis, microscopic images of the samples were also recorded using scanning electron microscopy (SEM).

ATR-FTIR and Raman spectroscopic techniques have been shown to be useful to relate the more important spectral features to phenolic extractability levels of wood samples. Moreover, scanning electron microscopy provided valuable complementary information that support the relationship between the structure of the wood and phenolic extractability levels.

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P11 SERS study of different species of p-aminothiophenol adsorbed on silver nanoparticles

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Different *Surface-enhanced Raman Scattering (SERS)* mechanisms can operate simultaneously or separately depending on both the molecule-metal system and the experimental conditions. Therefore systematic interpretations of SERS spectra can be a challenge, given that complex selection rules are derived from these enhancement mechanisms related to electromagnetic properties of the nanoparticles or resonance Raman effects involving the molecule-metal complex. [1]

In the present work we have focused the discussion on the experimental and theoretical SERS spectra of the organic compound pATP recorded on silver colloids. The huge SERS of pATP on metal substrates is significantly different from its ordinary Raman spectra due to the formation of a new specie namely p,p' –dimercaptoazobenzene (DMAB). The features of the SERS spectra of pATP are strongly dependent on many factors as i.e. the laser power density or the laser wavelength [2] but there are still important aspects to understand as, for example, the effect of the concentration that has already been studied before by our group. [3] In this case we have analyzed the effect of the concentration at different wavelengths on the SERS spectra of pATP on silver nanoparticles.

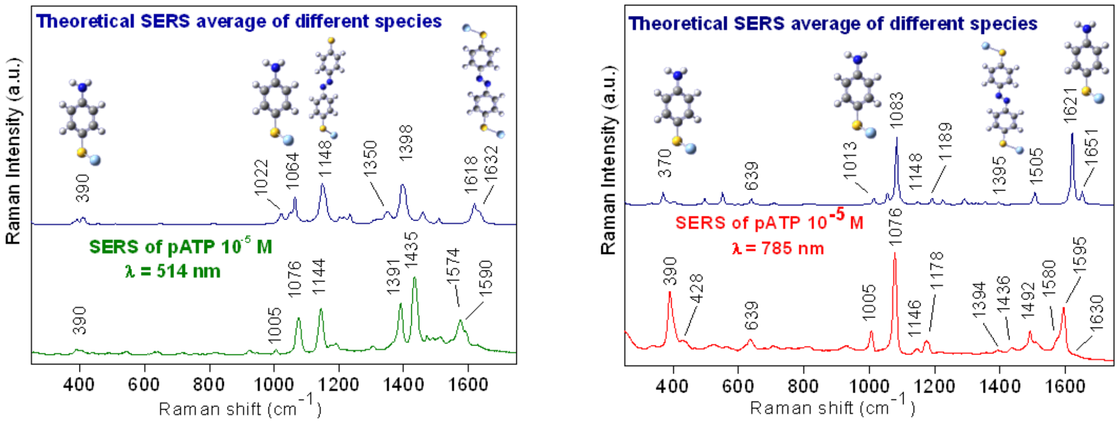

Figure 1. Theoretical and experimental SERS spectra of 10^{-5} M pATP at different wavelengths.

We have found that the Raman signals of the SERS of pATP arise from at least three different molecular species. At any concentration or wavelength we are able to detect SERS bands of pATP bonded to silver nanoparticles through sulfur atom (Ag_n-S^--Ph-NH_2). However we can only observe significant SERS bands from pATP bonded through both sulfur and nitrogen atoms (Ag_n-S^--Ph-NH_2-Ag_m) and the azo derivative in specific conditions.

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P12 Charge Transfer mechanism in the Surface Enhanced Raman Scattering of 2,2'-bipyridine recorded on a silver electrode

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Nowadays, Surface Enhanced Raman Spectroscopy (SERS) has become a powerful technique to investigate the electronic structure of surface-molecule hybrid systems due to the huge enhancement of the Raman signal. It is established that the origin of this enhancement has two main contributions; the electromagnetic (EM), related to surface plasmons, and the chemical mechanism, due to resonant charge transfer (CT) processes between the adsorbate and the metal. With the aim to investigate the SERS-CT of bipyridine and to identify charge transfer process, the spectra were recorded on silver electrode by using three different wavelengths (473, 532 and 785 nm) in a range from 0.0 up to -1.4 V electrode potential. The electrode potential was modelled in the calculations with atomic silver wires of different size and charge attached to the BPy molecule (Ag_nBPy^q, with q = 0 for n = 2 and q = ±1 for n = 3, 5, 7) and were computed with Density Functional Theory (DFT). Although BPy shows a trans conformation in solution, a cis conformation was chosen for its chelating properties. The results indicate that the intensification of the ~1550 cm^{-1} band at negative potentials is due the Franck-Condon factors related to the resonant CT process from the metal to the BPy molecule (Figure 1).

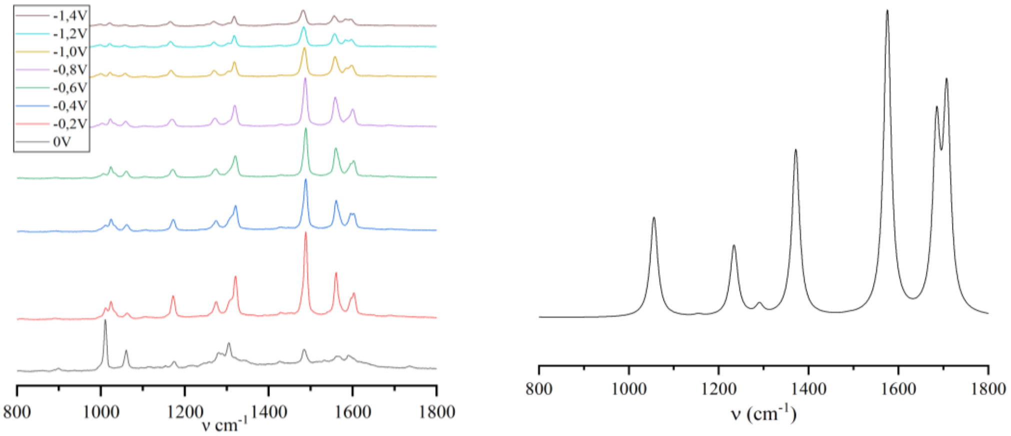

Figure 1: Experimental SERS Spectra of 10^{-3} M aqueous bipyridine solution at 532 nm (left), and calculated S_0-CT_0 resonant Raman spectrum (right).

Acknowledgements

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P13 SERS of complexes formed by fibrillogenic peptide hormone somatostatin-14 and emodin adsorbed on silver or gold nanoparticles

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Alzheimer disease [1] has been related with human amyloid disorders and more directly with the presence of brain plaques of β-amyloid peptides such as somatostatine-14 (SST-14) [2]. Concentration up to 20 to 60 mM range promotes high order self assemblies or denaturation of SST-14. To go deep down on the origin of the sickness a better knowledge on structural features of SST-14 on an aqueous environment will help to understand its molecular aggregation as well as the binding mechanism to peptide receptors.

Nanoparticles (NPs) represents nowadays an important role in the fields of biotechnology and medicine, drug delivery as much as diagnosis. They present a large surface/volume ratio allowing big concentration of medication to achieve disease tissues or changes in the rate of certain biological processes. In addition noble metal NPs exhibit enhancement of spectroscopic signals due to localized surface plasmon resonances (LSPR), being especially important SERS (Surface Enhanced Raman Spectroscopy) and SEF (Surface enhanced fluorescence), thus converting these systems in a good assembly to study structural features of low concentration solutions of biomolecules.

Gold and silver NPs exhibit, besides their enhancement spectroscopy properties related above, inhibition of the aggregation of short size αβ peptides, acceleration of fibrillation of cysteine-free peptides or retardation of insulin fibrillogenesis process. On a previous paper [3] we shown the ability of novel metal nanoparticles to bind SST-14 thus allowing detection of low traces of peptide and characterizing the vibrational markers arising from the group located in the vicinity or at the surface NPs.

In this work we present a novel SERS study, using gold and silver NPS, on the binding sites of SST-14 to NPs surface at different pH´s, trying to imitate physiological conditions. At the same time we also analyze influence of a second molecule (drug emodin) in the peptide-NP nanocarrier system or the presence of an aggregation agent. We check differences in the vibrational bands that could determine important features in structural architectures or in subsequent recognition of peptide receptors.

Acknowledgements

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P14 Determination of salivary cortisol and cortisone by ionic liquid-dispersive liquid-liquid microextraction

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Cortisol and cortisone are steroid hormones synthesized from cholesterol in the adrenal glands. The study of cortisol in plasma is important for diagnostic purposes but the estimation of the unbounded (fee) cortisol fraction in plasma is technically demanding. An alternative is saliva samples because salivary cortisol reliably reflects the biologically active free serum level. This approach represents an easier alternative to free cortisol determination in plasma, but high selective methods are required.

Immunoassay methods have been broadly used for the determination of steroids, but they suffer from lack of selectivity for similar analytes such as cortisol and cortisone. Liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) circumvents this problem and that is why it is widely accepted as the best available technique for the accurate analysis of endogenous steroid hormones in biological samples [1]. However, this technique is expensive, sophisticated, and does not avoid sample preparation. The use of ultra-violet (UV) detection is also possible but preconcentration steps are necessary to reach typical salivary cortisol and cortisone levels. Different extraction and preconcentration techniques, such as solid-phase or liquid-liquid extraction, have been proposed for this purpose but they are laborious, time-consuming and often require large amounts of organic solvents. These drawbacks can be avoided by using dispersive liquid-liquid microextraction (DLLME), which provides preconcentration of analytes in a rapid and simple manner. Moreover, the use of ionic liquids (IL) instead of organic solvents gives the way to IL-DLLME sub-technique. This approach takes advantage of the IL extraction potential and it is more environmentally friendly, but it has never been used for cortisol and cortisone extraction in salivary samples.

In this work, an IL-DLLME method was developed, for the first time, for the extraction of cortisol and cortisone in human saliva samples. The extracts were submitted to liquid chromatography (LC) with UV-vis detection for determination. The IL 1-butyl-3-methylimidazolium hexafluorophosphate [C_4MIM][PF_6] and methanol were used as extraction and dispersive solvent, respectively. The parameters that affect extraction, such as ionic strength, pH, amount of IL, volume of MeOH, vortex agitation and centrifugation time were optimized. Adequate enrichment factors to reach physiologically relevant levels have been achieved and quantitative recoveries in spiked saliva samples have been obtained.

Acknowledgements

Support for this work was provided by Ministerio de Economía y Competitividad (Spain) (project CTQ2016-78793-P) and Junta de Comunidades de Castilla-La Mancha (Spain) (project PEIC-2014-001-P).

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P15 Estimation of total phenols, flavanols and extractability of phenolic compounds in grape seeds using hyperspectral imaging and chemometrics

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Depending on varieties, grape seeds contain between 20 and 55% of the phenolic compounds of the berry, and they represent between 4 and 6% of the seed weight. These phenolic compounds play an important role in the sensory characteristics of wine. They are typically linked to the flavour (acidity, bitterness and astringency) and colour (*via* copigmentation phenomenon) of red wines [1]. Therefore, knowing the amount of phenolic compounds that are transferred from grape seeds to wine (i.e. extractable total phenolic content or extractable phenolic content) is an essential issue in the wine industry. There are a number of methods that allow obtaining the extractable or total content of the more important phenolic families. Among them, hyperspectral imaging is a potential tool for the screening of these parameters in oenological samples [2].

In this study, near infrared hyperspectral data were collected for 200 Syrah and Tempranillo grape seed samples. Next, a sample selection was carried out and the phenolic state of these samples was determined. Then, quantitative (modified partial least square regressions) and qualitative (K-means and lineal discriminant analyses) chemometric tools were applied to obtain the best methods for predicting the reference parameters.

Quantitative models for the prediction of total phenolic and flavanolic contents have been successfully developed with external validation errors similar to those previously reported. The application of these models to the whole sample set (selected and non-selected samples) has allowed knowing the distributions of total phenolic and flavanolic contents in this set. Moreover, a discriminant function has been calculated and applied to know the phenolic extractability level of the samples. In this way, the bases for the control of grape seeds phenolic state from their near infrared spectra have been stablished.

Acknowledgements

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P16 Selection of representative samples from near infrared hyperspectral imaging data to control grape quality

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Near infrared hyperspectral imaging (NIR-HSI) has been widely applied to the control of food quality in the last two decades [1]. This tool uses spatial and spectral information of the samples and allows developing different chemometric models for the screening of important parameters in the samples. Among a large number of applications, NIR-HSI is being also applied in the oenological sector [2]. Developing chemometric models from NIR-HSI requires the use of a calibration set that should be representative of the entire population. Therefore, the calibration procedure generally requires a large amount of resources, not only in the spectra acquisition step but also in the obtaining of reference parameters [3]. For that reason, there is a great interest in identifying the most representative samples within a complete set of samples in order to reduce the amount of resources necessary without losing spectral variability for the development of chemometric models.

In this study, different sample selection approaches have been tested (Figure 1). The calibration sets generated have been applied for the control of grape quality (technological maturity of grape and total phenolic compounds of grape skins in red and white cultivars). Finally, these different approaches have been compared with each other and with the entire set of samples predicting an external sample set. The results show that different sample selection procedures can be applied to reduce the number of samples that are necessary to analyse chemically without important loss of model accuracy.

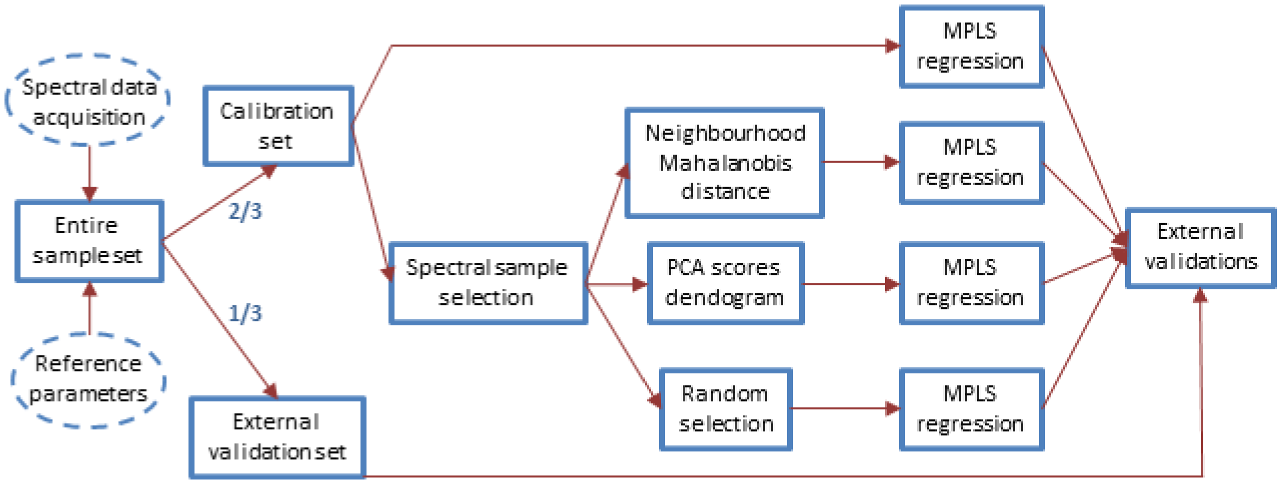

Figure 1. Procedure carried out in this study. MPLS: Modified partial least squares.

Acknowledgements

This work was supported by the Spanish MINECO [AGL2017-84793-C2] and Unversidad de Sevilla [VPPI-II.2, VPPI-II.4, VIPPI-EEBB-PIF 2017]; The authors thank the technical staff of Biology Service [Servicios Generales de Investigación (SGI), Universidad de Sevilla].

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P17 Chromium and nickel analysis in sprouted seeds of Brassicaceae species by ET – AAS: an exposure risk assessment

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Brassicaceae (or Cruciferae) sprouts are novel plant foods which have a high nutraceutical potential, due to the existence of bioactive compounds in its composition. Some of these compounds are glucosinolates, a group of specific sulphur compounds with a high nutraceutical potential, being exclusive to this plant family and present in their edible parts. Germinating seeds could contain from 2 to 10 fold increase of these phytochemicals depending on the species, cultivation, environmental conditions and time of germination [1]. On the other hand, these vegetables can be a good source of other trace elements such as selenium, calcium, chromium or nickel.

In relation with these two later trace elements (with nutritional and toxicological role), it has been developed a methodology to analyze Cr and Ni in sprouted Brassicaceae by electrothermal atomic absorption spectroscopy (ET – AAS) (model Agilent 240Z AA). Cr and Ni hollow cathode lamps were used as the radiation source at the wavelengths of 357.9 and 232.0 nm, respectively. The optimum temperatures of the drying step were studied in the ranges of 90 – 150 °C for temperature and 30 – 60 s for times. The pyrolisis temperatures were varied between 800 – 1100 °C at times of 8 s. Finally, it was used an atomization temperature of 2600 °C for Cr and 2400 °C for Ni. The optimized conditions for trace elements determination by ET – AAS are shown in Table 1. Standard calibrations were made with 5, 10 and 15 µg/L concentrations of Cr and 10, 25, 40 µg/L concentrations of Ni. Recovery experiments with Certified Reference Material were carried out with recovery percentages around 100%.

Table 1. Temperature programs for the graphite furnace

	Cr		Ni	
	T (°C)	t (s)	T (°C)	t (s)
Drying	110	55	110	55
Pyrolisis	1000	8	800	8
Atomization	2600	2.8	2400	2.8
Cleaning	2600	2	2600	2

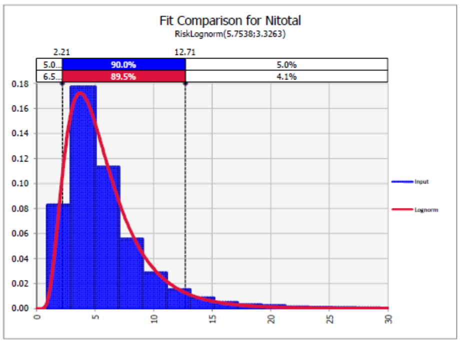

Figure 1. Simulated data and fitted probabilistic distribution

Trace elements contents in Brassicaceae sprouts ranged between 1.57 – 0.47 µg/g for Cr and 1.08 – 0.44 µg/g for Ni. A simulation software (@Risk) was used to determine the contributions of the above mentioned plant species to Dietary References Intakes (DRI) for these elements. It was found that intakes between 5 – 10 g of these dehydrated vegetables provided 12.1 µg of Cr and 10.3 µg of Ni for 95th percentile. These intakes do not exceed the safety recommendations for these elements [2].

Acknowledgements

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P18 Selectivity evaluation of methamphetamine based molecular imprinted polymer

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Nowadays, the illicit drug market has evolved by the rising of New Psychoactive Substances (NPS), substances in a pure form or preparation, that are not controlled by the 1961 Narcotic Drugs or the 1971 Psychotropic Substances Conventions.

Conventional methods for the analysis of drugs and NPS in biological fluids involved the use of gas (GC) or liquid chromatography (LC) as a separation technique coupled to mass spectrometry (MS) for the identification of those substances. In the last decade, Ion Mobility Spectrometry (IMS) has been employed for the identification of several NPS with a strong reduction in the analysis time [1]. However, IMS shows a lack of selectivity that can be improved by the use of analyte specific molecular imprinted polymers (MIPs).

Thus, we have developed a MIP able to hold back those NPS. Taking advantage of the similarities between the methamphetamine and those NPS, in this communication the MIP has been prepared by the mixture of methamphetamine as template, methacrylic acid as monomer, ethylene glycol dimethacrylate as cross-linker and azobisisobutyronitrile as initiatior in acetonitrile as porogenic solvent [2].

The main aim of this study is to evaluate the selectivity of the MIP fordifferent NPS which include amphetamine, methamphetamine, cathinones and phenetilamines derivatives and to study its application for the analysis of biological samples. Developed MIPs provided appropriate recoveries from 68 to 128 % for analysed amphetamines and cathinone derivatives (Figure 1). The non-imprinted polymer (NIP) provided recoveries lower than 50 % in all the cases. Other substances with different molecular structure have been studied showing no retention in the produced MIPs.

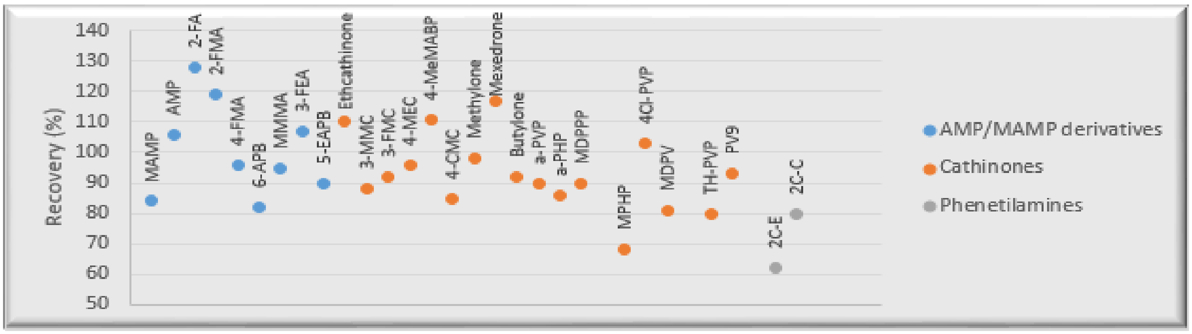

Figure 1. Recovery obtained for amphetamine (AMP), methamphetamine (MAMP) derivatives, cathinones and phenetilamines.

Acknowledgements

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P19 Partial least squares modelization of energy dispersive X-ray fluorescence

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The aim of this work is the development of a green methodology for the determination of calcium, potassium, iron, magnesium, aluminium, chromium, strontium, phosphorus and nickel in kaki peel samples by using and energy dispersive X-ray fluorescence (ED-XRF). Fifty-six kakis purchased in local supermarket (LLombay, Valencia) were employed for the study. ED-XRF is a non-destructive sample technique, avoid the use of toxic reagents and no generates any kind of waste [1]. This technique is very used in archaeological samples but is not very often in food samples [2].

For sample analysis by ED-XRF, the samples were measured directly without previous treatment, the peel of the kaki were only cleaned with water. As reference method Inductively Couple Plasma Optical Emission Spectrometry (ICP-OES) were used after acid microwave assisted digestion. XRF spectra combined with concentration obtained by ICP-OES using partial least squares (PLS) data treatment were used to develop chemometric models for prediction of mineral profile. Concentration obtained directly by internal calibration of ED-XRF (GeoChem Trace) were compared with those obtained by chemometric models for Ca, K and Fe because the rest of the elements were not quantified by the direct ED-XRF analysis. There is a solely good correlation in case of Ca being R^2 value 0.72.

Coefficients of determination obtained with the PLS calibration of Ca, K, Fe, Mg, Al, Cr, Sr, P and Ni were 0.997, 0.98, 0.9990, 0.994, 0.98, 0.990, 0.995, 0.95 and 0.990, respectively. Chemometric models allow quantify those elements with low concentration which were not possible to determine by direct ED-XRF analysis.

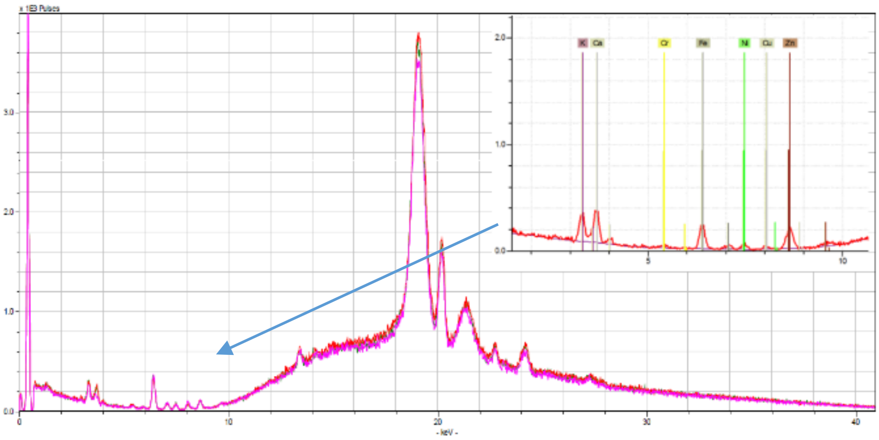

Figure 1. XRF spectra of a kaki sample.

Acknowledgements

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P20 Synthesis and Immobilization of Metallo-organic Structures to Capture and Convert CO_2

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Cascade complexes are formed stepwise by reaction of ligands with metal ions, which may in turn bind small molecules. Polyaza ligands have shown their versatility in creating, after coordinating two or three 3d cations, depending on their topological properties, a small cavity to bind anions. Nelson's cryptands[1] provide an example of a dynamic structure with useful applications, demonstrated by their ability to capture and convert CO_2 to carbonate following their coordination to two metal ions. On the other hand, the electrochemical reduction of CO_2 to other products with well-defined molecular catalysts has selectively produced compounds such as CO, formic acid, methane and methanol.[2] One of the strategies for catalytic CO_2 reduction is based on carbon nanotubes functionalisation through covalent grafting of metal complexes. Here we explore the conversion of CO_2 into CO by carbon nanotubes modified with Co(II) cryptates (Figure 1) that can capture CO_2 from the atmosphere. The syntheses of different Co(II) cryptates were performed under N_2 and CO_2 atmosphere. The new species characterised by FTIR, elemental analysis, and XPS. The redox properties of both the complexes and the modified carbon nanotubes were studied by cyclic voltammetry. The behaviour of the new materials under exposure to a CO_2 saturated atmosphere was investigated in aqueous medium.

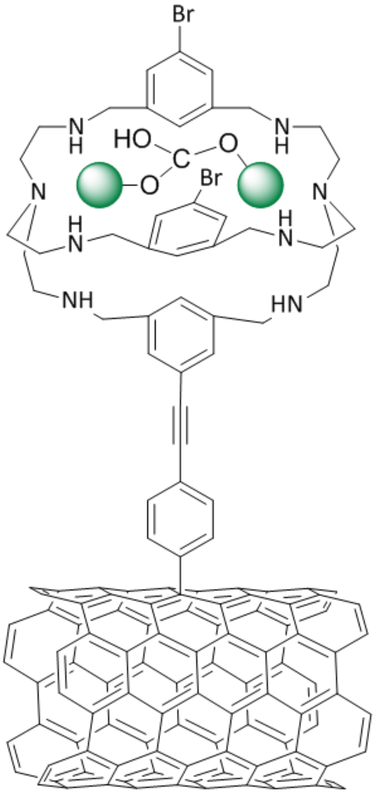

Figure 1 Modified carbon nanotube with Co(II) cryptate.

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P21 Inside Eu[TAP(G_n=0-3)]$_3$ dendrimers: a structural and theoretical assessment

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Lanthanide (Ln) complexes have unique advantages for OLED application. They have high emission quantum yield, relatively long luminescent lifetimes, narrow spectral width and they can emit red (Eu^{3+}), green (Tb^{3+}), blue (Tm^{3+}) and also white color. Many of these features can be achieved by a rational design of suitable ligands forming stable complexes with Ln ions and acting also as emission sensitizers [1]. However, the luminescence of Ln^{3+} is quenched via cooperative energy transfer processes (i.e. self-quenching) between the clustered Ln^{3+} ions [2] which limit their WOLED applications. The use of dendrimers is valuable in solving this problem because they can function both as light harvesting and as site-encapsulating nanocontainer [3]. Thus, new Ln-dendrimers with thenoylacetophenone (TAP) moieties with increasing generations of poly(benzyl aryl ether) dendrons are proposed. The synthetic protocol involved four steps, three to produce the dendritic b-diketone with a TAP core and with increasing generations of poly(benzyl aryl ether) dendrons (by the general route developed by Hawker and Fréchet[4]) and the fourth step to prepare the Eu-dendrimers by the conventional method[5]. Structural characterization of the synthetized Eu[TAP($G_{n=0\text{-}3}$)]$_3$ dendrimers was performed by several techniques. A systematic study with Eu[TAP($G_{n=0\text{-}3}$)]$_3$ dendrimers with different sizes in order to perform a rational quest of the favorable conditions for increasing the emission quantum yield was performed. In order to pursue the aforementioned studies quantifying the Ln[TAP($G_{n=0\text{-}3}$)]$_3$ emission quantum yields, a combined approach of semi-empirical methods with theoretical model of intramolecular energy transfer was performed. The calculated triplet energies and matrix elements were calculated for each dendrimer by using the theoretical mode described in terms of the well-known 4f-4f transitions. The photophysical behavior of the different Eu[TAP($G_{n=0\text{-}3}$)]$_3$ dendrimers were discussed in terms of molecular orbital description and energetics. The excited process as well as the singlet triplet energy transfer was theoretically explored (Figure 1).

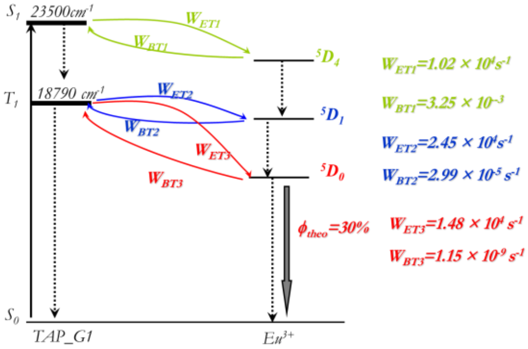

Figure 1. Energy transfer pathways predicted for Eu-TAP-G1

Acknowledgements

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P22 Test strips to the enzymatic determination of cadaverine and putrescine

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Cadaverine and putrescine are two biogenic amines (BA) responsible of the quality and freshness of food, and at certain levels, related with intoxications and intolerances processes. These is because food industry and public health agencies require rapid and economical methods for their control.

Our research group has developed a rapid analytical methodology based on the use of organic chromophores that change their spectroscopic properties when an enzymatic reaction with AB takes place (Figure 1A). The enzymes Diamino oxidase (DAO) and peroxidase (HRP) are involved. This reaction has been studied in solution using chromophores such as ABTS, TMB or Amplex red, with good results in the determination of cadaverine and putrescine, without incubation or tedious separation steps.

However, it would be very interesting to have disposable test strips that allow the *in situ* determination of these BA. To build up test strips, the above reagents must be immobilized in a solid support. Firstly, Whatman 1 paper was used as the support and the immobilization was carried out by adsorption. Later on, best results were obtained (Figure 1B) when the supporting paper contains the reagents entrapped; to do that, a solution containing cellulose, the enzymes (HRP and DAO) and the TMB was left to dry [1].

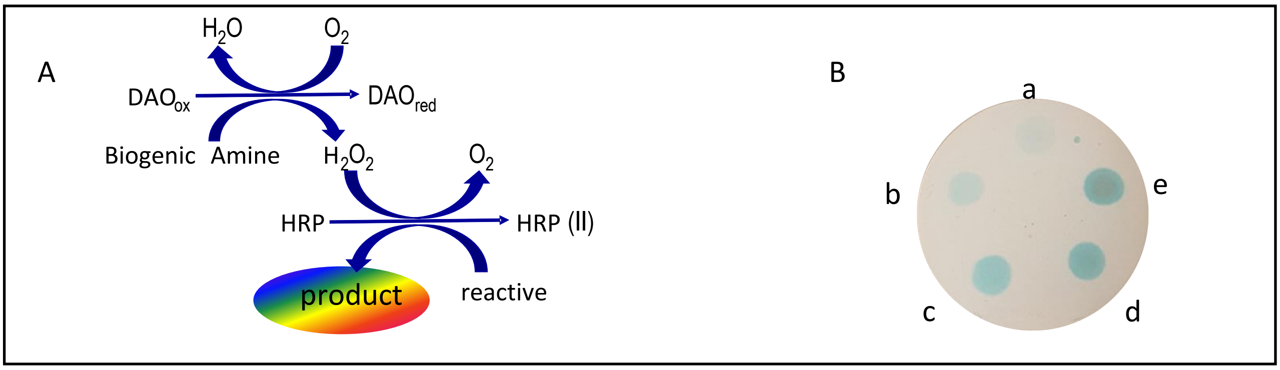

Figure 1. A. General scheme of the enzymatic colorimetric method for biogenic amines. B. Strip test for putrescine determination, concentrations (mg/L): (a)2, (b)4 , (c) 10,(d) 15, (e) 20.

At the present, we are working on the optimization of the system. Different parameters are being studied such as the cellulose type, quantity, treatment to activate the reactive groups, concentration of enzymes and chromophore, … The objective is the design of a test strip which responds, with a stable signal, to the presence of putrescine and cadaverine levels higher than the legally allowed. The signals could be quantified with both a smartphone or a photographic camera; the analytical figures of merit with both supports are being evaluated.

Acknowledgements

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P23 Vibrational portrait of a deep eutectic solvent: shape and hydrogen bonds

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The solids choline chloride and urea, mixed in a 1:2 molar proportion, form the iconic deep eutectic solvent "Reline". A combination of computational and vibrational spectroscopy tools, including inelastic neutron scattering (INS), have been used to probe intermolecular interactions in the eutectic mixture. Reline's experimental spectra were estimated using discrete and periodic ab initio calculations of a molecular aggregate with two choline chloride and four urea units. The INS spectrum of reline, compared with that of pure choline chloride, reveals a displacement of chloride anions away from their preferred positions on top of choline's methyl groups, whose torsional movement becomes less hindered in the mixture. Urea, which adopts a planar (sp^2) shape in the crystal, becomes non-planar (sp^3) in reline, a feature herein discussed for the first time. In reline, urea molecules form a wide range of hydrogen bonds, from soft contacts to stronger associations, the latter being responsible for the deviation from ideality. The chloride's interactions with choline are largely conserved at the hydroxyl end while becoming weaker at the cationic headgroup. The interplay of soft and strong interactions confers flexibility to the newly formed hydrogen-bond network and allows the ensemble to remain liquid at room temperature.

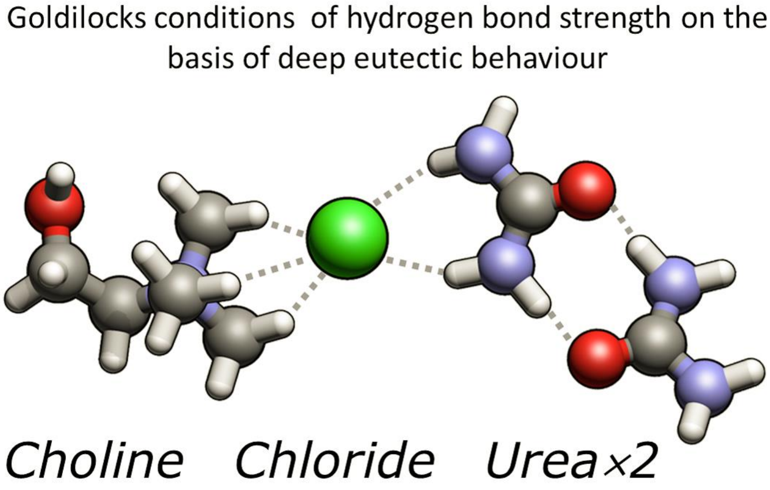

Figure 1. Ball and stick representation of choline chloride and urea. Dotted lines highlight important intermolecular contacts in the deep eutectic mixture.

Acknowledgements

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P24 The potential of near infrared spectroscopy to estimate the content of cannabinoids in *Cannabis sativa* L.

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Hemp (*Cannabis sativa* L) is one of the most ancient crops for fibre production. However, in the last years, different experiences have been developed in order to look for new uses and applications of hemp and its derived chemical compounds for biomedical purposes. Its production is becoming legalized and regulated in many countries, thus increasing the need for a rapid analysis method to assess the content of cannabinoids. Gas chromatography (GC) is the preferred analytical method for the determination of these compounds, according with the European law, an official method, (EC) No 1177/2000 of 31 May 2000 Annex C, although is a slow and costly technique. Near infrared spectroscopy (NIR) has the potential for the quantitative prediction of quality parameters, and also of pharmacologically active compounds. The aim of the present research was to develop a fast, economical, robust and environmentally friendly method based on NIR technology that allow the quantification of the main cannabinoids present in *Cannabis sativa* L. samples.

A total of 189 grinded and dried samples from different genotypes and registered varieties were used. The content of the cannabinoids CBDV, Δ9-THCV, CBD, CBC, Δ8-THC, Δ9-THC, CBG and CBN were determined by gas chromatography, which were used in the wet way. Spectra were collected in a dispersive NIR Systems 6500 instrument, and in a Fourier transform near infrared (FT-NIR) equipment. Excellent coefficient of determination of cross validation were obtained for the prediction of cannabinoids content, with standard error of prediction (SEP) values among 1.5 - 3 times the standard error of laboratory (SEL) using NIR and FT-NIR instruments. The results obtained allow to confirm that there is sufficient information in the NIRS spectral region for the development of cannabinoid prediction models in dried and ground Cannabis plant materials. Hence, the NIR technique has been proven as an alternative method to the conventional GC analysis for the assessment of Cannabis sativa L. varieties and genetic resources as regard to their cannabinoids contents. The major advantage of such spectroscopic technique is that the sample is measured with no or little pre-treatment (e.g. grinding, drying), is faster, simpler, and uses no pollutants for the environment compared with the reference analytical method. The comparison of the predictive ability of the models obtained with the dispersive NIR and the FT-NIR spectrometers show no significant differences between them.

Thus, this new analytical method would allow a simpler, more robust and precise estimation than the current standard GC.

P25 Identification by FTIR of microplastics in fish from the Portuguese coast

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Plastics comprise the largest part of marine debris and have been reported as important pollutants in marine as well as freshwater environments. The larger plastics gradually degrade into mesoplastics (5 – 25 mm) and microplastics (< 5 mm) [1,2]. This study aimed to characterize the type of litter present in the gastrointestinal tract of 5 commercial fish from the coast of Peniche (Portugal), two species of pelagic (Atlantic Horse Mackerel - Trachurus trachurus and Atlantic Chub Mackerel - Scomber colias) and three demersal fish (Poutine - Trisopterus luscus, species of the family Triglidae and Rajidae). The organic content present in the digestive tract of the fishes was examined and the organic matter present in the sample digested by using a solution of 10% potassium hydroxide (KOH). Microplastic polymers were identified using Fourier Transformed Infrared Spectroscopy (FTIR), which is a fingerprinting technique that provides characterization at the molecular level, allowing the identification and distinction of the different materials, through the interaction between infrared radiation and matter.

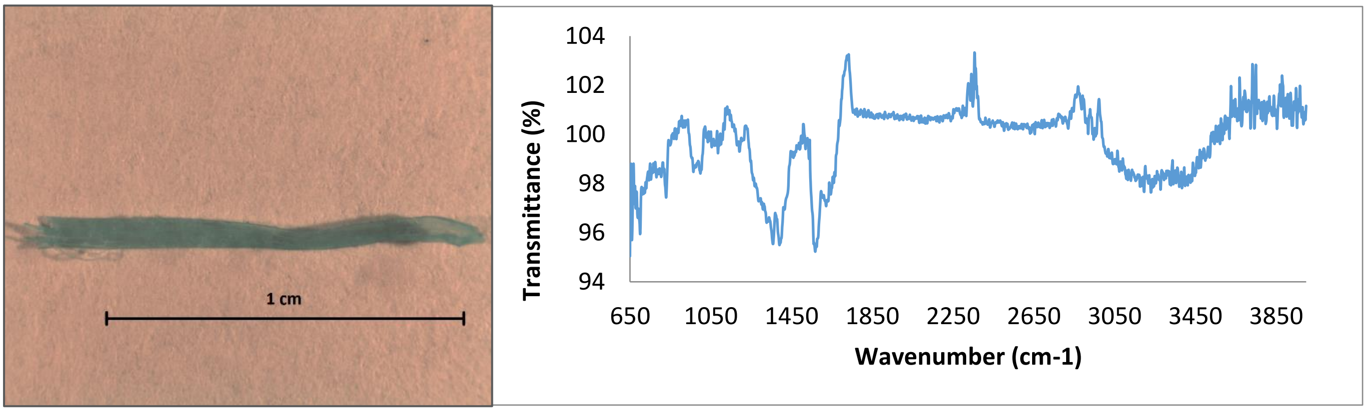

Figure 1. Photography of a polyester fiber and respective FTIR spectra

After analysis of several microplastic debris, it was concluded that polyurethane was the most abundant polymer present in the digestive tract of the fish analysed. This material may come from primary plastics, which are intentionally used as resin pellets or as ingredients of personal care products. The other plastics identified using FTIR analysis proved to be polyethylene, and polystyrene.

Acknowledgements

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P26 Polyphenols intrinsic fluorescence as a versatile tool to quantify their interaction with membranes at different pH

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Polyphenols have been attracting researchers from wide ranging fields of biophysics, biochemistry, pharmacology and medicine due to their health benefits. Phenolic acids and flavonoids are wide spread polyphenols in dietary plants and they display, *in vitro*, high antioxidant potential. I*n vivo*, the bioactivities of these polyphenols depend on their interaction with cell membranes. One of the reasons why their mode of action is still not fully elucidated is the low concentration range where they are physiologically relevant (nM to μM).

As polyphenols are intrinsically fluorescent, this property can be exploited to evaluate their mode of action using low concentrations, taking advantage of fluorescence high sensitivity / low background, and its strong dependence on compound microenvironment. For polyphenol-membrane interactions these two features acquire paramount importance. For example, the membrane-water partition coefficients (K_p), vital information to quantitatively interpret the impact of the compound on membrane structure and dynamics, can be obtained at low compound concentration, ensuring a regime close to infinite dilution. The large difference from the aqueous phase to a lipid bilayer milieu usually provides the environmental dependence of at least one fluorescence parameter that will be used to quantify the fraction of compound that is partitioning to the membrane under each condition studied.

We have studied the interaction of a flavonoid (quercetin) and three hydroxycinnamic acids (caffeic - CA -, rosmarinic - RA - and chlorogenic - CGA - acids) using different fluorescence techniques. While for RA the fluorescence intensity could be used to determine its membrane/water K_p (5.1×10^2 for lipid bilayers constituted by 1-palmitoyl-2-oleoyl-*sn*-glicero-3-phosphocholine (POPC) and 1.4×10^2 for POPC/Cholesterol 1:1)[1], for quercetin the most valuable property was its fluorescence anisotropy (1.5×10^4 for POPC and 3.6×10^3 for POPC/Cholesterol 1:1). Furthermore, all these compounds have several ionizable groups, which can also strongly influence their interaction with the membrane. Due to the influence of the ionization on compound fluorescence behavior, fluorescence spectroscopy was also useful to estimate the compounds pK_a values at 20 μM concentrations, much lower than those typically used with other techniques such as potentiometric titration. This concentration is closer to those used to assess the K_p values and in case of the more lipophilic quercetin, its impact on membrane biophysical properties. These spectroscopic pK_a values were also compared with *in silico* pK_a profiles, where the values are calculated along the membrane normal when the compounds are inserting into the lipid bilayer.

Conjugating the information concerning K_p, pK_a and changes in fluorescence properties of the compounds studied as a function of pH and lipid concentration allows to discriminate semi-quantitatively the contributions of each molecular form with variable ionization degrees to the interaction with the membrane.

Acknowledgements

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P27 Spectroscopical assessment of commercial and raw kaolin: is local kaolinite clay suitable for agriculture?

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In a World with a changing climate, several traditional crops are at risk, while many alternative and sustainable mitigation strategies are being envisaged to attenuate the losses, among which, kaolin, a white clay mostly formed from kaolinite, can be pointed, being widely used for this purpose due to its reflective properties. Kaolinite is a clay-mineral formed by aluminosilicates without isomorphic replacements, initially explored in ancient China. Since regarding plant protection this product is intended to form a shielding layer, a homogeneous grain size is desirable, while this feature will also interfere with the reflective properties. Therefore, kaolin is normally applied in the form of an imported commercial product, Surround - from BASF (USA), which is especially processed for this purpose, to be applied in a 5.0 % (w/v) water solution, in order to form a thin but continuous film, with established properties [1]. On the other side, there are noticeable deposits of kaolin in Portugal, which is presently used for other purposes, besides unexploited reserves [2].

Therefore, in the present work, it was intended to assess the structural properties of both Surround and local kaolin samples collected in Portugal, resorting to spectroscopical means, in order to evaluate the differences that may exist between these products. In this sense, samples of local kaolin were collected and assessed within the MIR interval, resorting to FTIR-ATR, while the diffuse reflectance spectra of these samples have been also registered resorting to a DRIFT accessory, within the NIR range. Concerning the reflectance spectra, the Surround spectrum displays much greater reflectance above 6000 cm^{-1} respecting local kaolin, reaching 90 %, while the Portuguese samples display more intense absorptions, concerning the peaks observable below 7500 cm^{-1}. Regarding the MIR spectra, the fundamental υ(OH) modes are visible in the interval between 3600-3750 cm^{-1}, while these peaks cannot be seen in the Surround spectrum. Moreover, the Portuguese samples display sharp intense peaks in the interval 800-1200 cm^{-1}, and below 600 cm^{-1}, while the surround spectrum displays a simpler set of broad peaks bellow 1300 cm^{-1}, which points to higher purity and structural uniformity. Finally, as both samples present a set of absorption peaks in NIR, between 7000-7400 cm^{-1}, which seems to be correlated with the 1st overtone of the υ(OH) modes, the absence of peaks corresponding to the υ(OH) fundamental in the Surround MIR spectrum points to a forbidden mode due to symmetry, showing that this material displays greater structural integrity, concerning their crystal periodic structure, with all the hydroxyl groups from the octahedrical sheets displaying the same orientation. Therefore, even though kaolin could be locally obtained, technical capabilities for its transformation are required for its use to be envisaged, so this product can undergo the necessary processing concerning structural integrity and homogeneity, to be applied as protective agent in agriculture.

Acknowledgement

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P28 Solvents in oxidation catalysis: probing specific interactions with neutron diffraction

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In nearly 80% of all compounds produced in chemical and pharmaceutical industries at least one catalytic step is essential during their synthesis. Catalysts speed up chemical reactions but directing it towards a specific product running at low temperature and pressure is still a challenge. This is a principle that is pursued with increasing emphasis and dedication leading to far more specific and cleaner processes. As part of ongoing research in the development of more selective and efficient (overall sustainable) oxidation catalysts, our work is aiming at understanding the key-roles of other reaction variables apart from substrate, catalyst and physical parameters (temperature, pressure, etc…).[1-4] To this respect, solvents are the obvious candidates as these, despite offering the reaction medium also have intrinsic properties (acidity, protic/aprotic, H-bond donor/acceptor) that are certainly relevant but have not been assessed in much detail so far.[5-7]

In this work we present a study where commonly used solvents (toluene and acetonitrile) were found to play key-roles in the kinetics and product selectivity of olefin oxidation reactions. The latter was observed for styrene oxidation where product selectivity was found to be dependent on the solvent used.

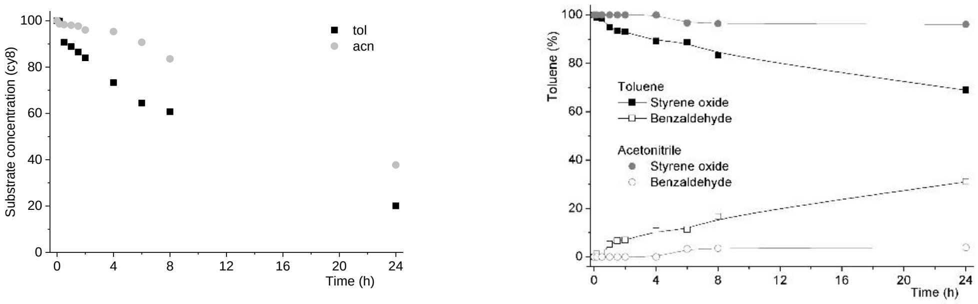

Figure 1. Reaction profiles for *cis*-cyclooctene oxidation in toluene and acetonitrile (left); The graph on the right shows the product selectivity profile for styrene oxidation in the same solvents. All reactions were carried out at 353 K, for 24 h, under air atmosphere and using *tert*-butyl hydroperoxide and an MCM41-based catalyst.

Using neutron diffraction data collected with the SANDALS instrument at ISIS Neutron and Muon Source – UK, as a state-of-the-art technique to probe the local structure we were able to demonstrate that there are differences correlated with the intermolecular interactions between styrene and the solvents (acetonitrile and toluene). When acetonitrile was used, experimental data revealed the existence of H-bonds, whereas these are absent when toluene was used instead. Only a few studies are known to assess the structure of solvents,[8] while to the best of our knowledge, no study has been devoted to correlate how solvents interfere in chemical processes at the local structure level.

Acknowledgements

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P29 A new fast photochromic: 2,2-Dimethyl-2*H*-1-benzopyran-6-carbonitrile

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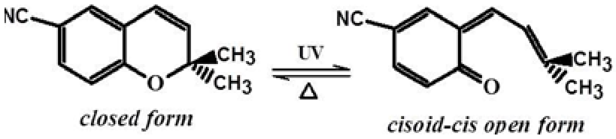
Fast photoreaction rates are crucial for practical applications of photochromic compounds in devices, such as optical switches, or photochromic lenses.[1,2] For the widely studied and commercially used family of chromenes, the photo-induced ring-opening forward reaction occurs in the sub-picosecond time range,[3] but the thermally-activated ring-closing backward reaction of the open form in the ground state is relatively slow, ranging from seconds to minutes or even hours.[4]

In this work, we studied the photochromic and thermochromic properties of 2,2-dimethyl-2*H*-1-benzopyran-6-carbonitrile (DMBPCN), a chromene with a cyano group substituted at the 6-position of the benzopyran moiety (Figure 1).



Scheme 1. Molecular structures of the closed and open forms of DMBPCN

Irradiation of DMPBC at low temperature (77 K) generated a relatively stable, but reversible, orange-red open form (absorption maximum at 467 nm), as found with other chromenes. At room temperature (293 K), the thermochromic ring-closure reaction occurs in 1.9 ms, much faster than that of other known chromenes.

Pump-probe data showed that the photochromic ring-opening reaction of DMBCN occurs on the femtosecond time range being followed by structural rearrangements in *ca.* 6 ps.

The much faster ring-closure reaction of DMBPCN at room temperature makes of it a potentially better photochromic than the commercially available 3H-naphtho[2,1-b]pyran.

Acknowledgements

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P30 A FT-IR and VCD study of the conformational landscape of monomers and H-bond dimers of (S)-Ketoprofen

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It is well established that the biological activity of drugs relies on a series of stereospecific interactions so that the study of the conformational arrangements of drugs, preferably in solution, is of capital interest in medicinal chemistry.

(S)-ketoprofen is a non-steroidal anti-inflammatory drug (of the same family as other of great analgesic importance such as ibuprofen, naproxen or diclofenac). The conformational landscape of the monomeric species was recently theoretically studied in the gas phase, in the framework of an ECD study focused in the interaction of the drug with albumins. [1] Nonetheless, although the records of the ECD spectra of the pure sample were performed in 1-propanol, the solvent-solute or solute-solute interactions were neglected.

The exquisite conformational sensibility of the VCD technique (contrasting its electronic counterpart, ECD) make its use and ideal approach for the study of conformationally flexible quiral species such as (S)-ketoprofen. Thus, in the present work, we have performed a thorough DFT conformational analysis of both the monomers and the H-bonded dimers (Figure 1) of the species the results of which have allowed the correct interpretation of its FTIR and VCD spectra in solution.

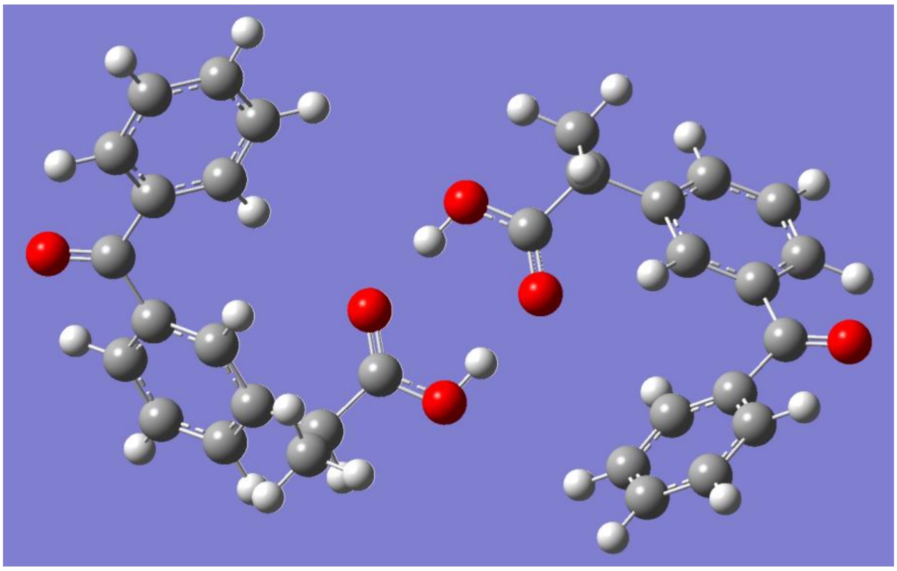

Figure 1. (S)-ketoprofen H-bonded dimer conformer

Acknowledgements

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P31 Sphingolipid headgroup impact on gel domains in Saccharomyces cerevisiae plasma membrane

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The presence of sphingolipid-enriched domains in the plasma membrane of *Saccharomyces cerevisiae* is currently acknowledged as physiologically relevant. These domains differ from the prototypical lipid domains both in composition, given that they are ergosterol-depleted, and biophysically, as they are highly rigid gel domains [1]. This finding was achieved by the use of two complementary fluorescent membrane probes, DPH and t-PnA. DPH is known to distribute evenly among most membrane domains, reporting global order of the membranes. On the other hand, the increased fluorescence quantum yield of t-PnA in ordered domains and its preference for gel domains makes this probe sensitive to changes in the amount and composition of ordered domains. Additionally, long lifetime component in t-PnA fluorescence intensity decay allows to distinguish gel domains (> 30ns) from liquid ordered domains (< 30ns) [2].

Current work is focused on which structural features of sphingolipids contribute to the stability of gel domains and for the action of antifungal agents. Thus, in this work the biophysical properties of the plasma membrane of wt cells and sphingolipid biosynthesis mutant strains, *ipt1*Δ, *csg2*Δ*csg1*Δ and *csg1*Δ*csh1*Δ, were studied, both *in vivo* and *in vitro*. In case of *ipt1*Δ, despite major change in the sphingolipid composition, the sterol composition is similar to the wt [3].

In *ipt1*Δ, *csg2*Δ*csg1*Δ and *csg1*Δ*csh1*Δ, the values of *t*-PnA long lifetime component and its amplitude are changed in comparison with wt cells. The global membrane order, as measured from DPH anisotropy, is also changed for *ipt1*Δ. These differences occur both in intact cells and isolated plasma membrane. However, using di-4-ANEPPS, a probe that reports sterol-dependent properties and reflects sterol composition [4], no significant differences could be observed.

In conclusion, changing the sphingolipid profile deeply affects gel domains and global membrane order in a manner largely independent of ergosterol. These results strengthen the recent suggestion that ergosterol and sphingolipids do not physically interact directly in yeast plasma membrane, and may in fact predominate in different membrane leaflets. Moreover, differences encountered between the wt cells and cells of the mutant strains concerning their sensitivity to membrane-active antifungals should be interpreted taking into account sphingolipid-enriched gel domains and their biophysical impact on membrane organization.

Acknowledgements

F. C.T., Portugal, is acknowledged for research grant PTDC/BBB-BQB/6071/2014, which includes a fellowship to J.T.M, UID/Multi/00612/2013, IF/00317/2012 (POPH, Fundo Social Europeu) and F.C.S. doctoral scholarship (SFRH/BD/108031/2015).

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P32 Evaluation of heat-not-burn tobacco effect on the quality of air and breath of smokers

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In recent years, there is an increasing interest to avoid the consumption of regular tobacco being several types of devices developed by manufacturers to decrease the impact of this practice on passive and active smokers and on the quality of air. To evaluate the new alternatives it is important to use monitoring devices to measure potential contaminants in both, ambient air and breath of active and passive smokers. Electronic cigarettes (ECs) are currently the most popular harm-reduction products, but still not all smokers find them effective or satisfactory enough in fully substituting smoking. In parallel to the emergence of e-cigarettes, new types of tobacco products have been proposed to generate an inhalable aerosol by heating tobacco instead of burning it, the so called "Heat Not Burn" (HNB) tobacco [1].

In this work, parameters as CO_2 and CO, the concentration of VOCs, NO_2, SO_2 and the levels of particulate material (PM) were analyzed for HNB by using portable devices, and compared with values obtained for other tobacco devices. The experiments were made in a clean and closed room of 40 m^3, where active and passive smokers were exposed to the smoke of HNB tobacco. The breath measurements of passive and active smokers were made at a distance of 20±2 cm based on previous experiments . The secondhand smoke of active smokers was also evaluated through breath measurements made on active and passive subjects.

On the one hand, from the comparison between HNB tobacco (Figure 1) and results obtained for electronic cigarettes and regular tobacco, it can be that the use of new devices decrease significantly the values of monitored contaminants in all cases, being the decrease 5 times lower for VOCs in HNB tobacco in front other devices and from 100 to 5000 times lower for the same comparison in the case of PM or CO_2.

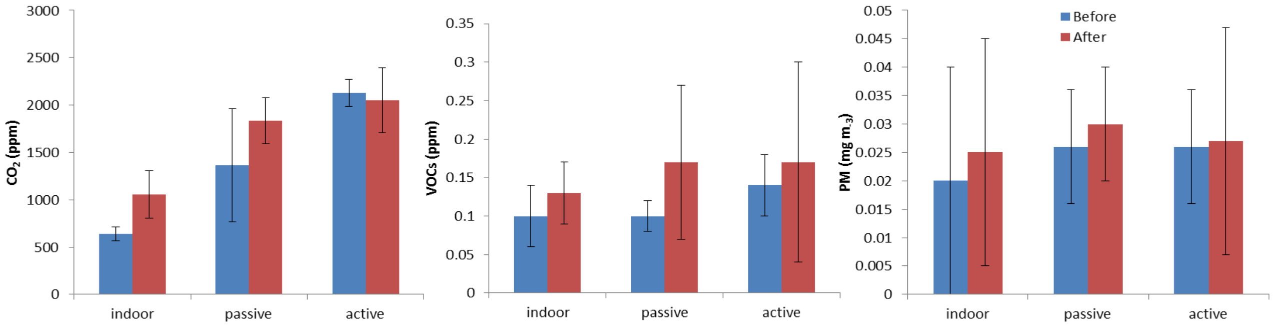

Figure 1. Concentrations of CO_2, VOCs and PM registered in the air and breath of active and passive HBN users.

On the other hand, it is clear that the employ of portable measuring devices based on infrared spectroscopy, electrochemical and photoelectric detectors provides fast, cheap, continuous and green methodologies to monitoring contaminants during these practices and assuring the quality of the air.

Acknowledgements

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P33 Inquiry based learning as a meaningful tool to apply IR spectroscopy and thermodynamic concepts in the chemistry lab

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Laboratory practices are key and integral part of the chemistry degree which are aimed at providing the students the necessary skills to get train in overall chemical procedures, understanding uncertainty in measurements, develop experimental designs, and, last, improve their scientific reasoning/ research abilities.

Despite the unquestionable capacity of hand-on lab experiences to achieve these goals, there is a general concern that, in many occasions, students are still somewhat immature in their ability to think things through even in the latter courses. [1] Considering that scientific reasoning is an innate human skill, the reason why even science students may lack this ability almost at the end of their academic undergraduate trajectory may lay in the way in which many of these courses are designed: as a follow-up recipe of a chemical process that, best case scenario, make the participants search for information and reflects about theoretical aspect related to the experiments carried out.

In this work we present an inquiry-based learning approach (IBL), which has been demonstrated to be a superior science teaching method that promote scientific, critical and creative thinking in students at different levels [2], to be implemented in spectroscopy courses intended for undergraduate chemistry students. The proposal starts with the introduction of a stimulus that invites the students to observe, describe and pose questions, hence, awaken curiosity. Within the context of the proposal the students are expected to use IR spectroscopy and apply thermodynamic concepts to study the H-bonded thermodynamic equilibria of benzoic acid in solvents of different polarity.

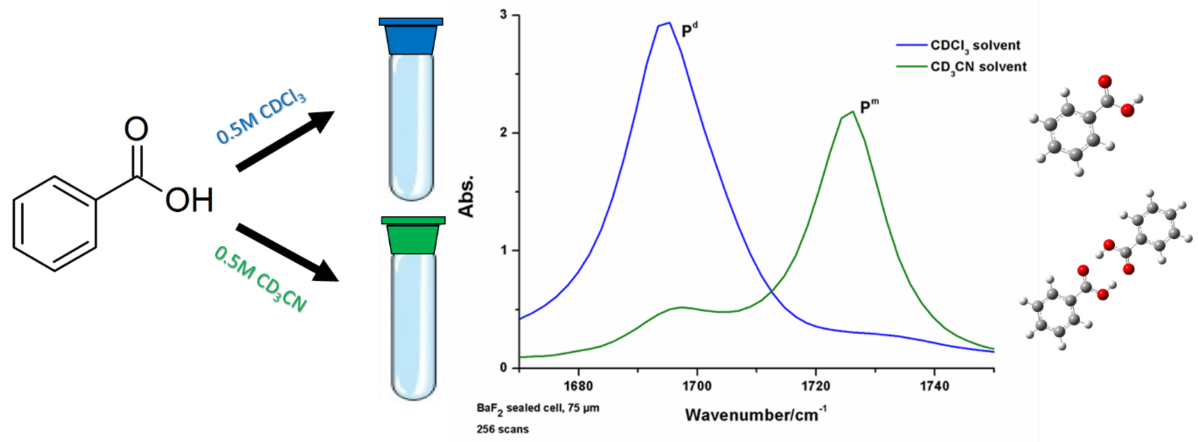

Figure 1. Differences observed in the experimental IR spectra recorded for 0.5M solutions of benzoic acid in CDCl3 (blue) and CD3CN (green) in the carbonyl region.

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P34 Carbon nanodots as next generation TPA probes

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Over the past decades, two-photon absorption (TPA) probes have attracted much attention due to their applications in biomedical imaging and biosensing. The application of TPA probes in multiphoton microscopy affords low background signal, deep tissue penetration depth, reduced photobleaching and low phototoxicity. However, to facilitate the use of two-photon excitation in biomedical research, there is a strong need for development of efficient, application-specific, two-photon responsive materials. Carbon nanodots (Cdot) are promising next generation TPA materials due to their unique properties, such as fluorescence emission, water solubility, high cell permeability and good biocompatibility.[1,2] However, exploration of C-Dot for two-photon imaging and sensing is hindered by the lack of fundamental understanding of their structure-optical properties relationship.

In this poster we discuss the optical properties of nitrogen-doped Cdots. The Cdots were produced by pyrolysis of citric acid in the presence of different amides. The final product is always an heterogeneous mixture of Cdots with excitation wavelength dependent emission upon one-photon excitation.[3] The emission spectrum is essentially dominated by two different emitting sites, with emission centred in the blue (440 nm) or in the green (520 nm). The most interesting observation of this study is illustrated in figure 1, where it is shown that for the same total excitation energy, the emission spectrum depends dramatically on the excitation mode. Excitation with one-photon is unspecific resulting in emission by the two emitting sites, while excitation by two-photon results in selective excitation of the green emitting site. The C-dots have TPA cross-section ranging from 200 to 1000 GM (Figure 1).

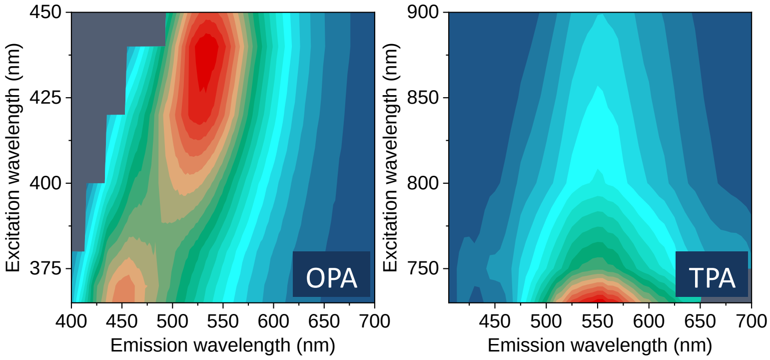

Figure 1. Excitation-wavelength dependence of the emission spectra of Cdots upon one-photon (OPEx) and two-photon excitation (TPEx).

Acknowledgements: Financial support from FCT is acknowledged (UID/NAN/50024/2013, SFRH/BPD/75782/2011, IF/00759/2013 and PD/BD/127805/2016).

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P35 Spectroscopic characterization of sensors based on Iron(II) coordination polymers

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Spin crossover (SCO) complexes show magnetic responses to subtle external stimuli, e.g., temperature, light, pressure and guest molecules, involving simultaneously changes in colour, dielectric constant or electrical resistance. These characteristics make them potential candidates for the detection of different organic and inorganic compounds, working as sensors. [1,2] These solids have more flexibility and ways of modifying porosity than inorganic porous compounds, allowing desorption and adsorption of guest molecules and, consequently, leading to the perturbation of various physical and chemical properties of the framework also affecting its SCO behaviour. Herein we present the spectroscopic study of the synthesized ligands and the corresponding coordination polymers by UV-Vis, fluorescence and FTIR.

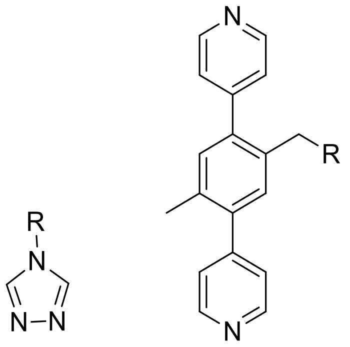

Figure 1. Text (Calibri, font size 10)

Acknowledgements

We thank Fundação para a Ciência e Tecnologia and the MOLSPIN cost action for financial support.

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P36 Spectroscopic studies of Hofmann structures based on donor/acceptor ligands

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Hofmann clathrates are bimetallic three-dimensional (3D) and two-dimensional (2D) coordination frameworks constituted by Fe(II) ions that are coordinated with cyanometallic anions [M(CN)x]y− (where M = Ni, Pd, Pt, Cu, Ag, Au, Nb) and N-donor heterocyclic ligands.[1] These pillared structures are appealing for potential chemical sensing applications since they can adjust their porosity.[2] Hoffman structures are commonly composed of units that make the bond in the crystal tridimensional structure are made by nitrogen atoms included in ligand that do the coordination to the metal centre, this structures have a big application in materials area because of their properties.

Spin crossover (SCO) complexes show magnetic responses to subtle external stimuli, e.g., temperature, light, pressure and guest molecules, involving simultaneously changes in colour, dielectric constant or electrical resistance.[3] These characteristics make them potential candidates for the detection of different organic and inorganic compounds. Hofmann clathrates, a class of metal-organic frameworks (MOFs) and their analogues are among the most known and well-studied for practical applications as SCO compounds. Our strategy on Hofmann clathrates consisted in inserting a photoactive unit (Figure 1) that has both acceptor and donor capabilities promoting the electronic and optic properties of the 3D structure envisaging a material with applications in photocatalysis, solar cells, LEDs and OFETs. Here we present the synthesis and characterization by Mossbauer spectroscopy and UV spectroscopy of Hofmann clathrates with thiazole-derived spacers and the magnetic and optical properties are also discussed.

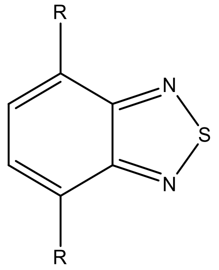

Figure 1. Donor/Acceptor unit used in the Hofmann Clathrates

Acknowledgments

The authors thank Fundação para a Ciência e Tecnologia for financial support UID/MULTI/00612/2013 and PTDC/QEQ-QIN/3414/2014

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P37 Reference measurements for trace elements in environmental candidate certified reference materials with Isotope Dilution-ICP-MS

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In this work, a new and simpler analytical methodology for fast and reliable reference measurements in marine environmental samples (*i.e.,* biota and sediments) using isotope dilution mass spectrometry (IDMS) is presented.

In the recent years the release of metal contaminants, toxic for the human being, into the marine environment has increased, specially from anthropogenic sources. This situation has led to an on-going requirement to develop analytical methodologies for their accurate determination in different types of environmental samples, which serve as reference materials in pollution and ecosystem conditions monitoring. The low levels at which trace metals are present in marine environment and the thin line between acceptable and dangerous concentrations mean that more accurate methods of analysis must be employed to successfully control the content of metals in these samples.

In this research, Isotope Dilution Inductively Coupled Plasma Mass Spectrometry (ID-ICP-MS) has been applied for the determination of the total mass fractions of priority (*i.e*. cadmium, mercury, methylmercury, nickel and lead) and essential (*i.e*., copper and zinc) trace elements in marine environmental candidate reference materials: IAEA-475 and IAEA-476, which are sediment and biota samples, respectively. Because of the complex matrix of the sample and the expected spectral interferences, special care was taken for the validation of the applied method, particularly for its measurement step. Reference isotopic measurements were carried out with a Sector Field Inductively Coupled Plasma Mass Spectrometer (ICP-SFMS).

The entire ID-ICP-MS measurement process was described by mathematical equations and the combined uncertainty estimated. All factors influencing the final results and their uncertainties were systematically investigated. Obtained results were compared with those derived from the worldwide inter-laboratory comparisons organized by the International Atomic Energy Agency (IAEA) on the same sample matrices and the agreement will further validate the reference methods developed in the Environment Laboratories of the IAEA.

Additionally, obtained results will be compared with those derived from the analysis on the same sample matrices using a new multiple nebulizer [1]. The nebulizer used in this study includes two independent liquid inlets: one is used for digested sample introduction and the remaining for introducing the spiking standard solutions. In this way, the spiking of the sample is performed directly into the spray chamber, and so the spiking step is avoided, reducing the time and human intervention in the analysis. This new multiple nebulizer will be evaluated as a fit-for-purpose alternative. Preliminary results will be shown.

Acknowledgements

The authors would like to thank the Spanish Ministry of Science and Innovation (project n. CTQ 2011-23968), Generalitat Valenciana (Spain) (project n. PROMETEO/2013/038) and the Government of the Principality of Monaco. M.A.A. is grateful to Generalitat Valenciana (Spain) (APOSTD/2016/076) for his Post-Doctoral fellowship and the financial support from the European Social Fund (ESF).

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P38 Mn(IV) Schiff base complexes for CO_2 electroreduction: a spectroelectrochemical study

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Mn(IV) complexes have been reported to be used as catalysts, more specifically in oxygen evolving complex (OEC) in photo-oxidation of water. Mononuclear Mn(IV) complexes with N_2O_4 donor atoms can also be used in electrocatalysis. [1] However, this type of compounds is still rare and only a few cases were studied over the last years. [2]

Many groups are currently working on CO_2 capture and conversion and researchers have been using first-row transition metal complexes as catalysts for CO_2 reduction. These first-row metal ions are a more sustainable alternative when compared to the second and third-row transition metal ions due to their abundance and low cost, for instances substituting Re(I) with Mn(I). CO_2 is reduced to other added-value products such as CO, formic acid, formaldehyde or methanol. [3]

In this work two Mn(IV) complexes (Figure 1) with N_2O_4 donor atoms were formed reacting $MnCl_2{\cdot}4H_2O$ and the different ligands in air. The ligands were obtained by reacting an amine with an aldehyde obtaining tridentate Schiff-base ligands. The compounds were also characterized by FTIR, UV-vis, NMR, elemental analysis and X-ray crystallography. The complexes were studied by cyclic voltammetry under N_2 and CO_2 saturated atmospheres and seen as good candidates to reduce this gas. Bulk electrolysis experiments were performed to reduce CO_2 into different gaseous and liquid products that could be detected by GC-TCD or NMR. Both IR-SEC and UV-SEC experiments were accomplished to understand the intermediates formed in both N_2 and CO_2 atmospheres after applying a potential.

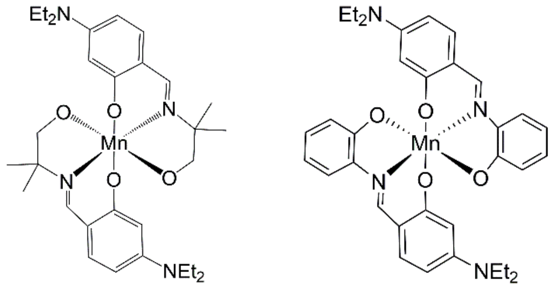

Figure 1. Mn(IV) Schiff base complexes

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P39 Phosphorus determination in beverages via PO molecule by High-Resolution Continuum Source Flame Molecular Absorption Spectrometry

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Phosphorous determination is a topic of interest in different fields such as clinical and food analysis inasmuch as this element controls relevant processes in the organisms. Most of the methods used for phosphorous determination are based on UV-vis molecular absorption spectrophotometry. Methods based on atomic absorption spectrometry (AAS) are limited due to the high energy required for phosphorus atomization and the fact that the most sensitive atomic lines of phosphorous appear in the vacuum ultraviolet region between 167 and 179 nm. The use of PO molecular bands can be an interesting alternative for phosphorus determination due to the lower energy required for the formation of diatomic molecules. The high-resolution continuum source atomic absorption spectrometers make easier the monitoring of molecular spectra for the quantification of non-metals compared to the use of conventional line-source AAS instruments [1-3].

The aim of this work is the optimization of a fast and simple analytical methodology for the determination of phosphorus in soft drinks via molecular absorption of phosphorus monoxide molecules using a high-resolution continuum source atomic absorption spectrometer, and an air-acetylene flame. To achieve this purpose, PO molecular bands at wavelengths of 246.4000 nm, 247.6200 nm, 324.6160 nm and 327.0400 nm were evaluated, and flame conditions were optimized in order to obtain the best analytical signal. Moreover, the introduction of sample in the spectrometer in a continuous and/or a discontinuous mode was investigated. The use of chemical modifiers such as titanium, EDTA and/or aluminium was investigated in order to eliminate or minimize the interferences due to the presence of calcium and magnesium in the samples. The figures of merit, such as sensitivity, limits of detection (LOD) and quantification (LOQ), reproducibility and linear working range for all PO molecular bands were estimated using both introduction sample modes. Finally, the proposed methodology was applied to determine phosphorous content in Cola drinks from different brands. The obtained results using the developed methodology were statistically comparable to those obtained with a UV-vis molecular absorption spectrophotometric method.

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P40 SERS Nanothermometry

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When illuminated near their plasmonic resonances, metallic nanoparticles can become effective heatsources that increase the temperature in their immediate vicinity [1]. This is an effect that can be controlled remotely using light, that has become increasingly important in several fields of modern science. The measurement of temperature with high spatial resolution, on the other hand, has also become a subject of interest [2], not only in the context of the miniaturization of devices, but also in the biological and medical fields [3]. The measurement and control of temperature at the subcellular scale, for instance, are crucial for the application of techniques like photothermal therapy and thermally-induced drug delivery. Not surprisingly, the development of non-invasive and high spatial resolution thermometers is now a very active field of research. Among the optical techniques that have been proposed to measure temperature with high spatial resolution we can mention those based on fluorescence, luminescence, and up-conversion [2-4]. To this end, we propose to exploit SERS spectroscopy: the idea is to measure the strengths of a Stokes and its corresponding anti-Stokes line, and use this information to calculate the temperature considering a Boltzmann distribution for the ground and first excited state populations.

In this work, we use the SERS signal of adenine to monitor the temperature increase of metallic nanoparticles under laser irradiation. The particles were produced by chemical methods and characterized by optical and transmission electron microscopy methods. Particles with various shapes, including nanospheres and nanostars have been produced [5,6]. Results for the estimated increase in the temperature of metallic particles under laser illumination will be presented. These results show that the temperature increases fairly linearly as a function of the incident irradiance. We also present calculations for the absorption cross sections of the nanoparticles, from which the temperature increase of the sample can be estimated. Employing a thermal model and fairly realistic assumptions, we are able to reproduce the experimentally observed behavior.

Acknowledgements

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P41 New developments in optically stimulated luminescence dating towards extending the age range

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The use of absolute dating techniques to establish a robust chronological record is a key tool in the study of Quaternary environmental evolution. Optically Stimulated Luminescence (OSL) dating, using mineral grains (quartz and feldspar mainly) as dosimeters has become one of the most useful techniques to do so. The age is given by the relation

$$Age\ [ka] = \frac{D_e\ [Gy]}{D_R\ [{}^{Gy}/_{ka}]}$$

where D_e is the accumulated dose and D_R is the environmental dose rate. The standard method is based on the detection of the luminescence signal (260-380 nm) from quartz during blue or green stimulation. The maximum age range is limited by the saturation of the dose response curve (Figure 1) which can reach up to doses equivalent to ~200 ka [1]. The infrared stimulated luminescence (IRSL) of feldspar saturates at a higher limit offering the possibility of extending the age range [2]. Unfortunately, the complex nature of feldspar and the instability of the IRSL signal compromises the reliability of this method. It has recently been reported that the luminescence signal of quartz during violet stimulation from deep electron traps, not accessible by blue light, has saturation values ~20 times larger than OSL [3].

VSL has been applied to the study of a clay pan in Atacama Desert where a 51 m core of sediment has been extracted. OSL and IRSL have provided ages coherent with the stratigraphy up to 6 m deep where saturation of the luminescence signals has been reached at ~500 Gy (approx. 200 ka). Initial VSL data show promising characteristics and may allow the development of a robust chronology for deeper sedimentary units.

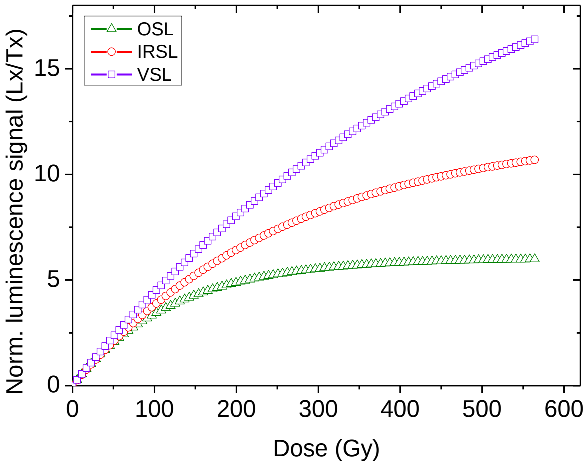

Figure 1. Dose response curves for OSL (triangles), IRSL (circles) and VSL (squares) signals from sediment from the Atacama clay pan under study. The plot shows the normalized signals as a ratio between the given dose and a fix test dose of 20Gy.

Acknowledgements

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P42 Charge Transfer mechanism in the Surface Enhanced Raman Scattering of 2,2'-bipyridine recorded on a silver electrode

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Nowadays, Surface Enhanced Raman Spectroscopy (SERS) has become a powerful technique to investigate the electronic structure of surface-molecule hybrid systems due to the huge enhancement of the Raman signal. It is established that the origin of this enhancement has two main contributions; the electromagnetic (EM), related to surface plasmons, and the chemical mechanism, due to resonant charge transfer (CT) processes between the adsorbate and the metal. With the aim to investigate the SERS-CT of bipyridine and to identify charge transfer process, the spectra were recorded on silver electrode by using three different wavelengths (473, 532 and 785 nm) in a range from 0.0 up to -1.4 V electrode potential. The electrode potential was modelled in the calculations with atomic silver wires of different size and charge attached to the BPy molecule (Ag_nBPy^q, with q = 0 for n = 2 and q = ±1 for n = 3, 5, 7) and were computed with Density Functional Theory (DFT). Although BPy shows a trans conformation in solution, a cis conformation was chosen for its chelating properties. The results indicate that the intensification of the ~1550 cm^{-1} band at negative potentials is due the Franck-Condon factors related to the resonant CT process from the metal to the BPy molecule (Figure 1).

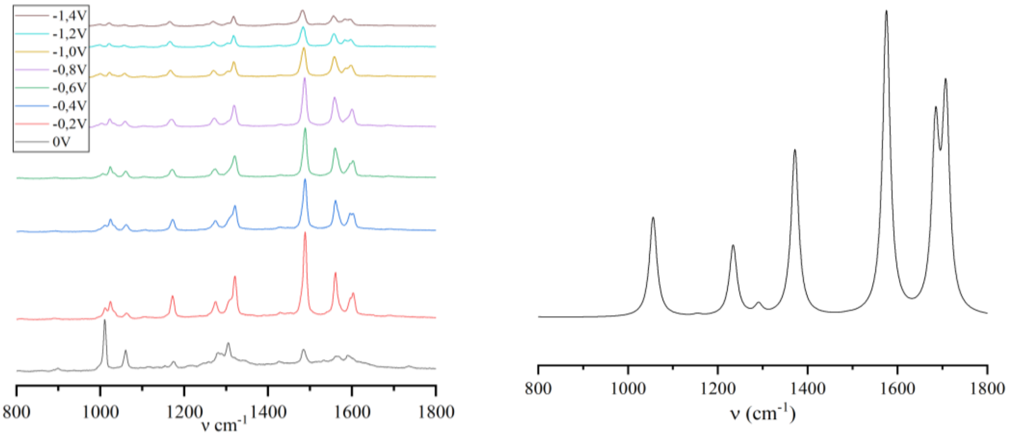

Figure 1: Experimental SERS Spectra of 10^{-3} M aqueous bipyridine solution at 532 nm (left), and calculated S_0-CT_0 resonant Raman spectrum (right).

Acknowledgements

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P43 Alkaline oxidation for elemental quantification of carbon materials

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With the development of new carbon materials such as nanotubes and graphene, the determination of sample-batch elemental concentrations is essential to promote quality control during the production of these materials as well as ensure reliability of their response when applied technologically [1].

We used alkaline oxidation (a.k.a. fusion) to digest the graphitic structure of carbon nanotubes and enable the subsequent reading of elemental concentrations with a routine analytical tool such as inductively coupled plasma optical emission spectroscopy (ICP-OES). The fusion method was validated using a standard nanocarbon, namely the SWCNT-1, which is produced by the Canadian National Research Council. Three certified elements were probed, namely Co, Ni and Mo, with recoveries attained in the order of 80% or higher. Furthermore, the fused remainders were collected and investigated with electron microscopy, Raman spectroscopy and nuclear magnetic resonance. Interestingly, there seem to be structural changes in the carbon lattice that are fairly different from those obtained using classical wet digestion methods.

The fusion method presents another possibility for digestion of nanoscaled materials when using ICP-based techniques and may be particularly useful when the option of wet digestion with acids is not feasible such as for refractory and graphitic materials.

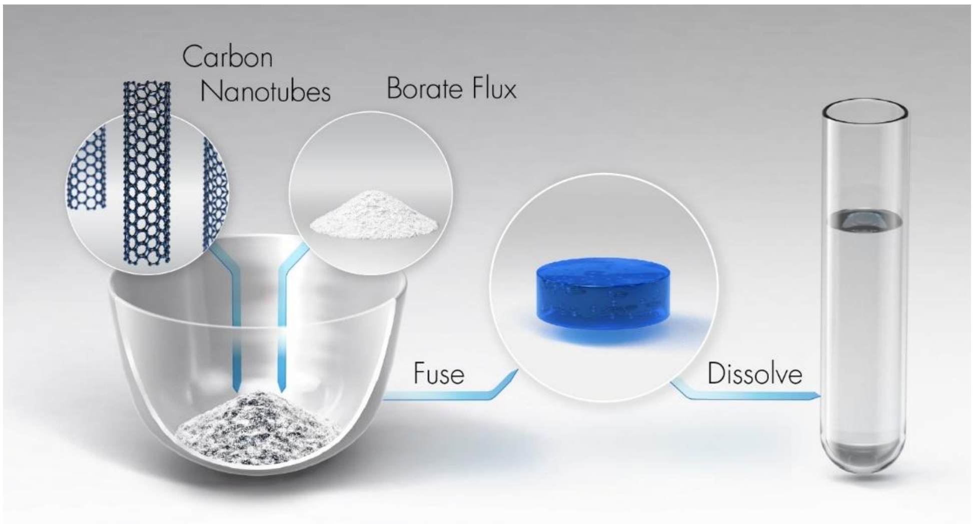

Figure 1. Illustration of the alkaline oxidation process.

Acknowledgements

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