Dipartimento di Chimica



# C'È FUTURO NELLA RICERCA! VIII CONVEGNO GIOVANI RICERCATORI

Dipartimento di Chimica, Sapienza Università di Roma Roma, 25 e 26 giugno 2019





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Antonio Di Nitto Injectable composite hydrogels for biotechnological applications

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Doping of LiNi 0.5 Mn 1.5 O 4 spinel as effective approach to improve the electrochemical performance of high voltage lithium battery

Mercoledì 26 giugno - Seconda sessione poster



# Martedì 25 giugno Keynote e presentazioni orali

# Supramolecular control of selectivity in C-H oxidation

# dr. Giorgio Olivo<sup>1\*</sup>

Giulio Farinelli<sup>2</sup>, Giorgio Capocasa<sup>2</sup>, Osvaldo Lanzalunga<sup>2</sup>, Stefano Di Stefano<sup>2\*</sup> and Miquel Costas<sup>2\*</sup> <sup>1</sup>QBIS-Cat, IQCC, Universitat de Girona, C/Pic de Peguera 15, 17003, Girona, Spain <sup>2</sup> Chemistry Dept, Sapienza University of Rome, P.le A. Moro, 5 - 00185 Rome, Italy

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Selectivity represents a longstanding challenge in aliphatic C-H bond functionalization. Most of the current methodologies target either the most (sterically or electronically) reactive positions, or rely on directing groups to force the reaction on one site close to the directing group. As a consequence, C-H bonds that do not meet these requirements are very difficult to functionalize. Bioinspired C-H hydroxylation, catalyzed by Fe and Mn coordination complexes with  $H_2O_2$  via the generation of a highly reactive yet selective high-valent metal-oxo intermediate,<sup>1</sup> is no exception, and suffers the same limitations on selectivity.

Seeking to overcome these limitations, we designed and

implemented a supramolecular strategy to target remote, non-intrinsically activated positions. We equipped a Mn catalyst with an 18-crown-6 ether receptor that can recognize protonated primary amines.<sup>2</sup> Such binding places C8 and C9 C-H bonds of the substrate in the range of the oxidizing species, thus enabling a geometrical control of the oxidation selectivity (Figure). Herein, the application of this strategy to the remote, selective oxidation of linear amines and more elaborated substrates will be presented. Moreover, the application of this strategy to an enzyme-like substrate-selective C-H oxidation will be described.



*Figure - Supramolecular control of C-H oxidation selectivity* [1] W.N. Oloo, L. Que Jr, *Acc. Chem. Res.* 2015, 48, 2612.

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# Low-cost materials for environmental applications: possible alternatives in groundwater remediation technologies

# Marta Maria Rossi PhD\*

Neda Amanat, Ludovica Silvani, Marco Petrangeli Papini Chemistry Department, University La Sapienza, Rome, Italy \* martamaria.rossi@uniroma1.it

Contaminated sites by mixture of contaminants are diffused worldwide: DNAPLs, VOCs or heavy metals are commonly revealed in the aquifer. Soil and groundwater's remediation technologies need to be more effective at lowering concentration imposed by local legislation, more sustainable and cost-effective [1]. For these reasons, the scientific community has turned the attention to products deriving from the thermal treatment of wastes with high environmental impact, like tires and plastics, or wastes from agriculture and breeding [2][3][4][5].

In this study four materials, obtained in small real plants for energy recovery, are investigated: a char obtained from pyrolysis of tires and rubbers (Krasnodar (RU)) and three materials obtained from the treatment of different biomass. A biochar from pine wood (Germany), one from rice husks in Indonesia and a biochar from *Eupatorium* shrubs plus Fe(OOH) (Nepal). The purpose of the study is the characterisation of

materials and the assessment of the adsorptive properties against organo-chlorinated contaminants (TCE) and heavy metals (Pb(II)) in aqueous solution. After observation at SEM-EDS and analysis for surface area determination and pores distribution, adsorption tests were performed in batch systems and in continuous systems. The former allow to study the kinetics and to draw the adsorption isotherm; the latter allow to realize a condition similar to the most used configuration (fixed-bed treatment columns) or possible innovative technology (direct injection of absorbent material into groundwater); moreover the study in continuous adds fundamental information: it allows to reason on the operating ability, linked to the limits imposed by local legislation. The columns, after tracer test, are fed from the bottom with a solution of TCE and Pb(II), respectively at 5 and 20 mg L-1: regular sampling allows the realization of the breakthrough curves.

The results are encouraging considering that these materials, compared with commercial activated carbon, have not undergone activation treatment, they are cost-free and can therefore be re-evaluated in a fundamental context, such as the improvement of the quality of groundwater.

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# Multi-block approaches for food and clinical data analysis

### Alessandra Biancolillo post doc\*,1

Patrizia Firmani<sup>1</sup>, Remo Bucci<sup>1</sup>, Jean-Michel Roger<sup>2</sup>, Federico Marini<sup>1</sup> <sup>1</sup> Chemistry Department, University La Sapienza, Rome, Italy - <sup>2</sup>ITAP, Irstea, Montpellier SuperAgro, University of Montpellier, Montpellier, France \*alessandra.biancolillo@uniroma1.it

When the same samples are investigated by different analytical techniques or at different time points, the outcome is a multiblock data set. In the presence of such kind of data, it has been demonstrated that it is more advantageous to process all the matrices together by data fusion techniques, rather than applying separate approaches for the individual sets of measurements. Consequently, due to the increase of the demand, in the last years, several multi-block approaches have been proposed into the literature, with the aim of overcoming some limitations of the standard data fusion approaches. In particular, two (relatively) new methods have been developed: Sequential and Orthogonalized Partial Least Squares (SO-PLS) [1-2] and Sequential and Orthogonalized Covariance Selection (SO-CovSel) [3]. Despite they can be applied on data of any nature, they found a wide application in food analysis, in particular to solve classification problems. In the present work, two applications in this context will be discussed, in order to highlight the advantages of these techniques. The first example is on grappa spirits: several pure and adulterated samples of

this liquor have been analyzed, and the novel techniques have been applied to detect non-pure spirits. On the other hand, in the second application, the above-mentioned approaches have been used to inspect chocolate bar samples with the aim of correlating chemical and sensory characteristics.

Due to its peculiar characteristics [3], the SO-CovSel algorithm is particularly suitable in estimating which variables contribute the most to a model, allowing a deep investigation of the system at study with the minimum number of descriptors. For this reason, it may find application also for sensor development and for the identification of biomarkers. For instance, it has been used to detect novel serum inflammatory biomarkers for the early identification of sarcopenia and physical frailty in elders [4].

In all the investigated examples, the multi-block approaches have provided better results (in terms of predictions) than the analysis of the individual blocks.

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L1 in the Henry reaction. The results we have collected will be discussed in the oral communication.



# *Figure - Employment of L1 in the asymmetric addition of diethylzinc to aldehydes.*

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# Multi-block approaches for food and clinical data analysis

## Ludovica Primitivo PhD\*,1

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Asymmetric catalysis is probably the most efficient method to obtain optical active compounds, and in the last decades many different catalysts have been developed, providing chiral products in high yields and enantiomeric excesses [1]. Given that, recovery of the catalyst from the reaction mixture is difficult and expensive. Thus, many efforts have been made in the field of heterogeneous catalysis, in which the catalyst is immobilized on solid support [2]. Among supports, magnetic nanoparticles potentially offer both high efficiency and simple recovery through magnetic decantation, thanks to their high dispersibility and superparamagnetic properties [3].

Since long the group I'm collaborating with has worked on this field, and developed ligand **L1**, potentially anchorable on magnetic nanoparticles, that showed high efficiency in the asymmetric addition of diethylzinc to aromatic aldehydes [4]. We have then studied the best magnetically recoverable support and immobilization strategies, together with the employment of

# Sodium cholate/PEO-PPO-PEO triblock copolymer mixed micelles as stealth nanocarrier for doxorubicin

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Polymer nanomaterials have received a great deal of interest as vehicles used for diagnostic and therapeutic agents [1]. The loading efficiency of a bile salt/block copolymer coformulation toward the fluorescent anticancer antibiotic doxorubicin has been studied. The coformulation is based on the anionic bile salt sodium cholate (NaC) and a nonionic triblock copolymer of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) denoted EO<sub>100</sub>-PO<sub>65</sub>-EO<sub>100</sub> (F127) that itself forms micelles in water with a core composed mostly of PPO and a PEO corona. Doxorubicin is usually administered as the hydrochloride (DX) to increase its solubility in water. This limits its partitioning to the corona region of F127 micelles. To promote its solubility in the hydrophobic core, NaC was introduced in the system. The resulting systems obtained by varying the NaC/F127 mole ratio were characterized by small angle X-ray and dynamic light scattering (SAXS and DLS) in combination with spectroscopic fluorescence techniques (steady state and time-resolved).

The host structure is not affected by the guest presence as deduced by SAXS and DLS data while in the presence of NaC, DX experiences a more apolar environment as indicated by its characteristic fluorescence behaviour (Figure 1). The stability against degradation of DX in the mixed micellar system was markedly enhanced relative to aqueous solutions without the coformulation [2]. The DX increased time stability in the NaC/ pluronic mixed micellar systems is a promising characteristic that could lead to an increase of the drug latency and protection against hydrolytic degradation. In addition, the PEO hydrophilic corona could provide a certain level of biocompatibility and stealth characteristics to the mixed system, thus being attractive from an applicative point of view.





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# A roman chemist in Germany – Challenges and opportunities

*Francesca Aulenta PhD Senior Product Manager* BASF SE, Ludwigshafen am Rhein, Germany

The step to enter the 'business world' at the end of the student career is often characterized by uncertainties and challenges, but also by new impulses that can be stepchanges in one person's life.

After my graduation in Chemistry at the University 'La Sapienza' of Rome, the opportunity to carry out a work placement abroad opened the door for a PhD in macromolecular chemistry in Reading, England and ultimately, a permanent contract in the headquarter of BASF SE, Ludwigshafen, Germany.

BASF is the world leading chemical company, in terms of sale, s with subsidiaries in over 80 countries and serving more than 90.000 customers across most application

#### segments.

In my presentation I will outline the company structure, area of activities, and give an insight on what it means working for BASF.

# Borate-based ionic liquids as electrolyte additives to improve the capacity retention of high voltage lithium batteries

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With improvement in the energy density of lithium batteries, safety and reliability of the electrolytes need to be enhanced. Especially when high voltage cathodes such as LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> (LNMO) are used, stabilization of the electrolyte/cathode interface becomes a critical issue. Ionic liquids (ILs) have been used as additives for carbonate-based electrolytes to suppress the latter's flammability.[1] More recently, borate-based ILs have been found also to form solid electrolyte interfaces (SEI) on both electrodes and suppress the decomposition of the electrolyte during cell cycling.[2]

In this study, we synthesized novel IL, namely *N*-methoxyethyl-*N*-methylpiperidinium bis(oxalato)borate (BOB-IL), and added this to 1M LiPF<sub>6</sub> electrolyte solution (LP71) employing ethylene carbonate : diethyl carbonate : dimethyl carbonate 1:1:1 vol.% as a solvent. When 0.3 M BOB-IL electrolyte was used in Li | LNMO cells as the electrolyte, the capacity of the cells converged to 120 mAh g<sup>-1</sup> after the 10<sup>th</sup> cycle, and the capacity retention rate at the 100<sup>th</sup> cycle was found to be 99.2% (**Figure**, blue). This value was higher than the cell with pristine LP71 solution (**Figure**, black). By means of impedance and infrared spectrum analyses, the capacity retention was confirmed to be supported by SEI formation. In addition, the ILs containing difluoro(oxalate)borate were synthesized, and their performances as the electrolyte additive were compared to those of BOB-IL.



**Figure** - Capacity retention of the Li | LNMO cells with LP71 and 0.3 M BOB-IL electrolyte. The cells were galvanostatically cycled within 5.0÷3.5 V at 1C rate.

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# Analytical chemistry: where there's a will, there's a way

## dr. Silvia Rocchi

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Si sottolinea spesso la mancanza di un ponte tra l'università e il mondo del lavoro. Se come ponte s'intende la ricerca di un'occupazione e il dialogo tra aziende e i giovani studenti universitari, concordo. Ma se come ponte s'intende la solida formazione che l'università ci fornisce per affrontare con sicurezza professionale il mondo del lavoro, allora devo dissentire.

Ripercorrendo brevemente la mia esperienza iniziata come studente del Dipartimento di Chimica dell'Università "La Sapienza", proseguita come dottoranda presso il Consiglio Nazionale delle Ricerche (con un periodo di formazione all'Università di Ginevra) e poi come ricercatore in Merck Serono, dove sono tutt'ora, saranno mostrate alcune delle sfide che ho affrontato studiando la chimica analitica. In particolare si illustreranno applicazioni di tecniche separative classiche e miniaturizzate, come la cromatografia liquida (LC) e la micro-LC/nano-LC, mediante il loro accoppiamento con la spettrometria di massa (MS).

Saranno inoltre discusse nuove frontiere della spettrometria di massa ad alta risoluzione per l'analisi untargeted di screening per la determinazione di impurezze chimiche.

## Glycosilated liposomes for targeting bacteria

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Biofilm associated bacterial infections are one of the most relevant health problems due to their high antibiotic resistance. In fact, bacterial cells are embedded in a complex polymeric matrix that, on the one hand protects the cells from external agents and, from the other confers to bacteria new powerful tools to survive, such as for example the ability to communicate among them by "Quorum Sensing", a system of stimuli and responses correlated to their proliferation that exploits specific signal molecules[1,2]. Several molecules, such as ferulic acid, gallic acid, arbutin and resveratrol have been shown to inhibit Quorum Sensing in *in vitro* studies [3] but an optimal formulation for their targeted delivery in living organisms has not been developed yet.

We have designed and prepared cationic glycosylated liposomes for the encapsulation of some of the most promising Quorum Sensing inhibitors. Sugar moieties (glucose, mannose, galactose) should in fact interact with specific proteins expressed on bacterial surface, lectins, that bear binding sites for specific monosaccharides.

Here we report on new resveratrol loaded liposomal formulation and on their biological evaluation.



Figure - Resveratrol

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# Insights in thermal transitions of polymers using Modulated Temperature Infrared Spectroscopy

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The increasing demand of polymers for high-tech applications and special transformation processes has favored the development of advanced characterization methods. Because of its applicative importance, the definition of polymer thermal properties is one of main issue in overall material characterization. It drives the synergistic union between fundamental and applicative research which favored the development of new instrumental techniques and interpretative models able to give new insight of material behavior. As far as the thermal analysis, in 1993 an innovative experimental apparatus, called Modulated Temperature Differential Scanning Calorimetry (MTDSC) has been proposed [1]. It is based on the calorimetric analysis carried out by applying a modulated temperature program, comprised of a linear heating or cooling ramp with superimposed a sinusoidal temperature variation. MTDSC offers the great advantage of the identification of the equilibrium and of the out-of-equilibrium thermodynamic transformation involved in polymer phase transitions. However, conventional or temperature modulated thermal analysis techniques acquire only one signal output and can give only an overall description of the sample thermal properties.

Differently, variable temperature FTIR (VTFTIR) performs a multi-signal analysis that permits to characterize materials in greater detail. The infrared spectroscopy, in fact, is sensitive to inter- or intra-molecular interactions, conformation or structure changes occurring during sample transformation. Therefore, the investigation of intensity variations of different absorption bands as a function of temperature can be employed to explore the sample thermal transitions at molecular level. The present contribution aims to introduce a new spectroscopic technique, developed in our laboratory, called Modulated Temperature FT-IR (MTFTIR) [2,3], able to improve the description of the thermal behavior of polymers. It is based on the acquisition of sample spectra sequentially during a modulated temperature program. By processing selected bands, the total signal variation as well as its reversing and non-reversing components as a function of the mean temperature are obtained. The reversing component is related to the sample transformation that can be reversed by temperature modulation while, the nonreversing component, to the spontaneous processes ( $\Delta G$ <0) that, once started, can't be reversed. In this way we explored at a molecular level the complex sample transformations involved in some transitions of polymers, such as the glass transition of poly(L-lactide) [2] and poly(ethylene terephthalate) as well as the crystallization of isotactic poly(propylene) [3]. The obtained results evidenced that MTFTIR is able to give new insights on polymer transformations otherwise not accessible by other conventional thermal analyses.

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# Simultaneous determination of 36 psychoactive substances in oral fluid by means of HPLC-HRMS/MS analysis

#### Flaminia Vincenti PhD\*,1,2

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The disorders deriving from the use of psychoactive substances, occur when one or more psychotropic substances are permanently introduced into a person life habits [1]. In recent years, multi-class analytical methods, that allow the simultaneous determination of several substances belonging to different chemical classes, have proved to be particularly advantageous to save time and resources in the cases of polydrug use [2], especially when sample volume is limited as is the case with oral fluid (OF). OF has become a valuable biologic specimen for toxicological analysis, especially in driving under the influence of drugs (DUID) investigations, because of easy and non-invasive collection procedures.

The aim of this work was the development of a multiclass method, for the simultaneous determination of 36 analytes in OF, including both natural and synthetic narcotic substances as well as New Psychoactive Substances (NPS). The method allows to perform both screening and confirmatory tests on the same sample as qualitative and quantitative analysis may be achieved simultaneously.

Sampling was carried out by using a sterile swab which is inserted directly in the mouth of the suspects, as is performed for DNA analysis. The extraction of the analytes was then carried out by consecutive washings of the dried swab with suitable solvent mixtures. The extract was then filtered and further diluted prior to injection into the UHPLC-HRMS/MS system. For the separation of the analytes a Hypersil Gold C18 column was used, allowing the separation of the 36 analytes in 8 minutes. The identification and quantification of the target analytes was performed with a high-resolution mass spectrometer with Orbitrap technology equipped with a H-ESI source operating in positive ionization mode.

Finally, the proposed method was validated according to the international EWDTS guidelines [3].

The method has been developed and is currently in use for DUID investigations as provided by the Italian Highway Code, article 187, which prohibits driving in a state of psychophysical alteration due to drugs or psychotropic substances consumption [4].

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# A Scientific Editor's Role: Behind the Scenes at Chemistry – A European Journal

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What happens when a manuscript is submitted to a journal? What is the role of a scientific editor in the peer review process? What happens once a manuscript has been accepted? This presentation will try to demystify the publishing process and answer some of the questions that editors are most frequently asked by giving an overview of the professional editors' daily work at *Chemistry- A European Journal*.

# Electrochemical sensor for screening analysis on extra-virgin olive oil

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In recent years, consumers and researchers are starting to turn their attention to olive oil quality. In Italy, olives or even oils from European and non-European sources are used to keep olive oil prices low. Traceability for these oils is poor, while scams and frauds are common. Numerous analytical methods have been proposed to solve this problem, ranging from polyphenol characterization [1] to DNA profiling [2]. Although these methods often succeed in identifying frauds, they are too expensive, time-consuming and difficult to apply to large-scale analyses. Our sensing proposal aims to develop a simple, economic environmentally-friendly system to perform quick screening analyses of edible oils. The proposed platform accurately described and characterized in our previous works [3,4], is based on screen-printed plastic electrodes modified with multi-walled carbon nanotubes and titanium oxide nanoparticles, using bio-derived ionic liquids as drop-casting medium.

The proposed platform has been used to perform cyclic voltammetry measurements on extra-virgin olive oils (EVOOs) of known origin and cultivar, processed in our lab.



#### *Figure -* Construction of the modified screen-printed electrode

The developed treatment mimes the industrial extraction procedure. Before the analysis, the EVOOs samples were incubated for 30 minutes in presence of lipase enzyme from *Candida Rugosa*. It is known that the lipase action on the olive oil triglycerides releases the antioxidant compounds [5], allowing their discharge at the electrode during the CV measures. For each oil sample analyzed, potential and current intensity of the anodic peak have been recorded. A clear classification of EVOOs has emerged, depending on the different cultivar of olives trees: all originated from olive groves in Lazio Region.

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# Comparative Evaluation of Polyhydroxyalkanates (PHA) Fermentability for Bioremediation Application

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In soil and groundwater naturally occurring microorganisms can effectively reduce chlorinated compounds, by the so-called Biological Reductive Dechlorination (BRD). Nevertheless, the lack of electron donors is usually recognized as a limiting factor in BRD. To overcome the problem, the in-situ bioremediation of chlorinated solvents has been used based on the injection of electron donors to speed up the reductive dechlorination natural processes. In this context, the use of biopolymers known as polyhydroxybutyrates (PHB), which are completely biodegradable polyesters, have been advantageously used as electron donors source for sustaining in-situ BRD [1]. These biopolymers are produced in very strictly conditions which cause high-cost of production. In recent years, more interest has been dedicated to polyhydroxyalkanates (PHA) obtained by selected mixed microbial cultures (MMC) which reduce the total costs by combing the wastewater treatment with bioplastic production [2]. This work is aimed to investigate, by monitoring of Volatile Fatty Acids (VFAs) production in microcosms, the anaerobic fermentability of three laboratorymade PHA (as obtained by MMC), in comparison with three commercial PHB. The lab-made materials were: (i) raw biomass

after PHA accumulation step, (ii) purified PHA extracted from the (i) and (iii) PHB blending with zero-valent iron particles to combine consolidated chemically reactive media with a slowreleasing carbon source [3]. The results show after some latency period, the VFAs production increased for both commercial and lab-made products, although the differences are the way that they arrive at the maximum quantity of production which can be attributed to the granulometry of the materials. Moreover, the behavior observed for the raw PHA is very interesting due to its immediate fermentation with quantity of VFAs comparable to commercial ones, and due to its possible environmental application, the cost of production is much lower as it has not been subjected of purification phase. Also, the PHB-ZVI showed a rapid fermentation with high quantity of VFAs production; the advantage that composite material could offer in the field of remediation resides in the synergistic effect is coupling of biotic and abiotic reductive dechlorination processes.

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# The structural response of Human Serum Albumin to oxidation: a biological buffer to local formation of hypochlorite

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The most abundant plasma protein, human serum albumin (HSA), plays a key part in the body's antioxidant defense against reactive species [1]. This study was aimed at correlating oxidant-induced chemical and structural effects on HSA [2]. Despite the chemical modification induced by the oxidant hypochlorite, the native shape is preserved up to oxidant/HSA molar ratio <80, above which a structural transition occurs in the critical range 80–120. This conformational variation involves the drifting of one of the end-domains from the rest of the protein and corresponds to the loss of one-third of the  $\alpha$ -helix and a net increase of the protein negative charge. The transition is highly reproducible suggesting that it represents a well-defined structural response typical of this multidomain protein.

The ability to tolerate high levels of chemical modification in a folded or only partially unfolded state, as well as the stability to aggregation, provides albumin with optimal features as a biological buffer for the local formation of oxidants.



*Figure* - *Representative dummy-residue models fitting the SAXS data* of the increasingly oxidized HSA monomer. The hypochlorite/HSA molar ratios are: 0 (blue), 80 (green), 90 (yellow), 105 (orange), 120 (red), 170 (violet).

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# Metal-organic crystal: shaping, uniformity and symmetry breaking

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The relationship between crystallization conditions, crystal structure and properties is a pivotal point in chemistry both for the investigation of fundamental aspects and for applications. The interest spans from the macro- to the nanoscale and the gamut of natural, laboratory-made, organic and inorganic systems.

In our study, we investigate the factors affecting the dimension and morphology of metal-organic crystals. [1] Typically, micro-nano crystals grown by additive-free synthesis are polydispersed in size, exhibit non-homogeneous shape or common polyhedral morphologies. We have developed a new additive-free synthesis that results in the formation of monodispersed crystals with a large variability of morphologies, while keeping the

crystallographic structure nearly identical. [2] The set of crystals generated include rare polyhedral shapes, hollow structures and unique morphologies not classifiable according to conventional rules. Interestingly, we prepared morphologically highly complex crystals from achiral components that exhibit single crystallinity and chirality at both the molecular structure and crystal morphology.

Moreover, metal-coordination chemistry was also exploited for the formation of superstructures assembled



from organic tubular crystals (Figure). [3]

Our work provides new fundamental insights in the growth of uniform and chiral crystals and aggregates, opening up opportunities for their use as 3D objects for nanotechnological applications.

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# Noble metal nanoparticles as a powerful tool for rational design of nanodevices

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In the last two decades, we have witnessed the advent and growth of nanostructured materials. In this field, functionalized Metal Nanoparticles (MNPs) has been the subject of intense research thanks to the properties that materials exhibit on the nano-scale. The interesting exotic features shown by nanoparticles, including the high chemical/physical stability, the ease of surface functionalization and the multitude of optical properties, have fostered applications in sensing, drug delivery, and cancer therapy, but intensive research effort is also directed to catalysis, electronics, and nonlinear optical processes [1,2]. In this work, narrow-sized noble MNPs (AuNPs, AgNPs, CuNPs and PdNPs) were synthesized from Au-, Ag-, Cu-, Pdsalts by a versatile wet chemistry method comprised of sequential reduction, nucleation and growth with mono- and bi-functional hydrophilic/hydrophobic thiols as capping agents. The particle size distributions were evaluated by DLS and confirmed with AFM, SEM and TEM. Extensive structural studies are possible through the use of conventional techniques

(UV-Visible, FT-IR, NMR), supported by modern techniques such as: XPS and electrical measurements. The conferment of peculiar surface characteristics is possibile through conjugation with foreign molecules such as dyes and drugs or entrapment in polymeric matrices. Surface ligand molecules enabling nanoparticles to disperse in both polar/nonpolar solvents, making them a versatile tool that can be adapted to the aqueous environment as well as to hydrophobic ones. The characterization results of the prepared colloids prove that MNPs are promising multi-functional systems, in which it is possible to combine electrical/photoelectrical and optical properties with biological activity, already proven by preliminary studies.





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# Occupational monitoring of legacy and emerging halogenated flame-retardants in an electronic waste recycling plant

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Halogenated flame-retardants (HFR) are chemical substances usually added to industrial products, such as polymeric materials, textile materials and electrical and electronic circuits, in order to prevent or reduce their flammability. Many of these compounds are associated with adverse health effects, including endocrine disruption and cancer. In 2009, the Stockholm Convention banned the production and use of the main brominated flame-retardants (PBDE e HBCD), which were afterwards replaced with alternative compounds of similar structure [1].

Several studies are focused on the investigation of this class of substances in environmental field; however, the exposure assessment of workers involved in flame-retardant production, in assembling industrial products containing HFRs or in recycling of electrical and electronic equipment (WEEE) waste is still insufficient and inadequate.

Thanks to a previously optimized analytical procedure [2], which includes the extraction and purification in a single step

and the analysis in GC-NCI-MS (Figure - left), of 28 "legacy" halogenated (PBDE, PCB) compounds and 10 new-BFR, we analyzed size-segregated atmospheric aerosol samples collected in a WEEE disposal facility during the processing phases.

Data showed significant concentrations of HFRs belonging to all three chemical classes, in ultrafine, fine, and coarse fractions of PM, with the higher concentrations in coarse fraction. The most abundant compounds are BDE 47 for the PBDE class, BTBPE for the new-BFR class and CB77 and CB138 for the PCB Therefore, the present findings imply a potential class. exposure of workers during disposal and recycling procedures to HFRs including the banned species, due to the treatment of obsolete and end-of-life products. Moreover, the present results can contribute to fill the lack of information on the concentrations of emerging BFRs in formal WEEE treatment facilities. Although exposure criteria for HFR in airborne particles of workplaces have not yet been established, the awareness of their negative effects on human health suggests the use of the present method for a wider occupational monitoring.



*Figure* - *Optimized analytical Procedure (left) Worker during dismantling procedures (right).* 

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# La mia esperienza nell'industria Chimica Farmaceutica

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# Mercoledì 26 giugno Keynote e presentazioni orali

# Oxidation of α-amino acids and peptides with H<sub>2</sub>O<sub>2</sub> catalyzed by nonheme metal based complex

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Oxidative functionalization of amino acids catalyzed by nonheme metal based complexes have received a great attention in recent years. [1] In this context we have investigated the oxidation of a series of N-acetyl amino acid methyl esters with H<sub>2</sub>O<sub>2</sub> using the iminopyridine iron (II) complex (Catalyst 1) [2] in order to obtain information on the reactivity and selectivity patterns in these oxidative processes (Figure 1A). Oxidation of aliphatic amino acids leads to exclusive C-H oxidation for N-AcAlaOMe and to both sidechain functionalization and C-H oxidation for N-AcValOMe and N-AcLeuOMe, with low efficiency. With N-AcProOMe the oxidation is more efficient and regioselective affording exclusively C-5 oxidation products in good yields. A surprising result was obtained in the oxidation of N-AcPheOMe, where a marked preference for the aromatic ring hydroxylation was observed leading to the formation of tyrosine and its phenolic isomers in high yields. [3]



#### *Figure 1 - (A)* Oxidation of N-acetyl amino acid methyl esters with Catalyst 1/H<sub>2</sub>O<sub>2</sub>, (**B**) site-selective oxidation of small peptides with supramolecular Mn-complex/H<sub>2</sub>O<sub>2</sub>.

Our studies have been extended to the site-selective oxidation of small peptides with H<sub>2</sub>O<sub>2</sub> catalyzed by a supramolecular nonheme manganese catalyst. The Mn-complex, which is equipped with two 18-benzocrown-6 ether receptors, is able to bind, via hydrogen bonding, a primary ammonium group of a Lys residue contained in the peptide (Figure 1B). This supramolecular interaction selectively exposes a specific C-H bond of the peptide to the oxidizing species and may result in a site-selective functionalization.

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# Injectable composite hydrogels for biotechnological applications

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In the last years the scientific interest towards the development of hydrogel materials for a variety of biotechnological applications has grown steadily [1]. Such materials are able to entrap a great amount of water, as much as 90-95% of their weight and exhibit a high biocompatibility. Peptide hydrogels are also able to mimic some properties of the extracellular matrix and they can be easily functionalized, both chemically or enzimatically.

Hydrogels can be prepared also from self-assembling low molecular weight oligopeptides able to self-assemble in water [2,3].

The goal of this project is to prepare injectable composite peptide hydrogels to deliver bioactive molecules able to promote the regeneration of the osteoarticular tissue.

In this project lipolytic enzymes have been used to biosynthesize self-assembling Fmoc-tripeptides by a reverse hydrolysis reaction in aqueous environment, starting from a dipeptide and an Fmoc protected amminoacid. The formed tripeptide self-assembles in water into a three-dimensional structure . In order to use the hydrogels in technological applications, it is required that these biomaterials have an appropriate structural stability and sufficient mechanical properties. So it has been added a commercial Graphene Oxide (GO) that is meant to stabilize the structure thanks to the  $\pi$ - $\pi$  stacking interactions with the aromatic moieties of the tripeptide [4].

In the first part of the work we studied the influence of GO on hydrogel formation and on the enzymatic reaction. In particular, the formation of the hydrogelator and the dependence of the reaction yield on the concentration of GO added were determined with HPLC-UV and HPLC-MS. In order to understand how GO concentration influences the chemical interactions within the hydrogel we carried out H-NMR measurements.

In the second part of the work we studied macroscopic properties such as the viscoelastic properties of the material with a rotational rheometer and the swelling abilities of the hydrogel composites.

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# Injectable composite hydrogels for biotechnological applications

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The determination of major and trace elements in non-invasive biological matrix samples (i.e. human hair, breast milk, meconium, and urine) is potentially useful for assessing an individual's health status and monitoring occupational and environmental exposure [1-3]. On the other hand, owing to the lack of standardised biological matrix analysis procedures (including sample treatment methods), it is difficult to compare and interpret the results (intervals and reference values) from different studies and reach significant conclusions. Analyte loss, contamination, and/or interferences may also lead to a decrease in the analytical accuracy of the results. Incomplete decomposition of the biological matrix samples involves an appreciable amount of residual C content in the resulting sample solution. In inductively coupled plasma spectrometry (ICP) techniques, this leads to the increased signal of some elements by C charge transfer reactions, especially for elements that have similar ionisation potentials to that of C [1]. Another source of error in biological matrix analysis by ICP with mass

spectrometry (ICP-MS) is the interference caused by the residual acidity in the digests, difference between the viscosity and acid concentrations of the calibration and sample solutions, and the presence of polyatomic ions in the plasma [1]. Considering these aspects, the aim of this study was to optimise and validate a fast screening analytical method for the multi-determination of elements (Al, As, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Rb, Sb, Se, Si, Sn, Sr, Te, Ti, Tl, U, V, W, Zn, and Zr) in biological matrix samples. The samples were subjected to HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> (2:1) digestion in an open vessel heated in a water bath and subsequently analysed by ICP-MS equipped with a collision-reaction interface.

The digestion process, which was performed directly in polypropylene tubes, presented a significant reduction in reagent and sample amounts, treatment time, and sample handling compared to those of microwave acid digestion. Thus, the proposed method is a precise and accurate method with a high sample throughput.

The in-field data can be employed as baseline information for the future elaboration of reference intervals and assessment of the nutritional status and environmental exposure of an individual.

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# Injectable composite hydrogels for biotechnological applications

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(+)-Oryzalexin S **1** is a stemarane diterpenoid isolated from Oryza sativa plant when attacked by the fungus Pyricularia Oryzae or when exposed to UV irradiation and heavy metals contamination [1,2]. Oryzalexin S **1** is a phytoalexin, displaying 7 stereocenters on the stemarane skeleton, of which 4 contiguous, and has not yet been synthesized. (Figure 1)



*Figure 1 - (+)-oryzalexin S* 

Our strategy for the total synthesis of **1** envisions as a key intermediate the compound **2**, which could be obtained from **3**, as illustrated in figure 2. We wish now to report on the synthesis of **3**, whereby 3 of the 7 stereocentres of Oryzalexin S **1** have been installed and whose absolute configuration has been confirmed by X-ray diffraction studies. **3** has been prepared from **4** (Fig.2), previously obtained by means of a D-amino acid mediated intramolecular aldol cyclization [3]. Some preliminary results in the obtaining of compound **2** are also reported.



*Figure 2 - Retrosynthesis of 2* 

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# Nanostructured TiO<sub>2</sub> based electrodes produced by electrochemical methods: characterization and possible applications

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In this contribution electrochemical approaches to synthesize two kinds of  $TiO_2$  based electrodes are illustrated. Bare  $Ti/TiO_2$  nanotubes (NTs) electrodes were obtained through a facile "one-step" anodization of titanium sheets, while composite  $Ti/TiO_2/Cu_2O$  electrodes were achieved through  $Cu_2O$  nanoparticles (NPs) electrodeposition employing the bare  $TiO_2$  electrodes as working electrodes [1]. Besides the cost effectiveness, these approaches allow by tuning the operating conditions to have control on morphology and sizes of the nanostructures, which could mainly influence the catalytic activity [2].

Two examples of applications for the synthesized electrodes are also showed. The first one is a photocatalytic application, where the electrodes were employed in photochemical (PC) and photoelectrochemical (PEC) cells for H<sub>2</sub> production [3]. In this framework the composite  $TiO_2/Cu_2O$  electrodes were specifically developed in order to overcome the bare  $TiO_2$ electrodes limitations respect to the visible light absorption. The second example showed is an environmental application for mine tailings (MTAW) treatment. Here the high aspect ratio  $Ti/TiO_2$  electrodes were employed as cathodes in an electrodialytic cell to sustain the removal of critical raw materials (i.e. As and W) from the MTAW, with the contextual recovery of the produced H<sub>2</sub> [4].



**Figure** - FE-SEM images of the synthesized electrodes. A) Ti/TiO<sub>2</sub> electrode, top view; B) Ti/TiO<sub>2</sub>/Cu<sub>2</sub>O electrode, top view. Inserts represent the cross-sectional view of the same electrodes

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# Sulfolipids profile of spirulina microalgae: graphitized carbon black enrichment and LC-High Resolution MS for a reliable identification

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Sulfolipids are polar glycolipids which possess a sulfate substituent bound to the sugar moiety. Recently, this lipid class is raising the interest of the scientific community for the promising bioactive properties, such as anti-inflammatory, immunosuppressive and anti-carcinogenic [1]. These compounds are constituents of the thylakoid membrane of plant and algae chloroplasts [2]; algae and microalgae have become a popular functional food and their healthy properties could be related to the abundance of sulfolipids. The most common analytical technique for their determination is high performance liquid chromatography (HPLC) coupled to mass spectrometry (MS). Despite the use of this powerful technique, usually a strong matrix effect is observed if sample treatment is not properly developed, thus affecting the detection and quantitation of sulfolipids. Moreover, if un-targeted analysis is

performed, a suitable database including the sulfolipid class is necessary for correct identification. The aim of the present work was to develop an enrichment procedure, based on graphitized carbon black (GCB) solid phase extraction, to obtain a clean-up of the extract derived from solid-liquid extraction of a spirulina microalgae sample (Arthrospira platensis). A comparison between an enriched sample and a simple non-enriched extract, was carried out in order to establish the enrichment efficiency, in terms of number of identified sulfolipids. Ultra HPLC coupled to high resolution MS and the up-to-date software Lipostar, with a proper database developed in a previous work [3], was exploited for reliable lipid structure assignment. A total of 199 sulfolipids were identified, which is the highest number ever reported for the A.platensis species. The analytical performances of the developed method were evaluated for some reference standards, representative of the sulfolipids class. Finally, a semi-quantitative analysis was carried out on the microalgae sample in order to characterize its sulfolipid composition and the relative abundances of the detected species.

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[2] M. Frentzen. Curr. Opin. Plant Biol. 2004, 7, 270-276.

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# Doping of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> spinel as effective approach to improve the electrochemical performance of high voltage lithium battery

Mario Branchi post doc\*

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Lithium-Ion Batteries (LIBs) represent one of the most promising technologies for the future of energy storage devices thanks to the high volumetric and gravimetric energy density of the cells.

The current lithium batteries technology, though widely spread in common electronic devices (mobile, laptop, etc), requires improvement in terms of electrochemical performances and extended life to enlarge their field to the automotive and stationary applications.

The research looks towards new cathode materials able to achieve raised capacity and high working voltage of the cell to increase supplied power of the device.

The spinel LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> (LNMO) is seen as one of the most promising cathode materials, instead of common LiCoO<sub>2</sub>. Indeed, LNMO permits to reach the theoretical capacity of

around 147 mAh g<sup>-1</sup> and a working voltage of 4.7 V using more friendly and cost effective elements than cobalt. Another advantage of LNMO is the possibility of loading extra lithium in the structure. This can be reached with different methods, electrochemically or directly from synthesis to achieve a Li-rich  $Li_{1+x}Ni_{0.5}Mn_{1.5}O_4$  spinel obtaining a higher capacity [1].

In this work the iron doping of spinel (LNFMO) was used as approach to improve the stability and cycling life of lithium cells. One of the major drawbacks is the disproportion of manganese and consequent dissolution of active element into the electrolyte during cycling. Doping with different elements such as Fe or Cr was already observed to be effective against loss of active material [2,3].

Here, we propose a simple solid-state synthesis employing a high energy ball milling for preparing reactive precursor of LNFMO, followed by heat treatment and annealing process. The thermic treatments and surrounding atmosphere have a huge influence on the morphology and the phase of final material [4], so that several experimental factors were studied in order to optimize the electrochemical performance of doped materials. Interestingly, the optimized doped sample showed a capacity loss of only 6% under prolonged galvanostatic cycling, with respect to 15% of undoped spinel.

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[2] M. Agostini, A. Matic, S. Panero, F. Croce, R. Gunnella, P. Reale, and S. Brutti, *Electrochim. Acta*, 2017, 235, 262-269.

[3] M. Agostini, S. Brutti, M.A. Navarra, S. Panero, P. Reale, A. Matic, B. Scrosati, *Scientific Reports*, 2017, 7, 1104.

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Acknowledgements: The financial support of "Bando di Avvio alla ricerca 2018" is gratefully acknowledged



# Martedì 25 giugno Prima sessione poster

#### ANDRONE - PIANO T EDIFICIO S. CANNIZZARO (CU014)

- P I.1 Andrea Cerrato (PhD student ): Innovative analytical platform for enrichment and identification of short peptides in urine
- PI.2 Elvira Cipriano (master student): Technique of micro-extraction of some explosives from complex matrices: a chemometric approach
- P I.3 Giorgia Conta (PhD student ): The evolution of infant gut microbiota metabolism during the breastfeeding and weaning as investigated on a mother-infant dyad by 1H NMR-based metabolomics
- PI.4 Alessandra Dagostino (master student): Profiling of cocaine seizures by GC-MS analysis of alkaloids and residual solvents with chemometric data analysis
- P I.5 Valeria Gallo (master student): Preparation, evaluation and characterization of a hydrophobic low transition temperature mixture for dispersive liquid-liquid microextractions
- P I.6 Ottavia Giampaoli (PhD student ): Identification by NMR spectroscopy of urinary metabolic profile and systemic metabolic changes due to direct-acting antiviral agents of HCV patients with severe liver disease

- PI.7 Giuseppina Gullifa (PhD student ): MicroNIR/ Chemometric screening system for cocaine detection
- P I.8 Lorenzo Massimi (PhD student ): Spatial mapping of PM10 element concentrations in Terni (Central Italy) by using spatially-resolved chemical data
- P I.9 Patrizia Firmani (PhD student ): Cheddar cheese ageing study by means of Low-Level data fusion coupled to ANOVA-Simultaneous Component Analysis
- PI.10 Flavia Pagano (master student): Simultaneous determination of Organic Gunshot Residues and stabilizers in forensic samples by means of UHPLC-HRMS analysis
- P I.11 Lucrezia Piccinini (master student): Characterization of morphological and compositional modifications during keratinocytes differentiation using Raman spectroscopy and chemometrics.
- P I.12 Martina Ristorini (PhD student ): Air quality biomonitoring in an urban and industrial hot-spot of Central Italy
- P I.13 Ilaria Serafini (research fellow): Dyes from the ashes: discovering and characterizing natural dyes from mineralized textiles

- P I.14 Elisa Sonego (PhD student ): Perfluorinated alkylated substances in house dust reference material
- P I.15 Carmela Maria Montone (PhD student ): Core shell molecularly imprinted polymers for selective magnetic enrichment of phospho-tyrosine-peptides.
- P I.16 Maria Agostina Frezzini (PhD student ): Optimization and application of the DPPH assay for evaluating reducing properties of particulate matter
- CORRIDOIO AULE PIANO I EDIFICIO S. CANNIZZARO (CU014)
- P I.17 Mirko Congiu (postdoc researcher ): Precursor Inkbased methods for depositing Zn1-xCdxS and M x S y thin films for CTZS and tandem Si-Solar Cells
- P I.18 Giuseppe Fazio (master student): Structural investigation of HgCl2 solvation structure using X-Ray Absorption Spectroscopy
- PI.19 Alessio Luongo (master student): Stabilization of Lead Halide Perovskites with Quaternary Ammonium Cations: Tetramethylammonium Lead Iodide
- P I.20 Giovanna Maresca (research fellow): Composite Tin-based anodes for solid state lithium ion batteries

- P I.21 Andrea Macchitella (master student): The role of hydrophobic interactions on the transfer of chirality from chiral lipids to achiral dye/surfactant aggregates
- PI.22 Adriano Pierini (master student): Ab-initio theoretical study of the disproportionation of superoxide radical anion
- P I.23 Ruggero Poiana (PhD student ): Electrolytes for safer high voltage lithium batteries
- PI.24 Luca Raganato (master student): Self-assembling hexa and octapeptide-polymer conjugates to use as drug carriers
- P I.25 Mariarosaria Tuccillo (research fellow): First principles study of Li-rich layered transition metal oxides for Li-ion battery applications
- P I.26 Antonio Greco (master student): Synthesis and characterization of polymeric nanoparticles for nanomedicine applications
- P I.27 Tommaso Alberto Salamone (master student): Electrospinning of thiol capped gold nanoparticles decorated polymeric nanofibers and sensing applications
- PI.28 Leandro Ardemani (postdoc researcher ): Fe-MOR prepared in aqueous or organic solvent for the simultaneous abatement of N2O and NOx with CH4  $\neg \pm$  O2

- P I.29 Ilaria Silvestro (PhD student ): Influence of Graphene Oxide Oxygen Content on properties of Chitosan/Graphene oxide scaffolds
- P I.30 Pier Giorgio Schiavi (postdoc researcher ): Production of nanostructured electrodes from spent lithium ion batteries and their application in new energy storage devices
- P I.31 Laura Lorini (PhD student ): High rate selection of PHA accumulating mixed cultures in Sequencing Batch Reactors with uncoupled carbon and nitrogen feeding
- PI.32 Laura Chronopoulou (postdoc researcher ): Innovative green chemistry approaches to recover and purify biopolymers from bacterial complex biomass
- P I.33 Flavio Marzolo (master student): Asymmetric supercapacitors based on Me-O x nanowires and graphite recovered from Li-ion battery waste
- P I.34 Cristina Porcu (master student): Sorption column characterization to increase CO 2 removal in a microbial electrolysis cell (MEC) aimed to biogas upgrading
- P I.35 Achille Antenucci (PhD student ): Green strategies in Br√∏nsted and Lewis acid catalysis

- P I.36 Chiara Biagini (PhD student ): Dissipative Catalysis with a Molecular Machine
- P I.37 Marika Di Berto Mancini (master student): A Self-Assembled Imine-based Iron (II) Complex as Potential Supramolecular Catalyst for Aromatic C-H Oxidations
- P I.38 Monica Messina (master student): Green synthesis of punctually chiral phosphoric acids as organocatalysts
- P I.39 Luis Claudio Pantaleone (master student): Photoresponsive Inhibitor for a Supramolecular Catalyst
- P I.40 Beatrice Marincioni (master student): Oxidative functionalization of polycyclic aromatic hydrocarbons catalysed by an iminopyridine nonheme Fe(II) complex
- P I.41 Lucrezia Lanciotti (master student): Stereocontrolled synthesis of pyrrolidine iminosugars' lipophilic derivatives
- P I.42 Tea Majnoni d'Intignano (master student): A Novel Approach for the Synthesis of new Chiral DMAP Catalysts
- P I.43 Simone Placidi (PhD student ): Organocatalytic Synthesis of Benzazetidines by Trapping Hemiaminals with Protecting Groups

ΡΙ

- PI.44 Claudia Metitieri (master student): Asymmetric Synthesis of Benzazetidines via Chiral DMAP Catalysts
- PI.45 Marika Iannoni (master student): New βaminoalcoholic catalysts for asymmetric additions to C=C and C=O groups
- P I.46 Myriam Alfonsini (master student): Synthesis and study of two new derivates of  $3-\alpha$ -cholic acid



# Mercoledì 26 giugno Seconda sessione poster

#### ANDRONE - PIANO T EDIFICIO S. CANNIZZARO (CU014)

- P II.1 Babino, Pamela (master student): Determination of several benzodiazepines collected from different items on drug-facilitated crime scenes
- P II.2 Aita, Sara Elsa (research fellow): Comparison of two enrichment procedures using GCB and WAX cartridges for the detection of phospholipids in olive oil by liquid chromatography-high resolution mass spectrometry
- P II.3 Bottillo, Grazia (master student): Double Bond in monounsaturated fatty acids of triglycerides: its role in human sebum
- P II.4 Antonelli, Michela (PhD student ): Polar lipidome microalgae research through optimized chromatographic separation, High-Resolution Mass Spectrometry, and Comprehensive Identification with Lipostar.
- P II.5 Castellani, Federica (research fellow): Troubleshooting of the analytical determination of mancozeb, a pesticide commonly used in agriculture, by high performance liquid chromatography tandem mass spectrometry
- P II.6 Cecinato, Angelo (PhD student ): Psychotropic substances in hospital interiors

- P II.7 Di Lorenzo, Francesco Valerio (master student): Classification of "Arancia Rossa di Sicilia" PGI by coupling different spectroscopies with chemometrics
- P II.8 Foglia, Miriam (master student): The Mystery of Ancient Drugs: a bridge between Forensics and Cultural Heritage Chemistry through HPLC analysis
- P II.9 Marsiglia, Riccardo (master student): Determination of Fosetyl-Aluminum in airborne particulate matter by hydrophilic interaction liquid chromatography coupled with tandem mass spectrometry
- P II.10Meschino, Martina (master student): Protonation of D-, DL-, L-Methionine
- P II.11 Minotti, Clarissa (master student): Simultaneous determination of psychoactive substances in urban waters by means dLLME extraction followed by HPLC-MS/MS analysis
- P II.12Pirau, Svetlana (master student): Fentanylderivatives: development of analytical methods for their determination in oral fluid by means (U)HPLC-HRMS/MS
- P II.13Scuto, Francesca Romana (PhD student ): Laccase immobilization on eggshell membrane
- P II.14Shabani, Egzontina (master student (Erasmus)): Voltammetric Determination Of Dopamine And Uric Acid In Serum Using Anionic Surfactants As A Surface Modifier Of Carbon Paste Electrodes

- P II.15Tomai, Pierpaolo (PhD student ): The potential of Bucky Paper for disc-solid phase extraction
- P II.16D'Annibale, Valeria (master student): Theoretical Computational Modeling of DNA-Nucleosides Reduction Potentials
- CORRIDOIO AULE PIANO I EDIFICIO S. CANNIZZARO (CU014)
- P II.17Lombardo, Lucia (postdoc researcher ): Nisupported three-dimensional microporous graphene as self-standing anode in lithium-ion batteries
- P II.18Mancini, Nicole (master student): Research, through theoretical calculations, of the Transition States in the Asymmetric Intramolecular-Aldol condensation, mediated by Amino Acid, for the synthesis of a new bicyclo-carbaldehyde
- P II.19Renga, Riccardo (master student): Iron-doped calcium titanate as co-catalyst in Fuel Cell cathodes
- P II.20Tavani, Francesco (master student): Coupled X-ray absorption/UV-vis monitoring of fast oxidation reactions Involving a nonheme iron–oxo complex
- P II.21Utrio Lanfaloni, Valentina (master student): A study of acoustic vibrations in bimetallic nanorods using femtosecond transient plasmon resonance spectroscopy

- P II.22Fioravanti, Raoul (PhD student ): Lipid membrane permeabilization induced by salmon calcitonin aggregates as a model to study the early molecular mechanisms of the amyloid neurodegenerations
- P II.23Luccisano, Giulia (research fellow): Ni supported on monoclinic ZrO 2 for the CH 4 -CPO
- P II.24Amatori, Simone (master student): Nanostructured Gold systems: an experimental and computational approach for the study of optical and conduction properties.
- P II.25Pica, Paride (master student): Functionalized gold nanoparticles blended with CuS in PMMA for switching memory devices
- P II.26Di Caprio, Fabrizio (postdoc researcher ): Microalgae biorefinery for the production of starch and lutein
- P II.27Cristiani, Lorenzo (PhD student ): Electric current's dependency on the organic loading rate in a tubular Microbial Electrolysis Cell
- P II.28 Alfano, Sara (master student): Extraction and characterization of poly-hydroxyalkanoates from mixed microbial cultures (MMC)
- P II.29Cianflone, Edoardo (master student): Synthesis and characterization of bioactive eugenol-based acrylate polymers

- P II.30Zanellato, Gianluca (master student): Electrochemical synthesis of nanostructured Cu/Znbased electrodes and their application in CO2 electroreduction
- P II.31Dell'Armi, Edoardo (master student): Bioelectrochemical treatment of CAHs contaminated groundwater under reductive and oxidative condition
- P II.32Casalese, Eleonora (master student): From spent lithium-ion batteries to new devices: a closed-loop recycling process
- P II.33Cataldi, Valerio (master student): Autonomous Motions of an Acid/Base Operated Molecular Machine achieved through a Prefuel Hydrolysis
- P II.34Semproni, Marianna (master student): Liposomes for dermal delivery of an estradiol derivative to promote wound healing
- P II.35Del Giudice, Daniele (master student): Controlled release of chemical fuel aimed to achieve the autonomous motion of an acid-base molecular machine
- P II.36Di Pietro, Federica (master student): Synthesis Of New 1,2-diaminic Ligand As Catalyst For Asymmetric Addition To Carbonyls

- P II.37 Todisco Fei, Ilaria (master student): Mannosylated liposomes for N-acetylcysteine delivery in antibacterial therapies
- P II.38 Agostinelli, Sonia (master student): A new approach to stereocontrolled synthesis of pyrrolizidin alkaloids
- P II.39D'Adamo, Andrea (master student): Studies to improve the enantioselective intramolecular aldolic reaction in the synthesis of (+)-Oryzalexin S
- P II.40 Pettazzoni, Luca (master student): Preparation of a key intermediate in the total synthesis of (+)-Oryzalexin S
- P II.41 Arena, Davide (master student): New multi-stimuli responsive methacrylates bearing the 2-(hydroxyimino)aldehyde group and their behavior in aqueous solution
- P II.42 Filippini, Dario (master student): Photochemical behavior of 2-(hydroxyimino)aldehydes
- P II.43Leone, Matteo (master student): Preliminary results on Ru and Ir catalyzed photostimulated [2+2] cycloaddition of allenes to enones
- P II.44Centrella, Barbara (master student): Stereocontrolled synthesis of piperidine iminosugars
- P II.45Zerbini, Adriano (master student): Synthesis of useful aromatic derivatives of bile acids through Click chemistry

P II.46Syeda, Rudaba Zaman Raya (master student): Cationic Liposomes For Drug Delivery To The Brain



# **Keynote speakers**

## **Giorgio Olivo**



Giorgio Olivo, born in 1988 in Formia (Italy), graduated in Organic Chemistry at Sapienza university in Rome in 2012 wih full marks (110/110 e lode). Later in the same year he begun his PhD, completed in 2015, in the group of prof. S. Di Stefano. His MSc as well as his PhD studies focused on the elucidation of structure-activity relationship in bioinspired oxidation reactions catalyzed by iron complexes. In 2016 he moved to Spain prusuing Post-Doctoral studies in the group of Prof. M. Costas at Universitat de Girona, first with an Italian fellwoship (2016) and then with a Juan de la Cierva fellowship (2017now). His research interests lie at the interface between organic, inorganic and supramolecular chemistry, and are aimed at the design and development of supramolecular catalysts to control the selectivity in oxidation reactions via substrate recognition.

#### Francesca Aulenta



Born in Rome on 21.12.1974, received her degree in Chemistry in May 1999 at the University of Rome 'La Sapienza' (degree dissertation on 'New methods of synthesis of molecularly imprinted polymers). After a three-months work placement (01.09.1999-31.12.1999) at 'Leatherhead Food Research Association', Leatherhead, UK, worked in the same company as a research scientist till 31.08.2000. From October 2000 till November 2003 completed successfully a PhD study in macromolecular chemistry (final dissertation: "Synthesis of novel dendrimers as fragrance delivery systems") at the University of Reading, Reading, UK. Then moved to the department of Chemistry and Biochemistry of the Free University of Berlin, Berlin, Germany, where she obtained a position of Post-Doctoral Researcher under the Marie-Curie Intra-European Fellowship Program. Since May 2006 she works at BASF SE, Ludwigshafen, Germany, covering

different positions, from Head of Laboratory to Senior Marketing Manager. Author of nine articles in peerreviewed journals and four patents.

### Silvia Rocchi



Silvia studied Analytical Chemistry and Applied Methodologies at the University "La Sapienza" in Rome having experience in method development for analysis of drugs and endogenous compounds in food matrices using high performance liquid chromatography coupled with mass spectrometry. During the PhD, at the Italian National Research Council, she worked with miniaturized separation techniques studying their coupling with mass spectrometry and new achiral and chiral stationary phases. Silvia joined Merck in 2015 in Guidonia site, introducing the approach for Extractables and Leachables (E&L) testing by liquid chromatography mass spectrometry. Her activity is focused on E&L studies for Merck Biotech products and process manufacturing materials. She also provides support to manufacturing sites for product and process changes and investigations.

## Luigi Bossa



Luigi Bossa, 32 years master's degree in Chemistry (Inorganic Chemical-Physics) obtained in 2013 at Sapienza University.

A few months after graduating, I started an internship at Janssen (Johnson & Johnson), at the manufacturing site for oral solid drugs located in Latina. Here I worked first in the Process Validation department (18 months) and later in the Quality Assurance (2 years).

Later I gained an experience of about 18 months as a Laboratory Assistant Technician at Newpark Drilling Fluids in Settebagni (RM), a leading multinational provider of drilling services and muds used in oil extraction.

In May 2018 I arrived at Merck in Guidonia Montecelio (RM) where in the Quality Control department I deal with

the planning, drafting and monitoring of chemical-physical analyses and stability studies performed on biotechnological drugs in development phase (pre-clinical and clinical phases) or marketed.

I was born professionally in a pharmaceutical production environment and, after a brief laboratory experience in the oil & gas sector, I returned to the pharmaceutical industry coming in a purely analytical context.

In this professional path I grew in contexts of international companies, often finding the opportunity to improve my technical and soft skills, also through the support of training courses offered by the companies themselves and to participation in project teams.

As personal information, I grew in "castelli romani" but now I live in Rome, from the marriage with Letizia in 2014. I like mountain hiking, running, guitar playing and music in general.



Leana obtained her PhD in Chemical Sciences in 2014 from the University of Rome "Sapienza", where she worked on the synthesis and self-assembly study of amphiphilic molecules under the guidance of Andrea D'Annibale and Luciano Galantini. She then joined the group of Luisa De Cola at the Institut de Science et d'Ingénierie Supramoléculaires of the University of Strasbourg. During this period her research focused on developing new mesoporous (organo)silica materials. Leana joined Wiley-VCH in 2018 as an Assistant Editor for *Chemistry – A European Journal*.

# Maria Chiara di Gregorio



Maria Chiara di Gregorio received her B.S., M.S. and Ph.D. in Chemical Sciences at Sapienza University of Rome, performing all the thesis researches under the supervision of Prof. Luciano Galantini. During her Ph.D. studies, she collaborated with Tel Aviv University and Ben Gurion University of the Negev in Be'er Sheva, Israel.

From 2015 to May 2019, she was a Postdoctoral Researcher at the Organic Chemistry Department of Weizmann Institute of Science (Israel), in the group of Prof. Milko Erik van der Boom. Currently she is a Researcher Associate in the same group. During her post-doctoral time, she was awarded the Dean of Faculty Fellowship and the Feinberg Graduate School Prize 2018 for outstanding achievement in postdoctoral research by the Weizmann Institute of Science. Her research interests include metal–organic frameworks, crystalline superstructures, self-assembly of surfactants and chirality in plasmonic systems.

### Cristina Rinaldi



Cristina Rinaldi is API TPM Manager in Abbvie site located in the south of Rome at Campoverde Aprilia, where two chemical and one pharmaceutical plant are located. She graduated in Industrial Chemistry at the University of Rome "La Sapienza" in 1996 at the Department of Chemistry under the supervision of Prof. V. Crescenzi in the field of polysaccharides. She performed research activities (1996-2001) after the degree in the same university; in 1997 she won a scholarship of one year abroad at Polytechnic Institute of NY in Brooklyn, working on the synthesis and characterization of Poly-acrylamide gels used as preparation matrix in electrophoresis of biomolecules. In 1999 she started a PhD in the University Rome "Tor Vergata" working on structural of characterization of Hydrogels based on Polyvinyl alcohol

through Dynamic Light Scattering spectroscopy and in 2001 she gave up the PhD to start working in Lamberti, a Chemical Company located in Albizzate in the north of Italy. In Lamberti she worked in R&D on the synthesis and characterization of polysaccharide derivatives used as thickening agents in several applications. The results of her studies were published in three scientific articles and three scientific magazines. In Lamberti she contributed in the achievement of 3 patents for the use of hydroxyalchylguar as rheologic modifier in paints, glue and cement fields. In 2005 she started working in Abbott in the Chemical plants where active ingredients, intermediates and anesthetics are manufactured, first as coordinator then as supervisor and finally as manager. The main responsibilities were to supervise process validation documents, troubleshootings, process and project improvements and supplier qualifications. In 2007 she obtained a certification as Internal Auditor of quality system (UNI EN ISO 9001/2003) by Certiquality-istituto di certificazione della qualità; she was project leader of Six Sigma Project "N-Acetyl Core Wing-A failure", the project lasted 8 months where a multifunctional team succeeded to identify and eliminate the route cause. With this project in 2008 she obtained the Six-Sigma Green Belt certification. In 2010 she obtained a master's degree

ottenuto la certificazione Six-Sigma Green Belt. Nel 2010 ha conseguito un master con certificazione in MPA (Master Pharmaceutical Administration) presso l'università LUISS di Roma. Nel 2011 ha ottenuto la certificazione PMP (Project Management Professional). Dal 2013 al 2018 ha iniziato a lavorare nell'impianto Farmaceutico nel ruolo di FG S&T manager con responsabilità analoghe al precedente ruolo di API S&T Manager. Tra il 2015 ed il 2018 è stata project leader di due progetti; il confezionamento di mini-tablets in sachets per studi clinici, per il quale Abbvie ha ottenuto l'autorizzazione al confezionamento da parte del ministero della salute italiano (AIFA) e all'avvio di una nuova linea di confezionamento primario e secondario di compresse in bottiglie nel reparto Farmaceutico, per il quale Abbvie ha ottenuto l'autorizzazione da parte di AIFA ed FDA. Da Settembre 2018 è entrata in un team internazionale nel ruolo di API TMP Manager a supporto delle produzioni dei fornitori esterni in Abbvie.



# **Comitato organizzatore**

### **Stefano Aiello**



Stefano Aiello was born in Rome on April 14<sup>th</sup> 1993 where he graduated at the "Liceo Scientifico A. Avogadro" in 2011. He obtained his bachelor degree in Chemistry in September 2014 with grade 109/110 under the supervision of professor Osvaldo Lanzalunga with the experimental thesis ""Studio di processi ossidativi catalizzati da complessi imminici di ferro noneme". He obtained his Master Degree cum laude in Chemistry in July 2016 under the supervision of professor Osvaldo Lanzalunga, the title of his thesis being "Studio dell'Ossidazione di Solfuri Aromatici Promossa da Complessi di Ferro Noneme".

Ph.D. student of the XXXII cycle under the supervision of professor Giovanna Mancini, he is author of five poster communications and one oral communication.

#### **Research activity**

The research activity is focused on the development of new glycosylated liposomes for the treatment of biofilm enhanced bacteria infections. Part of the research is also focused on the synthesis, purification and characterization of new glycosylated cationic amphiphile.

### Achille Antenucci



Achille Antenucci was born on June 11th 1991 in Campobasso, where he graduated with full marks from liceo "A. Romita". In December 2013 he obtained his Bachelor degree in Chemistry cum laude at University "Sapienza" of Rome under the supervision of dr. Riccardo Salvio. In May 2016 he graduated cum laude in Chemistry (Master Science, curriculum Organic and Biomolecular) under the supervision of prof. Marco Bella. The title of his Master Science thesis is "Enantioselective synthesis of biaryl compounds without the employment of transition metals". He has been awarded five working scholarships and two "Avvio alla Ricerca" grants (2017 and 2018); he is co-author of six scientific papers and author of three oral and one poster communications. From january to may 2018, he has joined Max Planck Institut für Kohlenforschung in Mülheim an der Ruhr as a "visiting PhD student", working in the laboratory of Prof. Dr. Benjamin List. In March 2019 he has furthermore been awarded an honorable mention during the second edition of "Premio Minerva" among the PhD students of the whole macro area A of "Sapienza" University.

#### **Research activity**

The research activity is focused on the development of new and eco-compatible catalytic systems, including cheap and easily handable metal salts as well as organic molecules (organocatalysts). A particular attention is dedicated to asymmetric organocatalysis, with synthesis, purification (column chromatography, crystallization, distillation) and characterization (NMR, ESI-TOF MS, HPLC-UV on chiral stationary phase, polarimetry) of new chiral molecules provided with stereogenic centres or axes.



Born in Roma in 1992, she achieved her bachelor's degree in Chemistry in July 2014 (110/110 cum laude, full marks) and her master's degree in Chemistry, Organic and Biomolecular chemistry course in July 2016 (110/110 cum laude, full marks) at Sapienza University of Rome. She is currently in the final year of her PhD in Chemical Sciences under the supervision of Dr. Stefano Di Stefano. Her research is mainly based on organic supramolecular chemistry and is focused on the design and synthesis of abiotic fuels for chemi- and photo-regulated molecular machines. In November 2017 she presented her work at the Molecular Machines Nobel Prize Conference in Groningen. From February to July 2018 she has been a visiting post-graduate researcher at the University of Manchester hosted by Prof. Dave Leigh. She is author of 5 scientific publications in cooperation with national and international groups in the field of molecular machines and fuels.

#### Laura Lorini



PhD (XXXII Cycle) in Chemical Engineering, research "Polyhydroxyalkanoates production activity: from renewable resources" on the following Horizon 2020 European projects: RES URBIS, SMART PLANT, NoAw, under supervision of Prof. Mauro Majone. 2016 Master degree in Industrial Chemistry (Curriculum ARES) at Sapienza University of Rome, experimental thesis: "Poliidrossialcanoato da colture microbiche miste in scala di laboratorio e pilota: produzione, estrazione e caratterizzazione", grade: 110/110 cum laude, under supervision of Prof. Mauro Majone. 2013 - Bachelor degree in Industrial Chemistry at Sapienza University of Rome, experimental thesis: "Sintesi e caratterizzazione di peptiti pegilati per drug delivery", grade 110/110 cum laude, under supervision of Dr Anita Scipioni.

#### **Research activity**

The research is currently focusing on the optimization of a PHA (polyhydroxyalkanoates) production process based on the use of mixed cultures, selected from activated sludge, and agro-industrial waste effluents, such as olive oil mill wastewaters, or domestic wastewaters as feedstock. This allows coupling biopolymers production to wastewater treatment and valorization. Moreover, the study involves the optimization of PHA recovery method through chlorine free reagents and the characterization of extracted polymers from different sources.





PhD (XXXII Cycle) in Environmental and Evolutionary Biology (Curriculum "Ecological Sciences"), research activity: "Monitoring and evaluation of Terni (Central Italy) air quality through innovative analytical methods". 2018 - Visiting Researcher at IRAS (Institute for Risk Assessment Sciences), Faculty of Veterinary Medicine of Utrecht University, research activity: "Spatial modelling of air pollution chemical data obtained through high spatial resolution analyses of PM". 2016 - Traineeship at GTS (Centre Grup de Tècniques de Separació en Química), Chemistry Department of Universitat Autonoma de Barcelona, research activity: "Evaluation of the effective removal of antimony from aqueous solutions using forager sponge® and SPION-loaded onto forager sponge®". 2016 -Scholarship for research activity at Chemistry Department of Sapienza University of Rome, research activity: "Evaluation of the adsorption properties of food waste and of innovative materials through analysis of physicalchemical characterization data". 2015 - Postgraduate degree Environmental Monitoring and Remediation, in experimental thesis: "Evaluation of the adsorption capacities of organic and inorganic pollutants from aqueous solutions by food waste", grade: 110/110 cum laude. 2013 -Bachelor degree in Environmental Science at Sapienza University of Rome, experimental thesis: "Monitoring of slope gully systems in the lower basin of the river Mignone (Lazio)", grade 110/110.

#### **Research activity**

Monitoring and evaluation of Terni (Central Italy) air quality through spatially resolved chemical analyses of particulate matter (PM). Mapping of the spatial variations of PM chemical species by innovative analytical methods for source apportionment studies. Evaluation of PM dispersion capacity and individuation of the PM chemical source profiles. Evaluation of PM effects on humans, animals and plants through oxidative potential assays, bioaccumulation analysis and genotoxicity assays.





Master's Degree in Industrial Chemistry (Environment Resources Energy and Safety ) on May 2016, defending the thesis "Cobalt electroplating on a nanoporous anodized alumina template", Supervisor Prof. Francesca Pagnanelli. During November of the same year accesses to the XXXII PhD course in Chemical Engineering. In November 2018 and March 2019 as a visiting PhD student he worked at the "Center for Environmental and Sustainability Research" of the Faculty of Science and Technology of the University of Li- sbon in the framework of the e.Through project (H2020-MSCA-RISE- 2017- 778045), with research activity focused on the synthesis and use of nanodioxide based electrodes in titanium structured electrokinetic processes ai- med to removals of critical raw materials, such as arsenic and tungsten, from mine tailings.

To date, the research activity carried out involves the production of electrodic nanomaterials through electrochemical methods for photocatalytic / electrocatalytic purpouses.

## Barbara Ticconi



Barbara Ticconi was born in Alatri on october 29 th 1992. She achieved her bachelor's degree in Chemistry in 2014 (110/110 with honor) and her master's degree in Organic and Biomolecular Chemistry in 2016 (110/110 with honor) at the University of Rome "La Sapienza". She is currently in the third year of PhD program in Chemical Sciences under the supervision of Prof. Osvaldo Lanzalunga.

Her research activity is focused on the study of oxidative functionalization of C-H bonds catalyzed by reactive oxygen species, such as *N*-hydroxy imides and biomimetic metal-oxo complex.

## Pierpaolo Tomai



PhD (XXXII Cycle) in Chemical Sciences at "La Sapienza" University of Rome under supervision of Prof. Alessandra Gentili with the project entitled "Evaluation of last generation materials for sample preparation". 2019 – Visiting Researcher at University of La Laguna (Tenerife, Spain) under supervision of Prof. Javier Hernandez Borges. 2018 – Visiting Researcher at University of Valencia (Spain) under supervision of Prof. Yolanda Picò. 2016 -Master's Degree in Analytical Chemistry with thesis entitled "solid phase extraction on buckypaper for multiclass analysis of organic micro-pollutants in surface water by HPLC-MS/MS" under supervision of Prof. Alessandra Gentili.

#### **Research activity**

The research is dedicated to evaluation of last-generation materials and development of innovative extraction techniques for sample preparation prior LC-MS analysis. The focus is onto nanostructured carbonaceous materials as alternative of conventional sorbents for solid-phase extraction (SPE) and deep eutectic solvents (DES) as extracting solvents in liquid-liquid microextraction (DLLME) techniques.

# Daniele Zappi



PhD (XXXII Cycle) in Chemical Sciences, research activity: "Development of new screening methodologies based on biosensors and X-ray techniques for quality control of edible oils". 7

2018 - Visiting Researcher at UBA-INQUIMAE (Universidad de Buenos Aires, Instituto de Química Física de los Materiales, Medio Ambiente y Energía) for Erasmus+ICM program, research activity: "The effect of ionic strength and phosphate ions in the construction of redox polyelectrolyte-enzyme self-assemblies". 2016 - Master's Degree in Analytical Chemistry in 2016, with an experimental thesis titled "Preparation and characterization of electrochemical biosensors based on fourth generation ionic liquids and enzymes", grade: 110/110 cum laude. 2013 - Bachelor's degree in Chemistry at University "La Sapienza" of Rome with an experimental thesis on "Study of Arginine as a binder for zinc in solution".

### **Research activity**

Development of innovative screening procedures to ascertain olive oil quality and origin using various easy-touse instrumentations. New screen-printed electrochemical platforms research and optimization using green and recyclable materials. Study regarding the influence of different nanomaterials on electrochemical performances of modified electrodes and interaction with green biological ionic liquids. Sampling and analysis of single-cultivar olive oils from different geographical and meteorological conditions. Development of a classification system for single-cultivar extra-virgin olive oils.