XXVII National Spectroscopy Meeting
XI Iberian Spectroscopy Conference

5 - 8 July 2022
Málaga - Spain

XXVII RNE – XI CIE
SPECTROSCOPY
MÁLAGA • JULY 5th–8th, 2022

BOOK OF ABSTRACTS

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WELCOME

It is a pleasure to invite you to attend to XXVII National Spectroscopy Meeting (RNE) and XI Iberian Spectroscopy Conference (CIE), which will be held at the School of Industrial Engineering (Dr. Ortiz Ramos St., Málaga, Spain).

This conference has been organized by Comité de Espectroscopia de la Sociedad Española de Óptica (SEDOPTICA) in collaboration with SEQA (Sociedad Española de Química Analítica), SEA (Sociedad de Espectroscopia Aplicada), SPQ (Sociedade Portuguesa de Química) and SPB (Sociedade Portuguesa de Bioquímica).

The principal goal of the meeting is to contribute to spread the latest developments in the spectroscopy field in fundamental aspects and applications, motivating the participation of senior and young researchers and students. Following the tradition of previous editions presentations will establish a forum to stimulate exchange of knowledge and scientific collaborations.

The program of the conference includes plenary and invited lectures delivered by well-known international speakers, as well as oral and poster presentations from participants in the following topics: Spectroscopy and Molecular Structure, Biomolecular Spectroscopy, Cultural Heritage, Chemical Analysis and Speciation, Food analysis, Instrumentation, Plasmonic, Sample Preparation, Sensors, Surfaces and Interfaces and Spectroscopy in Education.

The National Spectroscopy Meeting (RNE) had been held for many years ago, almost since the Spectroscopy Committee foundation in 1950, approximately. This meeting has been carried out in many scientific organizations and cities throughout Spain, being the first one in Barcelona in 1968. Here you can find a summary of the beginning:

I RNE (Barcelona 1968), II RNE (Alicante 1970), III RNE (Zaragoza 1972), IV RNE (Granada 1974), V RNE (Palma de Mallorca 1976), VI RNE (Madrid 1978), VII RNE (Santander 1980), VIII RNE (Córdoba 1981), IX RNE (Salamanca-Coímbra 1983), X RNE (Torremolinos 1986), XI RNE (Alicante 1988), XII RNE (Barcelona 1990), XIII RNE (Gandía 1992), XIV RNE (Baeza 1994), XV RNE (Oviedo 1996), XVI RNE (Sevilla 1998).

Since the year 2000 a new period of these meetings has also begun covering Portugal and thus introducing the first *"Iberian Spectroscopy Conference"* that was held in **León (XVII RNE - I CIE)**. After that, it has also been celebrated in:

2002 – Coímbra (XVIII RNE – II CIE)

2004 – Las Palmas (XIX RNE – III CIE)

2006 – Ciudad Real (XX RNE – IV CIE)

2008 – Murcia (XXI RNE – V CIE)

2010 – Porto (XXII RNE – VI CIE)

2012 – Córdoba (XXIII RNE – VII CIE)

2014 – Logroño (XXIV RNE – VIII CIE)

2016 – Alicante (XXV RNE – IX CIE)

2018 – Lisboa (XXVI RNE – X CIE)

The next meeting was planned for 2020 but unfortunately was canceled due to the pandemic caused by the COVID-19, being the first time since 1968 that a meeting was not held. It has been a hard period with a lot of uncertainty but happily, we are back with another in person spectroscopy meeting, motivated and with great pleasure to continue promoting research and science. We would like to express our special thanks to the plenary and invited speakers who have remained faithful to this meeting after this period of uncertainty and the essential support of the sponsors who have not abandoned us despite the poor projection of these two years ago.

As president of the Spectroscopy Committee of SEDOPTICA, I am proud to chair this meeting in Málaga as part of the history of this committee and on behalf of all my colleagues who have been part of it before me and have collaborated with other societies and made an effort to carry out the previous meetings. I would like to remember in this book the presidents who have preceded me:

1968-1970: Rafael Velasco Ferre – CSIC

1970-1975: Antonio Hidalgo Gadea - CSIC

1975-1981: José Mª Serratosa Márquez - CSIC

1981-1985: Manuel Rico Sarompas - CSIC

1985-1989: Juana Bellanato Fontecha - CSIC

1989-1993: José Vicente García Ramos - CSIC

1993-1998: Rafael Escribano Torres - CSIC

1998-2002: Jorge Santoro Said - CSIC

2002-2008: Juan Carlos Otero Fernández de Molina - UMA

2008-2012: Santiago Sánchez Cortés - CSIC

2012-2016: Belén Maté Naya – CSIC

Finally, we are delighted to have your presence and we hope you enjoy it both the scientific and the social program and of course your stay in Málaga.

Thank you very much for your participation.

María Rosa López Ramírez

President of Spectroscopy Committee (SEDOPTICA)

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CONFERENCE'S PROGRAM:

All scientific activities will take place at Salón de Grados A of the School of Industrial Engineering (EII) in the Campus of Teatinos of the University of Málaga

TUESDAY	**JULY 5, 2022**
18:30 – 19:30	**Workshop:** Remote and in-situ sampling with the Virsa Raman Analyser, a valuable tool in the science of Cultural Heritage. **Riccardo Tagliapietra, Sebastien Maussang** (RENISHAW) **Free registration. Send mail to:** mmontejo@ujaen.es
20:30	**Welcome reception / Registration** **Meeting point:** Casa Hermandad "Sepulcro", C/ Alcazabilla 5, 29015 Málaga

WEDNESDAY	**JULY 6, 2022**
8:00 – 9:00	**Registration**
9:00 – 9:30	**Opening Ceremony**
9:30 – 10:30	**CHAIR: Mª ROSA LÓPEZ RAMÍREZ** ***PL1:*** *Applied spectroscopy: Impact of organics in the chemistry of the Earth's atmosphere and the interstellar medium.* **Elena Jiménez Martínez** (University of Castilla-La Mancha)
10:30 – 11:15	**OC1:** Detection of biomarkers on lichens after Space and Mars like conditions with Raman **Rosa de la Torre Noetzel** (CSIC-INTA) **OC2:** XPS study of chemical evolution of glycine on pyrite (100) surface **Santos Gálvez Martínez** (CSIC-INTA) **OC3:** Subfemtogram detection power for single-trapped nanoparticles in laser-induced plasmas **Francisco Javier Fortes** (UMALASERLAB)
11:15 – 11:45	**Coffee Break (Hall in ground floor)**
11:45 – 12:15	**CHAIR: FRANCISCO ÁVILA FERRER** ***IL1:*** *A bright future for upconversion nanoparticles* **Marco Lurenti** (UCM – CSIC-ICCMM)
12:15 – 13:30	**OC4:** Polymeric (nano)composite papers as analytical platforms coupled to spectroscopic techniques **Ángela Inmaculada López Lorente** (U. Córdoba) **OC5:** Hyperspectral characterization of head and neck cancer in mice **Alba Martín de la Torre** (U. Cantabria) **OC6:** Electrospraying as Method for the Synthesis of Biocompatible PLGA@Ag2S and PLGA@Ag2S@SPION Nanocarriers with Drug Release Capability **Rafael Contreras Cáceres** (UCM) **OC7:** Molecular super-gluing: a straightforward tool for antibody labelling and its application to mycotoxin biosensing **Fernando Pradanas González** (UCM) **OC8:** Multiparametric Microanalyzer as a Warning System for Heavy Metals Monitoring in Water using Carbon Dots as Luminescent Reagent **Alex Pascual-Esco** (UAB)
13:30 – 15:00	**Lunch (EII Cafeteria)**
15:00 – 16:00	**CHAIR: JOSÉ MIGUEL VADILLO** ***PL2:*** *Mid-Infrared Photonics: From Emerging Technology to Enabling Tool* **Boris Mizaikoff** (University of Ulm)
16:00 – 16:30	**OC9:** FTIR and VCD assisted study of the speciation in solution of racemic and enantiopure NSAIDs: ketoprofen, naproxen and ibuprofen. **Magdalena Sánchez Valera** (UJA)

	OC10: Carbonaceous dust specific surface area determination using grazing-angle reflection-absorption IR spectroscopy **Belén Maté** (CSIC-IEM)
16:30 – 16:55	**Coffee Break (Hall in ground floor)**
17:00 – 17:30	**CHAIR: Mª VEGA CAÑAMARES ARRIBAS** **OC11:** Study of the aggregation behaviour and environmental stability of Platinum nanoparticles in water systems. **Armando Sánchez Cachero** (UCLM) **OC12:** Vibrational Spectroscopy Complemented with Chemometrics as a Tool for Auxiliary Diagnosis of Psychiatric Disorders **Gülce Ogruc Ildiz** (Istanbul Kultur University)
17:30 – 18:30	**Posters' Session (Hall in ground floor)**
19:30	**Conference's Social Program Activities:** **"Excursion, sunset and astronomical observation in "Torcal de Antequera"** **BUS DEPARTURE in Meeting point: EII - CONFERENCE VENUE**

THURSDAY	**JULY 7, 2022**
9:30 – 10:30	**CHAIR: BELÉN MATÉ NAYA** ***PL3:*** *IR-Induced and Tunneling-Driven Reactions in Cryogenic Matrices "Plastic Molecular Cryosurgery"* **Rui Fausto** (University of Coimbra)
10:30 – 11:15	**OC13:** Mid-infrared spectroscopy of aliphatic molecular ices exposed to UV radiation in dense molecular cloud **Guillermo Tajuelo Castilla** (CSIC-ICMM) **OC14:** Solution-Cathode Glow Discharge Optical Emission Spectrometry for Elemental Analysis: Novel Insights and Instrumental Approaches. **Jaime Orejas** (UNIOVI) **OC15:** Computation of Molecular Aggregates Vibronic Spectra with a Mixed Quantum/Classical Approach **Daniel Aranda Ruiz** (ICMol- UV)
11:15 – 11:45	**Coffee Break (Hall in ground floor)**
11:45 – 12:15	**CHAIR: MANUEL MONTEJO GÁMEZ** ***IL2:*** *Microenvironment sensing by multiparametric microscopy and nanoscopy* **Ángel Orte** (University of Granada)
12:15 – 13:15	**OC16:** Chirality from twisting **Francisco Javier Ramírez** (UMA) **OC17:** Comparative study of γ and δ alumina by vibrational spectroscopies **Íñigo González de Arrieta** (CNRS - Orléans) **OC18:** Mapping minerals in a Dhofar meteorite by Raman imaging **Ana Isabel Casado Gómez** (UCM) **OC19:** A detailed IR, Raman spectroscopic and DFT theoretical analysis of commercial additives monosodium glutamate and xylitol. **Vicente Timón** (CSIC-IEM)
13:15 – 13:45	**Posters' Session (Hall in ground floor)**
13:45 – 15:00	**Lunch (EII Cafeteria)**
15:00 – 15:30	**CHAIR: SANTIAGO SÁNCHEZ CORTÉS** ***IL3:*** *Innovation in Analytical Spectrometry driven by Nanotechnology* **Carlos Bendicho** (University of Vigo)
15:30 – 16:15	**OC20:** Analysis of two blue triarylmethane dyes by UV-Vis, FT-Raman and SERS spectroscopies. **Michela Rampa** (CSIC-IEM) **OC21:** Spectroscopic analysis and identification of Islamic and Christian materials and pigments in the church of Santa Catalina-convent of Santo Domingo (Jaén) **Alberto Sánchez** (UJA-IUIAI)

	OC22: Raman spectroscopy and SERS methodology for the analysis of a melamine admixture superplasticizer for concrete. **Ana Crespo** (CSIC-IEM)
16:15 – 17:00	**Coffee Break (Hall in ground floor)**
17:00 – 17:45	**CHAIR: ROSA DEL CARMEN RODRÍGUEZ MARTÍN-DOIMEADIOS** **OC23:** Hyperspectral infrared imaging of dystrophic mice muscles. **Verónica Mieites Alonso** (IDIVAL-UC) **OC24:** Spectroscopic monitoring of the stability of Phycoerythrin dye extract: influence of temperature, pH, light exposure and preservatives. **Ruperto Bermejo Román** (UJA) **OC25:** Electric field and charged cluster dual model for Potential Dependent Surface-Enhanced Raman Spectroscopy. **Francisco García González** (UMA)
17:45 – 18:30	**Societies' Assemblies**
21:00	**Conference's Dinner** **Meeting point:** Restaurante "El Balneario – Baños del Carmen" C/ Bolivia 26, 29018 Málaga

FRIDAY	**JULY 8, 2022**
9:30 – 10:30	***SPONSORED BY LASING*** LASING **CHAIR: VALENTIN GUADAÑO** ***PL4:*** *LIBS and acoustic measurements of rocks and regolith and the exploration of Mars* **Javier Laserna** (UMALASERLAB)
10:30 – 11:00	**OC26:** The crucial role of molecular emissions on detectability of organic biosignatures under Mars atmosphere conditions by LIBS **Tomás Delgado Pérez** (UMALASERLAB) **OC27:** Detection of A. platensis cyanobacteria in different inorganic matrices by LIBS under a simulated Martian atmosphere **Laura García Gómez** (UMALASERLAB)
11:00 – 11:25	**Coffee Break (Hall in ground floor)**
11:30 – 12:00	**CHAIR: Mª ROSA LÓPEZ RAMÍREZ** **IL4:** Studying Protein Stability in Ionic Liquids: Insights from NMR **Eurico J. Cabrita** (UCIBIO-NOVA)
12:00 – 13:00	**OC28:** Through the NMR looking glass: Unravelling role of water in DESs nanostructure **Ana Sofía Diogo Ferreira** (UCIBIO-NOVA) **OC29:** CPL and ROA: a rare couple together **Luis Palomo** (UMA) **OC30:** Concomitant Ion Impact on the Performance of A SCGD-OES Elemental Analysis Approach **Yinchenxi Zhang** (UNIOVI) **OC31:** Detection of the glyphosate pesticide by SERS: development of a new highly selective and sensitive detection method **Francisca Belén Fuenzalida Sandoval** (UPJS)
13:00	**Closing Ceremony**

POSTERS SESION PROGRAM:

All posters should be on display in the hall of the School of Industrial Engineering (EII) at the Campus of Teatinos of the University of Malaga from the morning of Wednesday, July 6.

P1: Combining nanotechnology and ultrasound: in situ synthesis of magnetic nanocomposites for mercury preconcentration.
I. Lavilla, I. de la Calle, J. Páez-Cabaleiro, V. Romero, C. Bendicho (UVIGO)

P2: Modification of cellulose filter paper with silver nanoparticles for Hg enrichment and determination by a direct mercury analyzer
I. Lavilla, I. de la Calle, H. Bartolomé-Alonso, C. Bendicho (UVIGO)

P3: The interaction between lysozyme and chlorogenic acid: a fluorescence approach
D. Leithardt, C. Tomaz, A. Mendonça (UBI)

P4: Biocompatible hybrid nanosystems with photoluminescent, magnetic and drug release activity
A. Alvear-Jiménez, L. Lozano-Chamizo, M. López-Romero, B. García-Pinel, R. Contreras-Cáceres, R (UCM)

P5: ICP-MS methodology to determine novel potential chemotherapy drugs based on Ruthenium derivatives
F. de Andrés, E. Domínguez-Jurado, C. Alonso-Moreno, I. Bravo, M. Zougagh, Á. Ríos (UCLM)

P6: Comparison of two theoretical models for simulating the charged metal-molecule interface in electrochemical SERS experiments
S. Valdivia, D. Aranda, J. Soto, I. López-Tocón, F. J. Avila, J. C. Otero (UMA)

P7: Silver nanostructures mediated by copper substrate for thin film microextraction coupled to surface enhanced Raman spectroscopy
L. Carrillo-Sánchez, A. I. López-Lorente, R. Lucena, S. Cárdenas (UCO)

P8: Structural in-depth analysis of iron complexes of plant gall polyphenols by spectroscopic techniques: Implications in the analysis of historical.
A. Espina, S. Sánchez-Cortés, M. V. Cañamares, Z. Jurašeková (CSIC-IEM)

P9: Characterization of Spanish PDO fortified wines by combining multidimensional fluorescence and chemometric approaches
R. Ríos-Reina, J. L. Pérez-Bernal, J. A. Ocaña, R. M. Callejón (US)

P10: Protonation effect on the ESIPT process of 2-(2'-hydoxyphenyl)pyrimidines.
M. P. Fernández-Liencres, R. Plaza-Pedroche, S. B. Jiménez-Pulido, N. A. Illán-Cabeza, S. Achelle, A. Navarro, J. Rodríguez-López (UJA)

P11: Branch detection in green and romano beans using reflection spectroscopy
A. Gracia Moisés, I. Vitoria, L. Castaño, A. Averillo, C. R. Zamarreño (UNAVARRA)

P12: Application of IR spectroscopy for assessing and characterizing organic and conventional virgin olive oils.
R. M. Callejón, C. Ortiz-Romero, R. Ríos-Reina, B. Jiménez-Herrera, L. Arce (US)

P13: Assessment of the potential of excitation-emission fluorescence and Chemometric approaches for characterizing olive oils of different qualities.
M. P. Segura-Borrego, R. Ríos-Reina, C. Ortiz-Romero, J. A. Ocaña, B. Jiménez-Herrera, L. Arce, R. M. Callejón (US)

P14: Aerosol pollen classification using laser-induced breakdown spectroscopy (LIBS).
F.J. Fortes, P. Purohit, T. Delgado, M. Villegas, J. García-Sánchez, M.M. Trigo, J.J. Laserna (UMA)

P15: Teaching Spectroscopy.
J.M. Suárez Muñoz, R. Pascual Juez (URJC)

P16: Detection of Ibuprofen and Caffeine Pollutants by Surface-Enhanced Raman Spectroscopy.
I. López-Tocón, M. Lemos de Souza, J. C. Otero (UMA)

P17: Aluminium doped zirconia nanoparticles-modified electrochemical sensor for authenticity controlling of vanilla flavours in food samples.
Y. Benmassaoud, R. Salghi, M. Zougagh, A. Ríos (UCLM)

P18: Determination of biological markers oxidative stress by capillary liquid chromatography mass spectrometry.
Y. Benmassaoud, R. Salghi, M. Zougagh, A. Ríos (UCLM)

P19: DFT assisted interpretation of the solid state VCD spectra of NSAIDs: ketoprofen, naproxen and ibuprofen.
M. Montejo, M. Sánchez-Valera, P. G. Rodríguez-Ortega (UJA)

P20: Introduction to meteor spectroscopy within the UMA/SMA Fireball and Meteor Detection Network.
A. Lozano-Fernández, A. Castellón-Serrano, J. L. Pérez-Bernal, M. R. López-Ramírez (UMA)

P21: Sample preparation effects on near infrared (NIR) data modelling of acidic and neutral forms of cannabinoids in Cannabis sativa flowers.
A. Palou, M. Pérez, M. Gómez-Cardoso, A. Castillejo, R. Valenzuela, J. Casals (UPC)

P22: Study by spectroscopic techniques of the process of protein corona formation onto platinum nanoparticles.
R.C. Rodríguez Martín-Doimeadios, N. Rodríguez-Fariñas, F. El Arnouki Belhaji (UCLM)

P23: The role of Optically Stimulated Luminescence (OSL) dating in archaeological sites
A. Medialdea, J. Rivera-Silva (CENIEH)

P24: Spatially resolved excitation temperature in the Solution-Cathode Glow Discharge.
C. Soto-Gancedo, Y. Zhang, J. Orejas, J. Pisonero, N. Bordel (UNIOVI)

P25: MRS and µEDXRF analysis on Roman wall paintings from the archaeological site of Cástulo (Linares, Spain).
J. Tuñón, P. Amate, B. Ceprián, D. Parras, M. Montejo, A. Sánchez (UJA)

P26: Monolayers of plasmonic nanoparticles prepared in electrostatically-driven self-assembly as effective substrates for surface-enhanced spectroscopic methods.
M. Oćwieja, N. Piergies, M. Sadowska, P. Gnacek, J. Maciejewska-Prończuk, M. Wasilewska, M. Nattich-Rak, C. Paluszkiewicz, M. Kozak (IKIFP)

P27: XPS and Raman Spectroscopy as a combined tool for study of N coordination in diluted InGaAsN.
M.C. López-Escalante, M. Gabás, V. González, B. Ściana, W. Dawidowski, D. Radziewicz and J.R. Ramos-Barrado (UMA)

P28: Spectroscopic analysis of mushrooms by Surface-enhanced Raman Scattering (SERS).
Federico Puliga, Veronica Zuffi, Alessandra Zambonelli, Ornella Francioso, Santiago Sanchez-Cortes (University of Bologna)

P29: Tuning robust hotspots in plasmonic chains.
Álvaro Buendía, J.A. Sánchez-Gil, Vincenzo Giannini (IEM-CSIC)

- PL -

PLENARY LECTURES

Applied spectroscopy: Impact of organics in the chemistry of the Earth's atmosphere and the interstellar medium

Elena Jiménez[a,b]

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Since 1970's, diagnosis techniques based on *absorption* and *emission spectroscopies* have been suitable tools to detect and monitor molecules, atoms and radicals in the Earth's atmosphere and in Space. Particularly, laser techniques are important in air quality management, while microwave rotational and infrared (IR) spectroscopies are commonly employed in radiotelescopes to detect molecules and lone-pair species in Space. Since 1990's, time-resolved laser techniques, such as the ***laser induced fluorescence*** (LIF) technique, have been employed in our laboratory to study the gas-phase kinetics of atoms and radicals with atmospheric pollutants (T=220-380 K) and interstellar molecules (T = 11.7-177.5 K) [1, 2]. In the past decades, our research is devoted to the reactivity of hydroxyl (OH) radicals, the main diurnal atmospheric oxidant in the atmosphere [3] and one of the first radicals detected in the interstellar medium (ISM) [4]. OH radicals are formed in the reactor by the ***ultraviolet (UV) pulsed laser photolysis*** (PLP) of a suitable precursor. The kinetic information obtained at tropospheric temperatures allows the estimation of the tropospheric lifetime (τ) of the pollutant. In addition to the laser techniques, in our research group ***UV and IR spectroscopies*** are employed to determine the absorption cross sections of pollutants in order to estimate the contribution of the photolytic degradation route to τ and to estimate its global warming potential, respectively [5,6]. Furthermore, the kinetic information at ultralow temperatures can be incorporated in astrochemical models to interpret the observed abundances of organics in extremely cold regions of the ISM where temperatures are in the range of 10-100 K.

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Mid-Infrared Photonics: From Emerging Technology to Enabling Tool

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Mid- infrared spectroscopy plays an increasingly important role in modern biodiagnostics. This has led to the evolution of mid-infrared photonics from an emerging technology in the clinical/medical domain to an enabling tool that finds its way into daily (bio)medical and clinical use.

With applications ranging from non-invasive exhaled breath analysis to the in-vivo assessment of cartilage damage, mid-infrared (MIR; 3-20 µm) photonics ranges among the most flexible molecular sensing platforms nowadays available. This development has been catalyzed by the emergence of quantum and interband cascade laser (QCL, ICL) technology providing miniaturized laser light sources based on quantum heterostructures that lend themselves to the on-chip hybridization and/or integration of entire MIR sensing systems with the perspective of IR-lab-on-chip devices. The inherent molecular selectivity of MIR signatures enables studying small molecules (e.g., volatile organic compounds; VOCs) in the gas phase, as well as biomacromolecules (e.g., proteins) or entire biological specimen (e.g., cells, viruses, microbes) in the liquid phase at yet unprecedented detail in a label-free and non-destructive fashion.

Finally, the combination with advanced multivariate data evaluation and deep learning algorithms facilitates analyses in real-world complex matrices of biomedical and clinical relevance. The discussion of latest MIR photonic technologies in this presentation we will be augmented by highlight applications underlining the utility of next-generation MIR photonic technologies.

References

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IR-Induced and Tunneling-Driven Reactions in Cryogenic Matrices "Plastic Molecular Cryosurgery"

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In this lecture, we will survey the major progresses in the field of IR-induced chemistry, and its entanglement with tunneling-driven chemistry. The narrative will follow a historical perspective, highlighting the interweaving of the two types of processes.
The story of this still ongoing fascinating scientific endeavour will be presented following closely our own involvement in the field for more than 30 years. It considers a large set of examples, from very selective IR-induced conformational isomerizations to bond-breaking/bond-forming reactions and successful observations of rare heavy-atom tunneling.
The lecture aims to introduce vibrationally induced chemistry as a powerful tool to manipulate molecular shapes and structures in a highly selective way ("plastic molecular surgery"), and demonstrate how to use and control quantum mechanical tunneling as a tool to explore the reactivity of organic molecules in an unprecedented way.

Acknowledgements
All members of the LMCB as well as my colleagues from abroad that contributed to the described studies are thanked. This work is being supported by Projects PTDC/QUI-QFI/1880/2020 and POCI-01-0145-FEDER-028973, funded by National Funds via the Portuguese Foundation for Science and Technology (FCT). The Coimbra Chemistry Centre is supported by FCT through projects UIDB/QUI/0313/2020 and UIDP/QUI/0313/2020, co-funded by COMPETE. Support from LaserLab Coimbra is also acknowledged.

LIBS and acoustic measurements of rocks and regolith and the exploration of Mars

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The SuperCam instrument of the NASA MARS 2020 rover combines a suite of atomic and molecular spectroscopies intended for an extensive description of rock, soils and minerals in the surroundings of the landing site of the mission – the Jezero crater. The microphone installed on the SuperCam allows the acquisition of acoustic signals resulting from the expansion of laser-induced plasmas towards the atmosphere. The acoustic signal has an additional component related to the surface and bulk properties of the target including hardness, deformation parameters, and elasticity, among others. This information is thought to be a valuable resource for characterization of the ablated material and may well complement the LIBS data gathered from coincident laser shots. This talk will present acoustic data of rock and mineral analogs and will discuss its correlation with LIBS spectra

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- IL -

INVITED LECTURES

A bright future for upconversion nanoparticles

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The synthesis of more efficient upconversion nanomaterials that absorb multiple low-energy photons in the near-infrared and then re-emit in the visible or ultraviolet is of key importance for the development of upconversion nanomaterials. The ability to efficiently convert near-infrared light to the visible or ultraviolet parts of the electromagnetic spectrum is potentially very useful for a host of applications including sensing, green energy conversion and imaging, as well as biomedical diagnosis and treatment.[1] Nevertheless, these bio-applications necessarily require the UCNPs to be transferred to aqueous media. Although many approaches have been explored for this purpose[2], luminescence losses related to water quenching, and dissolution or degradation of the UCNPs' host matrix, have been commonly reported as collateral effect.[3,4] These drawbacks, which are especially noticeable at low UCNPs concentrations, high temperatures, and under the presence of certain molecules (e.g., phosphates)[5], arise as a major limitation hampering the real bio-application of these promising nanomaterials. In this communication, we show several examples of the application of UCNPs, and a novel method developed by our group to protect the surface of UCNPs from these drawbacks that possibly limits their application.

Acknowledgements
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Microenvironment sensing by multiparametric microscopy and nanoscopy

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The striking property of highly marked solvatochromism, exhibited by several families of luminophores, has demonstrated a wide potential to develop sensing strategies to probe microenvironment features, as well as following biomolecular interactions and dynamics. We have been working in expanding the palette of solvatochromic luminophores by rational design and synthesis of new probes. Our attention has been driven to different families of fluorophores, such as acridones [1, 2], BODIPYs [3, 4], silicon-substituted xanthenes [5], and, specially, quinolimide derivatives [6-9].

The range of applications of the new probes is broad, covering from determining microenvironment polarity in subcellular structures [1-4], characterizing amyloid aggregation [5-7], studying the formation mechanism of supramolecular hydrogels [8], or following enzymatic activity [9], among others. These applications not only make use of spectroscopic techniques, but importantly they are designed for multiparametric luminescence microscopy, which provides robust quantitative information, with spatial resolution, by using orthogonal analyses of the luminescence events, such as spectral distribution, photoluminescence lifetime, anisotropy, etc. For all these experiments, the University of Granada launched a new Singular Laboratory called Nanoscopy-UGR (http://sl.ugr.es/nanoscopyUGR). The Nanoscopy-UGR laboratory holds a versatile super-resolution microscope, capable of STED-FLIM, STED-PLIM, and STED-anisotropy imaging, and an advanced confocal FLIM/PLIM microscope equipped with several visible and a tuneable fs-NIR excitation sources for one- or two-photon excitation, as well as spectral imaging. Within these facilities, a broad variety of experiments and settings are possible for a wide range of applications from cellular biology to new nanomaterials.

Acknowledgements

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Innovation in Analytical Spectrometry driven by Nanotechnology

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In the last years, Nanoscience and Nanotechnology (N&N) has emerged as an active research topic with application in many areas such as energy, medicine, catalysis, etc. N&N has spread to metrological disciplines such as analytical chemistry, where currently nanomaterials play an important role for improving characteristics of the analytical process such as sensitivity, selectivity, portability, etc. More importantly, this newly area has allowed relevant innovation to be achieved in order to solve current and future analytical problems, and in combination with miniaturization of analytical instruments, may allow on-site analysis. N&N has driven the development of novel nanosorbents, nanosensors, nanostructured stationary phases, nanocatalysts, etc., which take advantage of the unique electrical, optical, magnetic and catalytic properties inherent with the nanoscale dimension. In this presentation, the role of several nanomaterials employed for sorption (*e.g.* magnetic nanoparticles, Ag nanoparticles, graphene and graphene oxide, etc.), catalysis (quartz substrates coated with Pd or Ag nanoparticles) and chemical sensing (*e.g*. luminescent and plasmonic nanoparticles such as CdSe quantum dots, carbon quantum dots, Cu nanoclusters, spherical Au nanoparticles, Au nanorods, etc.) will be discussed. The synergic combination of nanotools possessing large surface area, increased density of active sites and enhanced optical properties with miniaturized analytical systems (atomic and molecular spectrometric techniques) will be emphasized. At a step beyond, strategies for integration of nanomaterial synthesis following 'bottom-up' approaches with sorption and sensing processes will be outlined. The potential of innovative paper-based analytical devices suitable for on-site analysis of environmental, food and biological samples will also be demonstrated. These systems may circumvent in many cases the use of conventional instrumentation for the detection of heavy metals, anions, organometals and organic compounds, being greener, simpler, cost-effective and with the ability of field analysis.

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Studying Protein Stability in Ionic Liquids: Insights from NMR

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Since the pioneering work of Hofmeister, more than 130 years ago, that ion specific effects are recognized as a mean to modulate the physical properties of proteins. In the last 10 years, a new type of designable solvents, Ionic Liquids (ILs), have added a significant new landscape for the interaction of ions with proteins[1]. Due to their extremely low vapor pressure and structure/property-tunability, ILs have been increasingly used as alternative solvents tailored for protein applications, *e.g.* as a reaction medium for biocatalysis, ILs have shown tremendous potential[2]. In fact, enzymes can be activated/stabilized by ILs and several enzymatic systems have been evaluated, including hydrolases, oxidoreductases, lyases, and even whole cells. Still, the interactions between ILs and enzymes may lead to inactivation of the latter due to i) competitive inhibition and blocking of substrate access, ii) (local) protein dehydration, iii) structural changes, iv) reduced protein dynamics, or v) protein denaturation. The molecular basis of these effects remains mostly unknown due to the lack of a thorough understanding of IL-protein interactions and their impact on structure, stability, and activity.

Using NMR methodologies, we have been investigating the molecular origins of stabilizing and destabilizing IL effects on proteins[3]. For this purpose, we study the interaction of model proteins with distinct stability and structural properties, with stabilizing or destabilizing ILs and salts. The data gathered provides a thorough understanding of IL-protein interactions as well as the mechanism by which they can affect protein stability and folding, which will be highlighted in this communication.

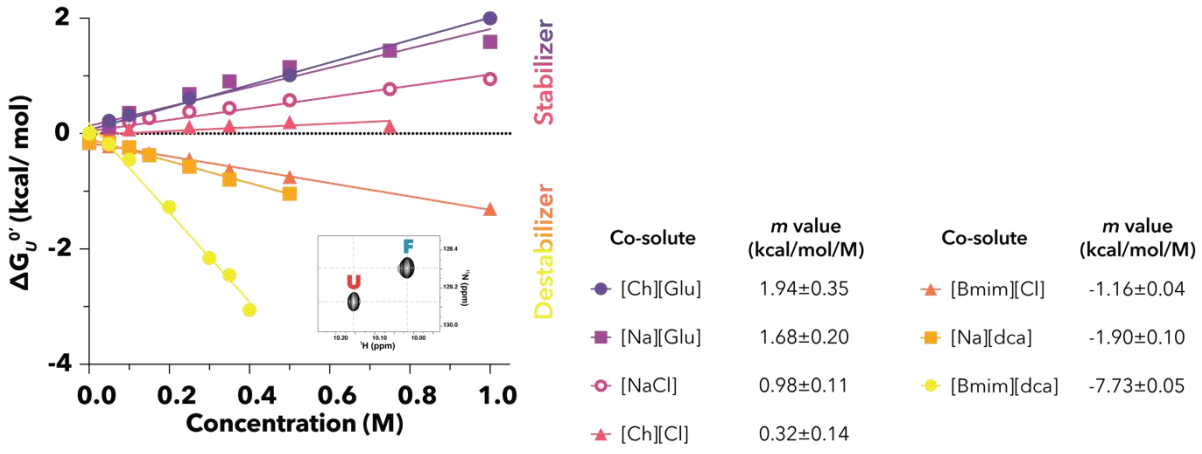

Figure 1. Salt or IL induced (de)stabilizing effect on the model protein drkN SH3 as determined by NMR. Stabilizing and destabilizing co-solutes have positive or negative *m*-value signs, respectively. The inlay shows the indole Trp peaks of the folded (F) and unfolded (U) states of drkN SH3 in an [^{1}H,^{15}N]-HSQC spectrum acquired in water.

Acknowledgements

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- OC -

ORAL COMMUNICATIONS

Detection of biomarkers on lichens after Space and Mars like conditions with RAMAN spectroscopy

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Exploration of the solar system is a priority research area of the AstRoMap European Astrobiology Roadmap, focusing on several research topics, such as "Life and Habitability" and another one is "Biomarkers for easy the detection of life". Space platforms and laboratories, installed outside the ISS, are essential to gain more knowledge of space- and planetary environments, which might be an essential basis for improvement of the robotic and human interplanetary exploration (Space, Moon, Mars, Enceladus, Titan, Europa). At the exposure platform EXPOSE-R2 on the ISS (2014-2016), the astrobiological model lichen *Circinaria gyrosa* as part of the BIOMEX experiment [2] (Biology and Mars Experiment, ESA), was exposed during 18 months to space and simulated Mars-like conditions, to investigate Mars' habitability and the resistance of the species to space conditions. After the return of the samples in June 2016, analyses of vitality was high at the dark control samples, but lower at the samples directly exposed to solar UV radiation. As reference, a correlative Mission Ground Reference Experiment (MGR) reproducing EXPOSE R2 conditions was performed at DLR with *C. gyrosa*: the samples were exposed to a simulated Mars-like and Space-like environments (DLR-Cologne) complementing the data of the space experiment. Analyses of these mission Ground Reference (MGR) samples, were performed to search for biomarkers, such as pigments, specific biomolecules and biominerals as secondary metabolites, at the inner part of the lichens, containing the medulla and algal clusters. Here we show the results obtained, which will contribute to detection of exposed biomolecules, by life-detection instruments, to an extraterrestrial environment, as ExoMars.

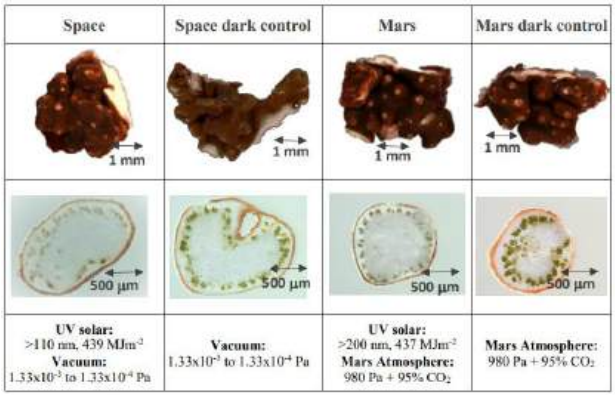

Figure 1. *Circinaria gyrosa* (CG) and the corresponding thin-sections exposed to different space parameters

Acknowledgements

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XPS study of chemical evolution of glycine on pyrite (100) surface

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Iron pyrite (FeS_2) is a common mineral on Earth, which has a reactive mineral surface that can catalyse reactions in chemical, geochemical and biological processes [1]. The presence of crystalline defects modifies the electronic properties of the surface and therefore its reactivity with adsorbed molecules. For that reason, understanding the mechanism of adsorption of bio-molecules on surfaces is a topic of highly interest in several fields such as materials science, surface chemistry, nanotechnology, prebiotic chemistry or catalysis [2].

In this study, we combine experimental and theoretical approaches to explore the reactivity of single-crystal pyrite (100) surface, modified by Ar^+ ion sputtering and annealing processes, besides its influence on the chemical species adsorbed and chemical evolution over time of glycine amino-acid molecule (NH_2-CH_2-COOH). The sample was placed in ultra-high vacuum conditions, then the generation of sulfur vacancies by Ar^+ ion sputtering and the functional groups of adsorbed glycine over time were monitored by X-ray photoemission spectroscopy (XPS). Furthermore, Density Functional Theory (DFT) simulates the electronic structure of the surface adding sulfur vacancies and iron dangling bonds, besides its effect on the adsorption of glycine molecule in zwitterion (NH_3^+ and COO^-) or anionic chemical form (NH_2 and COO^-).

Our results show that Ar^+ sputtering generates sulfur vacancies and metallic iron (dangling bonds) on pyrite mineral, driving electrostatic changes on its surface and increasing its reactivity [3,4]. Therefore, depending on the pyrite mineral treatment, the surface would drive the chemical species of glycine behaviour adsorbed on the surface. Well-ordered pyrite surfaces (i.e. no defects) promotes the adsorption of zwitterion form of glycine while sputtered pyrite (i.e. rough surface) favors the presence of the anionic form. However, both chemical species coexist during glycine adsorption, and in both cases molecules evolve from zwitterionic to the most stable anionic species over time. This study shows that surface defects enrich the chemical diversity of molecules adsorbed and insights the potential capability of pyrite to act as a surface catalyst.

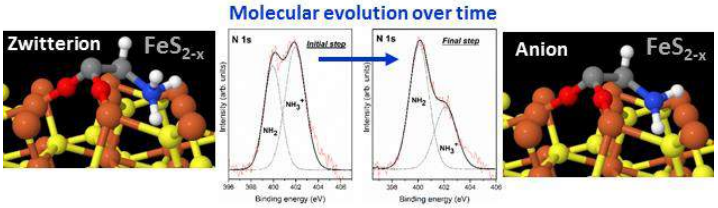

Figure 1. Non-stoichionetric sites on pyrite surface drives the chemical evolution of glycine from zwitterionic to anionic chemical form over time

Acknowledgements

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Subfemtogram detection power for single-trapped nanoparticles in laser-induced plasmas

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The interest in nanotechnology seems to be still far from over. Modern analytical techniques play a crucial role in detecting and characterizing nanoparticles (NP). The numerous singularities of nanosamples represent a challenge in constant evolution to the Analytical Chemistry community with recent research devoting special attention to single-particle analysis [1]. Recently, a LIBS-based platform, namely OC-OT-LIBS, has been evaluated to stably isolate, hold and probe single particles [2-3]. In OC-OT-LIBS, solid aerosols were created by optical catapulting. Ejected nanoparticles were stably trapped on-line in air at atmospheric pressure and then inspected by LIBS. An unprecedented LOD of 37 ag for single copper particles of 25 nm in diameter was reported by Purohit et al. [4]. Previously, authors inspected the dual role of air as the atomization and excitation source during single-particle LIBS analysis. The intensity of the signals corresponding to air decreased when a particle was also present within the laser-produced plasma, implying that a fraction of the plasma energy was transferred into the particle instead of being used to ionize peripheral air molecules which, along photon losses during signal collection could contribute to a decrease in the analytical performance. The calculation of electronic temperature (Te) for plasmas formed in the presence and absence of nanoparticles were calculated using ionic nitrogen lines from the air plasma, and indicates a heat transference into the nanoparticle [5]. Thermal effects are characteristic to LIBS inspection using ns pulsed laser. Therefore, the question of whether pulsed sources of shorter duration, which are becoming increasingly used, will be able to perform single NP analyses and what they can add to the equation arise immediately.

In this work, an extreme detection power via wavelength-resolved imaging analysis of optically trapped single nanoparticles in laser-induced plasmas has been investigated. Thus, limits of detection were calculated in the range of tens to hundreds of attograms (0.54 fg and 18 ag for graphite and copper, respectively) which indicates an improvement of up to 3 times over dispersive spectroscopic LODs. In addition, the employment of a picosecond laser instead of nanosecond for LIBS analysis has also improved the sensitivity in OC-OT-LIBS.

Acknowledgements

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Polymeric (nano)composite papers as analytical platforms coupled to spectroscopic techniques

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Paper-based analytical devices (PADs) are currently attracting great attention for microextraction and sensing due to the numerous advantages of paper as a support, such as their cost-effectiveness, versatility, flexibility, portability, high porosity, biodegradability, biocompatibility and non-toxicity, among others [1]. Common filter paper is widely available, while its easy modification via wet chemistry allows the fabrication of hybrid materials that synergistically combine the properties of both paper and the immobilized coating. Moreover, PADs can be coupled to different instrumental techniques, including spectroscopic ones.

Two examples of PADs modified with polymer (nano)composites coupled to spectroscopic techniques are presented. The first one is a molecularly imprinted PADs (MIP PAD) [2] obtained by a polymerization-free synthesis, which was coupled to a fluorimeter via a custom-built platform, which enables direct measurement of the fluorescence at the surface of the MIP PAD. Extraction efficiency of the MIP PAD was evaluated using quinine as model analyte, which was determined in soda drink samples. The second example is a silver nanoflower (AgNF) modified paper-based dual substrate for both surface-enhanced Raman spectroscopy (SERS) and ambient pressure paper spray mass spectrometry (PS-MS) [3]. AgNFs were immobilized on nylon-coated paper modified with silver and ethylenediamine. The densely packed nanoscale petals of the AgNFs lead to a large number of so-called hot spots at their overlapping points, which result in an enhancement of the Raman signal. In addition, the presence of the AgNFs produces an increase in the sensitivity of the mass spectrometric analysis as compared with bare paper and nylon/Ag-coated paper. The dual substrate was evaluated for the identification and quantification of ketoprofen in aqueous standards as well as human saliva from healthy volunteers. This dual substrate enables the simple and fast detection of ketoprofen with minimal sample preparation, providing complementary Raman and mass spectrometric information.

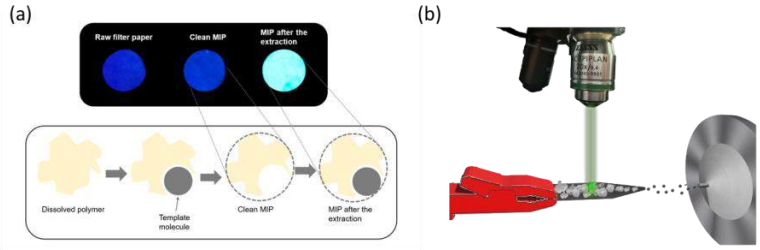

Figure 1. (a) Scheme of the MIP-PAD and fluorescence response upon extraction of the analyte, (b) AgNF-nylon PAD for both SERS and ambient pressure paper-spray mass spectrometry analysis.

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Hyperspectral characterization of head and neck cancer in mice.

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Head and Neck Cancer (HNC) represents the seventh most common cancer worldwide, with a 5-year relative survival rate of 50%. In particular, lip/oral cavity cancers exhibit the highest prevalence in this category [**1**]. HNC is diagnosed by physician examination followed by biopsy, and surgical intervention represents the primary form of treatment. We propose a hyperspectral imaging (HSI) device to characterize tissue absorption/scatter properties, allowing for non-invasive delineation of tumoral margins and avoiding local recurrence [**2**]. A recently developed HSI system [**3**] was used to obtain visible and near infrared (VisNIR, 400-1000 nm) images of a murine model of HNC (figure 1, b-d). A polarized light dermosopic image of a 4NQO preclinical model of oral carcinogenesis on a C57BL/6 mouse excised tongue is shown (figure 1.a) where leukoplakia and papilloma-like tumoral masses can be observed throughout the surface of the tongue [**2**]. These morphological features also appear in the tissue image reconstruction from the HSI dataset (figure 1.b), with which healthy/diseased ROIs were procured (figure 1.c). Different healthy/pathological spectroscopic features are observed (figure 1.e) where tissue reflectance at the absorption peak of the deoxymyoglobin (figure 1.d) shows enhanced contrast that foresees future non-invasive tumor delineation.

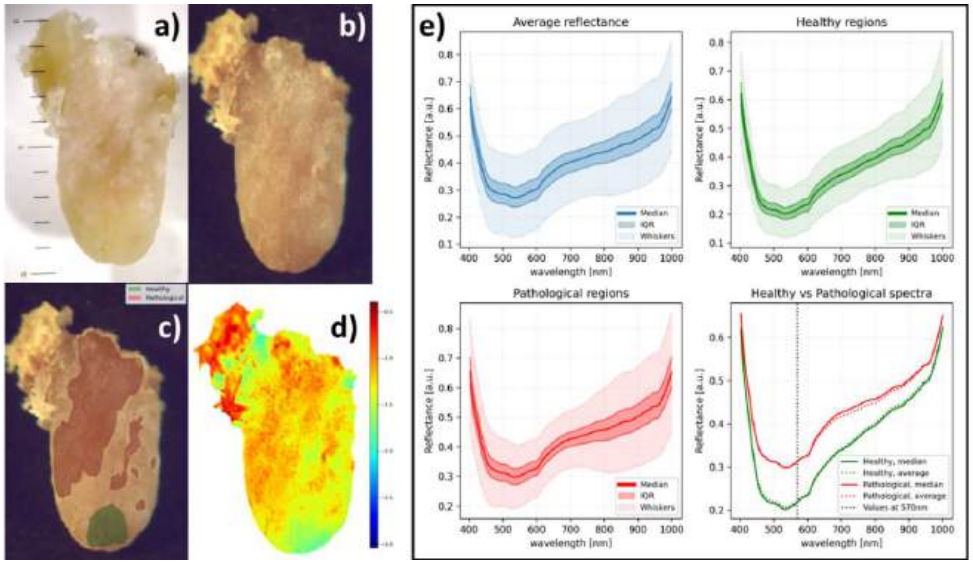

Figure 1. VNIR hyperspectral characterization of the mouse tongue: a) polarized light dermoscopic image; b) colorimetric reconstruction from the HSI measurement; c) ROI's identification; d) reflectance at 570 nm (log scale); e) reflectance spectra: whole tongue (blue), healthy tongue ROI (green), pathological tongue ROI (red) and comparison (bottom right).

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Electrospraying as Method for the Synthesis of Biocompatible PLGA@Ag_2S and PLGA@Ag_2S@SPION Nanocarriers with Drug Release Capability

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Electrospraying is an electrohydrodynamic atomization process used for the fabrication of biocompatible polymeric nanoparticles. In electrospraying, when a strong electrostatic field is applied to a polymer solution held in a syringe, the pendent droplet of the polymer solution from the injector is deformed into the Taylor cone. In this situation, multiple charged particles are sprayed and moved towards a collecting metal screen. As the solvent evaporates, a powder containing polymeric nanoparticles is formed on the collector screen. In function of the type of injector used during electrospraying process (simple or coaxial) two different routes are differentiated, simple or coaxial electrospraying. Here, we used poly(lactic-co-glycolic acid) (PLGA) as biocompatible polymer to produce hybrid PLGA@Ag_2S and PLGA@Ag_2S@SPION nanoparticles by simple and coaxial electrospraying. Ag_2S nanoparticles are near-infrared (NIR) probes providing emission in a spectral range of 1200 nm,[1] and superparamagnetic iron oxide nanoparticles (SPION) are colloidal systems able to respond to an external magnetic field.[2] Initially, we fabricate a hybrid colloidal nanosystem composed by Ag_2S NPs in connection with PLGA (PLGA@Ag_2S) by 3 different routes (R1, R2 and R3), showing good photoluminescent (PL) properties. Then, we incorporate SPIONs by coaxial electrospraying (R4 and R5), obtaining a PLGA polymeric matrix containing Ag_2S and SPION (PLGA@Ag_2S@SPION). Interestingly, the location of Ag_2S and SPIONs depends on the synthesis route. We also demonstrate encapsulation and release capabilities obtaining the kinetic release of a model chemotherapeutic drug (maslinic acid).[3]

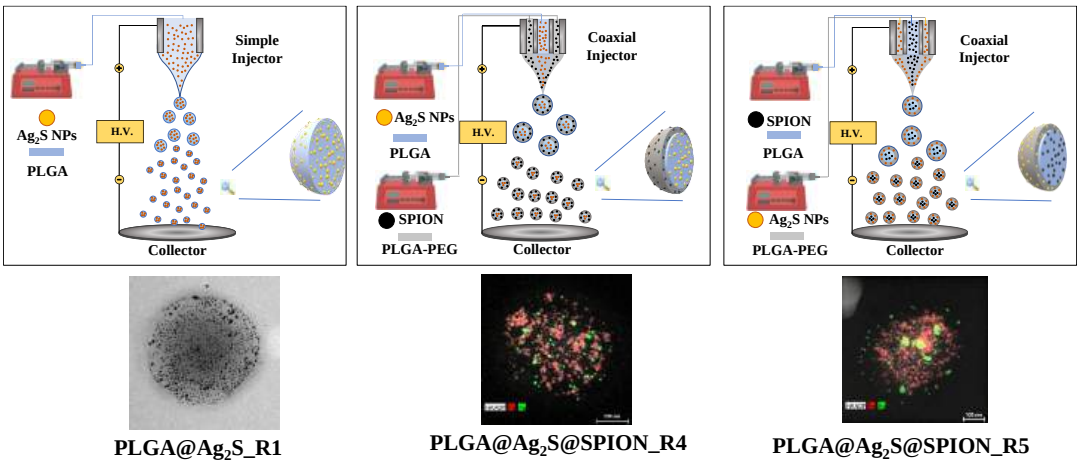

Figure 1. Schematic representation of the electrospraying routes used to obtained different conformations for hybrid PLGA@Ag_2S and PLGA@Ag2S@SPION systems, respectively.

Acknowledgments

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Molecular super-gluing: a straightforward tool for antibody labelling and its application to mycotoxin biosensing

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Mycotoxins are one of the most widespread and reported contaminants in cereal samples [1]. They are secondary metabolites produced by filamentous fungi, especially those of the genus *Fusarium, Penicillium, Aspergillus* and *Alternaria*, and their occurrence can be enhanced by poor harvesting practices and storage conditions. Their consumption may cause severe health problems, both in animals and humans. HT-2 toxin, is a type A trichothecene produced by different *Fusarium spp*. fungi, frequently found in cereals grains, such as oat, barley, wheat, etc. and products thereof [2].

In this work, we report a non-competitive fluorescence anti-immune complex (IC) immunoassay, based on the specific recognition of HT-2 toxin by a pair of recombinant antibody fragments, namely the antigen-binding fragment (Fab) (anti-HT-2 (10) Fab) and a single-chain variable fragment (scFv) (anti-IC HT-2 (10) scFv) selected by phage display [3]. The SpyTag and SpyCatcher system was applied for the first time as a bioconjugation tool for the analysis of mycotoxins. To this aim, a SpyTag-mScarlet-I (fluorescent protein) and scFv-SpyCatcher recombinant proteins were constructed, produced and fused *in situ* during the assay by spontaneous Tag-Catcher binding. The assay showed an excellent sensitivity with an EC_{50} of 4.8 ± 0.4 ng mL^{-1} and a dynamic range from 1.7 ± 0.3 to 13 ± 2 ng mL^{-1}, an inter-day reproducibility of 8.5 % and a high selectivity towards HT-2 toxin without cross-reactivity with other *Fusarium* toxins. The bioassay was applied to the analysis of the toxin in an oat reference material and in oat samples, with a LOD of 0.6 µg kg^{-1}, and the results were validated by analysing a certificate reference material and by HPLC-MS/MS [4].

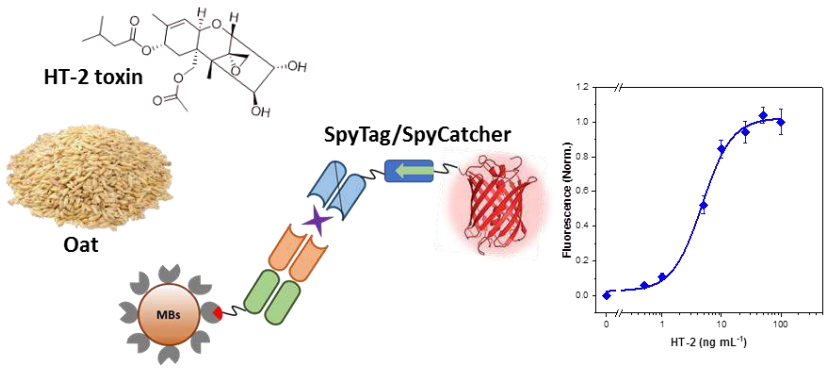

Figure 1. Scheme of the non-competitive fluorescence immunoassay for the analysis of HT-2 toxin in oat samples.

Acknowledgements

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Multiparametric Microanalyzer as a Warning System for Heavy Metals Monitoring in Water using Carbon Dots as Luminescent Reagents

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Contamination of water by heavy metals has been a critical environmental concern for decades. The commonly employed techniques for heavy metals detection require complex and expensive instrumentation and are not suitable for on-site analysis. Currently, it is very difficult to analyze simultaneously several heavy metal ions in water with low detection limits without using these techniques and it is still a challenge to develop a sensor for on-site and real-time monitoring of various heavy metal ions with high selectivity and sensitivity [1]. There is consequently great demand for regular water quality monitoring to identify and assess heavy metal pollution in water [2].

Microreactors based on Low-Temperature Co-fired Ceramics technology were developed to better control the synthetic conditions of CDs and thus improve synthesis reproducibility. They were fabricated by a multi-layered approach technology and temperature is controlled by an embedded heater and a PT100 sensor [3]. A microfluidic platform was designed to perform the heavy metals automatic analysis by using Computer-Aided Design software, and layers were micromachined onto Cyclic Olefin Copolymer substrate with a Computer Numerical Control micromilling machine. The platform was inserted in a customized miniaturized optical detection system.

For the detection of heavy metals, the fluorescence quenching effect of these ions on the emission of Carbon Dots (CDs) was studied by applying a reverse Flow Injection Analysis approach, where CDs are sequentially injected into a blank (buffer solution) and different samples (standard solutions, spiked tap water and soil extracts).

Five different heavy metal ions (Co^{2+}, Cu^{2+}, Hg^{2+}, Ni^{2+}, and Pb^{2+}) were selectively detected. Limits of detection between 2 and 12 ppb were obtained for all the heavy metal ions. Spiked tap water samples were analyzed obtaining recoveries between 98-134%. Polluted samples containing four of the five heavy metal ions studied (Co^{2+}, Cu^{2+}, Ni^{2+}, and Pb^{2+}) were also analyzed with no significant differences observed between both methods, the proposed microanalyzer and the reference method (ICP-OES), demonstrating the applicability of the proposal as an on-site warning system of heavy metals contamination.

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FTIR and VCD assisted study of the speciation in solution of racemic and enantiopure NSAIDs: ketoprofen, naproxen and ibuprofen.

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Ketoprofen, ibuprofen and naproxen belong to the family of drugs called NSAIDs (non-steroidal anti-inflammatory drugs) and are widely used due to their analgesic, antipyretic and anti-inflammatory activity. Currently, the behavior of this type of drugs in solution is a topic of interest in the pharmaceutical industry since the crystal growth and the potential incidence of crystalline polymorphs are affected by supersaturation and solvents [1] and must be controlled as they could lead to undesired pharmacokinetic changes (including bioavailability) and problems during the production process [2].

In order to obtain information about the supramolecular behavior of these species in solution, FTIR and VCD spectra of ketoprofen, ibuprofen and naproxen (enantiopure and racemic) were recorded at different concentrations in solvents of different polarity (namely deuterated chloroform and acetonitrile). Recently, the pharmaceutical industry chose VCD spectroscopy as the best option to determine the absolute configuration of drugs [3].

The DFT-assisted study of the experimental features observed in their respective spectra point out to different speciation in the set of samples depending on the solvent. For ketoprofen a monomer/dimer equilibrium operates in acetonitrile solution while in chloroform solution H-bonded open-chain dimers together coexist with oligomers of different size [4]. Similar results we found for ibuprofen. As regards naproxen, while in acetonitrile solution the speciation is the same than in the case of the other two analogues, our observations point out to the presence of cyclic H-bonded dimers in chloroform solution.

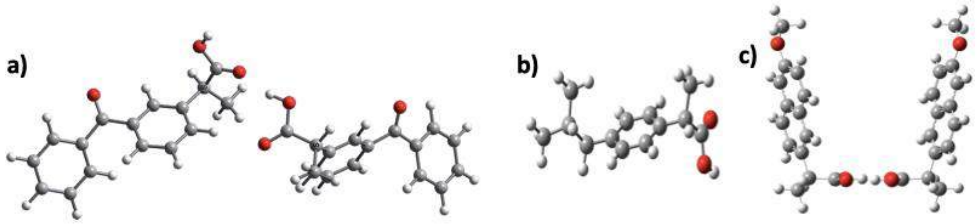

Figure 1. a) ketoprofen chain dimer b) ibuprofen monomer and c) naproxen cyclic dimer .

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Carbonaceous dust specific surface area determination using grazing-angle reflection-absorption IR spectroscopy

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The specific surface area of carbonaceous dust grains is a property that affects its physico-chemical behaviour. In the plasma laboratory at the IEM-CSIC carbonaceous dust is generated in a capacitive plasma reactor using acetylene as precursor [1]. The dust particles grown are good analogues of the interstellar dust, as revealed by its IR spectra, which compare well with astrophysical observations. As part of their characterization, and inspired by a recent work by He and coworkers [2], we have measured the specific surface area of the material monitoring CO absorption via grazing-angle reflection absorption infrared spectroscopy (RAIRS).

The procedure is the following. Dust is collected in Al substrates placed inside the plasma reactor, that subsequently are located in a sample holder in good thermal contact with the cold head of a closed-cycle He cryostat within a ultra-high vacuum chamber [3]. Controlled doses of CO vapor are introduced in the chamber and deposited on the dust surface held at 20 K. At this temperature it is assumed that CO diffuses efficiently on the surface, and the evolution of the CO grazing-angle RAIRS spectra with coverage allows distinguishing the beginning of formation of a CO multilayer. Similar experiments were performed for CO_2 keeping the dust temperature at 70 K in this case. Figure 1 shows the evolution of the 1300 cm^{-1} ν_4 band of CO in the RAIRS spectra with CO coverage. The appearance of the peak at 2141.6 cm^{-1} is taken as an evidence of the formation of a complete layer of CO on top of the dust surface, since it is the characteristic frequency of the RAIRS spectra of pure CO ice.

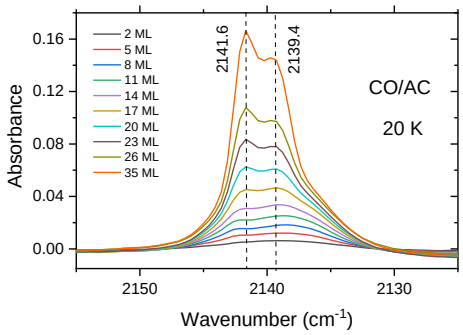

Figure 1. RAIRS spectra of the 1300 cm^{-1} ν_4 mode of CO ice grown on top of a carbonaceous dust deposited on an aluminum substrate. Different curves correspond to different doses of CO molecules deposited, as indicated in the legend, where 1 ML is defined as $1{\cdot}10^{15}$ molecules /cm^2.

Acknowledgements

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Study of the aggregation behaviour and environmental stability of Platinum nanoparticles in water systems

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Platinum nanoparticles (PtNPs) are widely used in several applications, being the catalytic converters of vehicles one of the most important. This widespread use has made their release into the environment unavoidable and the presence of PtNPs has been reported in all environmental compartments, especially those in the vicinity of roads. Then, they could be transported to rivers, lakes and other water systems [1].

Once in the waters, little is known about their behaviour or possible transformations. Dissolution, sedimentation or aggregation processes can occur. Aggregation is one of the most important processes, and it is dominated by the relationship of repulsive and attraction forces. NPs' physicochemical properties and media characteristics (ionic strength, pH or presence of organic matter, among others) can strongly influence their behaviour [2]. Nowadays, the greatest analytical challenges regarding the analysis of PtNPs are related to the correct characterization of those NPs in environmental matrices under relevant conditions.

Dynamic Light Scattering (DLS) is one of the most implemented techniques to study the aggregation kinetics of different NPs by measuring hydrodynamic diameter. Also, zeta potential could be a useful tool to interpret aggregation, since its study provides information about changes in the repulsion and attraction forces, which are directly related to aggregation. However, it has some disadvantages, as the requirement of high NP concentration, which are above of the environmental levels of any metallic NP. [3]. Other approaches, like the use of hyphenated techniques has been also proposed. One of the most promising strategies is asymmetric flow field flow fractionation coupled to inductively coupled plasma mass spectrometry (AF4-ICP-MS), which is advantageous in terms of separation size range, specificity or detection limits down to environmentally relevant levels.

In this present work, the influence of the ionic strength (testing different concentrations of NaCl), the water composition (using synthetic waters with different cationic and anionic composition). and the organic matter (using humic acid as role model) over the stability, aggregation behaviour and persistence of PtNPs (of different sizes) have been studied using AF4-ICP-MS and DLS (as complementary technique). Changes in their hydrodynamic diameters towards higher values and decreases in their Z-Potential values linked to an increase in the ionic strength were reported, while aggregation diminished in presence of organic matter.

Acknowledgements

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Vibrational Spectroscopy Complemented with Chemometrics as a Tool for Auxiliary Diagnosis of Psychiatric Disorders

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Mental disorders, such as schizophrenia and bipolar diseases, and neurodevelopmental disorders, like autism spectrum disorder (ASD) and attention deficit and hyperactivity disorder (ADHD), have an increasing impact on society in the last few decades and affect approximately 2% of the world population, while 10% of the world's children population have been diagnosed with ADHD. Due to the heterogeneity of their symptoms, accurate diagnosis of these disorders has been a challenge for the clinicians. In the case of schizophrenia and bipolar diseases, due to their similar symptomatology, their differential diagnosis ends up with a 70% error and may remain misdiagnosed for at least a decade since its first symptoms. ADHD also shares common symptoms and frequent comorbidities with other mental and neurodevelopmental disorders (e.g., autism spectrum disorder, bipolar disorder) which makes the accurate and timely diagnosis a difficult task. ASD is another neurodevelopmental disorder in which the early age identification has a fundamental importance for the treatment to be effective.

Current diagnosis of these disorders follows the Diagnostic and Statistical Manual of Mental Disorders (Fifth Edition; DSM-5) diagnosis criteria and is based on the clinical evaluation of the symptoms. The absence of auxiliary methods that can complement the clinical evaluation increases the probability of false identification of the disorders. Development of fast and cheap complementary molecular based analytical methods to help clinicians at the diagnosis stage thus has great importance for more accurate diagnosis. Spectroscopic methods, in particular Raman and IR spectroscopies, are promising tools for identification of biomarkers, through the analysis of body fluids. Body fluids are easily accessible, and their use for medical diagnostics is a common practice. The analysis of body fluids using vibrational spectroscopy has progressively gained the respect of clinicians as a complementary diagnostic tool, with advantages over other techniques, such as being a sensitive and reliable approach, but also cheap, fast and easily adaptable to the clinical environment. These approaches have already proven its success for the diagnosis of infectious diseases and cancer, as well as for Alzheimer's and Parkinson's diseases.

In this study, vibrational spectroscopy (either Raman or IR), is used as analytical tool, together with chemometric methods, for the diagnosis of the above mentioned mental disorders through the analysis of blood serum spectroscopic characteristics. Chemometrics is used to perform the scrutiny of the spectroscopic data obtained by IR or Raman spectroscopies, to find reliable statistical models to discriminate and classify the patients according to their diseases. In this work, the statistical models developed and tested for the cases of ASD, ADHD, schizophrenia and bipolar diseases (including subgroups: bipolar depressive episode, manic episode and otimic) will be presented.

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Mid-infrared spectroscopy of aliphatic molecular ices exposed to UV radiation in dense molecular clouds

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Dense molecular clouds (DMCs) are the densest regions of the interstellar medium (ISM), which are large amounts of gas and cosmic dust grains. On to the surface of these dust grains ice mantles are produced when the gas-phase species condense due to the low temperature (10 – 20 K) of DMCs. In addition, an active solid-phase chemistry in dust-ice systems is triggered by ultraviolet (UV) processing and leads to the formation of complex organic molecules. Moreover, aliphatic hydrocarbons are known to be widespread as a part of the carbonaceous cosmic dust and, recently the Rosetta mission has *in*-situ identified n-alkanes in comet 67P/Churyumov-Gerasimenko.

In this work, we have explored the UV (λ = 121.6 nm) photochemistry of n-C_6H_{14} and n-$C_{11}H_{24}$ by Fourier-Transform infrared (FTIR) spectroscopy at conditions mimicking those of DMs using INFRA-ICE module [1] of the Stardust machine, an experimental station devoted to simulate in the laboratory the long journey of cosmic dust from its formation in evolved stars to its processing in the ISM [2-4]. We elucidate the chemical pathways leading to the formation of olefinic moieties by a combination of FTIR spectroscopy, Thermal-Programmed Desorption (TPD) and *ab initio* calculations and show a preferential photocleavage of the C-C bonds over a dehydrogenation mechanism at the illumination wavelength employed. Finally, we have also derived kinetic constants from the quantitative analysis of the evolution of IR spectra that can be of interest to model the chemistry of n-alkanes in interstellar environments.

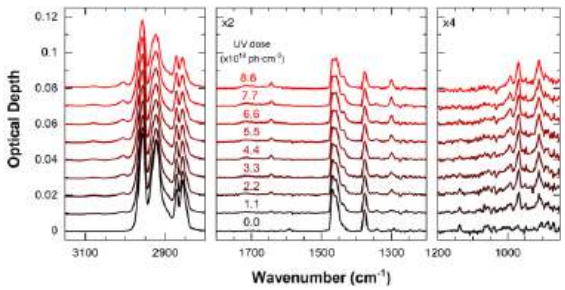

Figure 1. IR spectra of n-C_6H_{14} evolution by UV irradiation (right).

Acknowledgements

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Solution-Cathode Glow Discharge Optical Emission Spectrometry for Elemental Analysis: Novel Insights and Instrumental Approaches

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The demand for trace level elemental analysis has typically been fulfilled with benchtop instrumentation with long tradition and robust performance, such as Atomic Absorption Spectrometry (AAS) or Inductively Coupled Plasma (ICP) coupled with Optical Emission Spectrometry (OES) or Mass Spectrometry (MS). Nevertheless, the cost and/or consumption of this techniques restrict their use to laboratory environments. The development of Atmospheric Pressure Glow Discharge (APGD) sources searching for potentially miniaturized intruments has opened new perspectives, offering analytical features that make them viable alternatives to the aforementioned stablished approaches.

One such source is the Solution-Cathode Glow Discharge (SCGD), an APGD that makes use of a liquid electrode (typically the sample) that joins low electrical consumption (normally below 100 W), no need for pressurized gases and competitive limits of detection in the low ppb levels for many elements when coupled to OES. An important characteristic of this source arises from the plasma-liquid interaction, which eliminates the need for sample nebulization, simplifying the set-up. These characteristics offer possibilities for extensive continuous operation for elemental monitoring and even in-situ capabilities.

The present communication discusses fundamental information about the plasma-liquid interaction and its impact on the analyte solution-to-plasma transfer process, along with studies on plasma characteristics when introducing high amounts of concomitant ions that can induce matrix effects. Additionally, novel discharge geometries for improved light sampling efficiency are introduced and their analytical features presented.

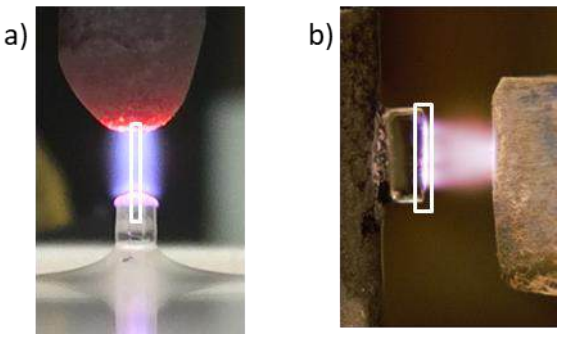

Figure 1. a) Radially view SCGD and b) Horizontally view SCGD approaches.

Acknowledgements

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Computation of Molecular Aggregates Vibronic Spectra with a Mixed Quantum/Classical Approach

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The computation of optical properties on excitonic molecular aggregates are very challenging, due to the large number of variables with relevant effect like conformational disorder, solvent effects, charge-transfer (CT) excitations, or excited state coupling.[1] In addition, conventional computational techniques are not applicable to this situation since the Born-Oppenheimer approach breaks down because of the large nonadiabatic coupling arising from the manifold of nearly degenerate excited states. In this work,[2] we present a computational protocol which rigorously takes into all the relevant parameters and the interplay between them. We separate the degrees of freedom in fast and slow by an adiabatic approach. Then, the slow degrees of freedom are sampled with classical Molecular Dynamics (MD) simulations in combination with parametrized *ab initio* force fields. For each MD structure (a total of 100), we characterized the fast degrees of freedom by Quantum Dynamics of vibronic wave packets on coupled potential energy surfaces described by a Linear Vibronic Coupling (LVC) Hamiltonian. We applied this method, named Ad-MD|gLVC, to a dimer of perilenebisimide (PBI) in water and acetonitrile. Our results nicely reproduce the observed trends upon aggregation and reveal that CT states have little impact on the spectra for this case. However, for specific orientations of the two monomers, these CT states can obtain up to 80% of population in about 50 fs, highlighting their relevance in charge separation and transport in PBI-based optical devices. A combined analysis of MD results and LVC parameters allows us to individuate the key structural parameters that rule the spectral shape and to perform an in-depth investigation of the effect of the flexibility of the aggregate on the spectral shape.

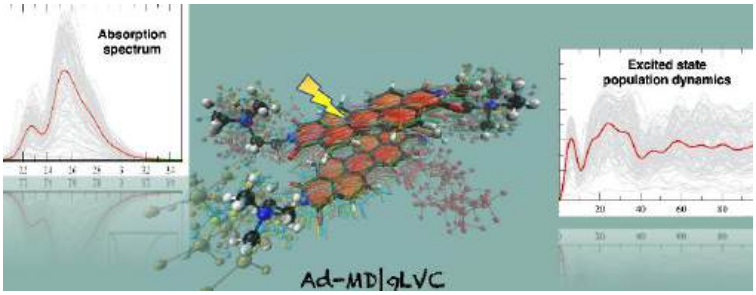

Figure 1. Cartoon of the Ad-MD|gLVC method. The inset shows the spectra (left) and population dynamics of a local excitation in monomer 2 after photoexciting monomer 1 (right). The average property is shown in red and the individual spectrum/population dynamics of the 100 structures from the MD appear in grey.

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Chirality from twisting

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Chirality is a ubiquitous property in nature, from molecules to galaxies, which is endowed in objects that are not superimposable with their mirror images. Although chirality is usually stated as a yes/no question, there is a growing endeavour to quantify this feature in molecules, aimed to relate chirality index with their properties. In this sense, twisting is a suitable way to endorse axial chirality in molecules without any stereogenic centre. This is the case of acenes (linearly fused benzenes), which are attractive systems to look at this issue because they allow us to modulate the backbone distortion in a highly controlled fashion [1]. As π-conjugated materials, the loss of planarity directly impacts in their photophysical and electronic properties, which can be related with the twisting-induced chirality.

Acenes are easily twisted by attaching bulky side groups in edge positions, as the required energy to deform the π-conjugated backbone out of planarity is quite low. A twisted acene, or twistacene, is then a chiral molecule with two possible enantiomers that differ on the sign of the twist angle: clockwise (*P*) or counter-clockwise (*M*). However, the chiroptical features of twistacenes have been scarcely explored due to the difficulty of isolating steady enantiopure samples. Recently, a witty strategy to prevent racemization is based on tethering the acene backbone with alkyl chains [2]. This gives us the chance of tuning the acene twist angle by using different tether lengths and, hence, of controlling the effect of twisting on its optoelectronic properties.

Raman spectroscopy has been very useful to study the electronic properties of π-conjugated systems due to the effect of the π-electron interaction on the C-C stretching bands. Raman Optical Activity (ROA), the chiral branch of Raman, is obtained from the subtraction between right and left circularly polarized incident of scattered Raman intensities. In this work, we present a Raman and ROA study of a series of helically-locked twisted anthracenes, Fig. 1 (left panel), in which distortion is managed by a tether alkyl group which length ranged from propyl to hexyl [3]. The ROA fingerprints of these molecules, Fig. 1 (right panel), will reveal information on their chiroptical properties in connection with the changes on electronic structure leaded by the π-core twisting.

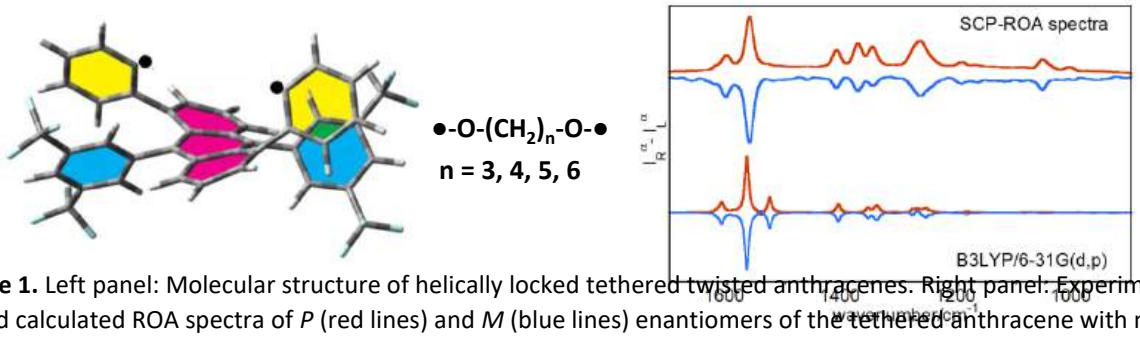

Figure 1. Left panel: Molecular structure of helically locked tethered twisted anthracenes. Right panel: Experimental and calculated ROA spectra of *P* (red lines) and *M* (blue lines) enantiomers of the tethered anthracene with n=5

Acknowledgements

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Comparative study of γ and δ alumina by vibrational spectroscopies

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Transitional aluminas, obtained by thermal decomposition of the mineral boehmite, are essential for catalytic applications due to their large surface areas and amphoteric nature. Three phases can be singled out in the so-called metastable cascade (γ -> δ -> θ -> stable α-Al_2O_3), with the structures of the first two being controversial and heavily dependent on the synthesis procedure [1]. In this work, we present infrared and Raman spectroscopic results on γ and δ alumina nanopowders that supplement structural identification by X-ray diffraction. The lattice contribution to the dielectric functions of both phases was extracted from infrared specular reflectance measurements on pressed pellets using an effective medium approximation. Despite their strong similarities, two more modes are clearly observed for the δ phase. The results have been compared to density functional theory (DFT) computations for suggested structures of γ-Al_2O_3. Comparison to theoretical results on δ is hampered by the absence of works dealing with this phase in depth. Finally, Raman spectroscopy allows distinguishing between two proposed structures for the δ phase, which were not resolvable by X-ray diffraction due to the small crystallite size. Factor group analysis suggests the observed Raman spectra are closer to those predicted by group theory for a *$P4_12_12$* structure (22 modes) [2] than to those corresponding to a *P-4m2* one (30 modes) [3]. This result is very significant because Raman spectroscopy is rarely used to characterize transitional aluminas due to well-known fluorescence problems. No such bands could be observed for the γ sample with lasers spanning the UV to NIR spectral ranges.

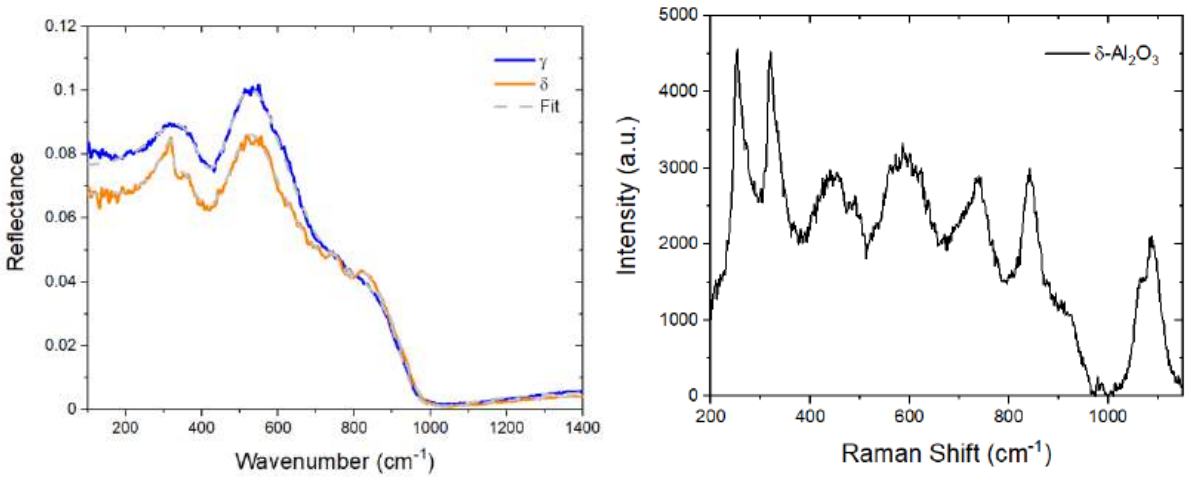

Figure 1. Infrared (left) and Raman (b) studies of the nanopowders.

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Mapping minerals in a Dhofar meteorite by Raman imaging

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In the era of space exploration, meteorite characterization has become an unvaluable source of information about solar system formation without need of carrying out special and costly missions. Traditional techniques, such as X-Ray or microprobe analysis cannot always answer where meteorites were formed, mainly because they do not provide compositional and structural information at the same time [1].

In this work, we outline our latest investigations in adapting Raman imaging to study meteorites. We will show how mapping Raman peak positions, intensity features and compositional distributions allow to disclose relevant geological information such as meteorite origin or the pressure and temperature conditions at which different mineral phases were originated.

Our results are focused on a meteorite was discovered in the Dhofar desert in 2009. This uncharacterized meteorite has been classified as ordinary chondrite. Briefly that means that Dhofar meteorite is composed by chondrules, millimetre-sized spheroids formed in the early stages of the Jupiter protoplanetary disk. Dhofar meteorite constitutes a test-bed example of the most common meteorites found on earth [2]. Our results show that six chondrule types are present: porphyritic olivine, porphyritic pyroxene, porphyritic pyroxene and olivine, barred olivine, radiating pyroxene, cryptocrystalline. This covers almost all the chondrule types described so far [3], and therefore provides a validation of our proposed methodology to be applied in other samples.

While presenting our results, we will see how it is possible to disclose crystallinity features of the mineral phases, as well as pressure and temperature effects. We will also propose that compositional Raman imaging can be used to deduce the fractional mineralisation order. All this information led us to conclude that the different chondrules of Dhofar meteorite were formed in separate sites in the protoplanetary disk, but so close that the accretion of the chondrules were in semiplastic conditions.

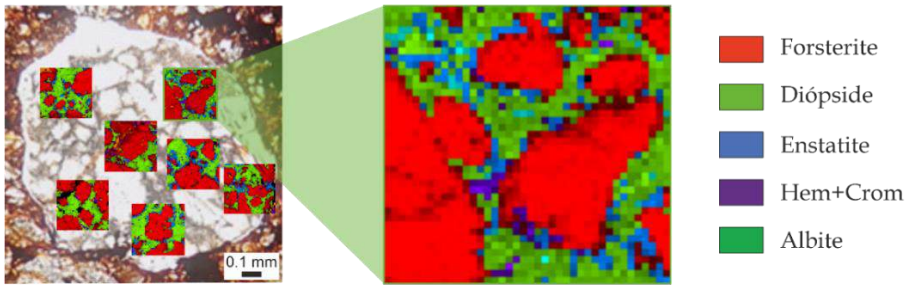

Figure 1. Example of a Raman image of a chondrule, where mineralogies are coloured differentiating forsterite (red), diopside (light green), enstatite (blue), hematite-cromite (purple) and albite (dark green).

Acknowledgements

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A detailed IR, Raman spectroscopic and DFT theoretical analysis of commercial additives monosodium glutamate and xylitol

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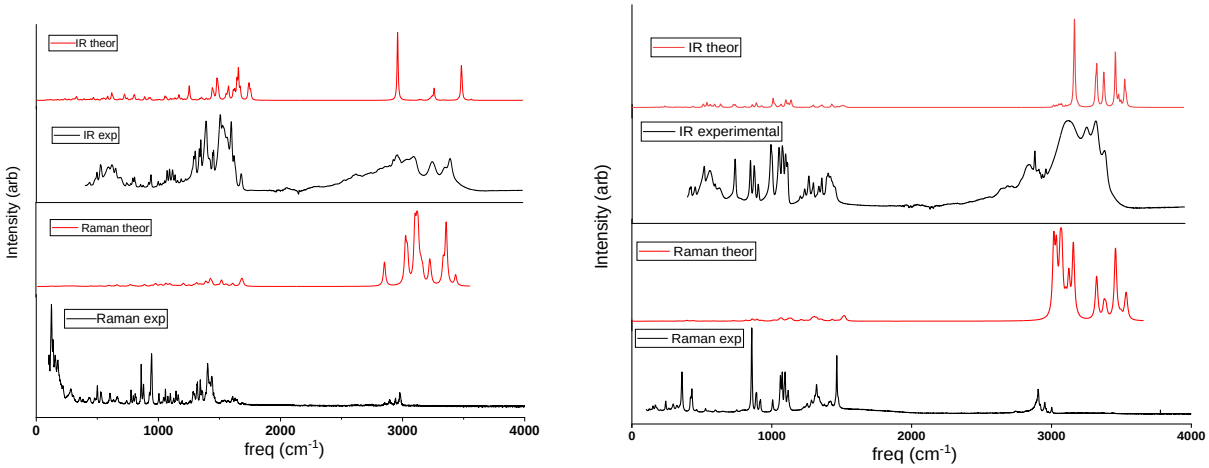
The use of organic additives added in small quantities to food is worldwide spread during food production or processing to improve their organoleptic quality (flavor, appearance, color, taste and texture). In between the most used Monosodium glutamate (MSG)(1), the sodium salt of glutamic acid, is used to seasoning while Xylitol a natural five-carbon-sugar alcohol is added to food as a sweetener used as a dietary additive and as a preventive of dental caries (2).

To understand more in depth, the structure and water role, hydrated and unhydrated crystalline phases, a spectroscopic research has been done on pure monosodium glutamate and xylitol, registering its spectra with a Bruker Vertex70 FTIR spectrometer and a using Renishaw inVia Raman microscope equipped with a Leica microscope, a CCD camera, and laser at 532 nm with 10 mW laser power. Besides, a theoretical structural and spectroscopic DFT study using the CASTEP code (3) has been carried out to understand the structures and to achieve an accurate assignment of the vibrational modes. As shown in Figure 1, a) and b) the corresponding IR and Raman spectrum of glutamate and xylitol display a good agreement between the predicted and the experimental spectra. Features form the hydrated and unhydrated resulting products of the compounds are also characterized.



a) Monosodium glutamate **b) Xylitol**

Figure 1. Calculated and experimental IR and Raman spectra of monosodium glutamate and xylitol.

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Analysis of two blue triarylmethane dyes by UV-Vis, FT-Raman and SERS spectroscopies

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The study of organic colouring materials used in cultural heritage objects provides useful information for dating, authentication, conservation treatments, and art history in general. Synthetic dyes are not as widely studied as natural dyes, since the latter are typically considered of more artistic and historic relevance. However, the study of modern and contemporary art is widely recognized as one of the most difficult and pressing challenges in conservation science. Indeed, the ease in production and employment of these materials was responsible for their huge widespread, accompanied by a lack of scientific knowledge and comprehension of adequate conservation treatments [1].

The aim of the study is to understand the behavior of Basic Blue 26 (Victoria blue B, VBB) and Basic Blue 11 (Victoria blue R, VBR) [2] under different pH conditions using UV-Vis, FT-Raman and SERS spectroscopies. The FT-Raman technique was applied for the Raman characterization of these dyes as they show a great fluorescence emission that prevents the use of other excitation lines. SERS spectroscopy was performed on Ag nanoparticles prepared by reduction by citrate. Various pH values and laser excitation lines were tested in order to find the optimal conditions for the study of the blue synthetic dyes.

At alkaline pH, the UV-Vis spectra show a great shift in the maximum absorption band of VBB, from 616 to 510 nm. However, only an intensity decrease of the main absorption at 611 nm is observed in the case of VBR. This is accordance with the change in the color of the VBB aqueous solution at basic pH.

The SERS spectra of both blue dyes show an intensity decrease as the pH increases, due to the deprotonation of the triarylmethane molecules. Regarding the excitation lines, the position of the absorbance maximum affects the resonance or pre-resonance conditions met by both dyes. Thus, the excitation at 532 nm leads to a pre-resonance conditions of the two species present at acid, neutral and basic pH, while the laser at 633 nm, met resonance conditions only with the VBB species at acid pH. Finally, the 785 nm laser lies far from any absorption maximum, being out of resonance. In the case of VBR, only one absorption maximum is observed in the UV-Vis spectra, meaning that only one is present in solution. Pre-resonance conditions are only met at 532 nm. The differences among the SERS spectra of the dyes at the different pH values were studied by mean of the vibrational analysis obtained from the results obtained by DFT theoretical calculations.

Acknowledgements

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Spectroscopic analysis and identification of Islamic and Christian materials and pigments in the church of Santa Catalina-convent of Santo Domingo (Jaén).

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In the year 2020, archaeological excavation was carried out in the Church of Santa Catalina (former convent of Santo Domingo) in Jaén, which resulted in the appearance of various materials from different historical periods dating between the 12th and 17th centuries. Of special interest were the remains of an arcade and wall coverings from the Almohad period belonging to the Islamic palaces located under the Church of Santa Catalina. The relevance of the archaeological remains discovered made it necessary to carry out research related to their composition for subsequent conservation and restoration work.
The analyses of mineral and elemental composition of the building materials and pigments belonging to both the Almohad and Christian phases were performed by Micro-Raman spectroscopy (µMRS), Micro-Energy-Dispersive X-Ray Fluorescence (µEDXRF) and Wavelength Dispersive X -ray Fluorescence (WDXRF). As a result of these analyses, gypsum was identified as the main raw material in the construction of the arch and walls, and hematite, cinnabar and amorphous carbon [1] in the composition of the decorations from the Almohad period. For the Christian period, the identification of nodules composed of plaster and lapis lazuli [2] stands out, surely used in the decorations of the walls and ceilings of the church.

Figure 1. Remains of the Almohad arch and selection of the decorated materials analysed.

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Raman spectroscopy and SERS methodology for the analysis of a melamine admixture superplasticizer for concrete

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Admixtures used in concrete are natural or artificial compounds which are added in the kneading water to improve some properties of the fresh and the hardened concrete, such as durability, workability, mechanical strength, etc. Admixtures are classified according to modified properties and are defined as plasticizers, air entrainers, accelerators, retarders or superplasticizers and are added in concentrations below 1%. Due to the low concentration of admixtures it is difficult to monitor them after the interaction with the cement particles. This work is focused on a methodology to study a superplasticizer admixture based in polymerized melamine with Raman Spectroscopy and Surface Enhanced Raman Spectroscopy (SERS). The admixture is commercialized as a transparent liquid of high density where the polymerized melamine is dissolved. A drop of admixture has been heated at 40ºC degrees during four hours to evaporate the solvent; the quantity of the solid in the commercial admixture has been calculated at 21% in mass. The polymerized melamine has been analyzed with Raman spectroscopy before and after a heating treatment at 40ºC, thereby Raman spectrums of the admixture have been obtained as liquid and as solid (Fig. 1a). Besides, a SERS study of the same molecule has been done analyzing the commercial liquid admixture, and the solid left after the heating treatment by diluting the polymerized melamine in distilled water at 21% in mass (Fig. 1b).

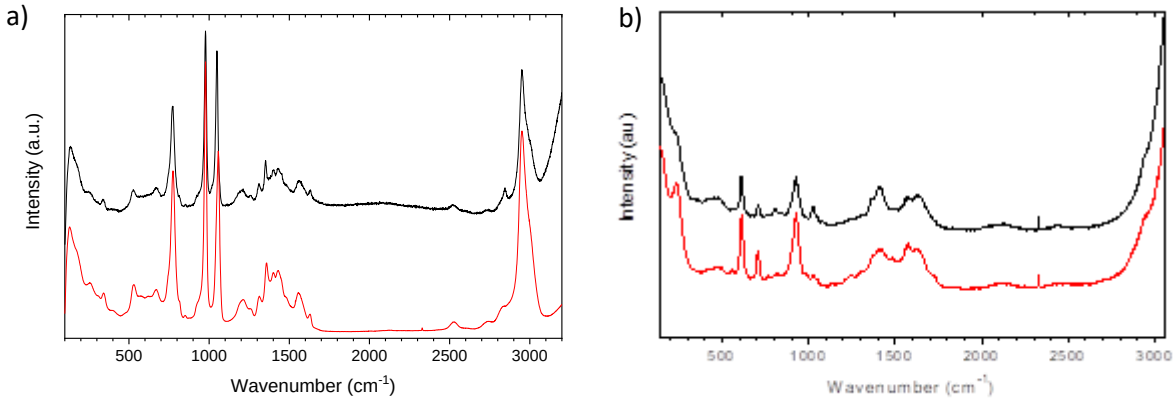

Figure 1. a) Raman spectrum of the melamine admixture before heating treatment (black) and after (red) and b) SERS spectrum of the melamine admixture before heating treatment (black) and after (red)

Results indicate that the polymerized melamine is not degraded during heating treatment, besides, Raman spectrum show signals which below to the aromatic ring at the melamine and other signals which correspond to the polymer. It has been tested that SERS technique is viable for the analysis of polymerized melamine as superplasticizer admixtures in the experimental conditions considered, being possible to identify characteristic signals of the aromatic ring of the melamine at 922 and 1030 cm^{-1}.

Acknowledgements

This study was funded by the Regional Government of Madrid, (S2018/NMT-4372 TOP Heritage-CM Programme) and by the Spanish Ministry of Science, Innovation and Universities (MICIU), the Spanish National Research Agency (AEI) and the European Regional Development Fund (ERDF) under project RTI2018-097074-B-C21-22. The authors wish to acknowledge the professional support of the Plataforma Temática Interdisciplinar del CSIC Patrimonio Abierto: Investigación y Sociedad (PTI-PAIS).

Hyperspectral infrared imaging of dystrophic mice muscles.

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Muscular dystrophies are rare, gene-related diseases which prevalence sits between 19 and 25 per 100000 of the male population [**1**]. Given their low incidence and high mortality, diagnostic devices and methods to monitor muscular dystrophies are in constant evolution. A recently developed hyperspectral imaging (HSI) system (figure 1), based on a pushbroom device combined with a high-precision rotating mirror [**2**], has been used to obtain short wave infrared (SWIR) spectra of mice muscles (figure 2, a-d). Mice population covers control (multiple ages), one-month and six-month-old dystrophic mice (alpha-sacroglycan deficit model). The two characteristic collagen peaks [**3**] (Figure 2, e-f), obtained from ex-vivo muscle measurements, show that one-month-old muscles have the highest presence of collagen, which is in accordance with the over-expression of collagen in pathological mice versus healthy mice. Nevertheless, a decline in collagen is present in the six-month-old mice that could be associated with the stabilization of the fibrotic process [**4**].

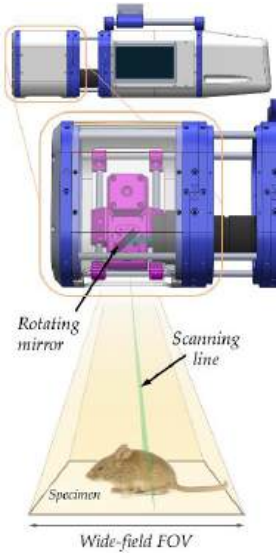

Figure 1. HSI-SWIR system setup schematic.

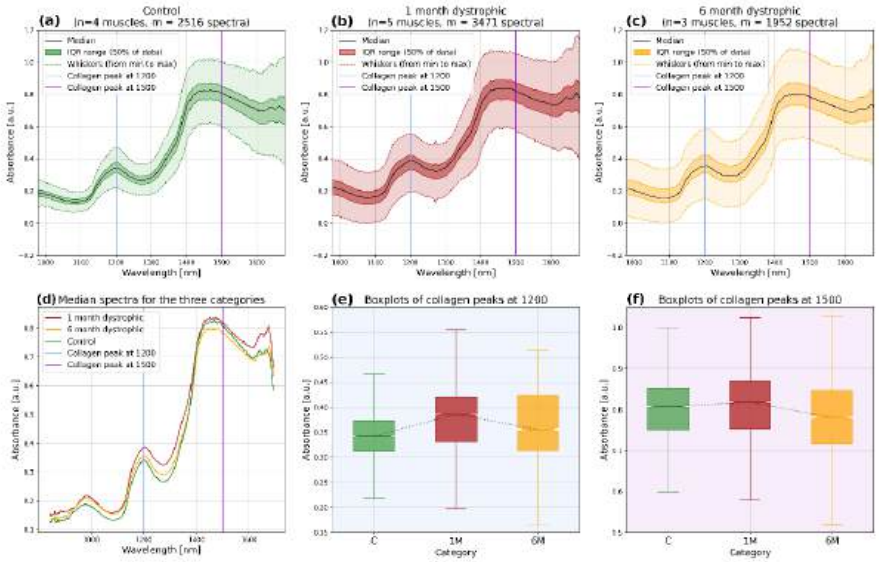

Figure 2. SWIR absorbance spectra for (a) control, (b) one month dystrophic and (c) six month dystrophic mice muscles. Median spectra are compared on figure (d). Figures (e) and (f) show the boxplots of the muscles' spectra at two significant collagen wavelengths: 1200nm (e) and 1500nm (f).

Acknowledgements

Support for this work was provided by the projects PREVAL 21/07 (FUSIOMUSCLE), SUBVTC-2021-0038 (HYPERfusionTRANS), DTS17-00055 (INTRACARDIO) and DISFOS (PID2019-107270RB-C21/ AEI / 10.13039/501100011033), financed by the ISCIII, the Fundación Instituto de Investigación Valdecilla (IDIVAL) and the Spanish Ministry of Science, Innovation and Universities, co-financed with FEDER funds.

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Spectroscopic monitoring of the stability of Phycoerythrin dye extract: influence of temperature, pH, light exposure and preservatives

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Phycoerythrin (PE) is a biliprotein from microalgae with application as colorant in many sectors [1,2]. The focus of the presented work was on improvement of PE extract as a potential natural pink colorant by enhancement of its stability. In this sense, temperature, pH and light exposure play an important role in the biliprotein stability. The PE stability was assessed by monitoring the extracts at different pHs, temperatures and light exposure, measuring the absorbance, fluorescence and colour of the protein solutions (Figure 1). Kinetic modelling was used to describe PE degradation under different conditions. The maximum stability of PE was in the pH range 3.5-9.0 and incubation at temperatures between 40 and 64 ºC caused the PE concentration and half-life of protein in solution to decrease rapidly. Regarding stability to light exposure, samples exposed to darkness showed better stability values than those exposed to light. Furthermore, the stability of PE in the presence of edible preservatives was studied, being found to be effective for improving protein stability in terms of increase the half-life and relative protein concentration. The pigment was successfully applied as colorant in beverages such as isotonics, tonics, gins and wines, using a pigment concentration between 4.4, 1.7, 1.5 and 3.0 mg L^{-1} respectively. This study highlights the potential of PE extracts for application in food and beverages.

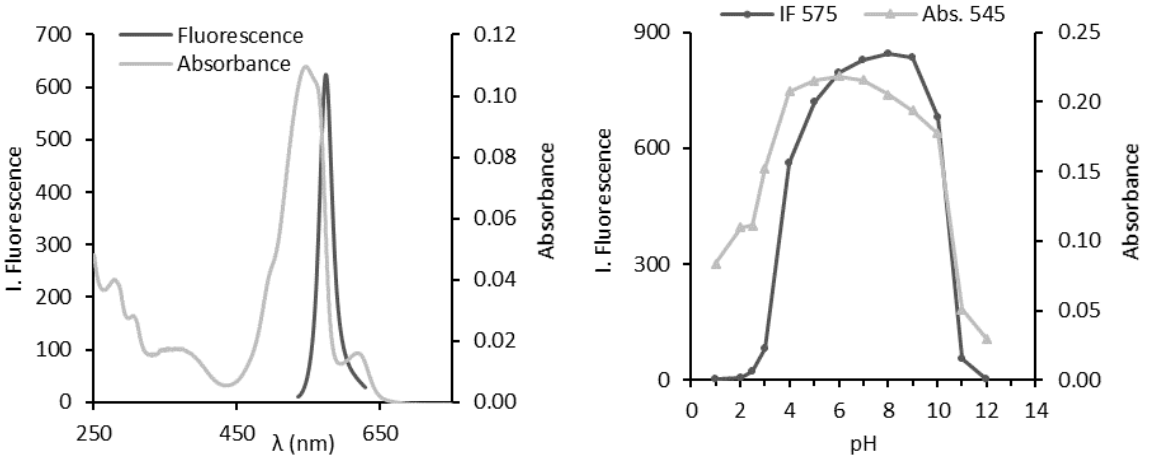

Figure 1. (a) Absorbance and fluorescence spectra of PE at pH 7.0; (b) variation of absorbance and fluorescence intensity of PE solution, at various pH values, in 20 mM phosphate buffer. Protein concentration = 0.015 mg mL^{-1}.

Acknowledgements

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Electric field and charged cluster dual model for Potential Depdendent Surface-Enhanced Raman Spectroscopy

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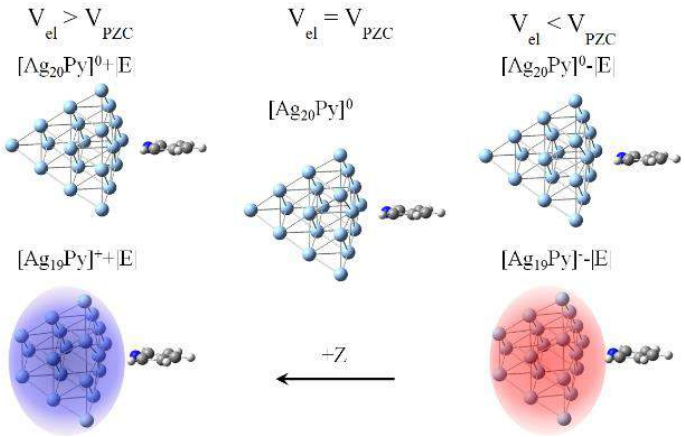
The computation of electrochemical systems is very challenging because of the many variables involved [1]. Among them, the effect of the electrode potential is particularly complex to be introduced in atomistic models. In this work, we propose a model where the surface excess of charge has been modelled with the tetrahedral-like clusters [Ag19]+, [Ag20]0 and [Ag19]-. We then modulate the effect of other surface charges implicitly as an external electric field and correlated a calculated magnitude like the electric charge on the adsorbate with the electrode potential, a purely experimental one.

This model is tested with the potential-dependent Surface-Enhanced Raman Scattering (SERS) of pyridine. Namely, we investigated the changes in the Raman shifts and relative intensities due to the potential, and evaluated the different contributions (electromagnetic, charge-transfer) to the SERS spectra. Our preliminary results nicely reproduce the experimental trends and reveal that enhancement factors up to 107 are achieved when the charge-transfer state interact with the bright local excitations of the metal cluster.



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The crucial role of molecular emissions on detectability of organic biosignatures under Mars atmosphere conditions by LIBS.

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If there was life in the past on the Red Planet, specific biosignatures might still be present only if preservation conditions have been favourable for them [1]. The recognition of the habitable past on Mars increases the exigency to identify and characterize modern analogues of these surroundings and to evaluate the mechanisms that can conserve biosignatures in them. The processes that originate and safeguard possible organic-type biosignatures in mineral phases are of crucial interest [2]. In the last few years, laser-induced breakdown spectroscopy (LIBS) has emerged as a powerful tool with an essential role in space exploration [3]. LIBS combines many of the required features for this application, including fast multi-elemental detection, no sample preparation, and an unlimited range of material capabilities. Although, in essence, LIBS can provide elemental information of a material, it has been shown to be a powerful tool for identifying and discriminating different types of organic compounds based on their intrinsic spectroscopic characteristics [4]. The classifying of these materials associated to optical emission signal from molecular emitting species such as CN, C_2, NH, CH and OH, among others, can be affected by the atmosphere surrounding the laser-induced plasma [5]. In this particular application, the CO_2-rich Martian atmosphere implies that the effect could be reduced, whereas other species formation processes attributed to dissociation of CO_2 and subsequent recombinations in plasma may occur. Modern geochemical and astrobiological studies mainly focus on the detectability of molecular biosignatures, which could be related to evidence of life on Mars. There is a wide variety and abundance of terrestrial rock-hosted life and fossil biomarkers to assist the search for life on the red planet. Some investigations have reported the difficulties of detecting organic compounds, in the presence of a carbon and oxygen rich atmosphere. In this sense, the formation mechanisms of emitting species of organic and C-containing inorganic compounds under Mars-like atmospheric conditions using LIBS have been evaluated.

Acknowledgements

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Detection of *A. platensis* cyanobacteria in different inorganic matrices by LIBS under a simulated Martian atmosphere.

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In recent years, the number of missions launched to the Red planet has been increased, as well as the interest in the search for evidence of past biological activity or biosignatures. The need for robust and reliable equipment that can operate in extreme conditions has led to Laser induced breakdown spectroscopy (LIBS) to prove to be one of the most versatile tools in the field [1].

Nevertheless, the identification of certain emissions by LIBS is often a complex process, due to the strong sensitivity of the technique to environmental conditions. Detection and identification of organic compounds in rich-CO_2 atmosphere is a challenge, that implies the potential contribution of different emission sources to LIBS signals, which can lead to the appearance of molecular and atomic species in the plasma plume from atmosphere or substrate ablation, besides the organic sample itself [2,3].

For this work, a mixture of different matrices with a complex organic sample (*A. platensis, cyanobacteria*) has been carried out, in order to identify what type of substrates can favor the detection and identification of biological material, with a view to the results that could be obtained in real scenarios, including samples with humidity, heterogeneity, different ablation rates and different counterions. For this purpose, atomic (C, H and N) and molecular (CN and C_2) emission signals have been monitored by LIBS to characterize the organic sample in these different substrates.

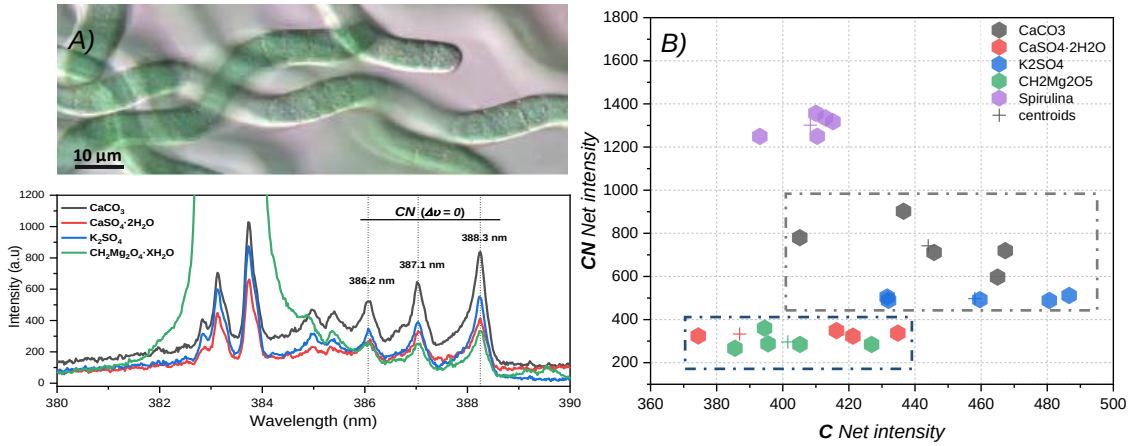

Figure 1. *A) Microscopic observation of the cyanobacteria sample described A. platensis [4], and LIBS spectra of the 380-390 region obtained from the 50% Wt. mixture of the substrates selected with the Cyanophyta. Representation of the CN/C ratio generated from the calculated net intensities.*

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Through the NMR looking glass: Unravelling role of water in DESs nanostructure

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Deep Eutectic Systems (DES) have been coined as the new sustainable alternative to conventional organic solvents for a myriad of applications, from biotechnology to material science[1,2]. These systems have shown to have similar properties to Ionic Liquids (ILs), but with a lower associated cost. One of the major problems in the applicability of DESs is their intrinsically high viscosity due to the nature of the DES 3D network. This problem can be circumvented by the addition of water, but what is the role of water in the hydrogen bond nanostructure, and how much water can be combined with DES to overcome the physicochemical properties limitations while maintaining most of the DES structure?

Nuclear Magnetic Resonance (NMR) spectroscopy is a key tool in unravelling unconventional solvent structures and dynamics, like ILs and DESs[3,4]. In this work[5], we studied aqueous solutions choline chloride:glycerol (at a 1:2 molar ratio) DES system, with water contents ranging from 1 wt.% (x_w=0.06) to 70 wt.% (x_w=0.94), with particular focus on low water contents (< 70 wt. %), mimicking industrial storage conditions. Using a combined NMR experimental approach, where information at the DES/water atomic level obtained by different NMR methods, like relaxation, diffusion, chemical shift, and NOE NMR, were combined with changes in macroscopic properties, namely viscosity. This allowed us to identify three distinct water behaviour domains. Up to 11 wt % H_2O, where the structure of the DES not only remains intact but is strenghthen by the addition of water; between 11 and 35 wt %, where the DES structure endures, in spite of the components starting to be solvated, and above 35 wt %, where the structure is disrupted and occurs the transition from a water-in DES to a DES -in-water system.

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CPL and ROA: a rare couple together

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It is known that the mutual presence of fluorescence and Raman is highly undesirable as they usually damage one the other. The opposite is however true with their chiral versions, CPL (Circularly Polarized Luminescence) and ROA (Raman Optical Activity), respectively, given their intrinsic interconnections with the electronic structure, which might give access to hidden molecular properties. However, the competitive origin of these two effects makes their simultaneous observation uncommon for organic molecules, since magnetically allowed transitions responsible of chiral bands are usually buried by those electronically allowed. Besides, by considering that this experiment must be recorded using a standard ROA spectrometer, it is limited to systems whose lowest-energy excited state is able to be populated enough with a 532 nm laser. As a consequence, CPL-ROA observation has been only recorded for heavy atom structures, such as lanthanides complexes, addressed by the high magnetic transition dipole moments associated to the *f-f* atomic transitions [1].
We present here the simultaneous detection of CPL and ROA in the lemniscular molecule shown in Fig. 1, hereafter [16]CPPL, an oligoparaphenylenic double cycle bridging by a 9,9'-bicarbazole group which freezes a chiral loop conformation and, more interestingly, allows the two enantiomers to be stable over time [2]. The inter-ring distortion and shape of this molecule finely triggered magnetic effects and makes the CPL-ROA couple to appear together. A right balance between π-conjugated electronic enhancing effect of the Raman signal and the magnetic exaltation effect of the cyclic/inter-ring distorting structure seems to be on the origin of this observation [3]. As far as we know, Fig. 1 shows the first reported example of combined ROA and CPL spectra successfully recorded for a pure organic molecule.

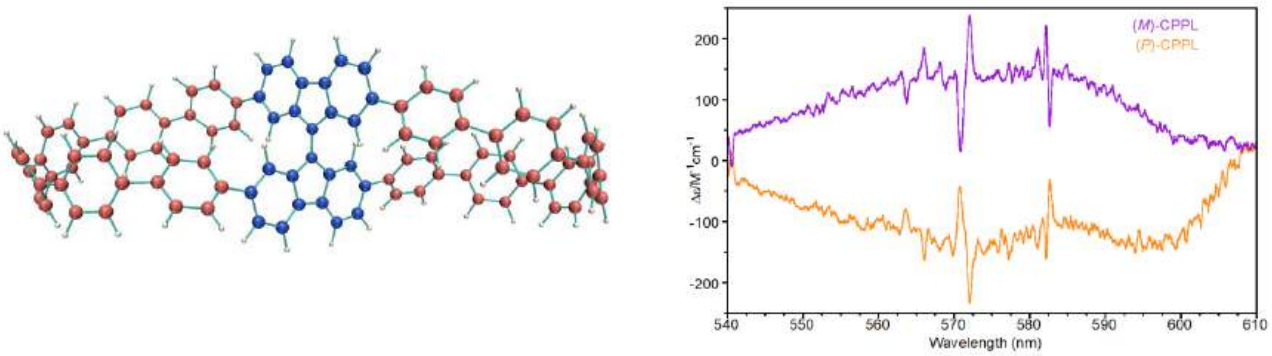

Figure 1. Left panel: Molecular structure of the lemniscular [16]CPPL. Right panel: CPL-ROA spectra of (*M*-) and (*P*-) enantiomers of [16]CPPL in dichloromethane solutions.

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Concomitant Ion Impact on the Performance of A SCGD-OES Elemental Analysis Approach

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The Solution Cathode Glow Discharge (SCGD) is a micro-plasma in contact with a flowing liquid working under ambient air. The SCGD represents a potential alternative for elemental analysis when coupled to optical emission spectroscopy (OES), since it provides competitive sensitivities compared to Inductively coupled plasma-OES (ICP-OES) or Atomic Absorption Spectrometry (AAS), with the possibility continuous and/or in situ operation thanks to its much lower running costs and its potential for miniaturization. This work systematically deals with the influence of NaCl on the analytical performance of SCGD-OES.

A 90-min discharge is realizable when the solution contains 3.5 g/L NaCl; nevertheless, a loss in stability was observed due to the electrode corrosion. Meanwhile, an accumulation of nanometric particles on the cathode pointed to the increased reductive capability at the liquid-plasma interface as a result of the presence of NaCl. Noticeably, NaCl improved the response of assayed elements (Zn, Cd, Fe, Ag, In, Sr and Li) slightly at the concentration of 0.0035 g/L and depressed the response when it surpasses 0.35 g/L. Experimental parameters for Fe, In, Sr and Li were optimized at NaCl level of 0 g/L, 0.35 g/L and 3.5 g/L, and the calibration curves of analytes were obtained for each NaCl concentration. Sensitivity for analytes were worsened ascribable to NaCl, though Li and Sr were less affected. In addition, HCOOH was observed to improve the analytes emission when NaCl is absent, while deteriorating the analytes response at high NaCl concentration (3.5 g/L). In this sense, further investigation concerning the influence of HCOOH on elemental response when other dissolved ions were present (KCl, $CaCl_2$, $MgCl_2$, Na_2SO_4, $NaHCO_3$, and NaBr) was carried out.

Acknowledgements

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Detection of the glyphosate pesticide by SERS: development of a new highly selective and sensitive detection method

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Glyphosate (glyph) is a broad-spectrum systemic herbicide widely known under its trade names Roundup® and Ranger Pro®. These products are used for weed control in agricultural production fields. In the 20th century, the use of glyph increased dramatically due to the introduction of pesticide-resistant crops [1]. As a consequence, in the last decade, glyph has been sprayed on more hectares planted with resistant crops as well as applied more intensively. Actually, it is the most widely sprayed pesticide in history [2,3]. Further, in the early 2000s, the practice of *green burndown* also began what affected significantly accumulation of glyph and its metabolites in food, water, and dust [3]. Toxicological studies indicate that chronic exposure to this herbicide is potentially carcinogenic and can induce different diseases, such as gluten intolerance, diabetes, heart disease, multiple sclerosis, Alzheimer's disease, autism, and birth defects [4,5]. In this context, on-site identification and quantification of chemicals such as glyph are essential to promote food safety, human health, national security risk assessment, and disease diagnosis. Surface-enhanced Raman spectroscopy (SERS) is a promising technique for in-situ analysis of glyph as it allows obtaining a true *fingerprint* of the analyzed compound with exceptional sensitivity [6]. In contrast to the techniques currently used for the sensitive detection of glyph, such as GC, HPLC, UV absorption, and fluorescence spectroscopy, the SERS technique has several advantages: no need for sample pre-treatment, fast and cost-effective measurements, and available portable equipments [7].

Many investigations were conducted so far on the theoretical and experimental characterization of glyph by Raman and SERS. However, the SERS of this pesticide shows rather weak signals leading to not so low limit of detection [7]. The reason for this low sensitivity is attributed to the high polarity of the molecule, what seriously hinders the approach of the pesticide to the surface of metallic nanostructures. In the present work, a method for the SERS detection of glyph proposed by Jan *et al.* [8] was tested and optimized. By modifying the environment of the metal colloid, we have observed a greater affinity of glyphosate for the metal surface and, consequently, a greater sensitivity of the SERS analysis of this important pesticide, being able to obtain a detection limit close to 1ppb.

Acknowledgments

This work was supported by the research grants provided by the Slovak Research and Development Agency (APVV-19-0580) and Faculty of Sciences of the P.J. Šafárik University in Košice (VVGS-PF-2021-1770), and by the project OPENMED (ITMS2014+: 313011V455) from the EU Structural funds. This work was also financially supported by the AEI Project number PID2020-113900RB-I00.

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POSTER COMMUNICATIONS

Combining nanotechnology and ultrasound: *in situ* synthesis of magnetic nanocomposites for mercury preconcentration

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Mercury is included in the priority list of pollutants, thus highly sensitive and selective methods are necessary for its determination, especially in drinking waters [1,2]. Lately, nanomaterial-based strategies have proved advantageous for sensing and enrichment of pollutants [1]. In this work, ultrasound energy has been combined with nanotechnology allowing integration of main steps: *i.e.* synthesis of magnetite NPs and Hg(II) enrichment. An *in situ* ultrasound-assisted co-precipitation method was applied to prepare magnetic nanocomposites for Hg(II) preconcentration in waters based on previous studies of the research group [3]. The novelty of this work lies on the combination of magnetite with noble metals for Hg(II) retention. Noble metals such as Ag(I), Au(III) and Pd(II) were added to the medium of synthesis allowing Hg(II) trapping. Then, easy magnetic separation of the Hg enriched-NPs from the aqueous phase was performed avoiding filtration or centrifugation steps. No elution was required either. Hg analysis was directly performed on 50 µL of the enriched magnetite nanocomposite in a direct mercury analyser (DMA) [4]. Among the noble metals attempted, best performance was provided by Pd. For a 5 µg/L Hg(II) concentration, a Hg/Pd ratio between 1:5 and 1:100 showed the highest increase in sensitivity. Characterization of the nanocomposite was performed by transmission electron microscopy (TEM), high-resolution transmission electron microscopy coupled to energy dispersive X-ray spectrometry (HR-TEM-EDS) and total reflection X-ray fluorescence spectrometry (TXRF). The particle size was in the range 7-10 nm. The limit of detection obtained was 3.2 ng/L Hg(II). The preconcentration factor achieved was 100 and the repeatability expressed as relative standard deviation (RSD, %) was 7 %. Trueness was evaluated using CRMs (water samples) containing different concentrations of Hg(II), namely, QC-1014, QC-1129 and QC-1205. Studies performed on real water samples yielded Hg recoveries in the range of 88-115 %. No satisfactory recoveries were found for wastewater samples due to the effect of organic matter on the direct synthesis of NPs in the water sample. The method is fast and efficient, allowing extraction and preconcentration of Hg in drinking water at ultratrace level.

Acknowledgements

Support for this work was provided by the Spanish Ministry of Science, Innovation and Universities (Project RTI2018-093697-B-I00), the Spanish State Research Agency and FEDER. I. de la Calle and V. Romero acknowledge financial support as postdoctoral researchers from the 'Universidade de Vigo' and the 'Xunta de Galicia', respectively.

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Modification of cellulose filter paper with silver nanoparticles for Hg enrichment and determination by a direct mercury analyzer

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Cellulose-based materials have found a plethora of applications in the different stages of the analytical process (sample treatment, preconcentration/separation techniques and detection) due to its abundance in nature, biodegradability, ease of chemical modification and excellent sorption properties [1]. Recently, nanostructured materials such as silver nanoparticles (AgNPs) have been used along with cellulose substrates for the preparation of antibacterial papers, substrates for surface enhanced Raman spectroscopy, colorimetry and catalysis, sorption of pollutants, etc. [2]. Different methods are available in the literature for the modification of cellulose with AgNPs: covalent methods, physical adsorption, thermal reduction and *in situ* chemical reduction [3]. A new application is described here using AgNPs-modified cellulose for the enrichment of Hg(II) after filtration and analysis by a direct mercury analyser following complete pyrolysis of filters and measurement of the Hg atomic absorption [4].

Parameters influencing the Hg preconcentration were carefully optimized, namely, i) Synthesis approach of AgNPs (i.e. *in situ* synthesis, physical adsorption, thermal reduction, amount of $AgNO_3$, amount of $NaBH_4$, time of immersion in different reagents, stability of the coating; ii) Type of cellulose material; iii) Variables involved in the filtration operation (filtration volume, type of filtration systems, sample pH).

After optimization, characterization of filter papers was performed by scanning electron microscopy (SEM) showing that the particle size was in the range of 30-60 nm. An enrichment factor of 3500 and a limit of detection of 0.2 ng/L Hg were achieved when using a sample volume of 100 mL. The repeatability, expressed as relative standard deviation (RSD), ranged from 5 to 9 %. Recoveries in the range of 92-105 % were achieved for certified reference materials and synthetic water samples. The developed procedure has proved to be a very efficient, sensitive and simple strategy for the enrichment of Hg(II) in a large variety of water samples (tap water, seawater, groundwater, etc.) without the need for a previous reduction of Hg(II) to Hg(0). Additionally, the possibility of direct analysis of Hg on the filter paper without resorting to elution or digestion procedures simplifies the whole procedure.

Acknowledgements

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The interaction between lysozyme and chlorogenic acid: a fluorescence approach

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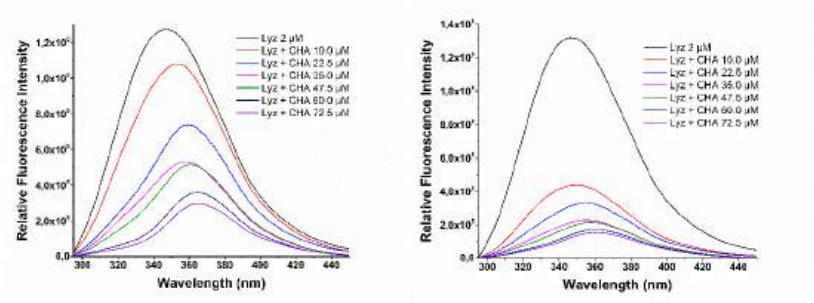
Egg white is a natural source of lysozyme (Lyz, EC 3.2.1.17), which constitutes about 3 to 4% of the total of its proteins [1]. The interactions between phenolic compounds and proteins can form soluble or insoluble complexes, changing the protein native structure and its properties [2]. Thus, in this work, the effect of the interactions of egg Lyz with chlorogenic acid (CHA) was evaluated on the protein tertiary structure as a conceivable way to promote changes in Lyz functional properties.

The fluorescence spectra of Lyz (2 µM) incubated 10 min, at 310 K, in 50 mM phosphate buffer pH 3.50 and pH 7.40, with different concentrations of CHA (10 µM to 72.5 µM) were recorded. The fluorescence extinction constant (K_{SV}) was obtained using Stern-Volmer equation and the binding constant (K_b) was given by Lineweaver-Burk equation [3].

The results showed an increase in fluorescence quenching with the increase of the CHA concentrations (**Figure 1**). In fact, the extinction of fluorophores in proteins occurs when aromatic residues (mainly tryptophan) are exposed to the solvent, which means that changes in the tertiary structure of the native protein occur. Moreover, K_{SV} values indicate that the fluorescence decrease is proportional to the CHA concentration (**Table 1**). Therefore, the interactions of Lyz with CHA giverise to changes in the tertiary structure of the protein.

A



B

Figure 1. Fluorescence spectra of Lyz (2µM) with CHA at pH 3.50 (A) and pH 7.40 (B) solutions.

Table 1. The binding (Kb), quenching (Kq) and Stern-Volmer (Ksv) between Lyz and the CHA.

Phenolic Acid	pH	Kb (M^{-1}) x10^4	Kq (M^{-1} s^{-1}) x10^{12}	Ksv (M^{-1}) x10^4
CHA	3.50	1.47	4.68	4.67
T (310 K)	7.40	1.51	8.98	8.98

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Biocompatible hybrid nanosystems with photoluminescent, magnetic and drug release activity

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Combining different nanoparticles (NPs) in a single system is a powerful strategy to complement each other's properties and obtain a multifunctional nanostructure (MF-Ns). Electrospraying is an electrohydrodynamic atomization process that can achieve this purpose by encapsulating NPs within highly stable polymeric nanoparticles. This technique allows a high encapsulation efficiency and high reproducibility.[1] The MF-Ns produced in this project are composed of the following elements: *i)* Ag_2S NPS are fluorophores working in the NIR-II optical biological window, allowing whit deep tissue penetration, low autofluorescence, and photon scattering [2], *ii)* superparamagnetic iron oxide NPs (SPION) able to respond to an external magnetic field and supplying molecular imaging by magnetic resonance techniques [3], *iii)* poly(lactic-co-glycolic acid) or PLGA a common polymer used for therapeutic devices owing to its biodegradability and biocompatibility and *iv)* Maslinic Acid, a natural triterpene extracted from the coating of olives that induces apoptosis in human colon cancer cells via the mitochondrial apoptotic pathway.[4]

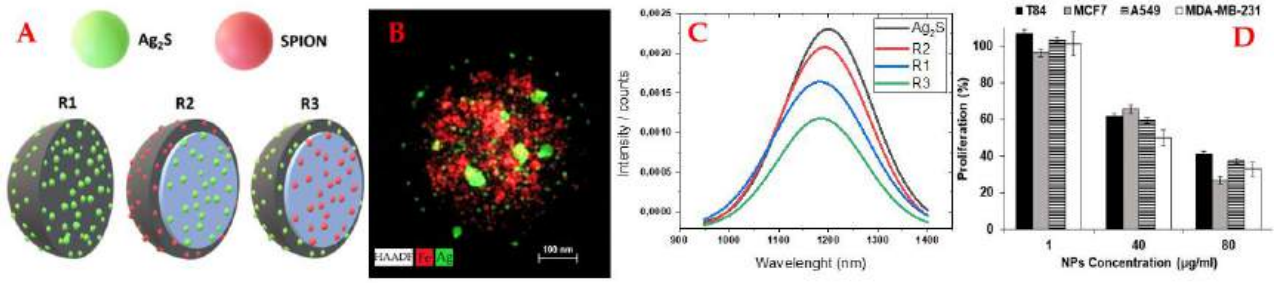

Figure 1. A) schematic representation of the different conformations. B) EDX elemental mapping of mixed iron and silver for the hybrid colloidal system R3. C) PL emission spectra of Ag_2S alone (black line), R1 (blue line), R2 (Red line), and R3 (Green line). D) Cell proliferation assay of A549. MCF7, MDA-MB-231, and T84 tumor cell lines treated with R1_Maslinic Acid

Five different conformations were printed with two types of injectors, simple and coaxial, allowing us to choose the location of each element. After characterization, it was proved that the different elements preserve their properties, as can be seen in figure 1. Results reveal that PLGA polymeric matrix barely affects the fluorescence emission, SPION maintains their superparamagnetic behaviour and, the desired conformation was achieved. *In vitro* cytotoxicity assays with different tumour cells lines also demonstrated that controlled release of Maslinic Acid could be achieved.

Acknowledgments

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ICP-MS methodology to determine novel potential chemotherapy drugs based on Ruthenium derivatives.

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Despite some limitations like long term side effects or the potential presence of intrinsic or acquired resistance, platinum compounds are key therapeutic components for the treatment of several solid tumours. To overcome these limitations maintaining the same efficacy, organometallic ruthenium (II) compounds have been proposed as a viable alternative to platinum agents as they have a more favourable toxicity profile and represent an ideal template for both, high-throughput, and rational drug design [1]. Novel ruthenium agents for further clinical development need to be evaluated against tumoral cells and compared to platinum agents. This is the case of bis-phosphino-amines Ruthenium (II) para-cymene complexes [2]. Unfortunately, the mechanism of action of these novel complexes needs to be studied. Herein, we report a simple and fast methodology for the qualitative and quantitative analysis of Ru content determined by inductively coupled plasma−mass spectrometry by inductively coupled plasma-MS which aim at analysing the pharmacokinetic and biodistribution of these novel ruthenium derivatives. Serum, liver, spleen, kidneys, heart, lungs, brain, prostate, ovary, and reproductive organs were collected from each mouse under treatment and the Ru content was determined. First, samples are digested in a microwave digestor by placing the biospecimen previously weighed in a digestion vessel, where 2 ml of 20% HNO_3 are added. 125 W of power per vessel using a 4-stage program is applied and digested solutions are then adjusted with ultrapure water to obtain a 10 mL solution with the correct acid concentration for the quantitative analysis, carried out using a 7900 Series (G8403A) Agilent ICP-MS instrument equipped with a MicroMist glass concentric nebulizer, a quartz Scott-type double pass-cooled spray chamber, and SPS4 autosampler. The Ru content is determined by flow injection analysis under these operating conditions: power 1550 W, carrier gas 0.99 L/min, make-up gas 0.00 L/min, sample depth 10 mm, nebulizer pump 0.1 rps and spray chamber temperature 2°C. The instrument is operated in He collision mode for unsurpassed interference removal, using 0.5 ng mL^{-1} Erbium as IS and monitoring the ^{101}Ru signal. The ICP-MS instrument is tuned using a solution containing 1 µg mL^{-1} each of Ce, Co, Li, Mg, Tl and Y, and calibration curves are obtained using aqueous standard solutions in identical matrix to the samples (about internal standard and 2% HNO_3) with appropriate stock standards dilutions. The LOD and LOQ are calculated, for instance, as 5.2 pg mL^{-1} and 22 pg mL^{-1}, respectively, for [RuCl(p-cymene)(N,N-bis(diphenylphosphino)-isopropylamine)][BF4]. Linearity was accordingly established in the 0.5-500 ng mL^{-1} range and precision values obtained were remarkably good (r = 0.996; RSD <2.5%).

Therefore, this work provides an adequate methodology to support the preclinical and clinical development of Ru-based potential metallodrugs for different types of cancer.

Acknowledgements

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Comparison of two theoretical models for simulating the charged metal-molecule interface in electrochemical SERS experiments

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A vibrational study of pyridine adsorbed on a silver nanostructured surface at a sequence of electrode potentials has been carried out [1]. This series of SERS spectra allows us to explore the dependence of the wavenumbers of the main bands on the electrode potential and, thus, analyze the wavenumber shifts of the bands. Two simple theoretical models of the metal-pyridine (Ag_nPy) interface have been used to simulate the effect of the applied electrode potential. In the first one, the charge density of the $[Ag_nPy]^q$ complex can be modulated as a function of the charge (q) and the number of silver atoms (n) by considering a linear metal cluster (Figure 1A). It allows us to define the parameter q_{eff} = q/n, which is comparable with the experimental electrode potential [2,3]. In the second model, an external electric field on a neutral Ag_2-Py complex (Figure 1B) and isolated Py molecule has been employed by using the keyword "field" in the Gaussian09 software [4]. All calculations have been done using the Density Functional Theory (DFT) at different levels of theory. Additionally, other theoretical conditions are explored, such as the effect of the solvent by using the Polarizable Continuum Model (PCM) and the shape of the metal cluster by employing a pyramidal silver cluster with twenty atoms. The wavenumber shifts calculated for both models are compared with the experimental ones. It is concluded B3LYP/LanL2DZ level of theory applied to the linear cluster model with different densities of charges shows the best concordance with the experimental results.

Figure 1. Theoretical models for simulating the effect of the electrode potential in electrochemical SERS experiments. A) Linear charged clusters and B) External electric field.

Acknowledgements

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Silver nanostructures mediated by copper substrate for thin film microextraction coupled to surface enhanced Raman spectroscopy

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Raman spectroscopy is a powerful spectroscopic technique which can provide structural information through the fingerprint spectra of a variety of species. The huge potential of this technique is hindered by its limited sensitivity due to the scattering cross-section. In order to overcome this limitation, in the last years the so-called surface enhanced Raman spectroscopy (SERS) has received great attention and a great variety of SERS substrates have been developed based on nanomaterials and nanostructured surfaces. The sample preparation step is critical and in the last years some attempts at combining the extraction and enrichment of the analytes from the matrix and the subsequent Raman or SERS detection have been reported, based e.g., on solid phase microextraction (SPME) techniques [1-3].

In this work, a method combining thin film microextraction (TFME) based on a silver nanostructure-modified copper foil with SERS has been developed and applied to the extraction and determination of crystal violet (CV) dye. Silver nanostructures with different shapes (Figure 1) can be obtained at the surface of the copper foil by immersion of the foil in a $AgNO_3$ solution due to the galvanic displacement process between Ag ion and Cu at room temperature [4]. The geometry of the silver nanostructures can be tailored from silver nanoplates to silver nanodendrites upon varying the concentration of $AgNO_3$ and reaction time. The morphology and composition of the SERS substrates have been characterized by different techniques, such as scanning electron microscopy (SEM) and X-ray fluorescence (XRF). It has been found that the synthesis in aqueous solution without the need of addition of further reagents led to the formation of Ag nanostructures which provided enhancement of the Raman signal of CV upon deposition on the SERS substrate. However, the substrate yielded poor extraction efficiencies when coupling the microextraction step with SERS detection. However, when the synthesis of the Ag nanostructures was carried out in the presence of an organic acid, namely, formic acid, acetic acid and propionic acid, the Ag-nanostructures-Cu substrate could be used for the TFME of CV with the subsequent SERS detection directly on the foil.

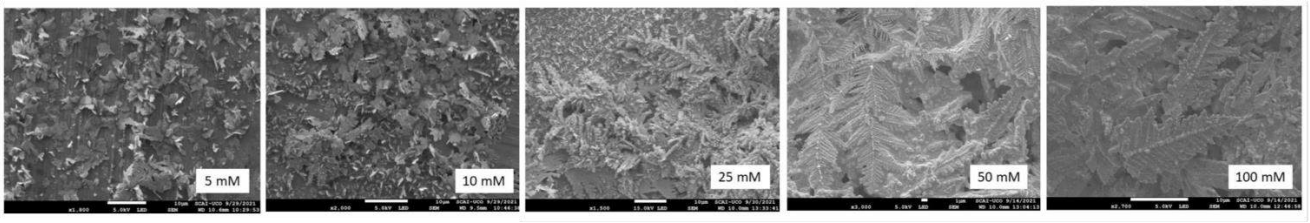

Figure 1. SEM image of the different Ag nanostructures obtained in aqueous solution by varying the concentration of $AgNO_3$ solution in contact with the copper foil

Acknowledgements

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Structural in-depth analysis of iron complexes of plant gall polyphenols by spectroscopic techniques: Implications in the analysis of historical manuscripts

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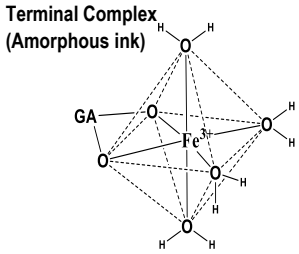
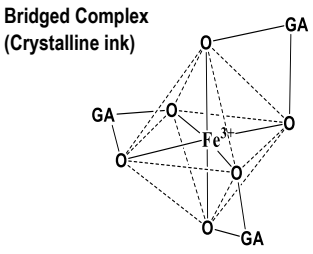
Phenolic compounds are the most abundant secondary metabolites in plants demonstrating many beneficiary properties and activities. Special attention deserves the phenolic compounds existing in plant galls, in particular, oak galls contain a large amount of tannis and gallic acid. These polyphenols were the basis for the preparation of iron gall inks (IGIs). The investigation of IGIs is of a great importance in the study of historical manuscripts with many implications in the Cultural Heritage. Raman spectroscopy (RS) has been demonstrated to be very useful in the identification of IGIs in historical manuscripts. Moreover, Raman and the Surface-enhanced Raman scattering spectroscopy was employed in the analysis of the chemical structure of many phenols [1]. Nevertheless, a less attention was devoted to an eventual structural characterization of IGIs by using the information provided by the Raman technique and the structure of the actual colorant in IGIs is still a matter of controversy. The main reasons are the intrinsic complexity of the studied materials and the lack of an appropriated and valid assignments of the vibrational bands.





In this work a structural analysis of polyphenol complexes with iron at several conditions is reported. The investigated polyphenols were tannic acid (TA), gallic acid (GA), pyrogallol (PY) and syringic acid (SA) being components and molecular models of the gallnuts usually employed in the past in fabrication of IGIs. PY and SA were employed as models to study the interaction of iron with similar structures to the GA one, and, more precisely, to evaluate the importance of the presence of both the carboxylic and the –OH groups in the benzene ring. This work was done by using Raman, FTIR, UV-Vis absorption and fluorescence spectroscopy at different conditions: pH, aging and stoichiometry. Besides, DFT calculations were performed for the first time on the gallic acid complex with iron to elucidate the structure of the IGIs, as well as to aid in the normal mode assignment of the IGIs Raman bands.

Acknowledgement

This work has been supported by the Scientific Grants Agency of the Ministry of Education of the Slovak Republic (APVV-19-0580), by the grant of the Faculty of Sciences of the P.J. Šafárik University in Košice (VVGS-PF -2021-1770) and by the project OPENMED (ITMS2014+:313011V455) from the EU Structural funds. This work has also been financially supported by the AEI Project PID2020-113900RB-I00.

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Characterization of Spanish PDO fortified wines by combining multidimensional fluorescence and chemometric approaches

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Fortified wine is a hight-quality product appreciated by its organoleptic characteristics which has increased its diversity in the market in the last years. Some of them have a great worldwide prestige, such as those Andalusian whose production is associated to the land and the growing area and are regulated by the European Union with a 'Protected Designation of Origin' (PDO). Furthermore, within the four Andalusian PDO fortified wines, there are different types according to their particular characteristics and winemaking conditions: 'Fino' and 'Manzanilla' wines that are produced by biological ageing, 'Oloroso' wines by an oxidative ageing, and 'Amontillado' and 'Palo Cortado' wines that share both types of ageing. The great diversity of fortified wines on the market, together with their high quality and high price, make them susceptible to fraud. To combat this problem, it is necessary to characterize them, establishing quality and authenticity control parameters that protect them and assure consumers that the product they are acquiring on the market has the quality declared, as well as to demonstrate and defend its identity. Consequently, there is a growing need to develop fast, inexpensive, robust and effective analytical methods that do not require any sample manipulation. Among them, excitation-emission fluorescence spectroscopy is an emerging competitive technique for food characterization, since it provides an excitation-emission landscape in a short time that may be used as a fingerprint of the wine [1,2]. This technique in combination with Parallel Factor Analysis (PARAFAC) allows to extract the most relevant information from the data allowing a simultaneous determination of fluorescent components useful for building robust models [3]. In this context, the aim of this work was to study, for the first time, the possibilities of multi-way fluorescence linked to PARAFAC in order to characterize and differentiate the different Andalusian PDO fortified wines. A visual assessment of the fluorescence landscapes obtained (Figure 1) showed that the shape of the excitation-emission spectra varies between PDOs and between the different types, which allows us to confirm a priori differentiation according to both parameters. Moreover, after developing chemometric models, the results obtained demonstrated the usefulness of the proposed methodology as a perfect combination to extract relevant chemical information and to differentiate the fortified wines considering their corresponding PDO and the different types.

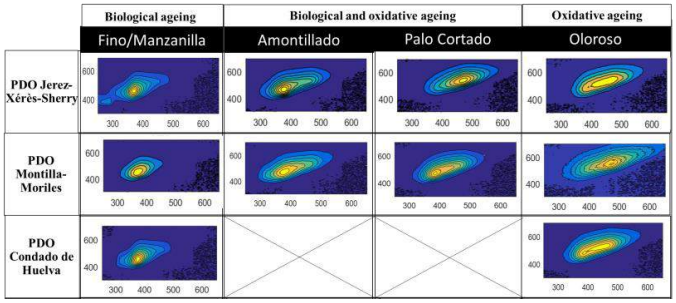

Figure 1. Example of fluorescence excitation-emission landscapes of PDO fortified wines.

Acknowledgements

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Protonation effect on the ESIPT process of 2-(2'-hydoxyphenyl)pyrimidines

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The development of fluorescence materials with switched on/off emission has attracted a great attention due to their potential applications in chemical sensing and, in particular, molecules undergoing excited state intramolecular proton transfer (ESIPT) have been widely investigated [1]. In this contribution, we summarize the theoretical and spectroscopic research about the photophysical properties of a new family of 2-(2'-hydroxyphenyl)pyrimidines that exhibit very little or no luminescence both in solution and in the solid state. The non-emissive behavior is explained by a fast ESIPT process from the OH group of 2'-hydroxyphenyl to the nitrogen atoms of the pyrimidine ring which leads to an excited tautomer (keto) with a different electronic and geometrical structure from the original excited form (enol). The protonation of the pyrimidine ring with trifluoroacetic acid provides a substantial enhancement in the fluorescence response due to the inhibition of the ESIPT process (Figure 1). This causes a reversible switch on fluorescence response detectable by the naked eye and, consequently, allows their use as solid-state acid-base vapor sensors and anti-counterfeiting agents [2]. Single crystal X-ray structure analysis allowed us to determine inter- and intramolecular interactions and molecular packing structures, which helped us to rationalize the different luminescent behavior in the solid state. All the results have been interpreted with the aid of extensive DFT and TD-DFT calculations.

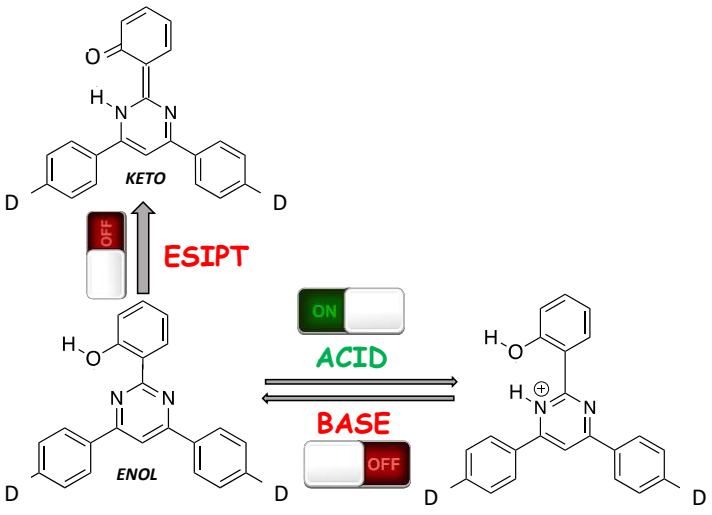

Figure 1. ESIPT and protonation processes.

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Branch detection in green and romano beans using reflection spectroscopy

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The main objective of this work has been the identification of branches among the green beans (*Phaseolus vulgaris*) and romano beans (*Phaseolus coccineus*) for the company *The Real Green Food by Gvtarra*© employing direct reflection spectroscopy measurements obtained from the samples [1]. Here, the light reflected from the samples provides information about the sample surface properties and colour that can be used to identify between branches and beans. The optical setup used consisted of an optical fiber reflectance probe (200µm, QR200-12-MIXED from Ocean Insight©), a TAKHI halogen light source from Pyroistech©, an HR4000 (368-1055 nm) and a NIR Quest (858-1721 nm) spectrometers form Ocean Insight©, see Fig.1.

Figure 1. Optical measuring setup

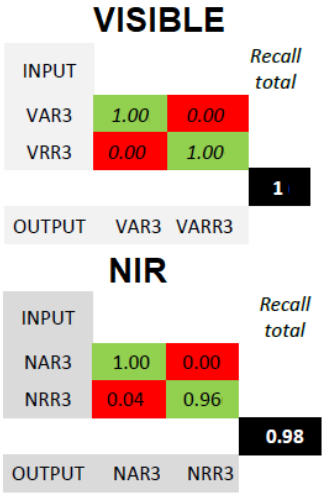

Figure 2. Results obtained for the classification of flat and round beans at stage 3 using visible and near infrared spectral information.

Round (*Phaseolus vulgaris*) and flat (*phaseolus coccineus*) bean samples were obtained from three different stages (stage1: before the product was cleaned; stage2: after the product is cleaned and cutted into pieces; stage3: after cleaning, cutting and scalding processes) of the production line and measured using the setup shown in Fig 1. Visible (VIS) and near infrared (NIR) spectral data collected from the samples (3778 samples) was used to train an artificial neural network (ANN) [2]. Obtained classification algorithm was able to detect branches with a success rate of 100% in both flat and round beans samples at stage 3 using only the VIS spectral information while using the NIR spectral information the algorithm was able to detect branches with a success rate of 98% under the same conditions (see Fig 2). Obtained results permit to foresee the utilization of a versatile and fast detection system to be used for branch detection in the production line.

Acknowledgements

This work was supported by *The Real Green Food by Gvtarra*©, Gobierno de Navarra (G20001-G2100-4701-467300), the Ministry of Science, Innovation and Universities of Spain (PID2019-106231RB-I00) and the Institute of Smart Cities PhD Student grants. Also, we thank *Pyroistech*© company for their help.

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Application of IR spectroscopy for assessing and characterizing organic and conventional virgin olive oils

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Olive oil companies, stakeholders and consumers need a proper and complete characterization of the olive oils (OOs) that are produced, marketed, and consumed in order to guarantee the quality and authenticity of the product and to avoid possible mislabeling and frauds or adulteration [1]. Within the olive oil products, some of them have a high-quality value, such as Extra virgin olive oil category and even more, the organic extra virgin olive oil (EEVOO). Those products are more susceptible to frauds due to their higher quality and therefore, their higher price [2]. Nowadays, the quality classification of OOs into the three different categories (extra virgin-EVOO, virgin-VOO and lampante-LOO) are based on the analysis of some combining physicochemical parameters and on a further sensory evaluation according to positive or negative attributes carried out by a "panel test" of experts [2], while the authentication of EEVOO is still more difficult, requiring costly and time-consuming process. Some alternative techniques have been tested in the last years in order to develop cost-efficient analytical methods able to complement these analyses. Among them, infrared spectroscopies are emerging techniques for solving food issues. In this context, the potential of infrared spectroscopies (near IR and mid IR) have been assessed for giving a rapid tool to the olive oil companies for evaluating the quality of its own products. Thereby, different olive oil samples (EVOO, VOO, LOO as well as EEVOO) were analyzed by MIR and NIR spectroscopic techniques. Spectra were preprocessed accordingly to each technique, and it was mean centered prior to modelling. The set of samples was divided into two new sets for calibration and validation approach. The best wavelength regions for predicting the authenticity criteria were selected and a proper chemical explanation of the assignment was provided to help in the interpretation of results. The ability of these bands for assessing the olive oil categories (EVOO, VOO and LOO) and for assessing the organic and conventional production (EEVOO vs EVOO) types was checked by Principal Component Analysis (PCA) and a classification approach was performed by partial least squares-discriminant analysis (PLS-DA). The satisfactory results obtained together with the advantages of this technology (e.g., fast and non-destructive methodology) would allow implementing this measurement as a rapid technique to carry out preliminary screenings of olive oil with different qualities or production process before a traditional or conventional technique (such as sensory test, gas chromatography coupled to mass spectrometry or ion mobility spectrometry).

Acknowledgements

Support for this work was provided by ["Consejería de Economía, Conocimiento, Empresas y Universidad" of the ''Junta de Andalucía" (Project P18-TP-2850)" and "Fondo Europeo de Desarrollo Regional (FEDER) y Consejería de Transformación Económica, Industria, Conocimiento y Universidades de la Junta de Andalucía, dentro del Programa Operativo FEDER 2014-2020", (US-1380836), Universidad de Sevilla].

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Assessment of the potential of excitation-emission fluorescence and Chemometric approaches for characterizing olive oils of different qualities

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In recent years, there has been a greater demand and interest on the part of the consumer towards healthier, quality foods whose production is respectful of the environment. That is, towards foods with greater added value. In this sense, the highest quality within olive oil is found in the extra virgin category (EVOO). But in addition, within this category, there are olive oils with a higher added value, such as those produced by an organic cultivation, that are organic extra virgin olive oils (OEVOO), whose production and presence on the market is increasingly greater time [1]. Moreover, other parameter that affects the quality of an olive oil is the irrigation modalities (irrigation management and dryland). Due to the high quality of these products, and, in consequence, their higher prices in the market, both EVOO and OEVOO are highly susceptible to fraud. At present, it is still sometimes difficult to distinguish between the three categories of olive oil, and even more so between the cultivation and irrigation modality. This fact makes it necessary to search for effective and robust analytical techniques able to make a characterization of these olive oils that serves to establish their quality and authenticity, and thus, protect and assure consumers that the product they are purchasing on the market has the quality declared. In this context, the techniques of selective fingerprint profiles (or "fingerprinting"), which uses spectroscopic techniques combined with chemometrics, has shown its ability to characterize and authenticate food products such as to discriminate between organic and conventional products [2,3]. Among them, multiway fluorescence spectroscopy, in combination to chemometric tools such as Parallel Factor Analysis (PARAFAC), is a powerful combination due to the technique has the advantage of being rapid and non-destructive providing an excitation-emission landscape used as a fingerprint of the olive oil, and PARAFAC allows a simultaneous determination of fluorescent components by extracting the most relevant information from the data. In this context, the aim of this work was to assess the potential of excitation-emission fluorescence linked to different chemometric tools in order to characterize and differentiate the different categories of olive oil (extra, virgin and lampante), the type of cultivation (organic EVOOs from the conventional ones), and even the irrigation modality (irrigation management versus dryland). Samples were analyzed by duplicate after a proper dilution with hexane, in the excitation range of 250—750 nm (each 5 nm) and the emission range of 250-750 nm (each 3nm). After preprocessing the data, different approaches were tested to find the best one for each of the differentiation issues (category, cultivation and irrigation modalities), considering different zones of the spectra, unfolding of the data or directly applying PARAFAC deconvolution. The results obtained demonstrated that the use of the proposed analytical with the appropriate chemometric approach could be suitable to characterize these olive oil samples as well as to differentiate them considering their category, or the cultivation and irrigation modality used.

Acknowledgements

Support for this work was provided by ["Consejería de Economía, Conocimiento, Empresas y Universidad" of the ''Junta de Andalucía" (Project P18-TP-2850)" and "Fondo Europeo de Desarrollo Regional (FEDER) y Consejería de Transformación Económica, Industria, Conocimiento y Universidades de la Junta de Andalucía, dentro del Programa Operativo FEDER 2014-2020", (US-1380836), Universidad de Sevilla].

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Aerosol pollen classification using laser-induced breakdown spectroscopy (LIBS)

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Ambient air contains a great variety of particles, including dust, spores and pollens among others that can affect the human health depending on both, their composition and size. Thus, the chemical characterization of biological and non-biological materials is strongly demanded nowadays. In the last few years, laser-based techniques, including Raman spectroscopy, laser-induced fluorescence (LIF) and laser-induced breakdown spectroscopy (LIBS), have been employed for aerosol analysis. The analysis of aerosols and particulate matter by LIBS has not been a trivial task, resulting in low sampling rates and a more than significant signal variability [1]. Fundamental aspects of the plasma-particle interaction, which plays a larger role than direct interaction with the laser pulse, and how it affects the analytical signal were reported by Hahn et al [2]. In the last few years, research is mostly focused on a critical and deeper understanding of the laser-matter interaction at the nanoscale. The use of chemometric tools and the design of new experimental set-ups have improved the performance of LIBS for this application [2]. In this sense, Fortes et al. [3] combined optical catapulting and LIBS for solid aerosols analysis. Using this technology, a solid aerosol was created inside a sampling chamber (without any mechanical contact and free from interferences from the substrate) and then, analyzed by LIBS. In a previous work, authors demonstrated a size-dependent seeding-like effect in aerosol analysis. Thus, the light coming from the core of several small-sized plasmas was synergistically added up to result in a more intense LIBS signal. Consequently, the size threshold for the complete particle dissociation turns crucial in the analysis of particulate matter [4].

In this work, different aerosolized pollen species were analyzed and detected by LIBS. Qualitative analysis reveals the presence of C, H and Ca as majority elements, while Cu, Al, Mg, Ba and Si were identified as minor species. Based on the chemical composition, the different species were classified using chemometric analysis.

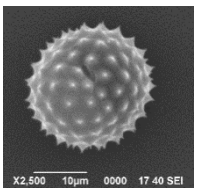

Figure 1. SEM image of *Ragweed pollen*.

Acknowledgements

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Teaching Spectroscopy

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Being spectroscopy an instrumental technique used in different fields of science and used to determine the composition, whether qualitative or quantitative, of a sample, it is necessary for students to know it even at an early age such as early or middle adolescence.

Based on Ausubel's theory of meaningful learning [1] or Carl Rogers' theory of personality development [2], adolescents are predisposed to learn concepts if they were able to understand the utility and its application to their daily problems, all this in a pleasant environment.

From adolescence, young people are capable of developing hypothetical-deductive thoughts and logic, both of which are essential for solving scientific problems.

Teenagers' way of thinking compared to children or adults is that possibility takes on a life of its own, every logical thought is a possibility even if that idea cannot be turned into reality. This means that the great ideas and theories of the modern world that the great geniuses developed in adulthood had a beginning in adolescence. Thus, Albert Einstein himself came to the theory of Relativity because as a child while he was running he wondered how he would see a ray of light if he could run at the same speed [3].

The first approach to the spectroscopic theory must take into account a problem or some situation in which they are involved as often as possible, such as the analysis of contaminants in fast food or analysis of the drinks most consumed by adolescents. The use of 3D images, computers, augmented reality glasses that make them feel like scientists solving a mystery, can increase their desire to learn about the different techniques used in spectroscopy.

Subsequently, the approach can be from different disciplines such as physics, chemistry or mathematics. Being mathematics the science that can be used at an earlier age, for example with the theoretical preparation of a calibration curve or the practical case of calculating heavy metals in a food sample from a given curve and intensities.

Due to the wrong idea that adolescents have of their importance in the social world, and the cognitive bias that this is associated with, all of this is translated into the personal fable. In this fable, adolescents see themselves as saviors of the world or winners of the Nobel Prize, this can be strengthen with the use of spectroscopic techniques since solutions to personal or social problems can be forged in their heads with the new techniques learned.

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Detection of Ibuprofen and Caffeine Pollutants by Surface-Enhanced Raman Spectroscopy

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Detection of emerging contaminants in aquatic environment, such as ibuprofen and caffeine, is studied by Surface-Enhanced Raman Spectroscopy (SERS) using Ag nanoparticles (AgNPs) synthesized with β-cyclodextrin (βCD) as reducing agent [1]. Different molar ratios of Ag^+:βCD in the synthesis route have been investigated by using trans-cinnamic as test molecule in order to select the AgNPs with a good signal/noise ratio. The effectiveness of the β-cyclodextrin colloids (Ag@βCD) as SERS substrate was also checked and compared with other silver sols obtained by other reducing agents such as citrate, borohydride and hydroxylamine. All synthesized SERS substrates have been characterized by TEM spectroscopy (Figure 1). The experimental results indicate that Ag@βCD with the more diluted Ag^+:βCD molar ratio (Ag@βCD3) shows the best SERS signal reaching a trace concentration of 0.5 μM in the case of trans-cinnamic acid. Ag@βCD3 sols also show the best sensitivity for detecting ibuprofen and caffeine, reaching the lowest limit of detection (0.1 mM). Thus, the synthetic route for Ag@βCD sols provides an improved SERS substrate to detect organic pollutants with better performance than other standard silver sols.

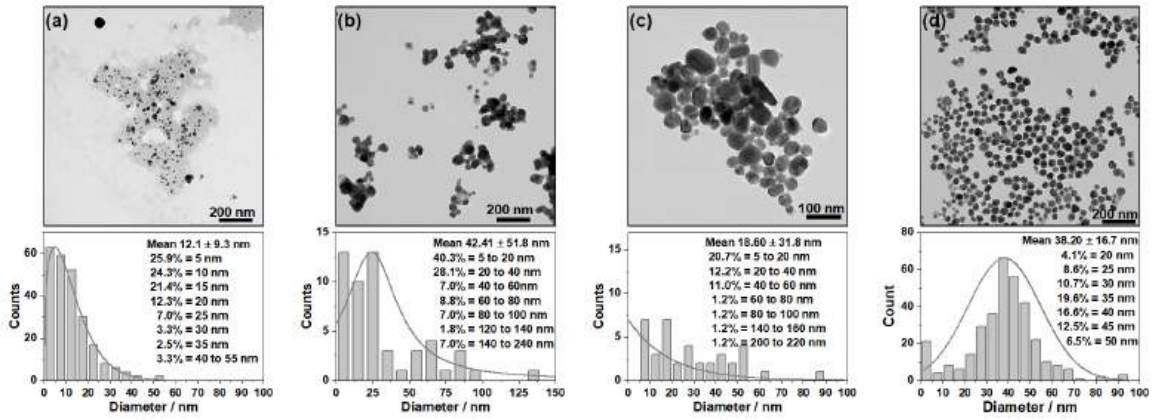

Figure 1. TEM images (above) and histogram distribution (below) for the different synthesized NPs, (a) Ag@BH; (b) Ag@HX; (c) Ag@Citr and (d) Ag@βCD3.

Acknowledgements

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Aluminium doped zirconia nanoparticles-modified electrochemical sensor for authenticity controlling of vanilla flavours in food samples

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Nowadays, mixed food products are becoming very popular in the food industry [1] and their consumption in Europe has significantly increased. Thus, the quality control in this area is crucial to avoid the occurrence of any side effects. Vanilla is a type of tropical climbing plant [2] considered a major flavoring product finding its application in many fields, namely food, cosmetics and pharmaceuticals. It is naturally obtained from vanilla plantifolia exctract and includes vanillin (Van) as the major constituent, together with several related compounds such as p-Hydroxybenzaldehyde (p-HB), p-Hydroxybenzoic acid (p-HBA), Vanillic acid (VA) and Vanillyl alcohol (V-OH) [3]. Given its popularity, the high demand and cost of natural vanilla give rise to many adulterations carried out using Ethyl vanillin (EVan) or synthetic Vanillin. In this work, a rapid and sensitive technique for frauds determination in vanilla flavors was developed. The method comprises separation by liquid chromatography followed by an electrochemical detection using a homemade screen-printed carbon electrode modified with aluminium doped zirconia nanoparticles (Al-ZrO2-NPs/SPCE). The prepared nanomaterials (Al-ZrO2-NPs) were characterized by using X-ray diffraction (XRD), transmission electron microscopy (TEM) and energy dispersive X-ray (EDX). This method allows the determination of six phenolic compounds of vanilla flavors, namely; vanillin, p-hydroxybenzoic acid, p-hydroxybenzaldehyde, vanillyl alcohol, vanillic acid and ethyl vanillin in a linear range between 0.5 and 25 µg.g-1, with a relative standard deviation value of 4.76%. While the limit of detection and quantification were 0.14 µg.g-1 and 0.48 µg.g-1, respectively. In addition, the Al-ZrO2-NPs/SPCE method displayed good reproducibility, high sensitivity and good selectivity towards the determination of the vanilla phenolic compounds, making it suitable for the determination of vanilla phenolic compounds in vanilla real extracts products.

Acknowledgements

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Determination of biological markers oxidative stress by capillary liquid chromatography mass spectrometry

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Oxidative stress is defined as the imbalance between reactive oxygen species (ROS) and the ability of the body to counteract with antioxidants [1]. Though, the formation of ROS is the main cause of the cellular damage occurrence in the organism. Oxidative stress mechanism can be caused by multiple factors, exogenous (high temperatures, ultraviolet radiation, food and chemical) or endogenous (mitochondrial action), which action, regardless of the type of source, might be harmful to living being [2]. In order to understand the mechanism of action of ROS it is required analytical methodologies and specific biological samples to carry out their detection and analysis. Distinct methods have been used to measure the extent and nature of oxidative stress, ranging from oxidation of DNA to proteins, lipids, and free amino acids. The present work describes an HPLC-MS method involving the separation of Tyrosine from 3-NItrotyrosine, 3-Chlorotyrosine, 8-hydroxy-2'-deoguanosine and 4-Hydroxynonenal by HPLC and MS quantification under positive-ion chemical ionization conditions. Determination of the biomarkers oxidative stress amounts was allowed in a concentration range of 5–500 µg.L-1. The limit of detection, limit of quantification and standard deviations achieved were lower than 2 µg.L−1, 6 µg.L−1 and 4.5 %, respectively. The described method was applied for the quantification of oxidative damage in DNA during an experimental induction of oxidative stress by exposing several birds to a pro-oxidative substance (diquat dibromide) when feathers were being developed and melanins produced.

Acknowledgements

Financial supports from the Spanish Ministry of Science and Innovation (PID2019-104381 GBI00), Junta de Comunidades de Castilla-La Mancha (SBPLY/17/180501/000262) and University of Castilla-La Mancha (2020-GRIN-28882) are gratefully acknowledged.

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DFT assisted interpretation of the solid state VCD spectra of NSAIDs: ketoprofen, naproxen and ibuprofen.

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Ketoprofen, naproxen and ibuprofen are propionic acid derivatives that belong to the family of the so-called non-steroidal anti-inflammatory drugs (NSAIDs) and can exist in two enantiomeric forms which exhibit different biological activity. It is well known that the pharmaceutical properties reside exclusively in their S-form. The nature of the inter/intra-molecular interactions present in the crystal structure and, thus, their crystal morphology and plausible polymorphs are of capital interest for the pharmaceutical industry [1], since their different physicochemical properties [2] will affect production process [3] and even their pharmacological properties.

In this work, we report and analyze the firstly recorded VCD spectra of the biologically active enantiomers of these species in solid phase. The interpretation of the spectral features has been assisted with DFT calculations simulating the main structural synthons present in the crystal structure previously obtained by X-ray diffraction [4-6]

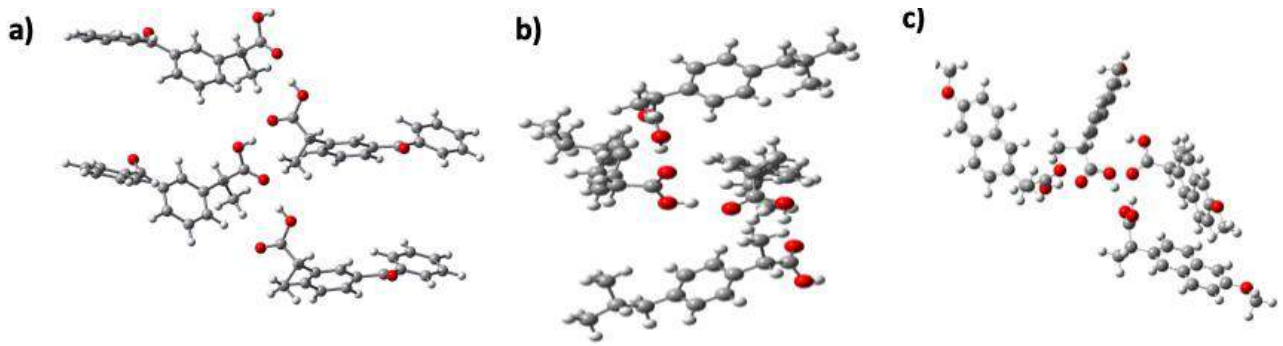

Figure 1. a) tetramer ketoprofen, b) tetramer ibuprofen and c) tetramer naproxen.

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Introduction to meteor spectroscopy within the UMA/SMA Fireball and Meteor Detection Network

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Spectroscopy is an important aspect of meteor studies as it enables the chemical composition of incoming meteoroids to be determined. For this purpose, the Fireball and Meteor Detection Network of the University of Malaga (UMA) and the Malaga Astronomical Society (SMA) is distributed in thirteen locations throughout Spain. Currently the network has fourteen stations in operation and another four are in the progress of being installed. In addition, this network has the possibility to use the allsky cameras of the Global BOOTES Network (IAA/CSIC). In all of them, the necessary software for the control of the instrumentation and for the processing of images and identification of meteors has been made by member of SMA and is free use by the network participants.

In this work we will try to obtain and analyse the emission spectra of several meteors captured from the station located at the El Torcal Observatory (OAT). In this camera a 200 lines/mm Star Analyzer 200 type diffraction grating (Paton Hawksley) has been adapted, which has been placed between a Sigma 4.5 mm fisheye objective and a Zwo ASI1600MM monochrome detector indicated for planetary and deep sky images due to its high sensitivity sensor. Meteors are particles that interact with our atmosphere, and they do not materialize on the earth's surface so we can only know their composition and nature using these detection techniques during the short period of time that the luminous phenomenon lasts. Typical spectra show the bright lines of metals such as calcium (Ca), sodium (Na) or magnesium (Mg).

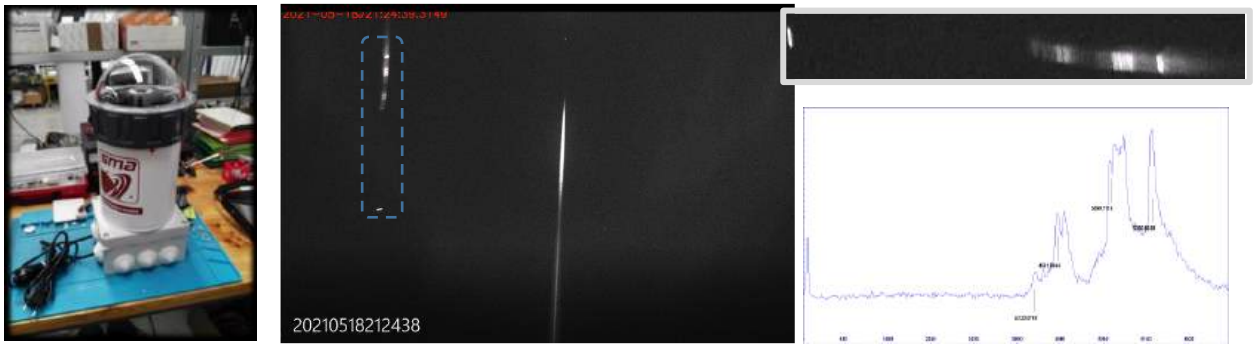

Figure 1. Detection camera and meteor spectrum image and profile.

Acknowledgements

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Sample preparation effects on near infrared (NIR) data modelling of acidic and neutral forms of cannabinoids in *Cannabis sativa* flowers

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Cannabinoids are a group of compounds with a high medical interest [1]. They are found in cannabis flowers mainly in their acid form. The conversion of acid forms into neutral is favoured by storage conditions, like heat or other degradation processes [2][3]. NIR spectroscopy has been proved as a suitable method for cannabinoids quantification [4]. Homogeneous sample composition and particle size joined to GC-MS reference method [3] are normally used. Due to intrinsic GC-MS sample heating, acid forms are lost and only total cannabinoid content can be assessed. The aim of this work is the development of NIR models to predict the cannabinoids content in *Cannabis sativa* ground dried flowers. The main novelty of the work is the separately modelling of acid and neutral forms and the comparison of the effect of different sample treatment protocols in models' performance. *Cannabis sativa* flower samples analysed by CTAEX were used, from 2 different experiments. In Exp. 1 samples were not homogenized and measured directly as received; samples of Exp. 2 were prepared following a standardized protocol. NIR spectra were acquired by a FT-NIR Antaris II (Thermo Fisher®), using a spinner module. Reference values were obtained by HPLC Agilent®1100. Reference values reveal differences between experiments and inhomogeneous data distribution along the working range (**Fig. 1a**), hindering the subsequent models' robustness. Spectra show poor differences between experiments (**Fig. 1b**), indicating that the use of the spinner module could compensate part of the inhomogeneity of the samples. Modelling total cannabinoid content with Exp. 1 data yielded similar calibration results than those reported previously [4] and some preliminary calibration models with separated forms showed good performance (r^2 values > 0.7). These initial results evidence the potential of NIR to quantify separately the acid and neutral forms of cannabinoids. Moreover, the comparison between Exp. 1 and 2 will allow to determine the effects of working with different ranges and sample treatments in the final models' accuracy.

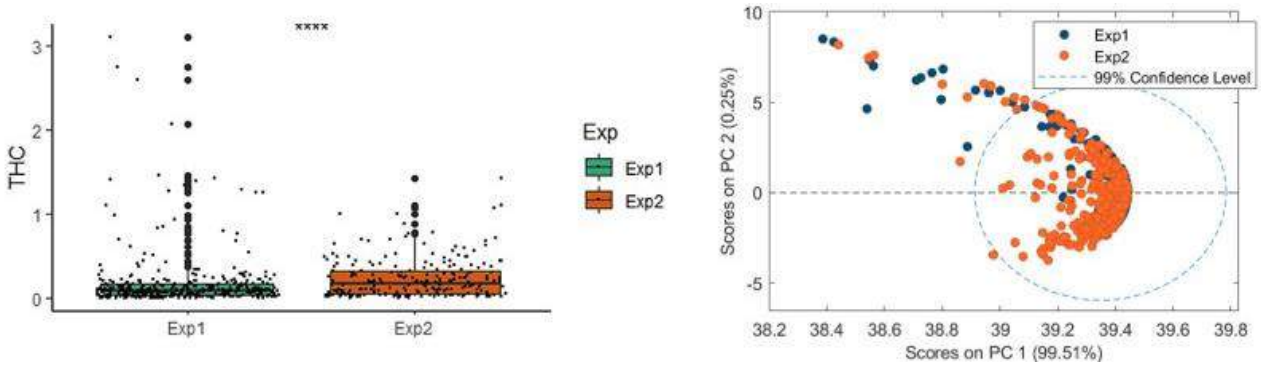

Figure 1. Samples comparison: a) Boxplot of neutral THC form contents and b) PCA of their SNV normalized spectra.

Acknowledgements

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Study by spectroscopic techniques of the process of protein corona formation onto platinum nanoparticles

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Platinum nanoparticles (PtNPs) have very interesting properties with applications in different fields, being the biomedical field one of the most important specially in relation to antitumoral therapies [1]. When PtNPs are dispersed in physiological media, they do not act as inert entities. In fact, different macromolecules, mainly proteins, present in this medium can be adsorbed on the surface of the NP and this process determines its behaviour in biological systems. This new nano-bio-identity is a dynamic structure called protein corona (PC). This structure is described to have two parts, known as hard corona (strong interactions between proteins and NPs) and soft corona (weaker interactions) [2]. Also, physico-chemical characteristics of PtNPs are important factors that influence the PC formation. Nowadays, the PC is considered as key parameter that must be investigated to understand the behaviour, fate, pharmacological profile, and toxicological risk of PtNPs in biological systems, but they are complex studies, and the currently available information is very limited.
The use of different techniques is required,and, among them, spectroscopic techniques stand out due to their simplicity and low cost, however they have been scarcely used. Therefore, the aim of this work is to study the potential of spectroscopic techniques, such as dynamic light scattering (DLS), absorption of ultraviolet-visible radiation (UV-vis) and fluorescence emission for the study of the process of formation of hard and soft PC onto PtNPs using bovine serum albumin (BSA) (the most abundant protein in plasma) as a model protein. The hard and soft corona was differentiated with a previous treatment by centrifugation. An increase in the hydrodynamic diameter related to the formation of the protein corona was observed by DLS technique, as well as differences in the formation process of the hard and soft corona. The adsorption process of BSA on PtNPs was confirmed by UV-vis absorption spectroscopy through changes in the wavelength maximum absorption of the protein. By fluorescence emission studies, it was possible to observe the quenching process carried out by PtNPs in the native emission of BSA. Thus, it has been proven that spectroscopic techniques can provide highly relevant information for the study of PC formation and can help in the comprehension of NP behaviour in future biomedical applications.

Acknowledgements
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The role of Optically Stimulated Luminescence (OSL) dating in archaeological sites

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Absolute chronologies provide key information for understanding archaeological sites. Luminescence signal (260-380 nm) emited from quartz when stimulating with blue light is correlated to the amount of ionizing radiation received over time. The age since burial is then given by the relation

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

where D_e is the accumulated dose estimated from the luminescence respose, and D_R is the environmental dose rate. The age range that OSL can cover is given by the dose response curve (Fig. 1), which generally covers from 50 years to 400 ka (in the most optimal conditions). We present here a series of archaeological sites were this technique has been applied.

At Casas del Turuñuelo site (Fig. 2), a Tartessian building where 41 buried horses were found, OSL is providing the ages of construction and abandonment of the building. At the Dolmenes de Antequera site, OSL has provided the age of construction, which could not be dated with any other technique due to the time range and the lack of other material but sediment. For Gorham´s cave complex, OSL is establishing the time of the Neanderthal occupation of the caves which spans over 100 ka. At the Olduvai Gorge and Atapuerca, both reference sites on human evolution, the technique is often applied at the highest dose range possible. The diverse nature of these sites and applications highlights the versatility of the technique.

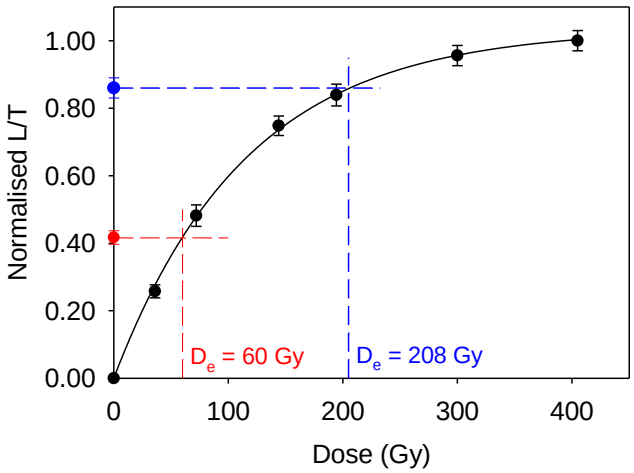

Figure 1. Dose response curve. Two natural signals and corresponding equivalent doses are indicated.

Figure 2. View of Casa del Turuñuelo, Guareña, Badajoz, Spain.

Acknowledgements

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Spatially resolved excitation temperature in the Solution-Cathode Glow Discharge

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The solution-cathode glow discharge is a liquid electrode atmospheric pressure plasma used in elemental analysis of aqueous samples, typically coupled to optical emission spectroscopy. Its simplicity and low consumption (less than 100 W of DC power and no requirement for plasma gas) together with its competitive limits of detection makes it an attractive alternative to established elemental analysis techniques, such as atomic absorption spectrometry or inductively coupled plasma atomic emission spectroscopy. As an atmospheric pressure glow discharge, it presents a spatial non uniform emission along the vertical axis of the plasma, with specific emission patterns for different atomic and molecular species [1, 2]. In the present communication the Cu emission intensity and excitation temperatures were measured/calculated with spatial resolution to provide a better understanding of the behaviour of the species within the plasma. Moreover, as real samples with variable salt contents lead to changes in the emission signals from the analytes (matrix effects) [3], different concentrations of NaCl were introduced in the solution to observe the change of Cu emission line profiles and excitation temperatures. The addition of NaCl changes the profile of Cu emission lines, depressing its emission near the cathode and increasing it near the anode. Consequently, the addition of NaCl modifies Cu excitation temperature, showing slight depression in areas close to the cathode.

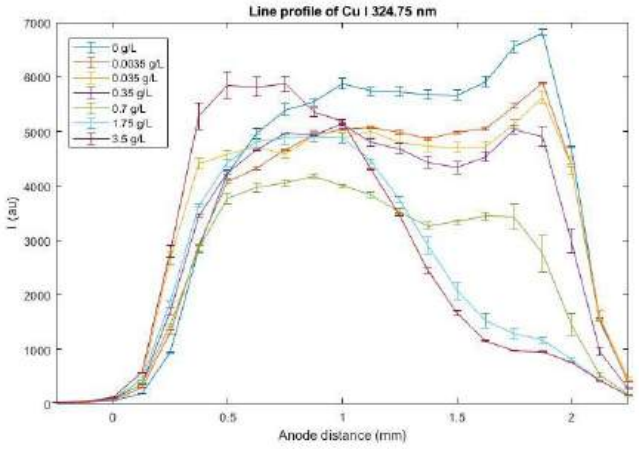

Figure 1. Cu I 324.75 nm emission line profile along the plasma vertical axis at variable NaCl concentrations.

Acknowledgements

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MRS and µEDXRF analysis on Roman wall paintings from the archaeological site of Cástulo (Linares, Spain)

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The archaeological complex of Cástulo (Linares, Spain) is one of the most significant and representative heritage assets of the Iberian and Roman presence in the Iberian Peninsula. Of special importance are the Roman wall paintings located in building D (late I- II A.D.), interpreted as the building for the imperial cult of the Roman emperor Domitian. New spectroscopic analyzes have been carried out on a new interesting Roman wall paintings group of this building, so increasing the results that had already been obtained previously [1]. The samples (Figure 1) represent various plant, human, and animal decorative motifs and have been analyzed using a non-destructive analytical approach, which includes Micro-Raman spectroscopy (MRS) (employing portable and laboratory equipment) and micro Energy Dispersive X-ray Fluorescence (µEDXRF) (mapping and one-pointed measurements).

The results obtained allow identifying and establishing the repertoire of raw materials used in the elaboration of these paintings: cinnabar, hematite and lead compounds (reds), goethite (yellow), Egyptian blue, green earths (rich in Cr in one case) [2], amorphous carbon (black) and calcite (white). The preference for cinnabar and Cr-based green over other more common pigments points to a special symbology, relevance and exclusivity of the decorated spaces in building D. On the other hand, knowledge of the materials used in the decoration increases the effectiveness of the conservation and restoration treatments applicable in the future.

Figure 1. Roman wall paintings from the archaeological site of Cástulo (Linares, Spain).

Acknowledgements

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Monolayers of plasmonic nanoparticles prepared in electrostatically-driven self-assembly as effective substrates for surface-enhanced spectroscopic methods

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The aim of the research was the formation of silver, gold, and platinum monolayers based on the electrostatically-driven deposition of nanoparticles on oppositely charged solid surfaces and the evaluation of the usefulness of these substrates for the detection of adsorption behaviour of erlotinib (drug introduced in the non-small cell lung cancer therapy). For this purpose, the technique that combines atomic force microscopy and infrared spectroscopy (AFM-IR) was applied to provide the detailed characterization with ultra-high spatial resolution. The nanoparticle monolayers were formed on poly(allylamine hydrochloride) (PAH)-modified Si/SiO_2 sensors under flow conditions using quartz crystal microbalance (QCM). The adsorption of erlotinib (ERL) molecules on the monolayers was investigated with the use of QCM and streaming potential measurements. Hereby, the mass of drug adsorbed on monolayers of given coverage and the electrokinetic properties of formed drug-metal nanoparticle systems were determined. The tapping AFM-IR mode was used for the collection of IR maps and spectra of the formed erlotinib-nanoparticle systems.

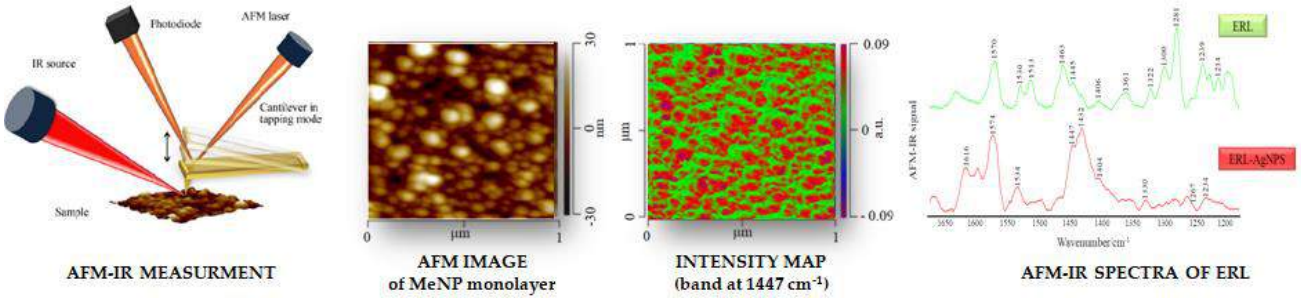

Figure 1. Experimental scheme.

It was found that erlotinib interacts with the silver nanoparticle monolayers through phenyl rings and methoxy moieties, while quinazoline, amino, and ethoxy moieties appear to be farther from the surface. In the case of gold nanoparticle monolayers, the interaction occurs through both the phenyl ring and the quinazoline moiety. The aliphatic groups of erlotinib directly participate in this interaction. Erlotinib indicates strong interaction with platinum nanoparticles mainly through the quinazoline and the amino moieties. The ethylene bridge takes part in the formation of the conjugate while methoxy moiety and phenylacetylene ring remain at a certain distance from the platinum surface. The comparison of obtained results showed that the adsorption behavior of erlotinib strongly depends on the type of plasmonic nanoparticle monolayers.

Acknowledgments

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XPS and Raman Spectroscopy as a combined tool for study of N coordination in diluted InGaAsN

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Dilute nitrides III-V-N alloys are arsenides and phosphides-based materials with a small nitrogen content which lends singular properties to the obtained semiconductor mainly with applications to telecom lasers and highly efficient multijunction solar cells. Nevertheless, the correct nitrogen incorporation into the semiconductor material is not something trivial owing to its electronegativity and smaller atomic size when it is compared to As. The presence of defects and the structural distortion of the GaAs matrix affect the material electronic structure and the band-gap. In particular, the nearest-neighbour bonding configuration of the N in InGaAsN has proven its influence on the band-gap [1,3]. One way to improve the suitable N bonding is by developing a final thermal treatment. In this work the influence of the different thermal treatment are studied by different spectroscopy technologies.

Dilute nitrogen samples have a small quantity of nitrogen; therefore, its quantification and the identification of its chemical environmental is always a difficult task. In that sense, XPS and mainly angle resolved-XPS have demonstrated as a valuable tool for such purpose [2,3]. Figure 1 shows that it is possible to fit the N 1s global signal in four different contributions: intersticial N-N, a share peak where N-As is involved and N-In. The N 1s core level peak assignation has been corroborated with the Raman spectra analysis for these samples.

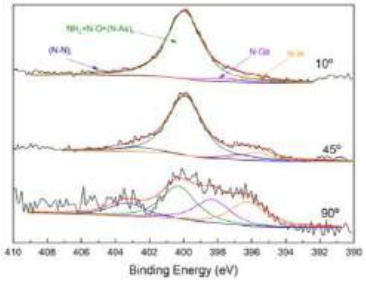

Figure 1. N1s core level deconvolution corresponding to a InGaAsN layer.

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Spectroscopic analysis of mushrooms by Surface-enhanced Raman Scattering (SERS)

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Mushrooms have always been considered an important source of food and biological active compounds with several medicinal properties. Nowadays, quite a few species of ligninocellulolytic fungi such as *Lentinula edodes*, *Ganoderma lucidum*, *Pleurotus cornucopiae* and *P. ostreatus*; and symbionts such as truffles (*Tuber* spp.) are successfully cultivated in the world.

In recent years, different methods were used to study the quality and chemical composition of fungi. Among these, Fourier transform infrared (FT-IR) and FT-Raman spectroscopy techniques has been successfully applied to identify different mushroom species (*Boletus* spp., *Ganoderma* spp., *Agaricus bisporus*, *Mucor rouxii* and *Mortierella* sp.) [1-3], for quantifying the total content of polysaccharides in the mycelium of *G. lucidum* [4] as well as the glucans and ergosterol contents in *Pleurotus* spp. [5] or to study the composition of mushrooms grown on different substrates [6]. However, the structural biomolecules components existing in the mycelium or in fruiting bodies may produce strong fluorescence emission that overlap the Raman radiation, thus avoiding their analysis by Raman.

SERS spectroscopy is a spectroscopic technique that uses metal nanoparticles (NPs) for the Raman signal enhancement of molecules adsorbed on the NPs surface. In addition, the ability of SERS is to quench the macromolecules florescence. Using the metal nanoparticles of different nature, we have performed a fast procedure to analyse and identify different chemical compounds from the fruiting bodies of six fungal species: *L. edodes*, *G. lucidum*, *P. cornucopiae*, *P. ostreatus*, *T. aestivum* and *T. magnatum*.

The results obtained showed that each analysed species is characterized by a species-specific spectrum. The vibrational assignments are proposed for the most important features, which can be mainly attributed to nucleic acids and aromatic polycyclic molecules. The present study demonstrated that SERS can be applied in the fast analysis of mushrooms based on their different biomolecular composition without any chemical treatment.

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Tuning robust hotspots in plasmonic chains

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Periodic arrays of metallic nanoparticles can host hotspots that are protected from disorder and perturbations. These resonances are robust because their frequency is fixed and they are isolated from the rest of the states i.e., they are in a gap in the spectrum. Geometry and material of the nanoparticles can be used to tune these plasmonic resonances. Previously, a chain of nanospheres, analogous to polyacetylene,
was studied [1]. These chains present robust hotspots at the surface plasmon frequency of the nanoparticle. Here we propose an alternative plasmonic analogue of polyacetylene: by considering periodic chains of equidistant spheroidal nanoparticles [2], we can use their orientations to tune the bonds between nanoparticles and open a gap in the spectrum. This will lead to robust plasmon resonances localised at the edges of the chain that can be excited separately or simultaneously by a external electric field.

Figure 1. Topological plasmonic chain of spheroidal silver nanoparticles

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M.V.	Cañamares	OC19	43
M.V.	Cañamares	OC20	44
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