26-28 DE OUTUBRO DE 2020

LISBOA

ANALÍTICA 2020

10º ENCONTRO DA DIVISÃO DE QUÍMICA ANALÍTICA

EVENTO VIRTUAL / ONLINE MEETING

https://analitica2020.events.chemistry.pt/

LIVRO DE RESUMOS

BOOK OF ABSTRACTS

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SOCIEDADE PORTUGUESA DE QUÍMICA

TÍTULO
Livro de Resumos do Analítica 2020 – 10º Encontro da Divisão de Química Analítica

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EDITOR
Sociedade Portuguesa de Química
Av. da República, 45 - 3º Esq
1050-187 Lisboa - Portugal
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DATA
Outubro 2020

Bem-Vindos / *Welcome*

O ANALÍTICA 2020, 10º Encontro da Divisão de Química Analítica da SPQ, começou por ser planeado para ter lugar em Lisboa, de 26 a 28 de Outubro de 2020. As circunstâncias especiais que surgiram, fruto da pandemia COVID-19, levaram a que a decisão sobre as instalações tivesse ficado em suspenso. Com o desenrolar dos tempos, o tradicional modelo presencial revelou-se uma hipótese remota, de difícil, se não impossível, implementação. Analisadas as várias implicações, avançamos para a realização um evento virtual.

O programa constará de lições plenárias, palestras convidadas, comunicações orais, apresentações em painel e debates sobre todos os temas da Química Analítica moderna, tanto na perspetiva de métodos e procedimentos de medição, como no que toca à tipologia dos sistemas materiais em estudo, visando entre outras, as áreas Ambiental, Forense, Alimentar, Farmacêutica, Industrial e Fundamental.

Sendo a Sustentabilidade Ambiental um grande objetivo da sociedade atual e as 17 metas estabelecidas pelas Nações Unidas para a década 2020-2030 um desafio para a Comunidade Analítica, a meta 14 leva-nos à redução da acidificação dos oceanos, o que requer o estabelecimento de metodologias de medição adequadas aos fins em vista, que permitam a comparabilidade de valores medidos, no tempo e no espaço. Tendo em conta este e outros aspetos emergentes, fundamentais e aplicados, de fortes implicações, considerou-se oportuno realizar a 26, um Dia do pH/ pH Day, na modalidade de curso pré-conferência. Conscientes do momento de grandes desafios e incertezas que globalmente atravessamos, empenhamo-nos em promover um evento de elevada qualidade, oportunidade de partilha e aprendizagem, para o qual convidamos a comunidade analítica a participar, contribuindo com a sua presença e com apresentações científicas e técnicas dentro das respetivas competências.

Christopher Brett, *Chair* e *Presidente da Divisão da Química Analítica*

Conteúdo / *Content*

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Sociedade Portuguesa de Química (Portuguese Chemical Society)
Av. República n º45, 3º Esq.
1050-187 Lisboa,
Portugal
E-mail: eventos@spq.pt
Phone: +351 21 793 4637
Fax: +351 21 795 2349

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Informação Geral / *General Information*

Apresentações orais

O encontro contará com Lições Plenárias (*PL*) de 60 minutos e Palestras Convidadas (*KN*) de 30 minutos. As Comunicações Orais (*OC*) terão uma duração de 15 minutos.

Apresentações em painel & Sessão Pitch

Os painéis estão disponíveis durante todo o Encontro na plataforma virtual da SPQ. Um dos autores das apresentações em painel (*PP*) irá apresentar o seu trabalho numa sessão pitch prevista na programação do Encontro. As apresentações *poster-pitch* consistem numa apresentação oral sucinta do trabalho, com uma duração de 3 minutos.

Prémios

Serão atribuídos:

- um prémio e duas menções honrosas para as melhores comunicações orais;
- um prémio e duas menções honrosas para as melhores apresentações em painel.

Programa / *Program*

	Um Dia com o pH (pH Day)	**ANALITICA2020**			
	26 outubro	**27 outubro**		**28 outubro**	
9:00	Introdução *Christopher Brett*				
9:30	Princípios químicos, conceitos e desenvolvimentos *Filomena Camões*	Sessão de Abertura / Opening Ceremony		PL 2	
10:00		PL1			
10:30				Intervalo / Break	
11:00	Intervalo / Break	Intervalo / Break			
11:30	Concepções, alternativas *Todos*	KN 1	KN 2	KN 4	KN 5
12:00		OC1 OC2	OC3 OC4	OC19 OC20	OC21 OC22
12:30	Almoço / Lunch				
13:00					
13:30					
14:00	Medição e cálculo - Métodos e procedimentos adequados e procedimentos adequados ao fim em vista *Filomena Camões*	OC5 OC6	OC7 OC8	OC23 OC24	OC25 OC26
14:30		Poster PITCH P1-P17 e P34	OC9 OC10 OC11	Poster PITCH P18-P33	OC27 OC28 OC29 OC30
15:00					
15:30	Intervalo / Break	Intervalo / Break		Intervalo / Break	
16:00	Exemplos de aplicação *Todos*			Debate / Discussion Prémios / Awards	
16:30	Projectos: 1 - Sustentabilidade Ambiental 2 - Escala Unificada *Filomena Camões*	OC12 OC13 OC14 OC15	OC16 OC17 OC18		
17:00				Encerramento / Closing Ceremony	
17:30	Debate / Discussion	KN 3			
18:00	Encerramento / Closing	Assembleia geral da Divisão de Química Analítica / GA ACD, SPQ			
18:30					
19:00					
19:30					
20:00					

Um Dia com o pH / pH *Day*

O dia será dedicado ao “parâmetro químico mais medido”, ilusoriamente fácil para muitos, pH.

Numa abordagem que pretende ser abrangente, clara, atual e cientificamente correcta, incutindo aos participantes a segurança da compreensão e a revelação das possibilidades e dos desafios a ele associados, serão focados aspetos tais como:

- Princípios químicos, conceitos e desenvolvimentos,
- Concepções alternativas,
- Métodos e procedimentos de medição e cálculo adequados ao fim em vista,
- A actualidade em projectos internacionais - Sustentabilidade Ambiental; Escala Unificada.

Programa Científico Detalhado / *Detailed Scientific Program*

	27 outubro	
[1]ID da reunião: 849 8307 0340		
9:30 h	**Sessão de Abertura / *Openning Session*** *Presidente da SPQ, Director da FCUL/ Chair e Co-Chair*	
10:00 h	**Moderadora: *Filomena Camões*** **PL1.** Unified pH – from concept to experimental realization ***Ivo Leito***, Universidade de Tartu- Estónia	
11:00 h	**Intervalo / Break**	
11:30 h	**Sessão / *Session* A** **[1]ID da reunião**	**Sessão / *Session* B** **[2]ID da reunião:** 818 6507 7273
	Moderadora: *Margarida C. Santos*	**Moderadora: *Cristina Oliveira***
	KN1. Magnetically responsive iron-carbon composites for micro-organic contaminants adsorption. ***Vânia Calisto***	**KN2**. Rethinking the teaching of analytical chemistry for industry 4.0. ***Manuel Matos***
12:00 h	**OC1**. Microwave-driven production of carbon adsorbents from biomass waste and their application to the removal of antibiotics from water. ***Luciana Rocha*** **OC2.** Antibiotics in aquaculture waters: Can carbon dots/titanium dioxide nanohybrids accelerate their photodegradation? ***Vitória Louros***	**OC3**. Analytical strategies to determine nanoparticles encapsulation efficiency and quantity. ***Sara S. Marques*** **OC4**. Microfluidic technologies for high throughput drug screening enzymatic activity and inhibition assays. ***Sarah A.P. Pereira***
12:30 h	**Almoço / Lunch**	
14:00 h	**Moderadora: *Vânia Calisto***	**Moderadora: *Ana Brett***
	OC5. Phenolic characterization of an hydroethanolic extract obtained from Satureja montana L. with an antibacterial activity and potential application on the control of plant pathogens. ***Daniel O. Carvalho*** **OC6**. Waste-based magnetic biochar/TiO2 as a catalyst in the photodegradation of antibiotics from aquaculture water. ***Diogo Pereira***	**OC7**. Hair analysis: The usefulness of microextraction for sample cleanup. ***Tiago Rosado*** **OC8**. Determination of urinary iron by colorimetric detection with a novel microfluidic paper-based analytical device. ***Francisca Ferreira***
14:30 h	**Poster Pitch*** **PP1 – PP17 e PP34**	**OC9**. Determination of aldehydes in beer using gas-diffusion microextraction and high-performance liquid chromatography with UV detection. ***Inês Ferreira***
		OC10. Infection markers in wounds. ***Fátima Mota*** **OC11**. Gumbos and nanogumbos: Tunable materials for chemical and biological applications. ***Ana M.O. Azevedo***
15:30 h	**Intervalo / Break**	

16:30 h	**Moderador: *Nelson Silva***	**Moderador: *António Rangel***
	OC12. Degradation of pharmaceuticals in aqueous solutions using a three-dimensional electrochemical process. ***Cristina Soares*** **OC13**. Removal of arsenic from contaminated seawater: A chemical and ecotoxicological study. ***Eduarda Pereira*** **OC14**. Human biomonitoring as a tool to assess firefighters´ total exposure to polycyclic aromatic hydrocarbons. ***Marta Oliveira*** **OC15**. Chemical quality of drinking-water in a Northeast region of Portugal**. *Andrea F. Afonso***	**OC16**. Diffusion and Removal Kinetics of Hydrogen Peroxide in Brain Tissue – a Study Using Ruthenium Purple Modified Carbon Fiber Microelectrodes. ***Ana Ledo*** **OC17**. Dual electrochemical immunosensor for the simultaneous analysis of two peanut allergens. ***Hendrikus P.A. Nouws*** **OC18**. Nanostructured poly(phenazine)-deep eutectic solvent/Fe2O3 nanoparticle film modified electrodes for (Bio)sensing applications. ***Wanderson da Silva***
17:30 h	**Moderador: *João Lopes***	
	KN3. Responsible Research & Innovation in a glimpse – Open science. ***Ana Mourato***	
18:00 h	**ASSEMBLEIA GERAL DA DIVISÃO DE QUÍMICA ANALÍTICA/GA ACD, SPQ** **ID da reunião:** 872 4275 3672	
20:00 h		

28 outubro

[3]ID da reunião: 872 1718 5074

9:30 h	**Moderador:** ***C. Brett*** **PL2.** Analytical Chemistry in 2020: challenges and opportunities. ***Marcela Segundo***, Universidade do Porto	
10:30 h	**Intervalo / Break**	
11:30 h	**Sessão / Session A** **[3]ID da reunião**	**Sessão / Session B** **[4]ID da reunião:** 871 6238 8693
	KN4 - Quality in chemical analysis: the key to the reproducibility CRISIS. ***Ricardo Bettencourt da Silva***	**KN5** - Pharmaceuticals, metabolites and degradation products in environmental waters: analytical trends for their determination. ***Cristina Delerue-Matos***
12:00 h	**Moderador:** ***Hugo Silva***	**Moderadora:** ***Marcela Segundo***
	OC19. Statistically Sound Identification of Oil Spills Origin: Simulation of Non-Normal Diagnostic Ratios by the Monte Carlo Method. **A. C. Rocha** **OC20**. Evaluation of the uncertainty of the characterization of large marine systems using Monte Carlo simulations. ***Carlos Manuel Barata da Fonseca Borges***	**OC21**. Electroactive polymer-deep eutectic solvent/carbon nanomaterials for electrochemical sensors and biosensors. ***Christopher M.A. Brett*** **OC22**. Study of antioxidant compounds in coffee using a low pressure chromatographic system with amperometric detection. ***Alexandra Rangel Silva***
12:30 h	**Almoço / Lunch**	
14:00 h	**Moderador:** ***Manuel Matos***	**Moderadora:** ***Filomena Camões***
	OC23. Chemical and metrological challenges of seawater acidity. ***Bárbara Anes*** **OC24**. Solidified floating organic drop microextraction for the quantification of three NSAIDs in environmental waters. ***Érika M.L. Sousa***	**OC25**. pHe measurement: What do ethanol measure? ***Fernando Fertonani*** **OC26**. Strategy for preparation of ethanolic buffering solution from lithium acetate/acetic acid. ***Natalia Cambiaghi Atilio***
14:30 h	**POSTER PITCH**** **PP18 – PP33**	**OC27**. Flow accuracy and traceability in a Lab-on-a-chip device. ***Elsa Batista*** **OC28**. Greener sequential injection method for Iron spectrophotometric determination in fresh and marine waters. ***Tânia Ribas V. Pedro***
		OC29. Development and validation of an UAE-HPLC-DAD-ECD method for simultaneous determination of parabens in cosmetic products. ***Lucía Abad Gil*** **OC30**. Immobilization of ionic liquids in solid phases and their application. ***Marieta L.C. Passos***
15:30 h	**Intervalo / Break**	
16:00 h	**Debate / Discussion & Prémios / Awards**	
17:00 h	**Cerimónia Encerramento / Closing Session**	

	*POSTER PITCH – 27 outubro, 14:30 h – 15:30 h	Apresentador/a
	Modern Analytical Methodologies	
PP 1	PRODUCTION AND ISOLATION OF BIOACTIVE* COMPOUND FROM TETRASELMIS CHUII AND CHLORELLA VULGARES	Sara Hussen
PP 2	RECENT DEVELOPMENTS ON WATERBORNE BACTERIA STRATEGIES FOR ENVIRONMENTAL ASSESSEMENT	Ana Machado
PP 3	ANALYTICAL APPROACHES FOR EVALUATING THE PHOTODEGRADATION OF GEOSYNTHETICS	Paulo J. Almeida
PP 4	CU(II) DETECTION BY FLUORESCENT CALIX[4]ARENE-OXACYCLOPHANE ARCHITECTURES	Patrícia D. Barata
PP 5	APPLICATION OF HEADSPACE MICROEXTRACTION TECHNIQUES TO MONITORING VOCS EMISSIONS FROM LEAVES OF FOUR PORTUGUESE TREE SPECIES UNDER EXTREME FIRE CONDITIONS	O.C. Gonçalves
PP 6	OPTIMIZATION OF SUBCRITICAL WATER EXTRACTION OF BIOACTIVE COMPOUNDS FROM VINEYARD PRUNING RESIDUES USING RESPONSE SURFACE METHODOLOGY	Manuela M. Moreira
PP 7	EXPLORING NEWLY SYNTHESIZED IRON CHELATORS AS COLORIMETRIC/FLUORESCENT SENSORS IN POLYMER INCLUSION MEMBRANES	Raquel B.R. Mesquita
PP 8	HIGH THROUGHPUT BAR ADSORPTIVE MICROEXTRACTION (HT-BAμE): PARALLEL MICROEXTRACTION OF KETAMINE AND NORKETAMINE FROM UP TO 100 URINE SAMPLES SIMULTANEOUSLY	Samir M. Ahmad
PP 9	FTIR CARACTERIZATION OF ANODIC ALUMINIUM OXIDE PROTECTIVE FILMS PRODUCED BY ANODIZING IN TANNINS	Carla S. Proença
PP 10	ANALYTICAL INVESTIGATION ON THE WRITING INK OF CODEX 99 FROM MANIZOLA COLLECTION	Margarida Nunes
	Biosensors	
PP 11	BIOINSPIRED LACCASE-POLYDOPAMINE FILMS FOR AMPEROMETRIC BIOSENSORS	Luís C. Almeida
PP 12	BRIGHT CARBON DOTS FROM CORK INDUSTRY WASTEWATER AS SENSORS OF HEMEPROTEIN	Alexandra I. Costa
PP 13	DEVELOPMENT OF A MICROELECTRODE ARRAY BIOSENSOR FOR MONITORING LACTATE DYNAMICS IN THE BRAIN	Eliana Fernandes
PP 14	MOLECULARLY IMPRINTED POLYMER-BASED ELECTROCHEMICAL SENSORS FOR THE DETECTION OF ANTIBIOTICS IN THE ENVIRONMENT	Patrícia Rebelo
PP 15	PAPER-BASED SUBSTRATES FOR WOUND INFECTION DETECTION	S. Sofia M. Rodrigues
PP 34	ELECTROCHEMICAL QUALITATIVE DETECTION OF STRESS BIOMARKERS IN SIMULATED AND REAL SWEAT SAMPLES	C.Cordas
	Health protection	
PP 16	NON-INVASIVE IDENTIFICATION OF POTENTIAL HUMAN STRESS BIOMARKERS BY LC-MSMS	M. João Nunes
PP 17	SPECIATION OF PT AND RH IN URBAN ROAD DUST LEACHATES	Carlos E. Monteiro

POSTER PITCH – 28 outubro 14:30 h – 15:30 h		**Apresentador/a**
	Health protection	
PP 18	CHARACTERIZATION OF ATMOSPHERIC AEROSOL (PM10 AND PM2.5) IN A CITY OF SÃO PAULO STATE, BRAZIL	Bruno Franzin
PP 19	PHYSICO-CHEMICAL CHARACTERIZATION OF EFFLUENTS FROM WASTEWATER TREATMENT PLANTS WITH DIFFERENT TREAMENTS AND ANTROPOGENIC PRESSURES	Ana Teixeira
	Examinology and metrology	
PP 20	EVALUATION AND OPTIMISATION OF THE UNCERTAINTY OF PHOTODEGRADATION KINETIC CONSTANTS DETERMINED BY THE MONTE CARLO METHOD	Cristina Oliveira
PP 21	EVALUATION AND OPTIMISATION OF THE UNCERTAINTY OF PH MEASUREMENTS ON A UNIPHIED SCALE	Ricardo Bettencourt da Silva
PP 22	A NOVEL AUTOMATIC METHODOLOGY FOR THE RELIABLE IDENTIFICATION OF MICROPLASTICS FROM AQUATIC ENVIRONMENT BY INFRARED SPECTROSCOPY	Vanessa Morgado
	Chemometrics	
PP 23	PORTUGUESE OCEAN ACIDIFICATION DATA - HARMONIZATION CHALLENGE FOR SEAWATER PH MEASUREMENTS	Marta Nogueira
PP 24	A NEW DATA-DRIVEN ALGORITHM FOR UNTARGETED METABOLOMICS ANALYSIS	Sandia Machado
PP 25	STUDY OF VARIABLES IN THE PRODUCTION OF BIODIESEL ETHYLIC-METHYLICY FROM RESIDUAL SOYBEAN OIL	Laurênio F. Lopes
	Method Validation	
PP 26	DEVELOPMENT AND VALIDATION OF AN INDIRECT GC-MS METHOD FOR THE QUANTIFICATION OF PSYCHOACTIVE SUBSTANCES IN SURFACE WATERS	Ivan M. Langa
PP 27	A METHODOLOGY FOR PEROXIDES EVALUATION IN COSMETIC CREAMS: A GREENER APPROACH	Valentina F. Domingues
PP 28	DETECTION OF THE ADULTERATION OF HONEY WITH SUCROSE SOLUTIONS BY FTIR SPECTROSCOPY	Amar Otmani
	Electroanalysis	
PP 29	ELECTROCHEMISTRY OF THE CALCIUM CHANNEL BLOCKER LERCANIDIPINE AT A CARBON BLACK MODIFIED GLASSY CARBON ELECTRODE	Ana-Maria Chiorcea-Paquim
PP 30	DISPOSABLE ELECTROCHEMICAL SENSOR FOR KETOPROFEN DETECTION	Álvaro Torrinha
	Separation Processes	
PP 31	ENANTIOMERIC PURITY OF NEW XANTHONE DERIVATIVES COMPRISING TWO CHIRAL MOIETIES BY LIQUID CHROMATOGRAPHY ON (S,S)-WHELK-O1 COLUMN	Joana Teixeira
PP 32	PH EFFECT IN BIOSORPTION OF DICLOFENAC IN WATER USING MORINGA OLEÍFERA SHELLS AS BIOSORBENT.	Agustina de Olivera
PP 33	COAGULATION AS SAMPLE PREPARATION FOR DETERMINATION OF SILVER NANOPARTICLES IN AQUEOUS MATRICES	Priscila L. Estevão

Lições
Plenárias

Plenary Lectures

UNIFIED pH – FROM CONCEPT TO EXPERIMENTAL REALIZATION

Ivo Leito

University of Tartu, Ravila 14A, Tartu, 50411, Estonia. ivo.leito@ut.ee

Acidity is one of the most important characteristics of liquids/solutions and its measurement is crucial to understand and control important processes in fundamental chemistry, industry and living organisms, such as catalysis, extraction, chromatography, processes in micelles/bilayers, etc. Acidity refers to the activity of the solvated proton and is expressed as pH. However, the conventional pH scale is well established only in dilute aqueous solutions at medium pH values. It has serious limitations in other solvents or more complex media where most of the real-life chemistry takes place. Most importantly, comparison of the conventional pH values between different media (solvents) is impossible.

In view of the above, a decade ago, the concept of “unified pH scale” was put forward, defining unified pH ($\mathrm{pH}_{\mathrm{abs}}$) via the absolute chemical potential of the solvated proton [1]. For easier comparability the $\mathrm{pH}_{\mathrm{abs}}$ scale was subsequently "aligned" with the aqueous pH scale [2], so that any medium/solution with $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H2O}}$ 7.00 has the same thermodynamic activity of the solvated proton as aqueous solution with pH 7.00. The merits of this approach are strict thermodynamic foundation and direct comparability of $\mathrm{pH}_{\mathrm{abs}}$ values between any solvents/media.

Initially the $\mathrm{pH}_{\mathrm{abs}}$ scale was a theoretical concept that had no practical implementation. However, in the recent years, to a large part thanks to the European Union UnipHied (17FUN09, www.uniphied.eu) project, the $\mathrm{pH}_{\mathrm{abs}}$ measurement possibilities for have been developed [2,3].

The presentation will give an overview of the $\mathrm{pH}_{\mathrm{abs}}$ concept and the principles of its current experimental realization.

[1] D. Himmel, S. K. Goll, I. Leito, I. Krossing. A Unified pH Scale for All Phases. *Angewandte Chemie International Edition*. **2010**, *49*, 6885–6888, http://dx.doi.org/10.1002/anie.201000252.

[2] A. Suu, L. Jalukse, J. Liigand, A. Kruve, D. Himmel, I. Krossing, M. Rosés, I. Leito. Unified pH Values of Liquid Chromatography Mobile Phases. *Analytical Chemistry*. **2015**, *87*, 2623–2630, http://dx.doi.org/10.1021/ac504692m.

[3] A. Heering, D. Stoica, F. Camões, B. Anes, D. Nagy, Z. Nagyné Szilágyi, R. Quendera, L. Ribeiro, F. Bastkowski, R. Born, et al. Symmetric Potentiometric Cells for the Measurement of Unified pH Values. *Symmetry*. **2020**, *12*, 1150, http://dx.doi.org/10.3390/sym12071150.

ANALYTICAL CHEMISTRY IN 2020: CHALLENGES AND OPPORTUNITIES

Marcela A. Segundo

LAQV, REQUIMTE, Departamento de Ciências Químicas, Faculdade de Farmácia da Universidade do Porto, Porto, Portugal. msegundo@ff.up.pt

Modern analytical chemistry is the "*interdisciplinary science of the generation of information about the composition and the structure of matter*" [1] or, in a more comprehensive way, it can be seen as the "*scientific discipline which develops and applies methods, instruments and strategies to obtain and evaluate information about the nature and composition of matter in space and time*" [2].

What is expected from analytical chemists in 2020? This lecture will address the main challenges faced today, including the need for sustainable methods, the involvement of citizens in science, the -omics fever, and the quest for the "lowest frontier": low level of analytes, low sample amount. Some selected examples will illustrate how these challenges can be met, namely through chromatographic methods coupled to tandem mass spectrometry. Other examples will address flow based methods that provide kinetically relevant information in studies dealing with bioactive compounds, and also how smart-phones can be incorporated in analytical sciences. Finally, some advanced automated methods will be discussed, introducing some opportunities that can be envisioned in the future of Analytical Chemistry, including technologies such as 3D-printing, artificial intelligence and internet of things (IoT).

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[1] Karayannis, M. I.; Efstathiou, C. E. *Talanta* **2012,** *102*, 7-15.
[2] Pérez-Bustamante, J. A. *Fresenius J Anal Chem* **1997,** *357*, 151-161.

Palestras Convidadas

Keynote Lectures

MAGNETICALLY RESPONSIVE IRON-CARBON COMPOSITES FOR MICRO-ORGANIC CONTAMINANTS ADSORPTION

Vânia Calisto[1], Luciana Rocha[1], Érika Sousa[1], María V. Gil[2], João A.B.P. Oliveira[1], Gonzalo Otero-Irurueta[3], María J. Hortigüela Gallo[3], Marta Otero[1], Valdemar I. Esteves[1]

[1]University of Aveiro & Centre for Environmental and Marine Studies, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal. vania.calisto@ua.pt
[2]Instituto de Ciencia y Tecnología del Carbono, INCAR-CSIC, 33011 Oviedo, Spain
[3]Centre for Mechanical Technology & Automation, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

The use of highly porous carbon materials, in particular powdered activated carbon (PAC), is an interesting option for advanced wastewater treatment, being the focus of significant attention mainly due to the ability of these materials to efficiently adsorb micro-organic contaminants. Yet, the generalized application of PAC in wastewater treatment plants (WWTP) is hampered by some relevant drawbacks: i) common use of non-renewable resources for PAC production; ii) difficult separation of exhausted materials from the treated aqueous phase; iii) difficult regeneration of spent PAC for reutilization, limiting their life-cycle. In order to surpass the referred disadvantages, a biomassic industrial waste was used in this work to produce magnetically responsive iron-oxide functionalized PAC, which can be efficient in the adsorption of micro-organic contaminants from wastewater, easily recovered from treated aqueous phase and further reutilized. The composite material was produced by *in-situ* iron oxide co-precipitation onto a previously prepared waste-based PAC. Optimal production conditions were selected by a multivariable process optimization through a fractional factorial design, allowing to assess the effect of production variables on the properties of the resulting materials. Based on the statistical analysis of the results, the material that best conciliated high saturation magnetization with adequate physico-chemical and adsorptive properties was chosen for application studies. For such evaluation, pharmaceuticals were considered as models of recalcitrant micro-organic contaminants, with special emphasis on the non-steroidal anti-inflammatory diclofenac. The kinetic and equilibrium adsorptive performance of the selected material was then tested in different matrices (ultrapure water and real WWTP effluents). Finally, the exhausted adsorbent was magnetically retrieved and subjected to a microwave-assisted regeneration and subsequently reutilized, being evident that its magnetic and adsorptive properties remained unchanged. The chemical composition of virgin, exhausted and reutilized composites was assessed by X-Ray photoelectron spectroscopy. The obtained results demonstrated the viability of producing waste-derived iron-carbon composites that simultaneously combine high efficiency for diclofenac removal with easy retrievability and successful regeneration/ reutilization.

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RETHINKING THE TEACHING OF ANALYTICAL CHEMISTRY FOR INDUSTRY 4.0

Manuel Matos[1], Nelson A. Silva[1,2], Hugo F. Silva[1,2], José Coelho[1,3], Cristina Oliveira[2]

[1]ISEL-CIEQB, R. Conselheiro Emídio Navarro, 1, 1959-007 Lisboa, Portugal.
manuel.matos@isel.pt
[2]Centro de Química Estrutural, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal
[3]Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Lisboa, Portugal

There is a considerable increase in regulatory issues in areas of society such as food, pharmaceutical, environmental, medicine and others. Analytical chemistry is the guarantee of quality of products and services for many of the industries that operate in these areas and, as a result, we have seen an increase in demand for chemical analysts at both global and local levels (Portugal and Europe).

New social challenges, for instance environmental issues, like the search for cleaner fuels and processes, the development of new batteries, the question of healthy eating, sustainable production and production of greener agrochemicals, among others, put some pressure in industries and in society that needs to use the knowledge of analytical chemistry to deal with these processes.

Also industries in their migration to Industry 4.0 need skills that support the increasing digitalization of data and information, intensive automation and modularity to respond to constant change.

How are we responding to these challenges in terms of the education/preparation of chemistry graduates in Portugal?

The analysis of higher education courses in Portugal directly linked to analytical chemistry shows that the content taught in this area has decreased over time. We are thus moving in a opposite direction to the demand for the knowledge in this field by the industries. The strong demand for analysts has even led some of the largest companies in Portugal to invest in training their analysts, in collaboration with Polytechnics and Universities. They seek skills essential to the profession but that are not yet taught in undergraduate courses (Bachelor's and Master's).

What can Higher Education in Analytical Chemistry do to respond to the demand for new 4.0 analysts?

The modernization of curricula seems essential. The introduction of subjects like method validation, quality control, GLP, regulation (REACH and others), operation in virtual environments (LIMS) and digital skills seem essential to reach this goal. But clearly accompanied by solid scientific knowledge. The only one that guarantees the understanding of nature and will endure, even when operational techniques change.

Courses in Portugal are difficult to change due to the lengthy, bureaucratic and costly accreditation process of A3ES (Regulatory Agency) so one of the solutions will be the creation of extracurricular courses. Some short courses will be proposed that may be taught involving colleagues from the industry and adapted to the needs of the new Industry 4.0.

RESPONSIBLE RESEARCH & INNOVATION IN A GLIMPSE – OPEN SCIENCE

Ana Mourato

Centro de Química Estrutural, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal. acmourato@fc.ul.pt

Responsible Research & Innovation (RRI) is included in Horizon Europe (2021-2027) as an operational objective and will be specifically outlined as a requirement of research and innovation in each program line of Horizon Europe. Additionally, it will be funded as a research and innovation action on its own terms in Reforming and Enhancing the European R&I system. Responsible Research & Innovation (RRI) refers to an approach rolled out in Framework Programs 7 & 8 (Horizon 2020) which intends to bridge gaps between science, research and innovation communities and society. In this frame, various stakeholders from, e.g. research, business, policy making, education and civil society are involved in R&I during all steps of the projects and system level to better align their processes and outcomes with the values, concerns, needs and expectations of society. In this way, co-design and co-responsibility for the outcomes of the research and innovation can be facilitated, increasing societal uptake and acceptability of research and innovation. RRI involves high ethical standards, gender equality in the scientific community, participation of policy-makers, engage citizens and ensure that they have the knowledge necessary to understand the implications by furthering science education and Open Access.

Open Access, is all about enabling easier access to scientific results. This includes access to academic information, such as publications and data, but also inter-institutional, inter-disciplinary and international collaboration among all actors in research and innovation.

In this presentation, the RRI and Open Science concepts, taxonomies and benefits will be addressed.

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QUALITY IN CHEMICAL ANALYSIS: THE KEY TO THE REPRODUCIBILITY CRISIS

Ricardo J.N. Bettencourt da Silva

Centro de Química Estrutural, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal. rjsilva@fc.ul.pt

Some authors and organisations have tried to attract the attention of the community to the so called "reproductivity crisis" of research [1,2]. Much research is not possible to be repeated and many conclusions are presented without an adequate support of sound evidence. The negative impact of reporting false information from a research work can go far beyond the team that produced the data or the specific entity that financed the study when the information affects the work of other scientists. An important scientific or technological development can be postponed for decades by an inadequate assessment of its merits in initial research.

Most research in chemistry and much research in other disciplines rely on the results of qualitative and quantitative chemical analysis, designed examinations and measurements in chemistry respectively [3].

This presentation discusses the socioeconomic relevance of chemical analysis and the way chemical information can be reported in an objective way. Only reliable and objective information will be binding, i.e. should be taken seriously.

Two key concepts for chemical information reliability and objectivity will be discussed: result traceability and uncertainty. The traceability of a result defines its reference that can be, e.g. a spectrum from a library or a chemical standard. This reference must be fit for the purpose in hand and presented together with the result.

The result uncertainty makes the reported information objective by expressing the impact of reference and analytical procedure quality on the reported information.

After presenting the general principles for reporting qualitative and quantitative chemical information in a reliable and objective way, some successful examples of the production of chemical information are reported. Discussion will take place on improving the reliability of the identification of active substances in human urine samples, assessment of composition variation of large environmental areas, and comparison of the efficiency of catalysts.

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PHARMACEUTICALS, METABOLITES AND DEGRADATION PRODUCTS IN ENVIRONMENTAL WATERS: ANALYTICAL TRENDS FOR THEIR DETERMINATION

C. Delerue-Matos

REQUIMTE/LAQV, Instituto Superior de Engenharia do Porto, Instituto Politécnico do Porto, Portugal. cmm@isep.ipp.pt

Pharmaceuticals play an important role in the prevention and treatment of many diseases. However, their use is not exempt from environmental problems that they can cause when they reach the environment, either in their original forms or transformed into metabolites or degradation products. In fact, everyday tons of these compounds are discharged into sewage systems and arrive at wastewater treatment plants (WWTPs). The WWTPs' removal efficiencies of pharmaceuticals and their derivatives has been studied and a large group of these compounds is not removed. Although they are not persistent pollutants, the continuous entry of these compounds in the environment make them omnipresent. Pharmaceuticals have been detected (at ng L^{-1} and µg L^{-1} levels) in a wide variety of water samples, such as effluents (hospital, landfills and municipal sewage), sea-, drinking-, surface- and groundwater [1].

Liquid chromatography with tandem mass spectrometric detection has been used in the analysis of these pollutants in environmental matrices at very low concentrations. Sample preparation is a very important step to preconcentrate the analytes and eliminate matrix effects. Solid phase extraction is still the most used extraction technique in water sample analyses. These methodologies are laborious and require sophisticated and expensive equipment and specialized operators. The development of (bio)sensors has increased significantly in recent years due to the need for simple analytical devices that are easy to operate and have the capacity to provide qualitative and quantitative information *in situ* with minimal sample treatment. Electrochemical techniques are of particular interest for the use in (bio)sensors. Several examples of these sensors for the analysis of pharmaceuticals in the environment [2, 3] are described in the literature but many challenges remain to convert them into real commercial alternatives.

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Comunicações Orais

Oral Communications

MICROWAVE-DRIVEN PRODUCTION OF CARBON ADSORBENTS FROM BIOMASS WASTE AND THEIR APPLICATION TO THE REMOVAL OF ANTIBIOTICS FROM WATER

Érika Sousa[1], Luciana Rocha[1], Guilaine Jaria[1], María V. Gil[2], Marta Otero[1], Valdemar I. Esteves[1], Vânia Calisto[1]

[1]University of Aveiro & Centre for Environmental and Marine Studies, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal. lrocha@ua.pt
[2]Instituto de Ciencia y Tecnología del Carbono, INCAR-CSIC, 33011 Oviedo, Spain

Multiple negative effects can arise from the presence of antibiotics in water systems, including bacterial resistance, which represents a huge menace and a major public health problem. Due to these adverse effects, there is a great demand for the development of environmentally friendly and cost-effective treatment strategies, capable of reducing the discharge of these micropollutants into the aquatic environment. Adsorption using powder activated carbon (PAC) prepared from industrial residues is currently considered an efficient and sustainable approach for wastewater treatment, ensuring high rates of pharmaceuticals removal, with no by-product formation. Typically, conventional pyrolysis has been applied in the production of PAC, but in recent studies, microwave-assisted pyrolysis has attracted considerable attention due to the lower energy consumption derived from the fast heating rate and to the higher production yields.

In the present work, microwave heating was used to produce carbon adsorbents from primary pulp and paper mill sludge (used as precursor) and their adsorptive performance towards the removal of the antibiotics amoxicillin (AMX) and sulfamethoxazole (SMX) from aqueous media was evaluated. To accomplish this goal, the impact of the production conditions, namely, temperature of pyrolysis, residence time and the ratio between the activating agent and precursor, on relevant responses such as product yield, surface area (S_{BET}), total organic carbon and adsorptive performance, were evaluated. The obtained results demonstrated the feasibility of microwave-assisted pyrolysis to produce energetically sustainable waste-based PAC, using a short residence time (20 minutes) and a low amount of KOH activating agent (KOH:biomass ratio of 1:5 *w*/*w*). The produced PAC exhibited a highly microporous structure with an S_{BET} of 1196 $\mathrm{m^2\ g^{-1}}$, being capable of removing up to 79% and 87% of SMX and AMX, respectively, using very small doses of material (25 mg $\mathrm{L^{-1}}$).

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ANTIBIOTICS IN AQUACULTURE WATERS: CAN CARBON DOTS/TITANIUM DIOXIDE NANOHYBRIDS ACCELERATE THEIR PHOTODEGRADATION?

Vitória Louros[1], Liliana Ferreira[1], Carla Patrícia Silva[1], Marta Otero[2], Valdemar I. Esteves[1], Diana L.D. Lima[1]

[1]CESAM & Department of Chemistry, University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal
[2]CESAM & Department of Environment and Planning, University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal

The emergent consumption of antibiotics worldwide, both in human and veterinary medicine, has triggered a remarkable increase in the occurrence of these pollutants in the environment. Aquaculture facilities are recognised as one of the major sources of the aquatic pollution by antibiotics. The main concern is that these micropollutants are very persistent in aquatic environment, and their presence can lead to bacterial resistance, which constitutes one of the most important health threats nowadays. Therefore, it is essential to draw possible strategies to remove antibiotics from aquaculture effluents before being released into the environment. Photodegradation of antibiotics plays a key role in the removal of these compounds.

In this work, carbon dots (CDs) were synthesized and later coupled with titanium dioxide (TiO_2) in an attempt to improve the photodegradation efficiency of two antibiotics widely used in aquaculture: oxolinic acid (OXA) and sulfadiazine (SDZ). The nano-hybrid materials of CDs with TiO_2 were prepared using two modes: *in-situ* (CDs@TiO_2) and *ex-situ* (CDs-TiO_2). For CDs synthesis, citric acid and glycerol were used and for TiO_2 synthesis titanium butoxide was used. Globally, 4 different materials were produced and tested for the photodegradation of SDZ and OXA: CDs, CDs@TiO_2, CDs-TiO_2 and TiO_2. The obtained results indicated that the presence of these materials enhanced the photodegradation of both SDZ and OXA. For SDZ, CDs@TiO_2 proved to have the best photocatalytic effect (96.9% *vs.* 23.4% of photodegradation in presence and absence of the catalyst, respectively, after 4 hours of irradiation), whereas for OXA, CDs-TiO_2 was found to be responsible for the highest photodegradation (59.4% *vs.* 22.4% in presence and absence of the catalyst, respectively, after 1 hour of irradiation).

This study provided a more detailed understanding of the possibility of using eco-friendly CDs/TiO_2 nanohybrids as a tool for the efficient removal of antibiotics from aquaculture effluents.

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ANALYTICAL STRATEGIES TO DETERMINE NANOPARTICLES ENCAPSULATION EFFICIENCY AND QUANTITY

Sara S. Marques[1], Maria R.M. Domingues[2,3], Marcela A. Segundo[1]

[1]LAQV, REQUIMTE, Department of Chemistry, Faculty of Pharmacy, University of Porto, Porto, Portugal. micf09213@ff.up.pt
[2]ECOMARE, CESAM, Department of Chemistry, University of Aveiro, Aveiro, Portugal
[3]Mass Spectrometry Center, Department of Chemistry, LAQV, University of Aveiro, Aveiro, Portugal

Several nanocarriers have been developed for drug delivery, aiming at providing more effective and safer therapeutic options. However, to advance in the translation of nanocarriers to clinical use, a set of analytical methods capable to accurately characterize nanoparticles without compromising their properties are required, along with orthogonal approaches to self-validate the obtained results. Hence, aiming at an improved characterization of nanoformulations´ dose, in this work analytical methods to measure nanoparticles encapsulation efficiency and quantity were developed.

An ultrafiltration-based protocol to separate nanoparticles from free drug prior to HPLC-UV quantification of both fractions was set to quantify the encapsulation of methotrexate (MTX), an anti-inflammatory drug, into nanostructured lipid carriers (NLCs) and polymeric nanoparticles. The influence of parameters (pH, concentration of surfactant, nanocarrier material) on the ultrafiltration process was studied. The established protocol enabled to assess the MTX associated to NLCs using a short ultrafiltration time (5 min), with recoveries > 85% and not requiring exhaustive separation. The amount of MTX associated to NLCs was also determined when these were dispersed in pig skin surrogate from permeation assays and cell culture media to monitor the stability of nanoparticles´ payload on these matrices.

Regarding nanoparticles quantification, a hydrodynamic size-based separative method resorting to a silica monolith and nephelometric-fluorescence detection was exploited to quantify rhodamine B-loaded NLCs and free rhodamine B in a single run by a "*dilution-and-shoot*" approach. Under the set conditions, nanoparticles´ quantification between 0.027 - 0.27 and 0.14 - 2.7 mg mL^{-1} (based on the mass of lipids) was feasible using 5- or 105-mm monoliths, respectively, along with the simultaneous quantification of free rhodamine. Analysis within 15 min was accomplished using the shorter column (5-mm) with a LOD and LOQ of 0.003 and 0.01 mg mL^{-1}, respectively.

Also, the lab-on-valve (LOV) platform was exploited to quantify PEGylated polymeric nanocarriers, based on the real-time measurement of optical density while nanoparticles passed through the LOV flow cell. Analysis of nanoparticles between 0.67 - 5.33 mg mL^{-1} (expressed as mass of polymer) and nanoparticle quantification in biological media were feasible, with a throughput of 36 samples h^{-1}. The results were compared to those attained by particle tracking analysis for method validation.

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MICROFLUIDIC TECHNOLOGIES FOR HIGH-THROUGHPUT DRUG SCREENING ENZYMATIC ACTIVITY AND INHIBITION ASSAYS

Sarah A.P. Pereira[1], Paul J. Dyson[2], M. Lúcia M.F.S. Saraiva[1]

[1]LAQV, REQUIMTE, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, Rua Jorge Viterbo Ferreira, nº 228, 4050-313, Porto, Portugal. sarah.pp@hotmail.com
[2]Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne (EPFL), 1015, Lausanne, Switzerland

Current analytical methods allow the screen of tens of thousands of drug candidates for their capacity to inhibit specific enzymes and the miniaturization of these approaches is extremely desirable to accelerate the drug discovery process with less costs.

Miniaturization techniques are of increasing interest in drug screening research with microfluidic-based devices whereas for enzymatic assays, these techniques have already shown an increase of sensibility and specificity, higher reliability and low risks of contamination comparing with the technologies presented in well-equipped laboratories [1].

The main of this work was to present the miniaturized techniques currently used to evaluate enzymatic activity and inhibition giving special attention of microfluidic technologies since they are systems that enable high performance, versatility, speed and integration, with negligible sample and reagent consumption, miniaturization and automation [2].

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PHENOLIC CHARACTERIZATION OF AN HYDROETHANOLIC EXTRACT OBTAINED FROM *SATUREJA MONTANA* L. WITH ANTIBACTERIAL ACTIVITY AND POTENTIAL APPLICATION ON THE CONTROL OF PLANT PATHOGENS

Rose Marie O.F. Sousa[1,2,3], Daniel O. Carvalho[4], Ana C. Torres[1], Luís F. Guido[4],
Fernando Tavares[1,5], Manuel Fernandes-Ferreira[1,2,3]

[1]Departamento de Biologia, Faculdade de Ciências, Universidade do Porto, Portugal
[2]GreenUPorto, Departamento de Biologia, Faculdade de Ciências, Universidade do Porto, Portugal
[3]CITAB, Universidade de Trás-os-Montes e Alto Douro, Portugal
[4]REQUIMTE/LAQV - Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Portugal. daniel.carvalho@fc.up.pt
[5] Centro de Investigação em Biodiversidade e Recursos Genéticos, Laboratório Associado (CIBIO-InBIO), Universidade do Porto, Portugal.

Xanthomonas euvesicatoria is a phytopathogenic bacteria of urgent phytosanitary concern, responsible for bacterial spot of tomato (*Solanum lycopersicum*) [1]. In this work, *Satureja montana* hydroethanolic extract was investigated as a possible source of antimicrobial compounds for the biochemical control of *X. euvesicatoria* and as a new eco-friendly alternative to synthetic pesticides with potential biotechnological application in agriculture.

S. montana hydroethanolic extracts from leaves and stems (Smtn-HEex) were prepared by solid-liquid extraction (70:30, EtOH:H_2O, v/v), with an extraction recovery of 15.8 % (dry weight), and the main phytochemicals were characterized by HPLC-DAD-ESI-MS/MS. The rosmarinic acid was identified as one of the main phenolic compounds in Smtn-HEex, together with salvianolic acid A and glycoside derivatives of the flavonoid luteoline.

The *in vitro* antimicrobial activity of Smtn-HEex against *X. euvesicatoria* LMG 905 was evaluated by the broth microdilution method [2]. Smtn-HEex exibithed moderate bacteriostatic (MIC = 4.5 mg/mL) and bactericidal (MBC = 9.1 mg/mL) activities after 24h. Furthermore, the phytotoxic impact of Smtn-HEex (0.4-12.8 mg/mL) on membrane integrity, oxidative damage, and photosynthetic pigments contents of young tomato plants (*Solanum lycopersicum* cv. Micro Tom) was evaluated 7 days after treatment, with no significant differences observed in treated plants comparing to controls. These findings suggest that Smtn-HEex may have a potential phytopathogenic protection without affecting plants integrity, and could be used as a source of antimicrobial agents for incorporation in plant protection products of botanical origin against bacterial spot disease in tomato.

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WASTE-BASED MAGNETIC BIOCHAR/TiO_2 AS A CATALYST IN THE PHOTODEGRADATION OF ANTIBIOTICS FROM AQUACULTURE WATER

Diogo Pereira[1], Carla Patrícia Silva[1], Vânia Calisto[1], Manuel A. Martins[2],
Marta Otero[3], Valdemar I. Esteves[1], Diana L.D. Lima[1]

[1]CESAM and Department of Chemistry, University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal
[2]CICECO and Department of Materials and Ceramic Engineering, University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal
[3]CESAM, Department of Environment and Planning, University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal

The ability of emerging contaminants to permeate several environmental matrices, such as water bodies, reveals the inefficacy of the currently applied water treatment systems. The removal of these contaminants, namely pharmaceuticals, has been an ever-growing topic of research due to their recalcitrant and potentially toxic nature. In this study, the effect of waste-based magnetic biochar/TiO_2 composite materials on the photocatalytic degradation of two antibiotics with relevance in aquaculture, oxolinic acid (OXA) and sulfadiazine (SDZ), in ultrapure water was evaluated. The biochar not only provides a solid surface for the generation of highly oxidizing species, namely hydroxyl radicals, through the irradiation of TiO_2, but also efficiently adsorbs pharmaceutical molecules facilitating the photolysis. The magnetic component of the structure allows for instant recuperation of the material. Four materials were produced mainly differing in the magnetization procedure: the BC_Mag refers to magnetized biochar; the BC_Mag_TiO_2 corresponds to the magnetized biochar (BC_Mag) which was functionalized with TiO_2; the BC_TiO_2_*in-situ* and BC_TiO_2_*ex-situ* refers to a biochar functionalized with TiO_2 and later magnetized using an *in-situ* an *ex-situ* approach, respectively. The materials were characterized by XRD, VSM, SEM and EDS and the two of them showing the most remarkable properties, were selected for photodegradation kinetic studies. For SDZ, half-life time considerably decreased from 11.2 ± 0.5 h in the absence of catalyst, to 2.9 ± 0.1 h and 3.3 ± 0.1 h for BC_Mag_TiO_2 and BC_TiO_2_*ex-situ*, respectively. For OXA, half-life times were 0.46 ± 0.01 h and 0.71 ± 0.03 h for BC_Mag_TiO_2 and BC_TiO_2_*ex-situ*, respectively, which are shorter when compared to the OXA half-life time (1.21 ± 0.08 h). Concluding, the presence of the magnetic biochar/TiO_2 heterostructures has a great capacity to enhance the removal of OXA and SDZ from water, being these materials promising catalysts for application in water treatment systems.

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HAIR ANALYSIS: THE USEFULLNESS OF MICROEXTRACTION FOR SAMPLE CLEANUP

T. Rosado[1,2,3], M. Barroso[4], D.N. Vieira[5], E. Gallardo[1,2]

[1] *Centro de Investigação em Ciências da Saúde, Faculdade de Ciências da Saúde da Universidade da Beira Interior (CICS-UBI), Covilhã, Portugal. tiago.rosado@ubi.pt*
[2] *Laboratório de Fármaco-Toxicologia-UBIMedical, Universidade da Beira Interior, Covilhã, Portugal*
[3] *C4 - Cloud Computing Competence Centre, Universidade da Beira Interior, Covilhã, Portugal*
[4] *Serviço de Química e Toxicologia Forenses, Instituto de Medicina Legal e Ciências Forenses - Delegação do Sul, Lisboa, Portugal*
[5] *Faculdade de Medicina, Universidade de Coimbra, Coimbra, Portugal*

Hair is one of the most important alternative matrices and has been drawing attention for several drugs analysis. The fact that this sample can be collected under supervision, with reduced tampering probability, and great stability of the analytes are pointed as its major advantages. As with conventional matrices, hair samples preparation is an important step for cleanup and analytes pre-concentration, significantly influencing the reliability and accuracy of analysis. Although hair testing is considered much more complex, technically is not more difficult or challenging than the analysis of other samples.

The use of miniaturized pre-concentration techniques, driven by the concept of ‘green chemistry’, has minimized the laboratorial waste usually associated to classic procedures. Microextraction techniques are known for lower solvent volumes and time consumption, but their applicability to hair samples is poorly explored.

This communication aims to demonstrate the practical applicability of microextraction by packed sorbent (MEPS) to hair samples with three different works: the determination of selected opioids; the determination of methadone and EDDP; and the determination of cocaine and metabolites using gas chromatography coupled to tandem mass spectrometry (GC-MS/MS).The novel methods were optimized and validated according to FDA, ICH and SWGTOX guidelines.

MEPS has proven to be an excellent alternative for toxicological analysis in hair samples. A comparison with the classic SPE approach was performed and the described works show that this miniaturized technique is quite advantageous, reducing the use of solvents and allowing sorbent reusage (> 100 extractions), which can be economically attractive for laboratories.

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DETERMINATION OF URINARY IRON BY COLORIMETRIC DETECTION WITH A NOVEL MICROFLUIDIC PAPER-BASED ANALYTICAL DEVICE

Francisca T.S.M. Ferreira, Karina A. Catalão, Raquel B.R. Mesquita,
António O.S.S. Rangel

Universidade Católica Portuguesa, CBQF - Centro de Biotecnologia e Química Fina – Laboratório Associado, Escola Superior de Biotecnologia, Rua Diogo Botelho 1327, 4169-005, Porto, Portugal

Iron is one of the most studied micronutrients in the world, since it plays several important roles in the human body, such as transport, storage and use of oxygen and DNA synthesis. Both deficient and overload of this metal can cause severe damages like anemia, hemochromatosis, cancer and neurodegenerative diseases, which is why its metabolism is very tightly regulated. Nowadays, urinary iron is mostly determined by Inductively Coupled Plasma, but this technique requires costly and complex equipment. Because, there is still a part of the world population that doesn't has an easy access to the basic healthcare, the development of practical and affordable devices and techniques is essential.

Microfluidic paper-based analytical devices (μPADs) are a recently developed platform used to perform analytical determinations in a simple, inexpensive, portable way. Furthermore, μPADs are rapid, disposable, and after being assemble don't require complex equipment or specialized personal to do the measurement, which makes them and interesting tool to be used in on-site analysis in locations of difficult access or with very few resources.

The focus of this work was to design a new μPAD for the quantification of iron in human urine samples. This device could ultimately be used as a screening option not only in healthcare facilities, but also to aid in the diagnosis of some diseases and health conditions in remote locations.

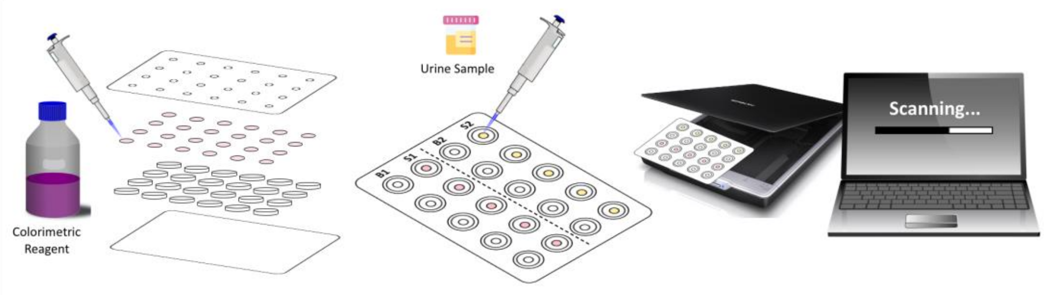

Figure 1: Schematic representation of the μPAD assembly and use.

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DETERMINANTION OF ALDEHYDES IN BEER USING GAS-DIFFUSION MICROEXTRACTION AND HIGH-PERFORMANCE CHROMATOGRAPHY WITH UV DETECTION

Inês M. Ferreira, Daniel O. Carvalho, Luís F. Guido

LAQV/REQUIMTE, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre 687, 4169-008, Porto, Portugal. *up201106585@fc.up.pt*

Beer flavour is a balance of organoleptic characteristics from malt, hops, and yeast. Thereby, it is not surprising that organoleptic quality of beer changes with time. For that reason, the majority of beer companies spend a lot of time trying to preserve the *"freshness"* of their products [1]. Carbonyl compounds are considered the main cause of the development of undesirable flavours during beer aging, despite they are present in very small amounts [2]. The development of analytical methodologies for the study and identification of these chemical species has been therefore very important. Gas-diffusion microextraction (GDME) was developed for the extraction of volatile compounds from liquid samples, particularly in alcoholic beverages [3, 4]. GDME is a sample preparation technique in which volatile compounds are transferred from the sample, through a gas-permeable membrane, into a liquid acceptor phase containing a derivatizing agent. Beer has several problems associated, that interferes in extraction, like the CO_2 level and foam. For this reason, this work aims at optimizing and validating a GDME methodology which may be applied to the analysis of carbonyl compounds in beer, subjected to different storage conditions (fresh beers and forced aged beers). The method enables the identification and quantification of acetaldehyde, 2-methylpropanal, 2-methylbutanal, 2-methylbutanal and furfural. Several parameters with influence on the extraction process were studied, such as: temperature, time of extraction, derivatizing agent, matrix effect and the calibration method. The use of an internal standard was shown to be crucial as volatile compounds loss may occur during the extraction. The optimized extraction parameters are: 40 ºC during 20 minutes of extraction with 4-hydrazinobenzoic acid (HBA) as derivatizing agent and 4-fluorobenzaldehyde as the added internal standard. For the validation of the current method, linearity range, detection and quantification limits (LOD and LOQ), intra and inter-day precision were determined. LOD values found in this study are in the range 7-2560 µg/L, and the LOQ values in the range 24–8532 µg/L for the mentioned compounds. The method showed good intra- and inter-day repeatability, showing RSD values below 10%.

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INFECTION MARKERS IN WOUNDS

Fátima A.R. Mota, Sarah A.P. Pereira, Marieta L.C. Passos, M. Lúcia M.F.S. Saraiva

REQUIMTE, Departamento de Ciências Químicas, Faculdade de Farmácia,
Universidade do Porto, Rua Jorge Viterbo Ferreira, No. 228, 4050-313 Porto,
Portugal. lsaraiva@ff.up.pt

After the occurrence of a wound, the healing process begins based on four distinct stages. A wound is a bodily injury caused by a rupture of a membrane and, consequently, damage to the surrounding tissues. However, one of the most serious problems associated with wounds is their infection, which leads to impairment of the healing process and poses risks to the patient [1].

It is essential to prevent the progression of a wound infection. For this reason it is very important that the detection and monitoring of the same occurs as soon as possible, although the availability of methods, as well as devices for rapid diagnosis is still very limited for this purpose [2].

The development of new and diversified methods of identifying infection in wounds is currently a huge challenge, which is why they have been studied to improve their identification [2].

Biomarkers can be used as a tool throughout the healing process, and in this way, new and current approaches and methods based on them, have been developed and discussed. There are several types of biomarkers, such as enzymes, bacteria and metabolites, and only a few of them are directly related to infection in the wound, acting as indicators of pathological or inflammatory processes. Among the biomarkers described, enzymes demonstrated a special role in the detection of infections in wounds, since they appear in very early stages of the inflammatory process and thus allow premature identification of the infection [2].

In this sense, different analytical methods are presented to identify and determine biomarkers in infected wounds and demonstrate their importance in this context. Actually, very few are, however, implemented for clinical use [2].

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GUMBOS AND NANOGUMBOS: TUNABLE MATERIALS FOR CHEMICAL AND BIOLOGICAL APPLICATIONS

Ana M.O. Azevedo[1], João L.M. Santos[1], Isiah M. Warner[2], M. Lúcia M.F.S. Saraiva[1]

[1]LAQV, REQUIMTE, Departamento de Ciências Químicas, Laboratório de Química Aplicada, Faculdade de Farmácia, Universidade do Porto, Rua Jorge Viterbo Ferreira, 228, 4050-313, Porto, Portugal. aazevedo@ff.up.pt*; lsaraiva@ff.up.pt*
[2]Department of Chemistry, Louisiana State University, Baton Rouge, LA, 70803, United States

GUMBOS (*g*roup of *u*niform *m*aterials *b*ased on *o*rganic *s*alts) share similar features to those of ionic liquids and offer extraordinary potential for expanding their applications. Although solid-phase (melting points between 25 and 250 ºC), these materials can be multifunctional and designed for a specific task by varying cation-anion combinations. GUMBOS can also be easily converted into nanomaterials (nanoGUMBOS), which combine the versatility of these solid-state compounds with the advantages of working at nanoscale [1, 2].

In this talk, we highlight the possibility of fine-tuning GUMBOS physicochemical properties, with emphasis placed on recent developments in areas such as solid-phase extraction and sensing. Here, we also describe available strategies for synthesis of nanoGUMBOS and their distinct outcomes in shapes and spectral properties, with pros and cons being discussed. An analysis is made of the opportunities and challenges encountered by this novel class of compounds. Finally, some of the research that has been conducted in our laboratory is presented, making use of these tunable solid-phase materials in tackling scientific challenges.

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DEGRADATION OF PHARMACEUTICALS IN AQUEOUS SOLUTIONS USING A THREE-DIMENSIONAL ELECTROCHEMICAL PROCESS

Cristina Soares[a], Luísa Correia-Sá[a], Henri Nouws, Manuela Moreira, Manuela Correia, Paula Paíga, Olga Freitas, Sónia Figueiredo, Cristina Delerue-Matos

REQUIMTE/LAQV, Instituto Superior de Engenharia do Porto, Politécnico do Porto, Portugal.
cmdss@isep.ipp.pt ([a]Authors contributed equally to the present work)

The occurrence of pharmaceutical products in the environment is a growing concern [1]. Pharmaceuticals and their metabolites present in hospital, industrial, and domestic effluents are not completely removed in conventional wastewater treatment plants [1]. These emerging pollutants, including antibiotics, can pose serious risks to human health and ecosystems, particularly when wastewater is reused, due to the possible incorporation of these compounds in crops, their bioaccumulation, and consequent diffusion in the food chain [2]. In recent years, electrochemical technologies, such as electro-Fenton, electro-flocculation, and electrochemical oxidation, have made remarkable progress in wastewater treatment because they present high treatment efficiencies, excellent flexibility, and no secondary pollution. However, these technologies also have shortcomings, such as high energy consumption, low current efficiency, and mass transfer limitations, restricting their applications [3]. Recent research on three-dimensional (3D) electrode processes provides a superior solution to the shortcomings of the two-dimensional (2D) electrode technology. The 3D method differs from the 2D process because of introducing a third particulate electrode, which is usually carbon-based. Compared with the 2D process, the introduction of the particulate electrode improves the treatment efficiency due to the simultaneous occurrence of different phenomena, such as adsorption/electrosorption, electrocoagulation, oxidation, and catalytic degradation [3]. Therefore, the performance of particulate electrodes plays a significant role in the degradation of pollutants in the whole 3D electrode system [3]. The objective of the present study was to test different anode and cathode materials, such as carbon felt, boron-doped diamond, stainless steel, and carbon-based (biochar and granular activated carbon) particulate electrodes in order to develop an economical and efficient 3D process for the degradation of different pharmaceuticals.

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REMOVAL OF ARSENIC FROM CONTAMINATED SEAWATER: A CHEMICAL AND ECOTOXICOLOGICAL STUDY

Eduarda Pereira[1], Francesca Coppola[2], Daniela Tavares[1], Bruno Henriques[1], Tito Trindade[3], Rosa Freitas[2]

[1]Chemistry Department & LAQV-REQUIMTE, University of Aveiro, 3810-193 Aveiro, Portugal. eduper@ua.pt
[2]Biology Department & CESAM, University of Aveiro, 3810-193 Aveiro, Portugal
[3]Chemistry Department & CICECO, University of Aveiro, 3810-193 Aveiro, Portugal

Several studies have demonstrated that intense urbanization and industrial activities, with their associated effluents, result in an increase of pollution load in the aquatic environments [1]. Often, the final destination of pollutants are low-lying coastal systems, with tendency to be accumulated in organisms inhabiting these areas [2]. Among the most common pollutants in aquatic environments are metal(oid)s, like arsenic (As), considered the most priority hazardous substance in the environment [3]. So, an important research topic is the development of new technologies for wastewater decontamination. Promising approaches to remove pollutants from water are based on the use of nanoparticles (NPs) [4], but knowledge in important issues are still missing, like the evaluation of the potential toxicity of NPs and the ecotoxicological evaluation of the remediated water, making crucial the assessment of decontaminated water potential impacts towards inhabiting organisms.

The present study evaluated the ecotoxicological safety of seawater previously contaminated with As and remediated with manganese-ferrite ($MnFe_2O_4$-NPs) NPs. Mussels *Mytilus galloprovincialis* were exposed for 28 days to different conditions. Results revealed that mussels exposed to water contaminated with As accumulated significantly more As than those exposed to remediated seawater. Biomarkers demonstrated that in comparison to remediated seawater mussels exposed to contaminated seawater presented significantly lower metabolic capacity, lower expenditure of energy reserves, increased antioxidant and biotransformation defences, higher lipids and protein damages, evidencing the potential use of these NPs to remediate seawater and its safety towards marine systems after discharges to these environments.

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HUMAN BIOMONITORING AS A TOOL TO ASSESS FIREFIGHTERS' TOTAL EXPOSURE TO POLYCYCLIC AROMATIC HYDROCARBONS

Marta Oliveira, Ana Bela Barros, Cristina Delerue-Matos, Simone Morais

REQUIMTE-LAQV, Instituto Superior de Engenharia do Politécnico do Porto, R. Dr. António Bernardino de Almeida 431, 4249-015 Porto, Portugal. Marta.oliveira@graq.isep.ipp.pt

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous organic compounds formed during pyrolysis or incomplete combustion of organic matter with recognized toxicity, mutagenicity, and carcinogenicity [1-2]. PAHs are absorbed through the skin, lungs and gastrointestinal track, being metabolized by enzymes from cytochrome P450 family through metabolic pathways that produce a complex mixture of hydrophilic intermediates (e.g., quinines, phenols, dihydrodiols, triols and tetrols) [1]. These hydroxylated metabolites are biotransformed to produce glutathione, glucuronide or sulphate conjugates to expedite their excretion from the human body (e.g., urine, milk, feces) [1]. In this work a method was developed to assess the concentrations of 6 PAH biomarkers of exposure (1-hydroxynaphthalene, 1-hydroxyacenaphthene, 2-hydroxyfluorene, 1-hydroxyphenanthrene, 1-hydroxypyrene, and 3-hydroxybenzo(a)pyrene) in the urine of firefighters. Urine samples are hydrolyzed (120 min; 37 ºC) with ß-glucuronidase/arylsulfatase and PAH biomarkers are extracted from urine through a solid-phase extraction and analyzed by liquid chromatography with a fluorescence detector [3-4]. Concentrations of PAH biomarkers of exposure are normalized with the urinary creatinine values which are determined by Jaffe colorimetric method [3]. The attained data show that human biomonitoring represents a crucial tool to assess PAHs total exposure regardless the route of exposure and environmental sources.

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CHEMICAL QUALITY OF DINKING-WATER IN A NORTHEAST REGION OF PORTUGAL

Andrea F. Afonso[1], Bruno Pires[1], Eugénia Afonso[1], Cristina Teixeira[2],
António Nogueira[3]

[1]Laboratório de Saúde Pública de Bragança, Unidade Local de Saúde do Nordeste (ULSNE), Rua Eng. Adelino Amaro da Costa, Bragança, Portugal. andrealfa@live.com.pt
[2]Unidade de Investigação em Epidemiologia (EPIUnit), Instituto de Saúde Pública da Universidade do Porto, Rua das Taipas, nº 135, 4050-600 Porto, Portugal
[3]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança (IPB), Campus de Santa Apolónia, 5300-253 Bragança, Portugal

The chemical and microbiological quality of drinking-water should be considered within overall public health priorities [1]. A poor quality of drinking-water, due to insufficient disinfection or by human contamination, can be a vehicle for transmitting diseases to consumers. Thus, the quality of both raw water (surface water and groundwater) and the drinking-water has a strong impact on the public health. Among the contaminants, nitrates (NO_3^-) and faecal indicators (such as thermotolerant coliforms, *Escherichia coli* and enterococci) represents a major concern because these factors have been associated with adverse health outcomes [1,2]. This study analysed contaminants in drinking-water samples (n=361), including surface water and groundwater in the district of Bragança (during the year 2019), according the standardized protocols [3]. We evaluated the relationship of NO_3^- concentration with microbial drinking-water parameters (heterotrophic plate count-HPC and faecal indicators), as well as, operational parameter used to assess the performance of a water-treatment process (chlorine residuals and pH) [1]. The nitrate concentration (3.38±5.79 mg/L) presented a significant relation with the presence of the fecal contaminant enterococci ($p=0.011$). There were significant differences ($p<0.001$) in regards to nitrate concentration between the water samples according to their provenience, such that groundwater presents higher concentration (mean varying from 4.51 to 6.48 mg/mL) than surface water (mean varying from 1.09 to 1.69 mg/mL). The results also showed that, beyond the presence of enterococci, HPC and coliform bacteria was associated with lower levels of residual chlorine ($p= 0.008$) and pH ($p= 0.004$), respectively.

The results suggest the relevance of chemical evaluation of drinking-water and the linking to the microbiological contamination and the operational control of water-treatment process.

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Diffusion and Removal Kinetics of Hydrogen Peroxide in Brain Tissue – a Study Using Ruthenium Purple Modified Carbon Fiber Microelectrodes

Ana Ledo[1,2], Eliana Fernandes[1,2], Christopher M.A. Brett[3], Rui M. Barbosa[1,2]

[1]University of Coimbra, Faculty of Pharmacy, 3000-548, Coimbra, Portugal
[2]Center for Neuroscience and Cell Biology, 3004-504, Coimbra, Portugal
[3]University of Coimbra, Department of Chemistry, Faculty of Sciences and Technology, 3004-535, Coimbra, Portugal. analedo@ff.uc.pt

Hydrogen peroxide – H_2O_2 – is recognizably a major biological oxidant which plays a pleiotropic role in redox regulation of biological activities. It is a messenger molecule both in physiological cell communication and deleterious neuroinflammatory response. Its concentration is maintained in the low nanomolar range through tight regulation of production and efficient removal systems which include catalase, glutathione peroxidase and peroxiredoxin systems [1].

Microelectrodes coupled to fast electrochemical techniques are an attractive approach towards real time *in vivo* monitoring of analytes in the extracellular space with minimal damage to living tissue. Carbon fiber microelectrodes (CFM) were modified by electrodeposition of ruthenium purple (RP) for monitoring of H_2O_2 concentration dynamics in brain tissue preparations. The RP-modified CFM (CFM-RP) showed catalytic activity for the reduction of H_2O_2 at −0.1 V vs. Ag/AgCl in aqueous electrolyte at neutral pH and physiological concentration of sodium cation (154 mM). Average sensitivity was 0.98 ± 0.37 μA cm^{-2} μM^{-1} and limit of detection of 70 ± 40 nM. Coating of the CFM-RP with a Nafion® layer extended the operational stability of the RP film to 3 h [2].The CFM-RP-Nafion® where used to study the diffusion of exogenously applied H_2O_2 in striatum slices. We found that diffusion of H_2O_2 followed a 1st order exponential decay function modeled by an equation describing diffusion from a spherical source. The diffusion coefficient was determined to be D=2.79 x 10-6 cm^2 s^{-1}, with $t_{1/2}$ = 2.51 ± 0.91 s. Inhibition of catalase did not change the decay kinetics of H_2O_2, while inhibition of glutathione peroxidase and peroxiredoxin increased the $t_{1/2}$ of H_2O_2 in striatal slices to 3.82 ± 1.22 s and 3.98 ± 0.90 s, respectively. Furthermore, metabolic poisoning of the brain tissue significantly increased $t_{1/2}$ to 5.77 ± 1.21 s, a value similar to that found in a 0.2% agarose slice ($t_{1/2}$ = 6.45 ± 0.75 s).

These result support the suitability of CFM-RP-Nafion® for monitoring H_2O_2 concentration dynamics in brain tissue and reveal details regarding how the brain tissue handles H2O$_2$ through energy-dependent enzymatic systems.

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DUAL ELECTROCHEMICAL IMMUNOSENSOR FOR THE SIMULTANEOUS ANALYSIS OF TWO PEANUT ALLERGENS

Marta M.P.S. Neves, Maria Freitas, Henri P.A. Nouws, Cristina Delerue-Matos

REQUIMTE/LAQV, Instituto Superior de Engenharia do Porto, Instituto Politécnico do Porto, Rua Dr. António Bernardino de Almeida 431, 4200-072, Porto, Portugal. *han@isep.ipp.pt*

Peanut (*Arachis hypogaea*) is included in many healthy diets due to its nutritional value, especially as a protein source [1], and its incorporation in food products has been increasing. However, precaution is essential since this can lead to serious health implications for people predisposed to its allergenicity [2]. Therefore, legislation was implemented and the presence of peanut in food matrices, even in trace amounts, must be declared on the label [3,4]. This has led to challenges such as efficient product labeling and the compliance of food manufacturers with legislation.

Therefore, we developed an electrochemical immunosensor for the simultaneous analysis of two allergenic peanut proteins (Ara h 1 and Ara h 6) in food products. The sensor was based on disposable dual screen-printed carbon electrodes as transducers and a sandwich immunoassay. The antibody-antigen interaction was detected by linear sweep voltammetry through the oxidation of enzymatically deposited silver, that was formed by using secondary antibodies labelled with alkaline phosphatase and a 3-indoxyl phosphate / silver nitrate mixture as enzymatic substrate. Within an assay time of 2 h 20 min, a linear relationship between peak current intensity and the allergens' concentrations was found between 25 and 1000 $ng\cdot mL^{-1}$ for Ara h 1 (i_p (μA) = 0.011 ± 0.0004 [Ara h 1] ($ng\cdot mL^{-1}$) + 0.719 ± 0.209; r = 0.997, n = 6), with a sensitivity of 0.175 $\mu A\cdot mL\cdot ng^{-1}\cdot cm^{-2}$, and between 0.05 and 1.0 $ng\cdot mL^{-1}$ for Ara h 6 (i_p (μA) = 7.098 ± 0.278 [Ara h 6] ($ng\cdot mL^{-1}$) + 0.283 ± 0.168; r = 0.998, n = 6), with a sensitivity of 113 $\mu A\cdot mL\cdot ng^{-1}\cdot cm^{-2}$. The limits of detection were 5.19 $ng\cdot mL^{-1}$ and 0.017 $ng\cdot mL^{-1}$ for Ara h 1 and Ara h 6, respectively. To assess the selectivity and possible interferents, several food constituents and other allergens were tested. The developed sensor was used for the analysis of the allergens in healthy snacks and cookies available in local supermarkets.

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NANOSTRUCTURED POLY(PHENAZINE)-DEEP EUTECTIC SOLVENT/ Fe_2O_3 NANOPARTICLE FILM MODIFIED ELECTRODES FOR (BIO)SENSING APPLICATIONS

Wanderson da Silva, Christopher M.A. Brett

University of Coimbra, CEMMPRE, Department of Chemistry,
3004-535 Coimbra, Portugal. wanderson-quimica@hotmail.com

Novel synthetic approaches for surface functionalisation and preparation of thin-layer coatings is the key principle of electrode modifications for electrochemical (bio)sensing applications. The sensitivity as well as the selectivity is mainly influenced by the kind and the nanostructure of sensitive electrode materials [1]. The preparation of electroactive polymer films, as redox mediators, in deep eutectic solvents (DES), a new class of green solvent, particularly acid-doped ethaline DES, increases the polymer surface uniformity and leads to more robust sensing capabilities, whilst also promoting better electrocatalytic and kinetic effects and more stable polymer films than those formed in aqueous electrolytes [2]. A nanocomposite of poly(phenazine) films and iron oxide nanoparticles (Fe_2O_3) is a novel nanomaterial combination that should have improved conducting and sensing performance, due to the complementary electrocatalytic properties of the components. Additionally, these novel nanostructured materials also offer a suitable microenvironment for biomolecule immobilisation leading to enhanced biosensing characteristics [3].

This work describes investigations into the formation by electropolymerisation and electrochemical properties of three electroactive poly(phenazine) dye films namely, poly(neutral red) (PNR), poly(methylene green) (PMG), and poly(Nile blue) (PNB). The poly(phenazine) films were electrodeposited in ethaline (1 choline chloride: 2 ethylene glycol molar ratio) DES on Fe_2O_3 nanoparticle modified glassy carbon electrodes. Characterisation of the modified electrode platforms by voltammetric, electrochemical impedance and surface analysis techniques will be described. Electrocatalysis and high analytical performance will be illustrated with antibiotic dapsone in electrochemical sensors, and also showing how they can be used as successful mediators with fast kinetics in catalase and acetylcholinesterase enzyme biosensors.

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STATISTICALLY SOUND IDENTIFICATION OF OIL SPILLS ORIGIN: SIMULATION OF NON-NORMAL DIAGNOSTIC RATIOS BY THE MONTE-CARLO METHOD

A.C. Rocha[1], C. Palma[1], R.J.N. Bettencourt da Silva[2]

[1]Instituto Hidrográfico, Rua das Trinas 49, 1249-093 Lisboa, Portugal.
catarina.rocha@hidrografico.pt
[2]Centro de Química Estrutural, Faculdade de Ciências, Universidade de Lisboa,
Campo Grande, 1749-016 Lisboa, Portugal

The frequent oil spills that occur along Portuguese coast and in many harbours are the result of intentional discharges (e.g. tank wash and ballast release), accidents in the fuel supply of vessels or other incidents (e.g. vessels collision and grounding). In addition to the known impacts that these types of incidents have on the marine environment, the cleaning operations and the limiting of the use (e.g. leisure, fishing and navigation) of the affected areas are generally very costly and time consuming, resulting in relevant socio-economic losses. For this reason, the identification of the spill origin is needed to, under the law, impute responsibility. However, in many cases it is difficult to produce the reliable evidence required by court proceedings.

In order to identify the source of the spill, chemical analysis on the spill and suspected source(s) are performed. These analyses assume that oils have singular compositional characteristics (*fingerprint*) enabling differentiations among crudes and derived products [1]. Gas Chromatography-Mass Spectrometry (GC-MS) is used in these assessments due to its ability to obtain a wide range of chemical data. However, the large amount of GC-MS data must be properly selected and interpreted.

As a part of the exhaustive data processing, ratios of chromatographic signals of different components (diagnostic ratios - DR) from samples of the spill and suspected source(s) are determined. Standard procedures indicate the use of Student's *t* tests for comparing DR therefore assuming that this variable is normally distributed [2, 3] which could lead to erroneous assessments if this assumption is not valid [4].

This work presents an alternative computational tool for the statistically sound assessment of the RD agreement of samples analysed in pollution incidents that does not assume ratio normality. This tool involves the simulation of the probability distributions of RD by the Monte Carlo method supported on the experimentally observed correlation and dispersion of signals combined in the ratio. It was compared the modelling of the RD by the t-distribution and MCM. The computational simulation allows a better assessment of the global performance of identifications based on various correlated RD and improved identification criteria significantly if RD is estimated from more than triplicates analysis.

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EVALUATION OF THE UNCERTAINTY OF THE CHARACTERISATION OF LARGE MARINE SYSTEMS USING MONTE CARLO SIMULATIONS

Carlos Borges[1], Carla Palma[1], Ricardo Bettencourt da Silva[2]

[1]Instituto Hidrográfico, Rua das Trinas 49, 1249-093 Lisboa, Portugal.
carlos.borges@hidrografico.pt
[2]Centro de Química Estrutural, Faculdade de Ciências, Universidade de Lisboa,
Campo Grande, 1749-016 Lisboa, Portugal

Chemical composition monitoring has a key role on environmental protection policies, but the interpretation of their results doesn’t usually account for the associated uncertainty. Furthermore, the influence of sampling in environment characterization may be the main source of uncertainty. Moreover, classical sampling strategies are not adequate to the marine environment due to two main factors: the system dynamics and the uncertainty of GPS positioning.

The present study intends to model and optimize the uncertainty of sampling in marine environments using Monte Carlo Simulations on a four step approach: collection of samples at a defined depth and known GPS coordinates; description of the collected information as a 3D surface (x, y, z), where x and y are GPS coordinates and z samples concentrations; randomization of the 3D surface given relevant uncertainty components of GPS coordinates and sample analysis; and scanning of the randomized surfaces to model the spatial variation of analyte concentration. Three types of sampling strategies were simulated: Single Sampling, Linear composite Sampling and Random composite Sampling using a user-friendly Microsoft Excel spreadsheet produced for this purpose [1-2].

Samples were collected on the Portuguese Continental slope during the IHPH-AQUIMAR2018-2 survey on board the Portuguese Navy’s R/V “NRP Alm. Gago Coutinho” as part of the work of AQUIMAR (Marine Knowledge supporting aquaculture) Project. For the specific purpose of this study, 20 samples of water were collected at a selected depth of 25 m and analyzed for nutrients’ contents.

The results obtained allowed to conclude that sampling uncertainty is a major contribution to the total uncertainty, accounting for 25 % to more than 80 % of the total uncertainty depending on the heterogeneity of the system.

The developed tool will allow the objective assessment of future composition trends of the studied environmental area.

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ELECTROACTIVE POLYMER-DEEP EUTECTIC SOLVENT/CARBON NANOMATERIALS FOR ELECTROCHEMICAL SENSORS AND BIOSENSORS

Berna Dalkıran, Isabel P.G. Fernandes, Melinda David, Christopher M.A. Brett

University of Coimbra, CEMMPRE, Department of Chemistry, 3004-535 Coimbra, Portugal. cbrett@ci.uc.pt

Electroactive and redox polymers have received considerable interest in recent years in sensors and biosensors, biofuel cells, and energy storage technologies. By acting as a redox mediator, they facilitate electron transfer. The growing demand for non-toxic, eco-friendly, biodegradable green designer solvents has led to increased interest in the use of deep eutectic solvents (DES) in polymer synthesis over the last few years; the use of DES leads to polymers with different chemical compositions and morphology [1, 2]. Carbon nanomaterials have been used for a long time in electrochemical applications, due to their important mechanical, catalytic and electrical properties. The combination of nanomaterials and electroactive polymers can improve the performance characteristics of sensors [3].

This study focused on the development of new matrices based on polymer-coated functionalized multiwall carbon nanotubes (MWCNT), in the modification of glassy carbon electrodes (GCE). The GCE was coated with MWCNT on top of which a film of the electroactive polymer poly(thionine) (PTH) was formed by electropolymerisation using potential cycling in acid-doped ethaline DES (choline chloride plus ethylene glycol) solution with the addition of acid dopants with different anions CH_3COO^-, SO_4^{2-}, Cl^-, NO_3^-, ClO_4^-, acetic acid being the best. This modified electrode, with the best architecture, was characterized by electrochemical voltammetric and impedance techniques. Surface characterization studies of the modified electrodes were carried out using scanning electron microscopy, and correlated with the electrochemical properties. The influence of electropolymerisation parameters was examined for the growth of the polymer film.

The applicability of the sensor platform with PTH prepared in ethaline DES was demonstrated using oxidation of ascorbic acid (AA). The new sensor is very promising for the determination of AA in real samples with good selectivity and detection limit equal or better than AA sensors in the literature. A uric acid biosensor platform was prepared by immobilising uricase enzyme and was successfully used to analyse uric acid in spiked synthetic urine samples with excellent recoveries.

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STUDY OF ANTIOXIDANT COMPOUNDS IN COFFEE USING A LOW PRESSURE CHROMATOGRAPHIC SYSTEM WITH AMPEROMETRIC DETECTION

Alexandra Rangel Silva, J.R. Santos, P.J. Almeida, J.A. Rodrigues

REQUIMTE/LAQV - Departamento de Química e Bioquímica, Faculdade de Ciências,
Universidade do Porto, rua do Campo Alegre s/n, 4169– 007 Porto, Portugal.
alexandrarangelsilva1@gmail.com

The coupling of short length monolithic columns in a flow analysis system, producing a low pressure chromatographic system, is an advantageous approach for compound separation in complex samples. This approach is sustained by the compatibility of monolithic columns with peristaltic pumps and the high superficial area (responsible for the high chromatographic efficiency). In a previous work, the determination of niacin in coffee was realized, using an ion chromatographic system, based on a 1 cm-length C_{18} monolithic column, and a boron doped diamond (BDD), as working electrode, for the amperometric detection [1].

In the present work, the main aim was the separation, identification and quantification of antioxidants present in green coffee beans, exploiting a low pressure chromatographic system with amperometric detection, similar to the one used in the cited work. Different studies were performed, with standard solutions and extracts of green coffee beans, regarding the elution conditions and electrochemical behavior of antioxidants, particularly 5-caffeoylquinic acid and caffeine, the two predominant antioxidants in green coffee, in different medium conditions. Also, the study of the eluate under different potential values at the BDD working electrode was performed.

The developed methodology allowed the separation of 7 antioxidants present in green coffee, having 6 of these compounds been identified by mass spectrometry. The antioxidants identified were caffeine, 5-feruloylquinic acid and 4 isomers of caffeoylquinic acid (3-, 4-, 5- and *cis*-5-CQA). Furthermore, the two most predominant coffee antioxidants (5-CQA and caffeine) were quantified in green coffee extracts.

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CHEMICAL AND METROLOGICAL CHALLENGES OF SEAWATER ACIDITY

Bárbara Anes[1], Maria Filomena Camões[1]

[1]*Centro de Química Estrutural, Faculdade de Ciências, Universidade de Lisboa,*
Campo Grande, 1749-016 Lisboa, Portugal

Anthropogenic emissions of carbon dioxide (CO_2) into the atmosphere result in instabilities to the ocean carbonate system and promote climate change. The increase in atmospheric concentrations of CO_2, hence in partial pressure of CO_2, $p\mathrm{CO}_2$, and in dissolved inorganic carbon, increases the seawater acidity, lowers the pH value, and affects the equilibrium concentrations of carbonate species in the oceans.

The free acidity, expressed by pH, is an important parameter for the characterization of seawater, affecting practically all the biogeochemical processes in the ocean. Although there is only one international recognized definition of pH [1], different conceptual definitions and alternative measurement procedures have been adopted and are in use by some, namely among oceanographers, often leading to confusion [2]. This leads to major difficulties with the use of data, e.g. on what concerns comparison of results in space and time, since different measurands, the chosen analytical methods and procedures, and the uncertainty associated to the experimental results conduct to small changes in the assessed composition values of ocean systems. Harmonization of methods and procedures is thus fundamental for future comparison purposes.

This work focuses on the different approaches currently used to measure seawater pH and related quantities. Key issues that must be considered for attaining a most needed harmonized international definition and method procedure to quantify ocean acidification, are being tackled by an international study grant (IAPSO) and will be discussed.

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SOLIDIFIED FLOATING ORGANIC DROP MICROEXTRACTION FOR THE QUANTIFICATION OF THREE NSAIDS IN ENVIRONMENTAL WATERS

Érika M.L.Sousa[1], Diana L.D. Lima[1], Lanna K. Silva[2], José H.G. Rangel[2], Natilene M. Brito[2], Valdemar I. Esteves[1], Arlan S. Freitas[2], Eliane R. Sousa[3], Gilmar S. Silva[2]

[1] CESAM, Department of Chemistry, University of Aveiro, Campus Universitario de Santiago, 3810-193 Aveiro, Portugal. erikamsousa@ua.pt
[2] Department of Chemistry, Federal Institute of Education, Science and Technology of Maranhão, Monte Castelo Campus, Getúlio Vargas Avenue, 65030-005 São Luis, Brazil
[3] Department of Chemistry, Federal Institute of Education, Science and Technology of Maranhão, Maracanã Campus, Av. dos Curiós, Vila Esperança, 65095-460 São Luis, Brazil

The extensive use of non-steroidal drugs (NSAIDs) is a major public health problem related to their toxicity and in some cases, bioaccumulation capacity. Environmental monitoring of NSAIDs is needed to evaluate their occurrence and risk assessment. Therefore, new extraction methods have been proposed, such as solid-phase microextraction (SPME) [1], which compared to liquid-liquid extraction and solid-phase extraction requires less time and solvent consumption. However, this strategy is not suitable for screening purposes, due to the high cost and time-consuming features. On the other hand, dispersive liquid-liquid microextraction coupled with solidified organic drop (SFODME) has numerous advantages comparing to conventional method, such as the use of less toxic solvents and easy removal of the extracting solvent.

Hence, the aim of this work was the optimization of a fast, simple and low-cost SFODME methodology coupled with high-performance liquid chromatography and UV/Vis detection for the simultaneous quantification of naproxen (NPX), diclofenac (DCF) and mefenamic acid (MFN) in environmental waters. The parameters that can influence the efficiency of the extraction process were evaluated, such as type and volume of the extracting and dispersive solvents, pH, stirring type and ionic strength. NPX, DCF and MFN calibration curves were obtained, providing limits of detection between 0.336 and 0.426 µg L^{-1}. The optimized method showed recoveries between 90 % to 116 % and enrichment factors between 149 to 199. The proposed method has been validated and satisfactorily tested in spiked tap water, surface water and seawater. Recovery rates ranging from 110 % and 120 % for seawater, 76 % and 107 % for tap water and 84 % and 120 % for surface water, demonstrated that the proposed method can be used to extract NSAIDs from aqueous samples with different characteristics.

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pHe MEASUREMENT: WHAT DO ETHANOL MEASURE?

Fernando Fertonani[1], Filomena Camões[2], Elcio Cruz Oliveira[3]

[1]*University of São Paulo State, **UNESP**, **IBILCE**- R. Cristóvão Colombo, 2265,*
S.J. Rio Preto/SP - CEP 15054-000 – Brazil. fertonan@gmail.com
[2]*Centro de Química Estrutural, Faculdade de Ciências, Universidade de Lisboa,*
Campo Grande, 1749-016 Lisboa, Portugal
[3]*Pontifícia Universidade Católica do Rio de Janeiro - **PUC-Rio / Petrobras**- R. Marquês de S. Vicente, 225, Gávea-Rio de Janeiro/RJ-CEP 22451-900 - 38097, Brazil*

Although the definition of pH is applied to aqueous systems, the measurement of ethanol pH (pHe) is a parameter of the quality of hydrous fuel ethanol (HEF). Brazil annually invests millions of reais in combined glass electrodes (CGE) for "on-line"/laboratories measurements. Thus, it is important to investigate what is actually being measured. For a long time our team and, recently, with the collaboration established with the University of Lisbon (UL) and PUC/PETROBRAS, have been working with the measurement of pHe with a focus on studying the variation in the composition of internal and external solution of CGE and applications. The measurement results obtained from these electrodes using NBR 10.891:2013 standard are compared with the results obtained using the ROSS pH Electrode (Orion 810007) requested in the ASTM D 6423: 2008 standard. These modified electrodes have been used in studies of ethanol - water mixtures, in the range values of (0 ≤ ethanol% ≤ 100). The results are very interesting when the ethanol content is above 95%, showing an effective change in the response of the electrodes. Another approach that we are investigating, as mentioned earlier, is the preparation of an CGE that contemplates a new paradigm, the complete modification of its internal and external electrodes with ethanol. In order to achieve this modification, it was necessary to prepare a buffer solution in an ethanolic medium to carry out the mentioned changes. Thus, we have been working on the preparation and characterization (homogeneity and stability) of a buffer of pH 4.7, prepared in ethanol and in water media for data comparison; the results are promising. Other tests have been carried out for the determination of pk_a for dyes in ethanol solution (97%) and anhydrous one. These dyes were applied for the spectrophotometric determination of the shortest pHe and pH range and make their comparison with the pHe and pH data obtained from the modified CGE electrodes and those originals. In parallel, we have been testing the measurement of pH and pHe of aqueous and ethanolic solutions prepared with HCl. Such measurements aimed to compare the results of pHe vs. pH values to evidence the pH behaviour of the solutions with the increase or decrease in the nH^+ added to the aqueous or ethanolic solution. The results of these experiments showed an effectively negative deviation for the correlation at pH values below pH 3. For higher pH values (4 ≤ pH ≤ 5), the pHe and pH are statistically equal. The observed deviation for the most acidic solutions (pH ≤ 3), may be related to the differences in the k_a values of the HCl solutions when it is aqueous or ethanolic solution. In general, the results have been promising and with the expansion of the partnership with the University of Lisbon, PUC-Rio/Petrobras, we will be expanding horizons for the theme of pH measurement of ethanol.

STRATEGY FOR PREPARATION OF ETHANOLIC BUFFERING SOLUTION FROM LITHIUM ACETATE/ACETIC ACID

Natalia Cambiaghi Atilio[1,2,3], Fernando Luis Fertonani[1,2], Elcio Cruz Oliveira[2]

[1]*University of São Paulo State, **UNESP**, **IBILCE**- R. Cristóvão Colombo, 2265, S.J. Rio Preto/SP - CEP 15054-000 – Brazil. nacambiaghi_@outlook.com*
[2]*Pontifícia Universidade Católica do Rio de Janeiro - **PUC-Rio**- R. Marquês de São Vicente, 225, Gávea - Rio de Janeiro/RJ - CEP 22451-900 - POBOX: 38097, Brazil*
[3]*SPR Soluções Metrológicas- Av. Vetorasso, 805, S.J. Rio Preto/SP-CEP 15035-470, Brazil*

The most used biofuel today is ethanol (Hydrous Ethanol Fuel, HEF), due to its low cost, good engine efficiency, etc. A criterion for assessing the quality of ethanol at the refinery is its pH, a parameter required in standards related to HEF performance in vehicles, and established in Brazil by the ABNT 10.891:2013 standard and internationally by the ASTM D 6423:2008 standard (anhydrous ethanol). The pH values are obtained from the combined glass electrode, containing a solution of saturated $H_2O/KCl_{sat.}$ or ethanol/$LiCl_{sat.}$, generating different values of net junction potential (E_{jl}) which compromises the measure pH values. The glass electrode was developed for measurements in aqueous media, and the HEF has an average of 6.9% in water, which approximates it to an organic solvent. So, is the combined glass electrode capable of correctly measuring the pH of ethanol? In response to the questioning, the electrodes were prepared: modified (ethanol/$LiCl_{sat.}$) and the conventional; and pH measurements were obtained in aqueous and ethanolic solutions with the exactly known number of moles of HCl. The relationship between $pH_{ethanol}$ vs. pH_{water}, for the solutions/HCl, $1 \leq pH \leq 5$, showed deviations from linearity to, $1 \leq pH \leq 3$, and equal values, within the experimental error, to $pH \geq 4$ (HCl presents: $Ka_{ethanol} > Ka_{água}$). However, the MRCs used to calibrate the mesuare system were conventional ones. Thus, the aim of the work was to prepare a reference material (MR): from LiAc/HAc in HEF solutions, to meet the need for a buffer solution prepared in ethanol. In view of the objective, buffer solutions (BS) of concentrations, C= 0.1 and 0.01 m (molal), were prepared in duplicates, in HEF and in water (only C= 0.1 m), for comparison; nominal value of BS: pH 4.40. The solutions were fractionated (5 vials) and kept under agitation at constant temperature (25±2) ºC, for the study of: 1- stability (ASTM E 691-99); 2- homogeneity (ANOVA-one way); and 3- uncertainty (botton-up). The pH values were measured 2 times/week (n= 5; for 4 months). Homogeneous and stable BS were obtained. The results of the pH and U measurements (k= 2; 95%) are shown in Table 1. The Δ values represents the absolute differences for the two media. The conventional electrode ($H_2O/KCl_{sat.}$) Showed the best results (less deviation between the means) compared to the modified one (ethanol/$LiCl_{sat.}$).

Table.1 pH values measured from different reference electrodes configurations obtained for the different BS.*

ST / Sol. Eletr.	**EtOH 0,1**		**EtOH 0,1**			**H_20 0,1**		**EtOH 0,01**		**EtOH 0,01**	
	s1	**U**	**s_2**	**U**		**s_1**	**U**	**s_1**	**U**	**s_2**	**U**
EtOH/$LiCl_{sat.}$	4,50	**0,072**	4,28	0,045		4,37	**0,061**	4,25	**0,065**	4,08	**0,053**
H_2O/KCl	4,49	0,073	4,33	0,037		4,35	0,079	4,39	0,076	4,31	0,073
Δ	**0,010**		**0,050**			**0,020**		**0,14**		**0,23**	

** arbitrary acceptance interval of 5% for the nominal pH 4.40; all values are accepted, except for EtOH 0.01 S2 solution.*

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FLOW ACCURACY AND TRACEABILITY IN A LAB-ON-A-CHIP DEVICE

Elsa Batista[1], João Alves e Sousa[1], Susana Cardoso[2,3], Vania Silverio[2,3]

[1]Instituto Português da Qualidade, IPQ, 2825-002 Caparica, Portugal, ebatista@ipq.pt
[2] Instituto de Engenharia de Sistemas e Computadores para os Microsistemas e as Nanotecnologias, INESC MN, 1000-029 Lisboa, Portugal
[3] Instituto Superior Técnico, Universidade de Lisboa, 1000-049 Lisboa, Portugal

Microfluidics is both the science which studies the behavior of fluids through micro-channels and the technology of manufacturing microminiaturized devices containing chambers and tunnels through which fluids flow or are confined. These devices are small, simple to use, portable and can be used in several emerging applications such as micro-liquid chromatography, (scaled down) process technology or micro-reactors, drug development, micro-implantology and Lab-on-a chip, to name a few [1,2]. At this scale, flow rate variability or erroneous flow rate of internal or external infusion systems has tremendous impact on the measurement accuracy. When external pumps are chosen, several important aspects must be considered to obtain the programmed flow rate, mainly the pump ability to control and maintain instant micro-flow and micro-flow changes. The minimum delivered volume, internal pressure, overall size, complexity, the compliance of these devices and their accessories may inevitably lead to long delays and unwanted large flow transients [3]. To ensure accuracy of flow through a lab-on-a-chip it is fundamental that the flow generator used is calibrated using the appropriate and traceable method. The most common calibration method used by NMI to measure low flow instruments is the gravimetric method [4]. Other methods can be used, such as optical methods, which trace flow rates down to 1 μl/h with very low uncertainty. This work experimentally compares the two methodologies when applied to syringe pump calibration and demonstrates its impact in the performance of a Lab-on-a-chip device.

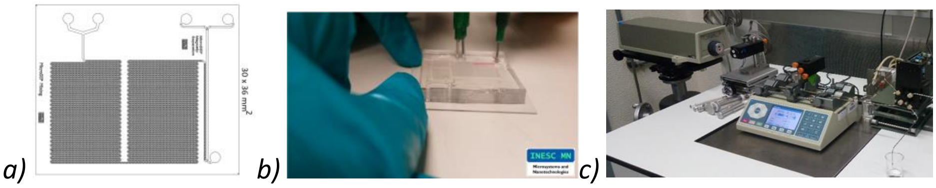

Figure 1: Microfluidic Lab-On-a-Chip device for passive mixing and magnetic separation of bioanalytes. *a*) CAD design, *b*) device after fabrication, *c*) experimental setup of the optical method (interferometry) for the syringe pump calibration.

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GREENER SEQUENTIAL INJECTION METHOD FOR IRON SPECTROPHOTOMETRIC DETERMINATION IN FRESH AND MARINE WATERS

Tânia C.F. Ribas[1], Raquel B.R. Mesquita[1], Tânia Moniz[2], Maria Rangel[2,3], António O.S.S. Rangel[1]

[1]Universidade Católica Portuguesa, CBQF – Centro de Biotecnologia e Química Fina – Laboratório Associado, Escola Superior de Biotecnologia, Rua Diogo Botelho 1327, 4169-005 Porto, Portugal. tpedro@porto.ucp.pt
[2]REQUIMTE - LAQV, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, 4169-007 Porto, Portugal
[3]REQUIMTE - LAQV, Instituto de Ciências Biomédicas de Abel Salazar, Universidade do Porto, 4050-313 Porto, Portugal

Iron is an important micronutrient for living organisms as it participates in a variety of biological functions. However, as it can be introduced in the environment by human activity, it may exceed the allowed limits. In high concentrations, iron affects water quality, causing aesthetic effects, namely water colour, taste and odour, thus making iron quantification of high interest. The spectrophotometric methods recommended for iron quantification often employ toxic reagents. Being green chemistry a concern nowadays, it is important to develop a more benign analytical chemistry. In this work, a sequential injection method for the spectrophotometric determination of iron, using the iron chelator [1], (1-(3'-methoxypropyl)-2-methyl-3-benzyloxy-4-(1H)pyridinone - MRB13), is described. Additionally, the applicability of the method to recreational waters with different salinity contents was accessed. For that purpose, two strategies were employed: one of them resorting to an on-line solid phase extraction (SPE) step targeting the sample matrix clean-up and/or iron enrichment, and the other without resorting to SPE. The SPE strategy was achieved by resorting to a nitrilotriacetic acid (NTA) resin column. The developed method proved to be an efficient tool for iron monitoring in different types of water.

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Development and validation of an UAE-HPLC-DAD-ECD method for simultaneous determination of parabens in cosmetic products

L. Abad Gil[1], S. Lucas Sánchez, M.T. Sevilla, M.J. Gismera, J.R. Procopio

Departamento de Química Analítica y Análisis Instrumental. Facultad de Ciencias
Universidad Autónoma de Madrid, Avda. Francisco Tomas y Valiente 7, 28049 Madrid,
Spain. lucia.abad@uam.es

Preservatives are added to a lot of products such as, cosmetic, pharmaceutical, food and industrial products to inhibit the microbial growth. Parabens are among the most used preservatives due to their low cost and broad antimicrobial activity. The use of cosmetic products has been increased due to the modern lifestyle, resulting in a potential risk for human health and the environment. Parabens have been detected in the environment, being the wastewaters from domestic-health care one of the main sources of contamination. Parabens exhibit estrogenic and carcinogenic activity, reproductive dysfunction effects and can cause allergic contact dermatitis. Since cosmetics are the principal source of human exposure to parabens, the European Union regulates their presence in these personal care products in the Regulation (EC) No 1223/2009 [1]. Considering the adverse effects of parabens on the human health, analytical methodologies should be developed and optimized to determine parabens in cosmetic products.

In this work, we present a HPLC method with dual detection (diode array (DAD) and electrochemical detection (ECD)) in combination with a simple and quick ultrasound assisted extraction (UAE) method for the simultaneous determination of six paraben in cosmetic products. Chromatographic conditions on a reversed-phase column were optimized using DAD. A 35% acetonitrile- 65% 0.01 mol L^{-1} phosphate solution at pH 2 was used as mobile phase at 1.5 mL min^{-1} flow rate. The ECD was performed in amperometric mode, using a thin-layer cell with disposable screen-printed carbon electrodes (SPCE). The use of these electrodes avoids passivation effects and polishing processes, hence the reproducibility of the measurements increases. A potential of +1.0 V (*vs.* Ag/AgCl) was chosen as the optimal for the detection. QuEChERS and UAE methods were optimized and compared for the extraction of the parabens from cosmetic samples. Better results were obtained for UAE method, using methanol as extraction solvent, 1.0 g to 9.0 mL as mass to volume ratio, 25 ºC and 10 min as temperature and sonication time, respectively. The total analysis time, including the sample pre-treatment and the HPLC run is less than 30 min. The UAE-HPLC-DAD-ECD method was successfully applied for the determination of the parabens in eight cosmetic samples with matrices of different complexity.

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IMMOBILIZATION OF IONIC LIQUIDS IN SOLID PHASES AND THEIR APPLICATION

Marieta L.C. Passos[1], Emília Sousa[2,3], M. Lúcia M.F.S. Saraiva[1]

[1]1 LAQV, REQUIMTE, Departamento de Ciências Químicas, Laboratório de Química Aplicada, Faculdade de Farmácia, Universidade do Porto, Rua de Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal. marietapassos@gmail.com
[2] Laboratório de Química Orgânica e Farmacêutica, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, Rua de Jorge Viterbo Ferreira 228, 4050-313 Porto, Portugal
[3] Centro Interdisciplinar de Investigação Marinha e Ambiental (CIIMAR/CIMAR), Universidade do Porto, Edifício do Terminal de Cruzeiros do Porto de Leixões, Av. General Norton de Matos s/n, 4050-208 Matosinhos, Portugal

In the proposed work, two solid-phases based on the immobilization of ionic liquids in an octadecylsilica matrix were prepared and characterized. The immobilization of these imidazolium based ionic liquids was performed based on a new and more environmentally friendly process, replacing a toxic reagent by UV-irradiation. The characterization was performed by nuclear magnetic resonance spectroscopy and elemental analysis. The applicability of these developed solid phases was studied by packing them in cartridges to test them in the solid-phase extraction processes for norfloxacin and ciprofloxacin. The aim was that by adding of the imidazolium group from the ionic liquids, these developed solid phases would exhibit additional ion-dipole interactions, hydrogen-bonding, electrostatic interactions and π-π interactions with analytes, apart from the hydrophobic effect usually used with the conventional C18 [1]. After the optimization of some parameters such as the elution solvent, the eluent volume and, the sample volume to be used during the loading step, the developed solid-phases with immobilized ionic liquids indicated high probabilities to be useful in solid phase extractions of other fluoroquinolones.

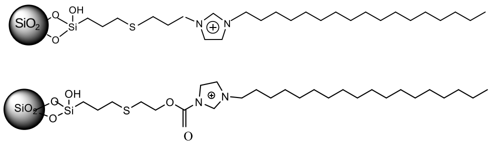

Figure 1: Silica-based octadecylimidazolium solid-phases.

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Apresentações em Painel

Poster Presentations

PRODUCTION AND ISOLATION OF BIOACTIVE COMPOUNDS FROM *Tetraselmis chuii AND Chlorella vulgaris*

Sara Hussen[1], Magda C. Semedo[1,2], Sónia Martins[1,2], Patrícia D. Barata[1,3],
Joana Laranjeira da Silva[4]

[1]Área Departamental de Engenharia Química, Instituto Superior de Engenharia de Lisboa, IPL, R. Conselheiro Emídio Navarro, 1, 1959-007, Lisboa, Portugal. msemedo@deq.isel.pt
[2]Unidade de Geobiociêcias, Geoengenharias e Geotecnologias (GeoBioTec), Faculdade de Ciências e Tecnologia, UNL, Campus da Caparica, 2829-516, Caparica, Portugal
[3]Centro de Química-Vila Real, Universidade de Trás-os-Montes e Alto Douro, 5001-801, Vila Real, Portugal
[4]Allmicroalgae, Av. Eng. Duarte Pacheco 19, 9º piso, 1070-100, Lisboa, Portugal

In recent years, there has been a growing interest focused on the biotechnological potential of microalgae, mainly due to the identification of several high value-added biomolecules synthesized by these microorganisms [1]. Thus, microalgae are a promising resource for a highly sustainable production of various compounds such as proteins, phenolic compounds, lipids, polysaccharides, pigments and vitamins. Its industrial production has been worldwide evolving due to their extensive application potential in renewable energy, animal feed, food, cosmetic, biopharmaceutical and nutraceutical industries [2]. Polysaccharides in general, and sulfated polysaccharides and β-glucans in particular, exhibit several biological effects such as antioxidant, anti-inflammatory, antiviral, antitumor and immunomodulating activities [3]. Numerous microalgae might also excrete into their environment exopolymers, which are mainly composed by exopolysaccharides (EPS) with several biological activities [4].

Tetraselmis chuii and *Chlorella vulgaris* were grown under autotrophic conditions, and biomass was collected in three different growth phases (lag, exponential, stationary) in order to evaluate the content of biomolecules produced by these species. With these purpose, aqueous extracts were obtained by using multistep extraction (with cold and boiling water, acidic and alkaline conditions) and conventional Soxhlet extraction (80% (v/v) ethanol). Their total polysaccharides, sulfated polysaccharides, β-glucans, carotenoids, chlorophylls, total protein and B-phycoerythrin contents were investigated [5,6]. EPS contents solubilized in culture media were also analysed.

The biomass collected at the exponential phase of both culture species, in general, showed higher contents in biomolecules, highlighting the alkaline fractions obtained by the multistep extraction method. Thus, the studied extracts due to their biochemical properties, could be suggested to be further exploited in the formulation of novel functional food or nutraceutical preparations.

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RECENT DEVELOPMENTS ON WATERBORNE BACTERIA STRATEGIES FOR ENVIRONMENTAL ASSESSEMENT

Ana Machado[1,2], Adriano A. Bordalo e Sá[1,2], António O.S.S. Rangel[3],
Raquel B.R. Mesquita[3]

[1]ICBAS—UP, Institute of Biomedical Sciences Abel Salazar—University of Porto, Rua Jorge Viterbo Ferreira 228, 4050-313 Porto, Portugal. ammachado@icbas.up.pt
[2]CIIMAR—UP, Interdisciplinary Centre of Marine and Environmental Research of the University of Porto, Novo Edifício do Terminal de Cruzeiros do Porto de Leixões, Avenida General Norton de Matos, S/N, 4450-208 Matosinhos, Portugal
[3]Universidade Católica Portuguesa, CBQF - Centro de Biotecnologia e Química Fina – Laboratório Associado, Escola Superior de Biotecnologia, Rua Diogo Botelho 1327, 4169-005, Porto, Portugal

Waterborne diseases have emerged as a stern global health burden worldwide, with more than 2.2 million associated deaths and an economic loss of nearly 12 billion dollars, per year [1]. Up to now, microbial water quality for drinking and recreational purposes has been solely evaluated based on the quantification of two fecal indicator bacteria (FIB), although concern with naturally occurring potential pathogens has been arising. For the purpose and although cumbersome, culture based methods remain the gold standard for bacterial monitoring. Nucleic acid-based and immunological techniques, coupled to colorimetry and chemiluminiscent approaches for signal acquisition, became broadly used in laboratories for detection of pathogens. Although a low detection limit is possible, the major limitations are the pre-enrichment and concentration requirement, the cross-reactivity, the associated costs, and the need of trained personnel [2]. Recently, detection strategies have been direct towards the development of efficient methods for low concentration, on-site and multiplex detection. Biosensor-based methods (optical, electrochemical, conductometric), and paper-based, microfluidic and lateral flow platforms revealed to be promising in the detection and quantification of waterborne bacteria. The main advantages of these analytical devices were the low cost, high throughput, easy to use, short time, minimal sample requirement, easy interpretation, and *in situ* applicability. The integration with smartphones for signal acquisition has been drawing the research and commercial attention. However, accuracy, resolution, sensitivity, and multiplexed detection require some improvements, being the principal drawbacks at this stage [3]. The aim of the present study is to discuss the advantages and limitations of the existing waterborne detection methods, with particular relevance to the new mobile devices with capacity for field use.

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ANALYTICAL APPROACHES FOR EVALUATING THE PHOTODEGRADATION OF GEOSYNTHETICS

Paulo Joaquim Almeida[1], José Ricardo Carneiro[2], Maria de Lurdes Lopes[2]

[1]Requimte, Faculty of Sciences, University of Porto, Rua do Campo Alegre 687, 4169-007 Porto, Portugal. pjalmeid@fc.up.pt
[2]Construct-Geo, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

The use of geosynthetics in the construction of civil and environmental engineering structures (e.g. waste landfills, roads or coastal protection structures) has become a common practice in the last decades. The advantage of using geosynthetics (instead of more traditional construction materials) include their ease of installation, low cost, high efficiency, high versatility and low environmental impact. These materials must often perform their functions for a long period of time (in many cases, over 25 years) and therefore must have a good resistance against degradation.

In their applications, the geosynthetics can be in contact with many agents capable of having a negative impact on their short and long-term behaviour. Polypropylene (PP), a polymer often used for manufacturing geosynthetics, has a quite good resistance against many chemical substances and biological degradation. However, it has a low resistance against oxidation and ultraviolet (UV) radiation. The oxidation process of PP follows a complex chain reaction mechanism, which is started by the formation of free-radicals, either produced by heat (thermo-oxidation) or by UV radiation (photo-oxidation)[1]. To retard the damage induced by UV radiation, chemical additives (e.g. UV-stabilisers or antioxidants) are often added to the composition of geosynthetics.

This work overviews some analytical techniques that can be used to evaluate the photo-degradation of geosynthetics. As an application example, 3 PP geosynthetics stabilised with different amounts of the additive Chimassorb 944 (C944) were exposed to UV radiation, both under natural (outdoor exposure) and accelerated (exposure in a laboratory weatherometer) conditions. The damage suffered by the geosynthetics (caused by the exposure to UV radiation) was evaluated by tensile tests, infrared spectroscopy and scanning electron microscopy with X-ray microanalysis. The evolution of the concentration of C944 during the UV-exposure tests was monitored by liquid chromatography with UV detection and by liquid chromatography with mass detection. The latter was also used to try to identify some degradation products of C944.

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Cu(II) DETECTION BY FLUORESCENT CALIX[4]ARENE-OXACYCLOPHANE ARCHITECTURES

Alexandra I. Costa,[1,2] Patrícia D. Barata,[1,2] Carina B. Fialho,[1†] José V. Prata[1,2]

[1]Departamento de Engenharia Química, Instituto Superior de Engenharia de Lisboa, Instituto Politécnico de Lisboa, R. Conselheiro Emídio Navarro, 1, 1959-007, Lisboa, Portugal
[2]Centro de Química-Vila Real, Universidade de Trás-os-Montes e Alto Douro, 5001-801, Vila Real, Portugal. jvprata@deq.isel.ipl.pt
[†]Present address: Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

Calixarenes are cyclic oligomers widely investigated due to their ability to recognize and differentiate neutral and ionic guests through the formation of inclusion complexes [1]. Various topologies of fluorescent sensors for metal cation recognition based on calixarene-derived molecular receptors have been developed [2]. Copper(II), lead(II) and mercury(II) ions are ubiquitous in nature, either associated to important physiological processes [3] or representing environmental hazards and health issues [4], making their sensitive and selective detection highly desirable.
In this communication we report the results of the chemosensing ability of calix[4]arene-oxacyclophane (Calix-OCP) receptor, either wired-in-series in arylene-*alt*-ethynylene conjugated polymers [5] (Fig. 1) or standing alone as a sole molecular probe [6], toward metal ions in solution.

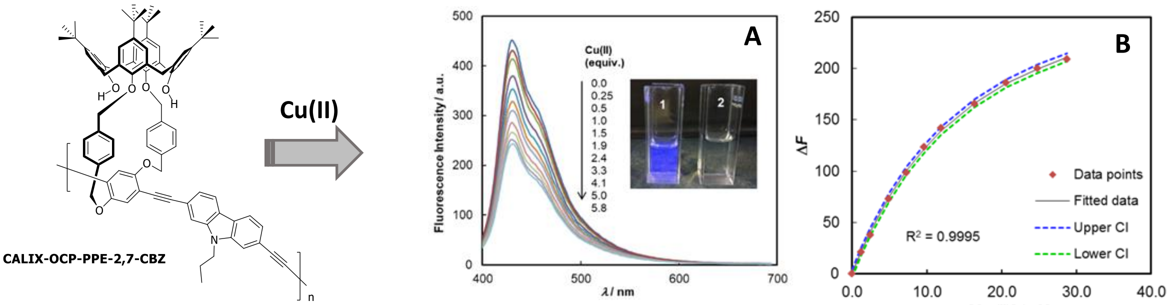

Figure 1: (**A**) Emission spectra of polymer **Calix-OCP-PPE-2,7-CBZ** (5.0 x 10^{-6} M in CH_3CN) upon addition of increasing amounts (0.25 - 5.8 equiv.) of $Cu(ClO_4)_2$ (λ_{exc} = 380 nm). Inset: photo of polymer fluorescence under UV irradiation (366 nm) before (1) and after (2) $Cu(ClO_4)_2$ addition (5 equiv.); (**B**) Binding isotherm for the fluorimetric titration of 5 with Cu(II) with fitted curve and confidence intervals.

The magnitude of the binding constants (K_a = 5.30-8.52x10^4 M^{-1}) and the free energy changes for the inclusion complexation (-ΔG = 27.0-28.1 kJmol^{-1}), retrieved from fluorimetric titration experiments, revealed a high sensitivity of Calix-OCP architectures for Cu(II) species.

Acknowledgements: We are grateful to Fundação para a Ciência e a Tecnologia/Ministério da Ciência, Tecnologia e Ensino Superior (FCT/MCTES) for financial support (UID/QUI/00616/2019) and Instituto Politécnico de Lisboa (IPL) for funding this work (Project IPL/2016/NoSeMeTox/ISEL).

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APPLICATION OF HEADSPACE MICROEXTRACTION TECHNIQUES TO MONITORING VOCs EMISSIONS FROM LEAVES OF FOUR PORTUGUESE TREE SPECIES UNDER EXTREME FIRE CONDITIONS

O.C. Gonçalves[1], N.R. Neng[1,2], J.M.F. Nogueira[1,2]

[1]Centro de Química Estrutural, Faculdade de Ciências, Universidade de Lisboa,
Campo Grande, 1749-016 Lisboa, Portugal. ocgp98@gmail.com
[2]Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa,
Campo Grande, 1749-016 Lisboa, Portugal

Ongoing climatic changes have created more frequent drought and heat wave conditions that trigger the occurrence of Extreme Wildfire Events. Many dramatic consequences of wildfires, particularly in terms of lives lost, are due to extreme fire behavior, with sudden changes in fire spread, in what have been termed as blow-up, eruptive or flashover fires. Studies have suggested that gases generated from heated vegetation, in particular volatile organic compounds (VOCs) may, under some topographic and atmospheric conditions, accumulate in locations where, after the arrival of the ignition source, they rapidly burst in flames as in explosions [1,2].
In this work, we proposed the application of bar adsorptive microextraction (BAμE) [3] and solid-phase microextraction (SPME) in the headspace (HS) mode, followed by gas chromatography coupled to mass spectrometry (GC-MS) analysis, to evaluate the VOCs emissions from the leaves (figure 1) of the four main Portuguese tree species (*Pinus pinaster*, *Eucalyptus globulus*, *Quercus suber* and *Quercus robur*) when subjected to aggressive environments at high temperatures. Preliminary data obtained, suggest that HS-BAμE technique seems to be the ideal analytical approach, to determine the majority VOCs from the leaf matrices and, in this sense, to study their flammability potential in fires that occur under extreme conditions.

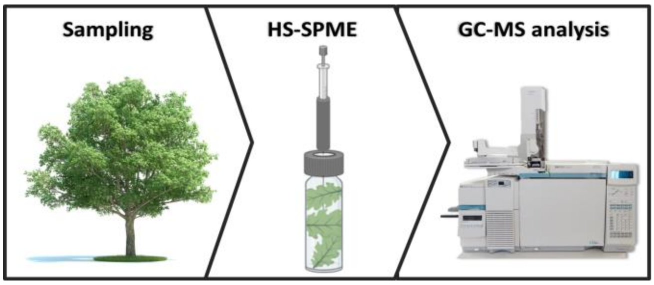

Figure 1. Analytical scheme proposed (HS-SPME/GC-MS methodology) to monitoring VOCs emissions from tree leaves.

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OPTIMIZATION OF SUBCRITICAL WATER EXTRACTION OF BIOACTIVE COMPOUNDS FROM VINEYARD PRUNING RESIDUES USING RESPONSE SURFACE METHODOLOGY

Olena Dorosh[1], Manuela M. Moreira[1], Elsa F. Vieira[1], Andreia F. Peixoto[2],
Cristina Freire[2], Cristina Delerue-Matos[1]

[1]REQUIMTE/LAQV, Instituto Superior de Engenharia do Instituto Politécnico do Porto,
Rua Dr. António Bernardino de Almeida, 431, 4249-015 Porto, Portugal.
manuela.moreira@graq.isep.ipp.pt
[2]REQUIMTE/LAQV, Departamento. de Química e Bioquímica, Faculdade de Ciências,
Universidade do Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal

Biomass represents a natural source of valuable components which could found application in many industries. Recently, it has been demonstrated that vineyard pruning residues can be used as a potential source of bioactive compounds, namely polyphenols [1,2].

In this study, an experimental design approach was used to optimize the total phenolic content and antioxidant activity from vine-canes from *Touriga Nacional* variety. Subcritical water extraction was employed, and the independent parameters studied were extraction temperature (150-280ºC) and extraction time (20-50 min). A central composite design was used to evaluate the influence of extraction parameters in achieving higher recovery of phenolics, as well as higher antioxidant activities (by FRAP and ABTS assays). Amongst the examined parameters, to maximize the phenolic content and antioxidant activity of the vine-cane extracts, the extraction temperature demonstrated to exerts the highest influence ($p < 0.05$). Preliminary results showed that the optimal conditions were 28 min extraction time and 280 ºC extraction temperature. The optimum subcritical water extraction conditions are currently being employed to different vine-cane varieties collected at different years to select the extracts with the highest antioxidant activity, which can be further applied to food or cosmetic industries in substitution of synthetic antioxidants. The results exhibited that subcritical water extraction technology is a time-saving, high yield, and bioactive environmentally friendly technique for obtaining phenolic compounds.

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EXPLORING NEWLY SYNTHESIZED IRON CHELATORS AS COLORIMETRIC/FLUORESCENT SENSORS IN POLYMER INCLUSION MEMBRANES

Raquel B.R. Mesquita[1], Andreia Leite[2], Maria Rangel[3], António O.S.S. Rangel[1]

[1]Universidade Católica Portuguesa, CBQF - Centro de Biotecnologia e Química Fina – Laboratório Associado, Escola Superior de Biotecnologia, Rua Diogo Botelho 1327, 4169-005 Porto, Portugal. rmesquita@porto.ucp.pt
[2]REQUIMTE - LAQV, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, 4169-007 Porto, Portugal
[3]REQUIMTE - LAQV, Instituto de Ciências Biomédicas de Abel Salazar, Universidade do Porto, 4050-313 Porto, Portugal

The determination of metal ions in natural waters is very important due to their potential toxicity. The latter is usually associated with the oxidation state so the total content is not as useful as speciation. Additionally, in dynamic aquatic systems, the matrix variability and the expected low concentrations may demand a pre-concentration and/or a clean-up step to separate the analyte from the matrix. This separation is frequently attained by solid phase extraction (SPE), either to retain the analyte or to retain potential interferences. Among the advantages of SPE, like the easiness to pack and potential manipulation of its selectivity, the potential to be used in a reusable mode is one of the most significant.

Recently, special attention has been devoted to the use of membranes, namely polymer inclusion membranes (PIMs), as selective liquid membranes. By exploiting this concept, we aimed to design a tailor-made solid phase to simultaneous extract and enable detection of the target analyte.

The idea of this work was to develop a PIM containing newly synthesized iron chelators, to extract iron(III) from the sample matrix, resulting in a coloured complex, that could be detected by optical fibres connected to a CCD detector. This approach would enable to simultaneously separate, pre-concentrate and detect the analyte with no need for eluent and/or colour reagents.

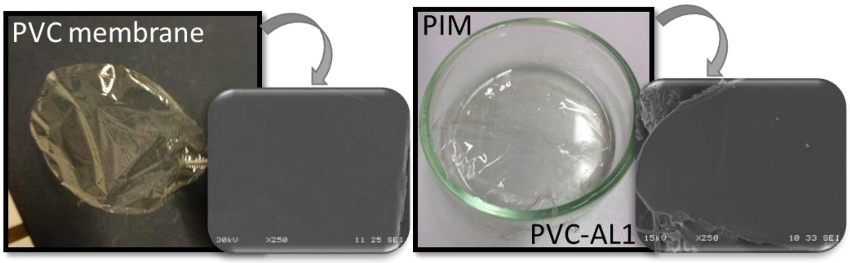

Figure 1. Visual and structural aspect (scanning electron microscope) of the membranes.

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HIGH THROUGHPUT BAR ADSORPTIVE MICROEXTRACTION (HT-BAμE): PARALLEL MICROEXTRACTION OF KETAMINE AND NORKETAMINE FROM UP TO 100 URINE SAMPLES SIMULTANEOUSLY

Samir M. Ahmad[1,2,3], Nuno R. Neng[1,4], José Manuel F. Nogueira[1,4]

[1]Centro de Química Estrutural, Faculdade de Ciências, Universidade de Lisboa,
Campo Grande, 1749-016 Lisboa, Portugal. smahmad@fc.ul.pt
[2]Molecular Pathology and Forensic Biochemistry Laboratory, CiiEM, Campus Universitário − Quinta da Granja, Monte da Caparica, 2829-511 Caparica, Portugal
[3]Forensic and Psychological Sciences Laboratory Egas Moniz, Campus Universitário − Quinta da Granja, Monte da Caparica, 2829-511 Caparica, Portugal
[4]Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa,
Campo Grande, 1749-016 Lisboa, Portugal

Modern sample preparation techniques such as sorbent-based passive or static sampling modes have gained more acceptance in almost all scientific areas, including solid-phase microextraction and stir bar sorptive extraction. Additionally, novel static-based microextraction techniques, such as bar adsorptive microextraction (BAμE), have also demonstrated to be a very effective and alternative analytical tool [1]. However, these techniques are not dedicated to routine analysis and have trouble coping with the simultaneous enrichment of large number of samples.

In this work, we present the development, optimization, validation and application of a simple, fast, reliable and cost-effective sample preparation approach using High Throughput Bar Adsorptive Microextraction (HT-BAμE) in combination with gas chromatography–mass spectrometry operating in the selected-ion monitoring acquisition mode, for the simultaneous enrichment of ketamine and its major metabolite (norketamine) from a large number of urine samples.

The target compounds were extracted in a HT-BAμE apparatus [2], which allows for simultaneous microextraction and subsequent back-extraction of up to 100 samples, resulting in a sample preparation time of only 0.45 min/sample. Under optimized experimental conditions, the developed methodology allowed for linear dynamic ranges between 5.0 and 1000.0 μg L^{-1} with determination coefficients of 0.997 and 0.999, as well as average recovery yields of 84.9-89.8 % and 96.5-97.8 % for norketamine and ketamine, respectively. The developed methodology was applied for the analysis of 24 samples (in triplicate), where no target compound was detected (< LOD).

Acknowledgements: Support for this work was provided by FCT through UIDB/00100/2020. Samir M. Ahmad acknowledges FCT financial support from SFRH/BD/107892/2015 and Nuno R. Neng his contracts established through DL 57/2016.

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FTIR CARACTERIZATION OF ANODIC ALUMINIUM OXIDE PROTECTIVE FILMS PRODUCED BY ANODIZING IN TANNINS

C. Sofia Proença[1,2], J. Correia[1], M.E. Araújo[1]

[1]Centro de Química Estrutural, Faculdade de Ciências, Universidade de Lisboa,
Campo Grande, 1749-016 Lisboa, Portugal
[2]ISQ – Instituto de Soldadura e Qualidade, Tagus Park, Oeiras, 2740-120 Porto Salvo.
csproenca@fc.ul.pt

The former conventional pre-treatment of AA2024-T3 aluminium alloy involves formulations containing chromium (VI) but REACH (Registration, Evolution, Authorization and Restriction of CHemicals) restricts the use of hexavalent chromium in EU, due to the negative impact of these compounds in environment and human health. In recent years there has been an increased interest in developing new corrosion protection alternatives, that could be efficient and more environmentally and human-friendly, to replace the chromium (VI) based treatments.

Numerous alternatives have been described in the literature, composed of mixture of inorganic/organic acids. For example, the process licensed by Boeing uses a mixture of boric/sulphuric acid and the Airbus employs the tartaric/sulphuric acid (TSA).

The conversion coatings formed on the aluminium alloy using several natural tannins obtained from renewable sources revealed that the use of these tannins, despite the differences in their chemical structures, provide a good corrosion protection, making this pre-treatment a promising alternative for chromium (VI) based chemical conversion coatings.

In this work the Fourier Transform Infrared Spectroscopy (FTIR) spectra of anodizing and anodizing and sealed samples of AA2023-T3 is presented and it can be observed that the shifts in the band position confirm that these compounds used as green inhibitor interacts with the metal surface. FTIR data confirms that the films are formed by interation between of OH groups belonging to the tannins molecules and the Al^{3+} cation.

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ANALYTICAL INVESTIGATION ON THE WRITING INK OF CODEX 99 FROM MANIZOLA COLLECTION

Margarida Nunes[1], Victoria Corregidor[2], Luís C. Alves[2], Fernanda Olival[3,4], Hermínia Vilar[3,4], Ofélia Sequeira[3], Ana Manhita[1], Ana Claro[5], Teresa Ferreira[1,6]

[1]HERCULES Laboratory, University of Évora, Portugal. tasf@uevora
[2]C2TN, Nuclear and Technological Campus, IST, University of Lisbon, Portugal
[3]CIDEHUS, University of Évora, Portugal
[4]History Department, Social Sciences School, University of Évora, Portugal
[5]CHAM, NOVA School of Social Sciences and Humanities, Portugal
[6]Chemistry Department, Science and Technology School, University of Évora, Portugal

Written in the first half of the 17th century by the Jesuit Father António Pessoa, “Orthographia Pratica de Varias Letras”, Codex 99 of Manizola collection, encompasses different pedagogical topics as orthography, alphabets, arithmetic’s, and even, recipes of iron gall ink (IGI) to be used on paper or parchment. This Codex is nowadays preserved in the Public Library of Évora but most of its prior custody and usage is unknown. The book was probably used in a pedagogical context, whether teaching or mission. From a conservation point of view, the book represents an interesting case study since the use of IGI led to different results: while the first half of the book is very well preserved, the second part presents dramatic degradation patterns such as yellowing, loss of paper strength and fragmentation on the inked areas. To prepare this ink, iron was used as green vitriol (ferrous sulfate) and sometimes salts of other metals like copper and zinc were added to adjust the final hue of the ink. Gum Arabic, the most frequently used binder, was added to increase the viscosity, facilitating the flow of the ink [1]. The ink’s colour could vary from blue to dark violet, and after deposition onto the substrate, it turned to different hues of brown or black as a result of oxidation. Although it was first thought as a long-lasting ink, its degradation effects were rapidly brought to light. Oxidation and acid hydrolysis of cellulose are among the main degradation mechanisms that this polymer may undergo, due to variation of relative humidity and temperature and the presence of transition metal ions, among others [2]. Using microscopic and spectroscopic techniques, namely, micro-Fourier transform infrared spectroscopy (µ-FTIR), micro-Raman spectroscopy and scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (VP-SEM/EDS), a selection of samples from the Codex was analyzed to gather information on the surface morphology and the chemical composition of the ink and the support, and the observed pathologies. Particle Induced X-ray emission (PIXE) was used to try to establish differences in the ink composition from different pages of the book. High-performance liquid chromatography with diode array and mass spectrometry detection (HPLC-DAD-MS) was carried out for tannins’ identification. Preliminary results showed that different inks were used and conservation work, not documented, to the best of our knowledge, was probably performed on the manuscript.

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BIOINSPIRED LACCASE-POLYDOPAMINE FILMS FOR AMPEROMETRIC BIOSENSORS

L.C. Almeida[1], R.D. Correia[1], G. Squillaci[2], A. Morana[2], F. La Cara[2], J.P. Correia[1], A.S. Viana[1]

[1]Centro de Química Estrutural, Faculdade de Ciências, Universidade de Lisboa, Campo Grande 1749-016 Portugal. lmalmeida@fc.ul.pt
[2]Istituto di Ricerca sugli Ecosistemi Terrestri (IRET), Consiglio Nazionale delle Ricerche, Via Pietro Castellino 111, 80131 Napoli, Italy

Polydopamine (PDA) aroused in the last decades as an extremely versatile bioinspired functional material, possessing catechol and amine groups, mimicking the mussel adhesive properties. Polycatecholamines are commonly synthesized through the chemical oxidation of the catechol ring in aerated basic media, coating a wide variety of materials [1,2]. They have been used in many fields, e.g. self-healing for biomedical purposes. However, it is accepted that PDA films are quite heterogeneous and mostly insulating, which is a drawback for many applications, namely to electrochemical biosensing. The poorly explored electrochemical synthetic route can be extremely advantageous to control the structure, thickness and conductivity of these coatings [3]. Electrosynthesized PDA is an excellent immobilization matrix to accommodate and bind active enzymes for biosensing purposes, allowing a good electrochemical transduction.

Herewith, a one-step electrode functionalization is reported, to prepare hybrid PDA-Laccase films for phenols detection. The enzyme laccase is immobilized during potentiostatic deposition of PDA on carbon surfaces. The catalytic activity of the films is firstly tested by chronoamperometry, for 2,2′-azino-bis-(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS) detection, a renowned substrate of laccase. A clear improvement of the analytical parameters (apparent Michaelis-Menten constant and sensitivity) for the catalytic detection of ABTS was obtained with one-step modified electrodes regarding those prepared in two steps: immobilization of Laccase on pre-synthesized PDA films. The developed methodology was reproducibly applied to disposable graphite electrodes, aiming the detection of phenolic compounds (e.g. caffeic acid, rosmarinic acid and gallic acid). The performance of PDA-Laccase graphite biosensor was evaluated in terms of reproducibility, sensitivity, limit of detection and linear range.

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BRIGHT CARBON DOTS FROM CORK INDUSTRY WASTEWATER AS SENSORS OF HEMEPROTEIN

Marta R. Alexandre[1†], Alexandra I. Costa[1,2], Mário N. Berberan-Santos[3],
José V. Prata[1,2]

[1]Departamento de Engenharia Química, Instituto Superior de Engenharia de Lisboa, Instituto Politécnico de Lisboa, R. Conselheiro Emídio Navarro, 1, 1959-007, Lisboa, Portugal
[2]Centro de Química-Vila Real, Universidade de Trás-os-Montes e Alto Douro, 5001-801, Vila Real, Portugal. jvprata@deq.isel.ipl.pt
[3]Institute for Bioengineering and Biosciences, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal
[†]Present address: Hovione, SA, Portugal

Carbon nanodots are a recent class of spherical-shaped nanosized carbon materials reaching average typical diameters < 10 nm and a variety of methods for their synthesis and applications are reported [1,2]. Sustainable production of high-valued carbon materials from industrial low-valued and problematic wastes materials is particularly appealing and highly desirable. Following eco-friendly and expedite hydrothermal processes, we have been able to synthesize highly luminescent carbon dots (C-dots) directly from cork industry wastewater (CIWW) [3] in excellent yields.
Herein we report the sensing abilities of as-synthesized C-dots toward haemproteins (*e.g.* haemoglobin) via direct turn-off fluorescence-based experiments. The haemoglobin in an oxidised state of haem iron (Fe(III), metHgb) is able to quench the C-dots fluorescence as retrieved from spectrofluorimetric titrations (Fig. 1).

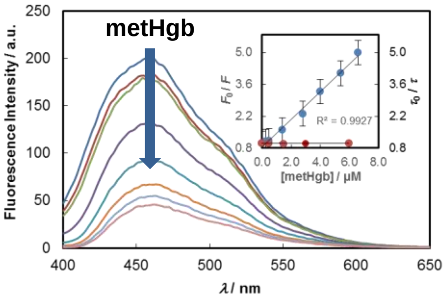

Figure 1. Emission spectra of C-dots (0.2 mg/mL) upon varying the amount of metHgb (0.25- 6.6 µM) in phosphate buffer (pH = 7.2) at 25°C. Inset: Stern-Volmer plots obtained from steady-state (blue dots; F_0/F; λ_{exc} = 380 nm) and time-resolved (red dots; τ_0/τ; λ_{exc} = 340 nm) fluorescence data. Error bars indicate the standard error.

High quenching efficiencies was observed for all the metalloproteins evaluated, although a higher response was found for haemoglobin ($K_{SV} = 6.1 \times 10^5$ M^{-1}) [4].

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DEVELOPMENT OF A MICROELECTRODE ARRAY BIOSENSOR FOR MONITORING LACTATE DYNAMICS IN THE BRAIN

Eliana Fernandes[1], Ana Ledo[1,2], Rui M. Barbosa[1,2]

[1]Faculty of Pharmacy, University of Coimbra, 3000-548 Coimbra, Portugal.
eliana.fernandes2604@outlook.com
[2]Center for Neuroscience and Cell Biology, University of Coimbra, 3000-504 Coimbra, Portugal

The previously considered metabolic dead-end L-lactate has since been identified as a key metabolic intermediate, formed under fully aerobic conditions and used by diverse cells as a metabolic fuel. In the brain, lactate is the predominant glycolytic substrate trafficked between the distinct cell constituents and plays also a role as an important signaling molecule [1]. Furthermore, changes in lactate concentration dynamics have been linked to situations of neural distress and disease. Hence, monitoring extracellular lactate concentrations is of surmount importance to understanding its role in brain physio(patho)logy.

A biosensor for the detection and monitoring of lactate in a real time mode and with high spatial resolution has been design and developed by immobilizing lactate oxidase (LOx) using the cross-linking agent glutaraldehyde (GA) in the presence of bovine serum albumin (BSA) onto the surface of ceramic-based platinum multisite microelectrode arrays (MEA), as essentially described in [2]. The biosensors were further coated with a diffusional layer of polyurethane (PU), to extend the linear range for the substrate detection. The *in vitro* evaluation of MEA-based LOx biosensors for monitoring lactate was performed by amperometry at +0.7 V *vs* Ag/AgCl. Analytical performance and kinetic parameters were determined by adding stock lactate solution until final concentration in the range of 0.05 - 50 mM. The enzyme loading, BSA concentration and the PU layer properties were evaluated and optimized. The optimum conditions were found to be a cocktail solution consisting of 1 mg/mL LOx, BSA 10% and GA in water, with 3 layers of PU (2%). The biosensor exhibited an apparent K_M of 15.3 ± 9.8 mM (n=8), a sensitivity of 1.8 ± 0.2 nA. mM^{-1} (n=8) and a LOD of 2.5 ± 0.3 µM (n=4).

Prior to insertion the biosensor into the rat brain, it was coated with an exclusion layer of *m*-phenylenediamine (PPD) by electropolimerization, to minimize the interference of undesired compounds such as ascorbate, for which a selectivity of 1: 6.7 ± 2.1 (n=4) was attained. The microbiosensors were successfully used for detection and monitoring of lactate with high temporal and spatial resolution in the hippocampus of anesthetized rats in response to local lactate changes and upon stimulation.

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MOLECULARLY IMPRINTED POLYMER-BASED ELECTROCHEMICAL SENSORS FOR THE DETECTION OF ANTIBIOTICS IN THE ENVIRONMENT

Patrícia Rebelo[1,2], João G. Pacheco[1], Iuliia V. Voroshylova[2], André Melo[2],
M. Natália D.S. Cordeiro[2], Cristina Delerue-Matos[1]

[1]REQUIMTE, LAQV, Instituto Superior de Engenharia do Porto, Instituto Politécnico do Porto, Rua Dr. António Bernardino de Almeida 431, 4200-072 Porto, Portugal
[2]REQUIMTE, LAQV, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, s/n, 4619-007 Porto, Portugal.
patricia.rebelo@graq.isep.ipp.pt

The over-use and misuse of antibiotics is one of the most alarming problems the world faces nowadays. Many studies have confirmed the presence of antibiotics in the environment, including surface water, underground water and seawater [1]. The remaining of antibiotics in the environment, even at low concentrations, is of uppermost concern because of their known and unknown associated adverse effects in nontargeted organisms. Consequently, it is crucial to develop fast, selective and cost-effective analytical sensing devices for their monitoring. Due to their high specificity, chemical and physical stability, low cost and easy preparation protocol, molecularly imprinting polymers (MIPs) have shown great potential for environmental target analysis [2]. In our work, the combination of electrochemical biosensing strategies with MIPs allowed for development of electrochemical MIPs sensors for the quantification of pharmaceuticals. Prior to experimental test, quantum mechanical calculations and molecular dynamics simulations were performed to select the optimal functional monomer and to establish the best pre-polymerisation mixture composition. Using different methods of polymerisation and sensing platforms, two examples will be presented for azithromycin (AZY) and furazolidone (FDZ). The sensors exhibited a limit of detection (LOD) for AZY and FDZ of 0.08 µM and 0.03 µM, respectively, and high selectivity to recognise the target antibiotics. The proposed sensors were successfully applied in spiked water samples, proving that these MIPs sensors could be a promising technique for monitorization of AZY and FDZ in environmental waters.

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PAPER-BASED SUBSTRATES FOR WOUND INFECTION DETECTION

S. Sofia M. Rodrigues, M. Lúcia M.S. Saraiva

LAQV, REQUIMTE, Department of Chemical Sciences, Laboratory of Applied Chemistry, Faculty of Pharmacy, Porto University, Rua de Jorge Viterbo Ferreira 228, Porto, 4050-313, Portugal. gisofi@gmail.com

The early diagnosis of an incipient wound infection is imperative to assure an appropriate intervention. This would allow the timely treatment of the infection, thus avoiding the complication of the infectious condition and the consequent severity of the disease [1].

Currently there is a lack of routine diagnostic options for a quick assessment of wound condition. This type of diagnosis could provide a great support, for both the attending physician and the patient, in their subsequent decisions.

Paper-based biosensors are affordable, easy-to-use, rapid, robust and inexpensive point-of-care devices [1]. One of the most challenging steps in the development of these type of sensors is the immobilization of appropriate biomolecules in the paper surface. This is crucial to ensure the functionality of paper biosensors.

In this study, paper modified with two different polysaccharides, chitosan and alginate, was used to immobilize a chromogenic substrate, aiming the visual detection of elevated elastase activity, a useful biomarker for wound infection.

The chromogenic substrate N-Succinyl-Ala-Ala-Ala-p-nitroanilide was selected and an efficient hydrolysis by elastase resulted in a colorimetric reaction. Preliminary results showed that, 2 h after the incubation of paper with elastase in a buffer solution, it may be observed the release of colored hydrolysis products. Hence, this study demonstrates the elastase potential for wound infection diagnosis leading to the conclusion that this strategy should be further evaluated for incorporation in point-of-care diagnostic devices.

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NON-INVASIVE IDENTIFICATION OF POTENTIAL HUMAN STRESS BIOMARKERS BY LC-MSMS

M. João Nunes, Cristina M. Cordas, José J.G. Moura, Luís Branco,
João Paulo Noronha

*LAQV, REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia,
Universidade Nova de Lisboa, 2829-516 Caparica, Portugal. mjm.nunes@fct.unl.pt*

Stress both physical and psychological has been related to several diseases and discordant social behaviour [1]. Biomarker molecules detection is an important field of research [2] since has implications in the development of new methods and devices with interest in medicine. Less invasive methods such as sweat analysis have been pursued for continuous health monitoring. In the current study, sweat is the target biological fluid for biomarkers detection. The aim is the identification of potential stress biomarkers that can lead to a rapid detection and monitoring of stress and/or disease states related with exercise. In this context, a simple, rapid, and versatile method able of identifying stress biomarkers in sweat by ultra high-performance liquid chromatography (*UHPLC*) coupled with multiple-reaction monitoring (MRM) tandem mass spectrometry (LC-MSMS) was developed.

This study has been performed for a global identification analysis on pooled sweat samples collected from ten healthy individuals. The sweat pool was attained from the healthy young male volunteers after a football game (university students aged between 22 and 26, that typically play one 90 minutes football per weak).

The composition profile provided the identification of 26 potential biomarkers by LC-MSMS. From the identified molecules some already described stress related biomarkers were found such as epinephrine or cortisol. The major potential identified biomarkers are NTs and other molecules [3]. This identification is an important achievement for further studies and selection of most important biomarkers in sweat, not only for stress, but also for other conditions/pathologies and/or early diagnosis. Also, from this study, it was possible to show that NTs are possible to detect in the composition of sweat body fluid after exercise.

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SPECIATION OF Pt AND Rh IN URBAN ROAD DUST LEACHATES

Carlos E. Monteiro[1,2], Antonio Cobelo-García[3], Miguel Caetano[2],
Margarida Correia dos Santos[1]

[1]*Centro de Química Estrutural, IST-UL, Av. Rovisco Pais 1, 1049-001 Lisbon, Portugal.*
carlos.e.monteiro@tecnico.ulisboa.pt
[2]*IPMA, Rua Alfredo Magalhães Ramalho 6, 1495-165 Algés, Portugal*
[3]*Bioxeoquímica Mariña, IIM-CSIC, Eduardo Cabello 6, 36208 Vigo, Spain*

Platinum and Rh occur naturally in the environment and their concentrations are among the lowest that can be found in the Earth’s crust. Nevertheless, their concentrations in several environmental compartments have steadily increased over the past decades due to anthropogenic inputs, mainly related to their use in automotive catalytic converters (ACC). Consequently, road dust and roadside soils are a major reservoir of Pt and Rh and their spreading in the environment easily occurs due to wind transport of particles and/or urban runoff. The forms in which Pt and Rh are emitted from ACC are not yet clear. Some studies indicate that they are released mainly as particulate material but a soluble fraction has also been measured. In addition, it is important to elucidate how Pt and Rh mobilization occurs in the environment after ACC emission.

In this work, a composite sample of road dust (<63 µm) was thoroughly characterized. Subsequently, the road dust was incubated over seven days in synthetic rainwater and seawater. In the leachates obtained after filtration (<0.45 µm), truly dissolved Pt and Rh concentrations were measured by adsorptive cathodic stripping voltammetry (AdCSV), while total dissolved concentrations were determined by inductively coupled plasma mass spectrometry (ICP-MS).

Truly dissolved species corresponded to a minor fraction of total Pt and Rh in the road dust leachates, relatively constant over time (7 days). Non-dissolved filter-passing Pt (nano)particles predominated by a factor of 10, whereas Rh increased about 2-3 times. Temporal variations were observed for Pt, as opposed to Rh. This suggests particle aggregation plays a role in the fate of Pt in both aquatic media.

The relevance of Pt and Rh truly soluble species vs. (nano)particles is still not well understood, namely for their mobility in environmental compartments and potential toxicity for the biota. Moreover, the reported results highlight that Pt and Rh speciation in aquatic systems can be obtained by a combination of suitable techniques.

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CHARACTERIZATION OF ATMOSPHERIC AEROSOL (PM_{10} AND $PM_{2.5}$) IN A CITY OF SÃO PAULO STATE, BRAZIL

Bruno T. Franzin[1,3,4], Filipe C. Guizellini[1], Ossamu Hojo[1], Iêda A. Pastre[2], Mary R. Marchi[1], Fernando L. Fertonani[1,2], Cristina Oliveira[3]

[1]São Paulo State University (Unesp), Instituto de Química-IQ, Departamento de Química Analítica Araraquara, SP, Brazil. bruno@sprqualidade.com.br
[2]Departamento de Química e Ciências Ambientais, Instituto de Biociências, Letras e Ciências Exatas, Universidade Estadual Paulista (Ibilce / Unesp), São José do Rio Preto, SP, Brazil
[3]Centro de Química Estrutural, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal
[4]SPR Soluções Metrológicas, Box 04, 15035-470, São José do Rio Preto, SP, Brazil

The atmospheric contamination by aerosols is a very important environmental problem affecting millions of people, mainly in urban areas, with significant impacts in the human health and wellbeing and high economic repercussion. Aerosols are mixtures of particles emitted from natural or anthropogenic sources with different sizes and different chemical compositions [1].

The present work allowed the characterization of PM_{10} and $PM_{2.5}$ aerosol of Araraquara city in the center of São Paulo state, Brazil.

The aerosol mass, determined by gravimetric analysis presented average values 3 to 4 times higher than the guide values recommended by the World Health Organization (WHO) [2]. A morpho-structural analysis carried out by SEM-FEG coupled to EDS identified in the coarse fraction elements from minerals and from soil resuspension, organic spherical particles originated from combustion processes as well as Ti, associated with long distance transportation.

The results of the ionic chemical composition obtained by Ionic Chromatography were correlated by PCA analysis with meteorological data and air masses backtrajectories obtained by the HYSPLIT model (NOAA), in order to identify the probable emitting sources of the urban atmospheric aerosol sampled in the city.

This study contributes to a better understanding of the complex composition of the aerosols in the atmosphere of Araraquara city, resulting from the combination of local and long distances sources and serves as a basis for the comparison with future studies related to the air quality at this and other regions in the world.

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PHYSICO-CHEMICAL CHARACTERIZATION OF EFFLUENTS FROM WASTEWATER TREATMENT PLANTS WITH DIFFERENT TREAMENTS AND ANTROPOGENIC PRESSURES

Ana Teixeira[1], Cristina Couto[1], Ariana Pereira[1], Maria Elizabeth Tiritan[1,2,3],
Cláudia M.R. Ribeiro[1,2]

[1]CESPU, Instituto de Investigação e Formação Avançada em Ciências e Tecnologias da Saúde, Rua Central de Gandra, 1317, 4585-116 Gandra PRD, Portugal.
claudia.ribeiro@iucs.cespu.pt
[2]Centro Interdisciplinar de Investigação Marinha e Ambiental (CIIMAR), Universidade do Porto, Edifício do Terminal de Cruzeiros do Porto de Leixões, Av. General Norton de Matos s/n, 4050-208 Matosinhos, Portugal
[3]Laboratório de Química Orgânica e Farmacêutica, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, Rua de Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal

Wastewater treatment plants (WWTP) aim to protect human health and prevent environmental degradation by the safety disposal of industrial and urban wastewaters. Nevertheless, wastewater effluents are also major contributors to a variety of water pollution problems [1,2]. In fact, poor quality or inadequate treated effluents can contain hazard substances or cause changes in the physico-chemical characteristic of the receiving waters causing degradation of aquatic systems and decline of both fauna and flora diversity [2,3]. Main purpose of WWTP is to reduce the amounts of nutrients, organic content and eliminate pathogenic microorganisms. Currently, WWTP should be able to ensure effluent discharge limits of chemical oxygen demand (COD), total suspense solids (TDS), nitrogen (N) and phosphorus loads set by legal regulation established by each country and the recommended limits for human and environmental protection. However, the level of treatment and monitoring required is based on the population the WWTP serves and where the effluent is discharged. Thus, WWTP do not have to comply all limit values and depends on the stipulated by its license. In this work, the physicochemical characterization of industrial and urban effluent samples from three wastewater treatment plants with different sewage treatments were evaluated. The physicochemical parameters assessed included pH, TDS, turbidity, COD, dissolved oxygen (DO), N, nitrates, nitrites, phosphate, ammonium, and conductivity. Samples were collected in winter, spring, and summer to evaluate possible seasonal variations. All WWTP showed physico-chemical parameters within the recommended by the Portuguese regulation except one where N and ammonium levels were higher than the established limits. Nevertheless, this WWTP does not have to comply with these limits. However, high levels of N and ammonium may cause eutrophication of the receiving waters. The highest values were found in summer. These results show that effluents might be sources of pollution to their respective receiving water systems and may threat public and environmental health.

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EVALUATION AND OPTIMISATION OF THE UNCERTAINTY OF PHOTODEGRADATION KINETIC CONSTANTS DETERMINED BY THE MONTE CARLO METHOD

Diogo Ferreira, Virgínia Ferreira, Ricardo J.N. Bettencourt da Silva, Cristina Oliveira

Centro de Química Estrutural, Faculdade de Ciências, Universidade de Lisboa,
Campo Grande, 1749-016 Lisboa, Portugal. cmoliveira@fc.ul.pt

The presence of PPCPs (pharmaceutical and personal care products), and the products of their transformation in waters for human consumption depends on the efficiency of the treatment carried out in the wastewater treatment plants, which for now is not entirely adequate.

Several studies point to the possibility of implementing a wastewater treatment methodology that involves the addition of catalysts that, under solar radiation or through an artificial lighting of proper energy, allow the photodegradation of emerging pollutants into less toxic degradation products (preferably into CO_2 and H_2O) [1]. This approach can be an alternative to treatment techniques that are currently not efficient enough to remove these pollutants [2,3].

One of the questions that arises is which catalyst systems should be used to maximize the removal of those species and their degradation products in the shortest possible time and if possible using less resources.

This work describes the use of a tool to produce a metrological model based on Monte Carlo simulations, capable of determining the uncertainty associated with the speed constant of the photodegradation process of the methylene blue (MB) dye and the drug sulfamethazine (SMZ) using different combinations of photocatalysts namely nanostructured titanates and titanium dioxide (TiO_2) and incident radiation energy or to compare the effect of a photocatalyst on a set of various compounds.

The developed tool was implemented in a user-friendly MS-Excel file.

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EVALUATION AND OPTIMISATION OF THE UNCERTAINTY OF pH MEASUREMENTS OF NON-AQUEOUS SOLVENTS ON A UNIPHIED SCALE

R.J.N. Bettencourt da Silva, B. Anes, C. Oliveira, M.F.G.F.C. Camões

Centro de Química Estrutural, Faculdade de Ciências, Universidade de Lisboa,
Campo Grande, 1749-016 Lisboa, Portugal. rjsilva@fc.ul.pt

Chemical process that depend on H^+ activity in aqueous and non-aqueous solvent should be monitored for this parameter, pH.

Himmel et al. [1] proposed an absolute pH scale, pH_{abs}, applicable universally to any type of solvent or physical state. This scale allows comparing the acidity of solutions from different solvents.

The determination of the pH_{abs} of a liquid solution involves measurements by differential potentiometry anchored in reference pH values of aqueous solutions. The pH_{abs} of various solutions can also be determined simultaneously by the numerical treatment of a set/ladder of differential potentials anchored in one or more reference aqueous buffers.

The uncertainty of the determined pH_{abs}, and to some extend the measurand, depends on the measurement procedure. The relevant uncertainty components of these measurements are the ones affecting the determination of the practical Nernst slope and intercept of the used H^+ selective electrode, potential measurements precision and liquid junction potential. The characterisation of the electrode response is function of potential measurements precision, reference pH buffer value and response linearity. For pH_{abs} measurement based on the numerical minimisation of differences from a ladder of differential potentials where all solutions are compared potentiometrically with each other, the numerical method also introduces some uncertainty to the collected information. Some of these uncertainty components have complex correlations such as when the same electrode is used in various differential potential measurements of the pH_{abs} ladder, or the same reference pH buffer is used to characterise electrodes and anchors the pH_{abs} ladder.

This work describes the simulation of the uncertainty of pH_{abs} measurement results based on a single or a complex ladder of differential potentiometry by the Monte-Carlo method. The developed tool was implemented in user-friendly MS-Excel file.

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A NOVEL AUTOMATIC METHODOLOGY FOR THE RELIABLE IDENTIFICATION OF MICROPLASTICS FROM AQUATIC ENVIRONMENT BY INFRARED SPECTROSCOPY

Vanessa Morgado[1,2], Carla Palma[2], Ricardo J.N. Bettencourt da Silva[1]

[1]Centro de Química Estrutural, Faculdade de Ciências, Universidade de Lisboa,
Campo Grande, 1749-016 Lisboa, Portugal
[2]Instituto Hidrográfico, Rua das Trinas, 49, 1249-093 Lisboa, Portugal.
vanessa.morgado@hidrografico.pt

Currently about 1.15 to 2.41 million tons of plastic enters oceans every year from rivers leading to more than 60 % of the global composition of marine litter being plastic [1,2]. Microplastics are characterised according to their physical and chemical properties and can be identified from collected infrared spectrum. This spectrum is unique for a specific plastic type, working as a molecular fingerprint. The manual interpretation of the infrared spectra can be very time-consuming due to its complexity.

A novel methodology for the automatic and valid identification of microplastics from river sediments by quantifying the correlation between particle and reference spectra is described in this communication.

The minimum correlation coefficient, *M*, above which identification is associated with a true positive result rate, *TP*, not lower than 95 % was estimated by simulating correlation coefficient, *CC*, distribution by the bootstrap method from experimentally observed spectra agreement. The false positive result rate, *FP*, of identifications was estimated by the probability of a particle not from the polymer of the reference producing a *CC* greater than *M*. Identifications are considered fit for purpose if the *TP* and *FP* is not lower or greater than 95 % and 5 %, respectively. This work presents results of the identification of microplastics from Mondego river sediments, supported on the quantification of correlation by different unweighted or weighted correlation coefficients from original or transformed spectra, improving the preliminary results on the polymer type identification already reported [3].

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PORTUGUESE OCEAN ACIDIFICATION DATA - HARMONIZATION CHALLENGE FOR SEAWATER pH MEASUREMENTS

Marta Nogueira[1], Bárbara Anes[2]

[1]Instituto Português do Mar e da Atmosfera, IPMA, Av. Alfredo Magalhães Ramalho, n. 6, 1495-165 Algés, Portugal. mnogueira@ipma.pt
[2]Centro de Química Estrutural, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal

The Intersessional Correspondence Group on ocean acidification (ICG-OA) is an international working group under the OSPAR convention (Convention for the Protection of the Marine Environment of the North-East Atlantic), in which Portugal is a member (as a Contracting Party), with the aim to develop a proposal for an ocean acidification assessment and monitoring strategy for OSPAR region. Ultimately, the main goal will be the development of an Ocean Acidification (OA) indicator for the Quality Status Report 2023 (QSR 2023).

One of the challenging features of this group is to define how to harmonize data for presentation and trend statistics approach (winter, deseasonalised, in situ T, etc...). In Portugal, the most common measurement of the OA parameters is pH. Several data have been reported in literature and generally different calibration procedures and pH scales have been used.

Field and laboratory pH measurements also differs in terms on how the data is reported. In general cases, pH is reported at in-situ temperatures and in other situations pH is harmonized to a reference temperature, usually 20 ºC or 25 ºC.

To be able to report good quality data, some questions remain unanswered:

- Which is the recommended procedure for pH measurements in seawater and which one minimizes analytical errors?
- How to harmonize previous data obtained through different method procedures (using different pH buffer standards) and reported at different temperatures?

This work aims to present a clear example on the current state of pH published data for the Portuguese Coast and estuaries as well as the challenges ahead regarding harmonization, reporting and future monitorization.

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A NEW DATA-DRIVEN ALGORITHM FOR UNTARGETED METABOLOMICS ANALYSIS

Sandia Machado[1], Luisa Barreiros[1,2], Ricardo N.M.J. Páscoa[1], Marcela A. Segundo[1], João A. Lopes[3]

[1]LAQV, REQUIMTE, Departamento de Ciências Químicas, Faculdade de Farmácia da Universidade do Porto, Porto, Portugal. sandia_machado@hotmail.com
[2]Escola Superior de Saúde do Instituto Politécnico do Porto, Porto, Portugal
[3]iMed.ULisboa, Research Institute for Medicines, Faculdade de Farmácia da Universidade de Lisboa, Lisboa, Portugal

Metabolomics aims at studying metabolites present in a sample, which all together form the metabolome [1]. Mass spectrometry has emerged as an extremely useful tool in metabolomics and is usually performed according to a targeted or untargeted approach. The untargeted approach is often neglected because its ability to access the entire metabolome of a sample, generating a fingerprint, increases the complexity of data and its interpretation becomes challenging [2]. Data-driven approaches are known for the capacity to extract valuable information from chemical systems data and could be very useful in the study of data retrieved from untargeted analyzes. However, for the treatment of mass spectrometry data no ultimate data-driven strategy has been proposed to date [3]. In this work we present an algorithm capable of extract relevant chemical information from data of untargeted analysis.

The algorithm was developed in Matlab and its efficiency was evaluated by comparison with the results obtained in MZmine software for mass spectrometry data analysis. The algorithm was tested with mass spectrometry data obtained from grape samples collected at different developmental stages, specifically during berry formation and berry ripening. Samples were analyzed by liquid chromatography coupled to mass spectrometry (LC-MS) using an untargeted method. The algorithm was developed with the aim at excluding undesired signals and noise, thus putting in sight chemically relevant signals. The aim of this strategy is to generate a more understandable data matrix for further study. Results were obtained by considering all grape samples simultaneously (n = 24). The output is a matrix containing the m/z values typical of each developmental stage as well as the m/z values present in all grape samples. The algorithm was also able to assess minor compounds because it does not use any threshold level, thus do not exclude any signal based on intensity. The proposed algorithm is suitable to access all the relevant m/z values of samples, thus paving the way for the study of unknown compounds from complex data.

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STUDY OF VARIABLES IN THE PRODUCTION OF BIODIESEL ETHYLIC-METHYLICY FROM RESIDUAL SOYBEAN OIL

Laurênio Ferreira Lopes[1], Carlos Michel dos Anjos dos Santos[1],
Thays da Silva Folly[2]

[1]Universidade Federal Fluminense, Rua Passo da Pátria, 156-Niterói/RJ, Brazil.
laurenio_lopes@id.uff.br
[2]Centro Universitário Anhanguera de Niterói, Av. Visconde do Rio Branco, 123-Niterói/RJ, Brazil

Many scientific studies have shown higher yields when using methanol as a molar ratio in the biodiesel synthesis process compared to ethanol, it is based on the decantation stage due to the immiscibility in the mixture, separating the material into two phases, glycerin and biodiesel, facilitating the separation in purification process [1]. However, methanol is a toxic and imported material while ethanol has low toxicity and is easily produced in Brazil [2]. This study aimed to analyze during the biodiesel synthesis the influence of the ethyl-methyl composition in order to increase the mass yield. The methodology was divided into qualitative and quantitative, part with research in recent sources that address the theme, verifying that the synthesis of biodiesel via methyl has high yields in low molar ratios, thus formulating an experimental design 2^3 totaling 8 experiments in triplicate, with variations: molar ratio (RM) oil: alcohol (1: 3 and 1: 9), mass ratio ethanol / methanol (10:90 and 30:70) and percentage of catalyst, NaOH, (0.5 and 1.5%), keeping the reaction time (60 minutes), temperature (60 ± 2 °C), magnetic stirring, pH (7.0) and the residual oil mass constant. With the results obtained, the experiment with an average yield of 93.70% stood out, it is worth noting that for this yield, RM (1: 9), NaOH (0.5%) and mixture between alcohols in 10% ethanol and 90% methanol, by weight. However, the worst performance was when the percentage of the catalyst was increased from 0.5 to 1.5%. It was concluded that for yields above 90%, the greatest influence is on the percentage of catalyst used, the higher, the lower the result. Regarding the use of the mixture between alcohols, these in the established percentages, did not present negative variations, being viable its use by ethanol is less toxic which facilitates its manipulation.

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DEVELOPMENT AND VALIDATION OF AN INDIRECT GC-MS METHOD FOR THE QUANTIFICATION OF PSYCHOACTIVE SUBSTANCES IN SURFACE WATERS

Ivan Marcelino Langa[1], Cláudia Maria Rosa Ribeiro[1,2], Maria Elizabeth Tiritan[1,2,3]

[1]CESPU, Instituto de Investigação e Formação Avançada em Ciências e Tecnologias da Saúde, Rua Central de Gandra, 1317 Gandra, PRD, Portugal. claudia.ribeiro@iucs.cespu.pt
[2]Centro Interdisciplinar de Investigação Marinha e Ambiental (CIIMAR), Terminal de Cruzeiros do Porto de Leixões, Avenida General Norton de Matos, s/n, Matosinhos, Portugal
[3]Laboratório de Química Orgânica e Farmacêutica, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, Rua de Jorge Viterbo Ferreira, 228, Porto, Portugal

The changes in the law to keep drug trafficking and consumption under control have boosted the synthesis and introduction of new psychoactive substances (PS) in the illegal market [1]. Many of this NPS are chiral and available as racemate or enantiomerically pure. These substances reach the environment through different ways such as direct disposal by industry, illegal discharges and as humans excretion products (of parent compounds and their metabolites) being a potential threat to non-target organisms [2, 3]. Occurrence of these substances in surface waters may also give insights about their consumption in a specific region.

The aim of this work is the development and validation of indirect method based on the application of solid phase extraction (SPE) followed by gas chromatography-mass spectrometry (GC-MS) for enantiomeric quantification of 9 PS (5 synthetic cathinones and 3 amphetamine like substances) based on the formation of diastereomers using (R) - (-) - α-methoxy-α- (trifluoromethyl) phenylacetyl chloride (MTPA-Cl) as chiral derivatization reagent. Two illicit piperazines (PP) were also included. PP were also derivatized with MTPA-Cl improving signal identification and detection. The optimized conditions allowed the quantification of the target PS (a total of 18 diastereomers and two PP) in less than 23.0 min.

The method was validated according to the International Conference on Harmonization and showed to be linear ($R^2 > 0.98$). Limits of detection ranged from 17 to 100 ng/L and limit of quantification varied between 50 and 300 ng/L. The method will be used to evaluate the occurrence, spatial distribution, and the enantiomeric fraction of the PS in Portuguese surface waters in the Great Porto region. Data will allow to evaluate their environmental impact, determine/ verify the consumption of recreational drug by the population and their potential sources.

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A METHODOLOGY FOR PEROXIDES EVALUATION IN COSMETIC CREAMS: A GREENER APPROACH

Inês Sousa, Cristina Soares, Cristina Delerue-Matos, Maria João Ramalhosa,
Valentina F. Domingues

*REQUIMTE–LAQV, Instituto Superior de Engenharia do Porto, Instituto Politécnico do Porto,
R. Dr. António Bernardino de Almeida 431, 4249-015 Porto, Portugal. vfd@isep.ipp.pt*

Lipid oxidation in products with high-fat content such as skin-care products is well known for causing changes in odor and for some of the deterioration processes that affect product quality and safety [1]. The oxidation process produces many by-products, and hydroperoxides are the primary oxidation products when fat and oils undergo oxidation [1]. The peroxide value (PV) analysis is usually determined by titration of the iodine released from the reaction of peroxides with potassium iodide. Alternatively, spectrophotometric methods are currently widely used to determine the PV in fatty foods, commonly using the oxidation of Fe(II) to Fe(III) ions that, once formed, can react with various reagents producing colored complexes. These complexes include the Fe(III)-thiocyanate in the International Dairy Federation (IDF) method. These methods are displacing classical volumetric methods, such as iodometry [2]. Whatever principle is chosen for determining the peroxide content, all methods involve first, the extraction of the fat phase of the product, traditionally using chloroform. The study's objective was to evaluate alternatives for the quantification of the PV by the iodometric method in cosmetic creams and compare it with the IDF method. Furthermore, the study encompassed the evaluation of possible substitute solvent, less harmful, used for extracting lipids from the creams. The wet chemical titration method has disadvantages in meeting an increasing demand for rapid, clean, and cost-effective PV measurements. Per titration, each sample produces at least mL of residues, while in the IDF method, less than 2.5 mL are generated in the determination of PV in the same samples. Besides, in the titration method, organic solvents like acetic acid and isooctane are used. The time necessary to perform this analysis using the IDF method adapted to a microscale with a microplate reader allows the determination of PV in more than 50 samples (in triplicate) in four hours, while to perform the same number of samples using the titration methods would take at least 18 hours. Also, to dissolve the samples and extract the fats, less toxic solvents like alcohols, were used instead of chloroform. This study has shown that there are greener alternative analytical methods capable of replacing the standard titration procedure currently in use for determining PV in creams.

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DETECTION OF THE ADULTERATION OF HONEY WITH SUCROSE SOLUTIONS BY FTIR SPECTROSCOPY

Amar Otmani[1,2], Salim Ouchemoukh[1], Maria Eduarda Araújo[2,3]

[1]Laboratoire de Biochimie appliquée, Faculté des Sciences de la Nature et de la Vie,
Université de Bejaia, 06000 Bejaia, Algeria. otmaniamar2015@hotmail.com
[2]Centro de Química Estrutural, Faculdade de Ciências, Universidade de Lisboa,
Campo Grande, 1749-016 Lisboa, Portugal
[3]Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa,
Campo Grande, 1749-016 Lisboa, Portugal

Honey is among the leading adulterated products. The phenomenon affects not only large producers of honeys but also small-scale local artisanal production.

In this work we investigated the use of ATR-FTIR spectroscopy to identify adulteration of honeys with sucrose syrup. The spectra of 56 pure honeys were recorded between 4000 and 750 cm^{-1}. FTIR spectra present six main characteristic bands: bands 1 and 3, with maximum absorption of 3311 cm^{-1} and 1646 cm^{-1}, corresponding, respectively, to the stretching and the deformation vibrations of (O-H) in H_2O; band 2, broad, with absorption maximum at 2936 cm^{-1}, corresponds to the stretching vibrations of (C-H) of carboxylic acids and the stretching vibrations of (NH_3) of free amino acids; bands 4, 5 and 6, appear in the most important absorption region of sugars and organic acids present in honey, the region ranging from 1500 to 750 cm^{-1}.

The comparison of the spectra of pure and adulterated honeys revealed a significant increase in the intensity of the band at 1646 cm^{-1} in honeys adulterated with distilled water and sucrose solution of 50% (w/v). Furthermore, in the spectra of honeys adulterated with sucrose solutions of 100, 150 and 200% (w/v), it can be observed the appearance of peak at 987 cm^{-1}, which is a marker of D-(+)-sucrose, and the increase of its intensity with increasing concentration of sucrose in the adulteration solution.

The results obtained show that pure honeys have the same spectral profile, with 6 characteristic bands, and reveal significant differences between the two groups of honey, pure and adulterated. From these results it is possible to conclude that analysis by ATR-FTIR spectroscopy can differentiate pure honeys from honeys adulterated with sucrose syrup after harvest.

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ELECTROCHEMISTRY OF THE CALCIUM CHANNEL BLOCKER LERCANIDIPINE AT A CARBON BLACK MODIFIED GLASSY CARBON ELECTRODE

Ana-Maria Chiorcea-Paquim, Isabel Garrido Fernandes, Ana Maria Oliveira-Brett

University of Coimbra, CEMMPRE, Department of Chemistry, 3004-535 Coimbra, Portugal.
anachior@ipn.pt

Lercanidipine is a third generation calcium channel blocker belonging to the dihydropyridine group of compounds, and is used to treat mild to moderate hypertension, chronic stable angina pectoris and Raynaud's syndrome.

The lercanidipine electrochemical behaviour at different carbon electrodes, in a wide pH range, was studied using cyclic, square-wave and differential pulse voltammetry, Figure 1 [1]. A comparison was made between unmodified glassy carbon electrode (GCE) and boron doped diamond electrode (BDDE), and GCE and BDDE modified with carbon black (CB) nanoparticles embedded within a dihexadecylphosphate (DHP) nanostructured film (CB–DHP/GCE and CB–DHP/BDDE).

The lercanidipine oxidation, for 3.4 < pH < 9.5, was pH-dependent, diffusion-controlled, irreversible, and took place at the N1 and C4 positions from the 1,4-dihydropyridine ring. Two consecutive steps were observed, each involving the transfer of one electron and one proton. For pH > 9.5, both oxidation processes were pH-independent, and a pKa = 9.40 was determined.

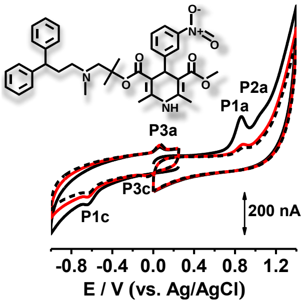

Figure 1: Cyclic voltammograms at a GCE, in N_2 saturated solutions of 50 µM lercanidipine in pH = 7.0, at v = 100 mV s^{-1}: (▬) first, (▬) second and (▪▪▪) third scans [1].

The lercanidipine reduction was irreversible, and the lercanidipine reduction products were also electroactive, following a reversible electron transfer reaction.

Based on the lercanidipine oxidation, with no need for N_2 purging, the electroanalytical determination at a nanostructured CB–DHP/GCE was achieved.

A detection limit of 0.058 µM (3.58×10^{-5} g L^{-1}) and a quantification limit of 0.176 µM (1.08×10^{-4} g L^{-1}), more than ten times lower than previous described, was obtained.

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DISPOSABLE ELECTROCHEMICAL SENSOR FOR KETOPROFEN DETECTION

Álvaro Torrinha, Marco Martins, Cristina Delerue-Matos, Simone Morais

REQUIMTE-LAQV, Instituto Superior de Engenharia do Porto, Instituto Politécnico do Porto,
Rua Dr. António Bernardino de Almeida, 431, 4249-015 Porto, Portugal.
alvaro.torrinha@graq.isep.ipp.pt

The uttermost necessity to preserve the environment relies on efficient methods for monitoring and control of environmental pollutants. Electrochemical sensors have enormous potential for contaminants detection and be established in the near future as techniques of choice, overcoming the more conventional analytical ones. Pharmaceuticals are a relevant group of contaminants of emerging concern due to their increasing presence in the environment and risk to cause negative effects on ecosystems and human health [1]. Therefore, the main objective of this work was the development of a disposable carbon paper-based sensor for detection of ketoprofen, a widely consumed anti-inflammatory drug. The working sensor consisted simply in an unmodified paper-based carbon substrate connected in one end to an aluminium foil. The electrochemical characterization of the paper-based carbon sensor was firstly assessed by cyclic voltammetry in a standard solution of $Fe(CN)_6^{3-/4-}$ and compared with other commonly used electrodes. The sensor was then applied for ketoprofen detection by differential pulse voltammetry (DPV) in a buffered solution at *ca.* pH 5. The sensor presented high sensitivity and low limit of detection even when used unmodified, being suitable for application in clinical and environmental analysis of pharmaceutical drugs.

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ENANTIOMERIC PURITY OF NEW XANTHONE DERIVATIVES COMPRISING TWO CHIRAL MOIETIES BY LIQUID CHROMATOGRAPHY ON (*S*,*S*)-WHELK-O1 COLUMN

Joana Teixeira[1], Ye Zaw Phyo[2,3], Maria Elizabeth Tiritan[1,3,4], Anake Kijjoa[2,3], Madalena M.M. Pinto[1,3], Carla Fernandes[1,3]

[1]Laboratório de Química Orgânica e Farmacêutica, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, Rua de Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal. cfernandes@ff.up.pt
[2]ICBAS-Instituto de Ciências Biomédicas Abel Salazar, Universidade do Porto, Rua de Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal
[3]Interdisciplinary Centre of Marine and Environmental Research (CIIMAR), Edifício do Terminal de Cruzeiros do Porto de Leixões, Av. General Norton de Matos s/n, 4050-208 Matosinhos, Portugal
[4]CESPU, Instituto de Investigação e Formação Avançada em Ciências e Tecnologias da Saúde (IINFACTS), Rua Central de Gandra, 1317, 4585-116 Gandra PRD, Portugal

Enantioseparation has become an emerging topic in several research fields, such as Analytical and Medicinal Chemistry. Considering all the phases of drug discovery and development, even at early stages, enantioseparation is a key step for diverse studies of chiral bioactive compounds [1]. Chiral liquid chromatography is a broadly applied technique for analysis and purification of diverse types of analytes. Several types of chiral stationary phases (CSPs) have been developed and, among them, more than a hundred are currently commercially available [2]. One of the most successful CSP is the (*S,S*)-Whelk-O1 [3], a Pirkle-type CSP, with enantioselectivity for a broad range of chiral analytes. Recently, (*S,S*)-Whelk-O1 CSP demonstrated high enantioselective performance for a series of bioactive chiral derivatives of xanthones [4].

Herein, the determination of the enantiomeric purity of new synthetized xanthone derivatives [5], comprising two chiral moieties, is reported. Liquid chromatography analyses were performed with the (*S,S*)-Whelk-O1 CSP in polar organic mode. A high enantioselectivity (α values ranging from 2.28 to 2.46) and resolution (R_s values ranging from 7.28 to 9.38) were achieved. The enantiomeric ratio (e.r.) values were higher than 99% for all the analyses.

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pH EFFECT IN BIOSORPTION OF DICLOFENAC IN WATER USING MORINGA *OLEÍFERA* SHELLS AS BIOSORBENT

Agustina De Olivera[1], Cristiane Kreutz[2], Ramiro Martins[3]

[1]*Universidad Nacional de Misiones (UNaM), Misiones, Argentina.*
agustina.deolivera@gmail.com
[2]*Federal University of Technology-Paraná, Campo Mourão, Brazil*
[3]*Polytechnic Institute of Bragança (IPB), Bragança and LSRE-LCM, FEUP, Porto, Portugal*

The role of Analytical Chemistry in dealing with environmental issues, such as energy issues, air, soil and water pollution, is of paramount importance to achieve a more sustainable future [1]. One of the most serious global issues nowadays is the contamination of water currents by emerging pollutants. In the present paper, we focus on the environmental damage caused by drugs, specifically the anti-inflammatory Diclofenac (DCF). In recent years, concentrations within the range of ng /l-mg/l have been recorded. Even though it appears at very low values, it is highly dangerous because excessive intake causes the development of a gene resistant to the active effects of the drug [2]. The Biosorption method arises as a possible solution. It is a pollutant removal process that stands out for its simplicity, low cost, and the fact that it is environmentally friendly as it uses biodegradable material as an adsorbent [3]. On this occasion, it was decided to assess the adsorption capacity of Moringa *oleífera* (MO) shells due to its coagulant, nutritional and medicinal properties [4,5].

The Moringa *oleífera* shells were collected in Angola, Africa. A concentration of 1 mg/l of DCF, 100 mg of MO powder in 50 ml of solution was employed. Tests of influence of pH and physicochemical characterization of MO were carried out to achieve a better understanding of the possible interactions between adsorbent and adsorbate.

The adsorbent surface charge was assessed by varying the pH of the solution. Moringa *oleífera* is positively charged for pH values < 6 and negatively for alkaline zone. Furthermore, it has been confirmed that the removal process is highly dependent on pH. It was evaluated within a range of pH 2-10 and it was observed that, as the pH increased, the percentage of adsorption decreased, obtaining a maximum percentage of removal of DCF at a pH of 2. These tests allowed us to establish a possible mechanism of action responsible for the drug biosorption process using Moringa *oleífera* shells as biosorbent.

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COAGULATION AS SAMPLE PREPARATION FOR DETERMINATION OF SILVER NANOPARTICLES IN AQUEOUS MATRICES

Priscila Lagner da Silveira Estevão, Patricio Peralta-Zamora, Noemi Nagata

Federal University of Paraná, Av. Cel. Francisco H. dos Santos, 100, Curitiba, Paraná, Brazil. priscilalagner@hotmail.com

The growing production and the indiscriminate use of silver-based Nanomaterials (nano-Ag), due to their antimicrobial activity, has resulted in inevitable environmental contamination. However, the environmental monitoring of nano-Ag in low concentrations is still being a challenge. Techniques such as Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) can be used, but the instrumental sensitivity is far from environmental levels (ng L^{-1}), making the use of pre-concentration techniques essential. This work aims to investigate the potential use of coagulating agents (commonly used in water treatment systems) in the sample preparation for the extraction and pre-concentration of nano-Ag from natural waters followed by ICP-OES analysis. Nano-Ag with different coatings, citrate and polyvinylpyrrolidone (PVP, MW=40000), were synthesized according to the literature [1,2], purified, characterized, quantified via ICP-OES (Thermo Scientific ICAP 6000), and then used to fortify aqueous samples. The efficiency of the sample preparation using the liquid Tanfloc SG® coagulant (Tanac S.A) aiming at the extraction and pre-concentration of nano-Ag was also assessed by ICP-OES. The preliminary tests were carried out with 45.0 mL of aqueous samples, separately fortified with 90.0 µg L^{-1} of Ag^+, Ag-PVP, and Ag-Citrate. The samples were added with 100.0 µL of Tanfloc SG, the pH was adjusted to 6 with tetramethylammonium hydroxide (25% w/v in water, Sigma-Aldrich), and were manually stirred and centrifuged. The supernatant was decanted and stored for later analysis. The extracts obtained were digested with 5.00 mL of H_2O_2 (35% w/v in water) in a medium of 1% (w/v in water) of HNO_3, followed by vigorous manual agitation, stored at room temperature, and then analyzed by ICP-OES after 24 h. Silver concentration over the instrumental limit of quantification was not detected in any of the analyzed supernatants, indicating the high efficiency of the coagulant in the removal of both ionic silver and nano-Ag in the investigated conditions. Also, high recoveries values (>82%) were observed for all analytes in the digested extracts, indicating the potential of the method in determining the total silver content in the sample. Future trials using Graphite Furnace Atomic Absorption Spectrometry (GFAAS) will be conducted to improve the enrichment factors (EF) of the method, due to the greater sensitivity of this technique and the possibility of analyzing the samples without previous digestion. We estimate that will be possible to achieve EF approximately 450 fold higher by GFAAS, which will make be possible the determination of nano-Ag in aqueous samples at the expected environmental levels. Also, future trials aiming to distinguish ionic silver from nano-Ag by modifying the method will be conducted.

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ELECTROCHEMICAL QUALITATIVE DETECTION OF STRESS BIOMARKERS IN SIMULATED AND REAL SWEAT SAMPLES

Cristina M. Cordas[1], Maria João Nunes[1], Gabriel N. Valério[1], Alejandro Samhan-Arias[1†], José J.G. Moura[1], João Paulo Sousa[2], Carlos Rouco[2]

[1]LAQV, REQUIMTE, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Campus de Caparica, 2829-516, Caparica, Portugal cristina.cordas@fct.unl.pt
[2]CINAMIL, Academia Militar, Estado Maior do Exército, MDN, Rua Gomes Freire, 1150-244 Lisboa, Portugal
[†]Present address: Departamento de Bioquímica, Universidad Autónoma de Madrid e Instituto de Investigaciones Biomédicas 'Alberto Sols' (CSIC-UAM). C / Arturo Duperier 4, 28029-Madrid, Spain.

Detection of stress biomarkers molecules through non-invasive methods is an important field of research. Sweat is a potential diagnostic fluid for early and continuous human health monitoring, not only for stress-related conditions directly, but also other pathologies (e.g. associated to chronic diseases) [1]. The simultaneous detection of multiple potential biomarkers in sweat samples, using simple and low cost electrochemical methods (detecting patterns or “electrochemical fingerprints”) requiring no samples preparation and its correlation with physiological conditions is an attractive methodology, although not straightforward, since the multiple possible biomarkers present very close oxidation potentials among other factors that hamper the detection [2]. Disposable screen-printed electrodes (SPE) can be useful to overcome the difficulties and to build a future (bio)sensor. In the current study, a set of selected potential stress related (non-protein) biomarkers (Tyr, Phe, DO, 5-HT, Cor), was used for a qualitative electrochemical detection on different screen-printed carbon-based electrodes (Figure 1). The detection was attained in simulated and real sweat samples and the most promising SPE carbon-based electrodes were selected.

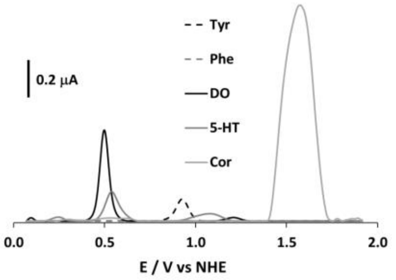

Figure 1: DPV individual responses of a set of molecules (Tyr, Phe, DO, 5-HT and Cor) on C-SPE.

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Lista de autores / *Authors list*