ISA 2023

Incontro di Spettroscopia Analitica

Milano, 14-16 Giugno 2023

Book of abstracts

Impressum

Organizzatori:

Comitato Organizzatore dell’Incontro di Spettroscopia Analitica ISA 2023
Dipartimento di Chimica, Università degli Studi di Milano
Via Golgi, 19, Milano, Italia

Sito web:

https://www.soc.chim.it/it/divisioni/analitica/ISA2023

Editori: Paola Fermo, Valeria Comite
Dipartimento di Chimica, Università di Milano
Via Golgi, 19, Milano, Italia

ISBN: ISBN 978-88-94952-36-0

9 788894 952360

Società Chimica Italiana

UNIVERSITÀ
DEGLI STUDI
DI MILANO

Comitato Scientifico

Paola Fermo, Università degli Studi di Milano
Emilia Brabanti, Istituto di chimica dei composti organometallici iCCOM-CNR
Rosaria Anna Picca, Università degli Studi di Bari “Aldo Moro”
Roberta D’Agata, Università del Studi di Catania

Comitato Organizzatore

Valeria Comite, Università degli Studi di Milano
Vittoria Guglielmi, Università degli Studi di Milano
Alfonsina D’Amato, Università degli Studi di Milano
Andrea Bergomi, Università degli Studi di Milano
Chiara Andrea Lombardi, Università degli Studi di Milano
Mattia Borelli, Università degli Studi di Milano
Carlo Dossi, Università degli Studi dell’Insubria
Sandro Recchia, Università degli Studi dell’Insubria
Damiano Monticelli, Università degli Studi dell’Insubria
Andrea Pozzi. Università degli Studi dell’Insubria
Giuseppe Spoto, Università degli Studi di Catania

Indirizzo:
Comitato Organizzatore dell’Incontro di Spettroscopia Analitica ISA 2023
Dipartimento di Chimica
Via Golgi, 19, Milano, Italia

Premio Mazzucotelli

In occasione dell’Incontro di Spettroscopia Analitica (ISA), il Gruppo di Spettroscopia Analitica (GSA), appartenente alla Divisione di Chimica Analitica della Società Chimica Italiana, conferisce il Premio intitolato al Prof. Ambrogio Mazzucotelli, prematuramente scomparso e già aderente al Gruppo, attraverso il quale ha operato per promuovere e valorizzare le ricerche in questo settore della chimica analitica.

Il Premio viene assegnato con cadenza biennale a giovani studiosi la cui attività di ricerca nel campo della Spettroscopia Analitica risalti particolarmente sia per l’originalità e qualità dei metodi che per la rilevanza dei risultati.

Invited lectures

Invited Lecture I

Felipe Conzuelo

Scanning Photoelectrochemical Microscopy for the Study of Light-Dependent (Bio)electrochemical Reactions

Instituto de Tecnologia Química e Biológica António Xavier, Universidade Nova de Lisboan, Oeiras, Portugal

Invited Lecture II

Federica Pozzi

The Visconti-Sforza tarocchi cards: unveiling court secrets through analytical spectroscopy

Centro per la Conservazione ed il Restauro dei Beni Culturali "La Venaria Reale", Italia

Scanning Photoelectrochemical Microscopy for the Study of Light-Dependent (Bio)electrochemical Reactions

F. Conzuelo

Instituto de Tecnologia Química e Biológica António Xavier, Universidade Nova de Lisboa,
Av. da República, 2780-157 Oeiras, Portugal
felipe.conzuelo@itqb.unl.pt

Oxygenic photosynthesis is a highly advanced process occurring in nature, which enables a large number of different organisms to achieve the conversion of water and CO_2 into O_2 and sugars using sunlight as the only energy source. The process is driven by two key protein complexes, the so-called photosystems, acting as natural photodiodes for the excitation of electrons across the thylakoid membrane upon absorption of visible light. Taking advantage of these biomolecules, the photosystems can be interfaced with electrode materials for the fabrication of biophotovoltaic devices able to produce electrical current and assist in the synthesis of renewable fuels. The biological photosystems also serve as inspiration for the development of synthetic materials for solar water splitting. The characterization of both, natural and artificial systems is of capital importance to understand and improve possible limitations related to slow kinetics and poor charge separation. To attain more detailed information on the characterization of biophotovoltaic devices, an advanced scanning photoelectrochemical microscopy (SPECM) setup has been implemented (Fig. 1) [1]. As it will be presented, SPECM is a versatile tool for the local assessment of light-dependent electron transfer reactions at the micro-scale, allowing the local evaluation of photocurrents and evolved products at electrode surfaces modified with diverse photoactive materials. By using a tip microelectrode that performs simultaneously as the source for local irradiation of the sample and as an electrochemical probe, different photoelectrochemical reactions can be easily resolved, allowing a deeper understanding of light-induced electron transfer processes [2,3]. Examples including the analysis of semiconductor materials based on ternary and quaternary metal oxides as well as biological photosystems integrated into suitably designed redox polymers will be shown.

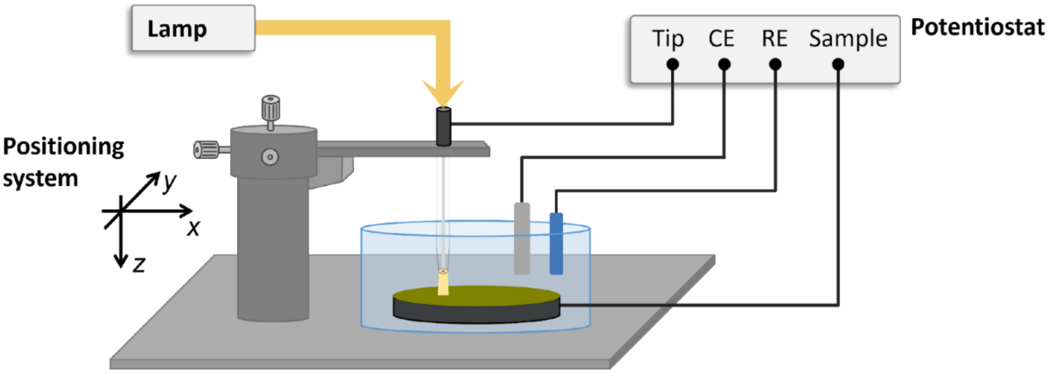


Figure. 1. Schematic representation of the scanning photoelectrochemical microscopy (SPECM) setup. A microelectrode is used simultaneously as the local illumination source and as an electrochemical probe for the analysis of photoactive sample materials. CE: counter electrode, RE: reference electrode.

References:
[1] F. Conzuelo, K. Sliozberg, R. Gutkowski, S. Grützke, M. Nebel, W. Schuhmann, *Anal. Chem.* 89 (2017) 1222
[2] F. Zhao, N. Plumeré, M.M. Nowaczyk, A. Ruff, W. Schuhmann, F. Conzuelo, *Small* 13 (2017) 1604093
[3] F. Zhao, S. Hardt, V. Hartmann, H. Zhang, M.M. Nowaczyk, M. Rögner, N. Plumeré, W. Schuhmann, F. Conzuelo, *Nat. Commun.* 9 (2018) 1973

The Visconti-Sforza tarocchi cards: unveiling court secrets through analytical spectroscopy

F. Pozzi

Centro per la Conservazione ed il Restauro dei Beni Culturali "La Venaria Reale", Italia
federica.pozzi@ccrvenaria.it

Beginning in 2021, conservators, conservation scientists, and curators from the Morgan Library & Museum, Yale University, the Metropolitan Museum of Art, the Art Institute of Chicago, the National Gallery of Art, and the Centro per la Conservazione ed il Restauro dei Beni Culturali “La Venaria Reale” partnered for a collaborative research project aiming to compare the three earliest known and most complete surviving sets of *tarocchi* cards. These sets of cards, which are known collectively as the Visconti-Sforza decks, were used to play trick-taking or gambling games. Portions of one deck, also known as the Colleoni-Baglioni deck, are held between the Morgan Library and the Accademia Carrara, while the Visconti di Modrone and Brambilla decks are respectively located at Yale’sBeinecke Rare Book and Manuscript Library and at the Pinacoteca di Brera. Generally attributed to artist Bonifacio Bembo and his workshop, all three decks were created in the mid-15th century. The Visconti di Modrone and Brambilla decks were likely commissioned by Filippo Maria Visconti, duke of Milan, prior to his death in 1447, while the Colleoni-Baglioni deck was commissioned by Francesco Sforza and made around 1456-58. These invaluable objects, displaying a rich color palette and intricately-tooled gilded backgrounds, have been the subject of endless fascination and numerous art historical studies, but have never undergone in-depth technical analysis. This contribution presents a cross-continental, multi-institutional, interdisciplinary endeavor aiming to fulfill the knowledge gap on the technical production of illuminated Italian *tarocchi* cards. A combination of non-invasive and minimally invasive analytical tools, heavily relying on analytical spectroscopy, was used both in the laboratory and *in situ* to investigate the elemental composition, molecular fingerprint signatures, as well as the physical structure of the three Visconti-Sforza *tarocchi* decks held in United States and Italian collections. The preliminary findings of such technical analysis, illustrated herein, inform a comparison of the cards’ materials and techniques, shedding light on how they were created, placing them in the context of contemporary Northern Italian illumination, and contributing to the ongoing conversation and body of research about their manufacture and attribution.

Premio Mazzucotelli

Nel corso dell'ISA 2023 il GSA ha conferito il Premio Ambrogio Mazzucotelli, dedicato a giovani studiosi la cui attività di ricerca nel campo della Spettroscopia Analitica risalti particolarmente per l'originalità e qualità dei metodi sia per la rilevanza dei risultati.

Presenta il vincitore
Walter Giurlani
walter.giurlani@unifi.it

Application of computational methods to analytical spectroscopy techniques for the characterization of films and metal alloys

Department of Chemistry "Ugo Schiff", University of Florence

National Interuniversity Consortium of Materials Science and Technology (INSTM)

Application of computational methods to analytical spectroscopy techniques for the characterization of films and metal alloys

W. Giurlani[a,b]

[a] Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 3, 50019 Sesto Fiorentino (FI), Italy; [b] National Interuniversity Consortium of Materials Science and Technology (INSTM), Via G. Giusti 9, 50121 Firenze (FI), Italy.
walter.giurlani@unifi.it

The compositional characterization and determination of thickness in metallic and non-metallic films are of fundamental importance in numerous scientific, technological, and industrial applications such as electronics, automotive, cultural heritage, and decorative field. There are several analytical methods available for characterizing metallic films, but many of them are destructive, have high costs, and require highly specialized technicians [1].

The use of analytical spectroscopy techniques, such as Energy-Dispersive X-ray Spectroscopy (EDS) and X-ray Fluorescence Spectroscopy (XRF), combined with Monte Carlo simulations, can prove decisive in meeting various needs for the characterization of metals and alloys due to their extreme versatility [2,3]. The possibility of simulating standards to build a calibration curve frees us from the limitations of having certified samples with a specific composition, without having to rely on necessary approximations using physical standards or analytical models.

By combining this analytical method with design of experiment (DoE), it is even possible to mitigate matrix effects through multivariate analysis. This allows for accurate analysis even of multilayered samples [4].

Although the spectra recorded with EDS and XRF two techniques have the same physical origin (the X-ray emission), the different probes used allows for the analysis of different portions of the sample. In EDS, the probe is electrons, which have low penetration, resulting in a surface-sensitive analysis. On the other hand, XRF utilizes high-energy X-rays with greater penetration. The use of XRF has proven successful compared to current commercial methods in measuring metallic layers typically used in the electroplating industry, where the thickness ranges from hundreds of nanometers to tens of microns. EDS, on the other hand, allows for the analysis of much thinner layers, on the order of a few nanometers [5].

By combining the characteristics of these two techniques, it has been possible to analyze minimal variations in the surface composition of gold deposits on copper substrates [6]. By applying Fick's law, this approach enables the measurement of intermetallic diffusion coefficients in a simple manner, with significant applications in the study of new alloys or the evaluation of barrier layer performance.

MUR PNRR and NextGenerationEU are acknowledged for funding the "3A-ITALY - Made-in-Italy circolare e sostenibile" project (Code PE_00000004, CUP B83C22004890007).

References:
[1] Giurlani, W.; Berretti, E.; Innocenti, M.; Lavacchi, A. Coatings 2020, 10, 1211, doi:10.3390/coatings10121211.
[2] Giurlani, W.; Innocenti, M.; Lavacchi, A. Coatings 2018, 8, 84, doi:10.3390/coatings8020084.
[3] Giurlani, W.; Berretti, E.; Innocenti, M.; Lavacchi, A. Coatings 2019, 9, 79, doi:10.3390/coatings9020079.
[4] Giurlani, W.; Berretti, E.; Lavacchi, A.; Innocenti, M. Anal. Chim. Acta 2020, 1130, 72–79, doi:10.1016/j.aca.2020.07.047.
[5] Fabbri, L.; Giurlani, W.; Biffoli, F.; Bellini, M.; Miller, H.; Fontanesi, C.; Vizza, F.; Innocenti, M. Appl. Sci. 2021, 11, 8403, doi:10.3390/app11188403.
[6] Giurlani, W.; Biffoli, F.; Fei, L.; Pizzetti, F.; Bonechi, M.; Fontanesi, C.; Innocenti, M. Anal. Chim. Acta 2023, 1269, 341428, doi:10.1016/j.aca.2023.341428.

Elenco Contributi

Orale	O1	**Functional antifouling coating on plasmonic platform for Lysozyme aptamer-based detection in food sample** *N. Bellassai[a,b], R. D'Agata[a,b], G. Spoto[a,b]* *[a]Dipartimento di Scienze Chimiche, Università degli Studi di Catania, Viale Andrea Doria, 6 – 95125 Catania; [b]Istituto Nazionale di Biostrutture e Biosistemi (I.N.B.B.), Viale delle Medaglie d'Oro, 305 – 00136 Roma*
Orale	O2	**Characterization of black crusts from the Monumental Cemetery (Milan) using a combined LIBS and Raman approach** *A. Bergomi[a], V. Comite[a], C. Della Pina[a], P.M. Carmona-Quiroga[b], L. Maestro-Guijarro[b], M. Oujja[b], A. Crespo[c], C.A. Lombardi[a], M. Borelli[a], M. Castillejo[b] and P. Fermo[a]* *[a]Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133 Milano, Italy; [b]Instituto de Quimica Fisica Rocasolano, IQFR-CSIC, C/Serrano 119, 28006 Madrid, Spain; [c]Instituto de Estructura de la Materia, IEM-CSIC, C/Serrano 121, 28006 Madrid, Spain*
Orale	O3	**Unravelling the composition of surface films formed on Ni-free DIN 1.4456 stainless steel for orthodontics by XPS** *D. Biggio[a], B. Elsener[a], G. Usai[a], M. Fantauzzi[a], A. Rossi[a]* *[a]Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari, Cittadella Universitaria, 09042, Monserrato, Cagliari, Italy*
Orale	O4	**A spectroscopic investigation of palladium recovery from electroplating solutions using carbon materials and electrochemical reduction** *M. Bonechi[a], I. Maggini[a], W. Giurlani[a,b], M. Savastano[a], A. Meoli[a], A. Bianchi[a], M. Innocenti[a,b,c,d]* *[a]Department of Chemistry "Ugo Schiff", University of Florence, via della Lastruccia 3, 50019 Sesto Fiorentino, Italy; [b]National Interuniversity Consortium of Materials Science and Technology (INSTM), Via G. Giusti 9, 50121 Firenze, Italy; [c]Center for Colloid and Surface Science (CSGI), Via della Lastruccia 3, 50019 Sesto Fiorentino, Italy; [d]Insititute of Chemistry of Organometallic Compounds (ICCOM) – National Research Council (CNR), via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy*
Poster	P1	**Chiral "doped" MOFs: an electrochemical and spectroscopic study** *M. Bonechi[a], D. Bettoni[a], I. Maccioni[a], W. Giurlani[a,b], T. Salzillo[c], R. Kawondera[d], C. Fontanesi[e], W. Mtangi[d], M. Innocenti[a,b,f,g]* *[a]Department of Chemistry "Ugo Schiff", University of Florence, via della Lastruccia 3, 50019 Sesto Fiorentino, Italy; [b]National Interuniversity Consortium of Materials Science and Technology (INSTM), Via G. Giusti 9, 50121 Firenze, Italy; [c]Department of Industrial Chemistry "Toso Montanari", University of Bologna, Viale del Risorgimento, 4, 40136, Bologna, Italy; [d]Institute of Materials Science, Processing and Engineering Technology, Chinhoyi University of Technology, P Bag 7724, Chirundu Road, Chinhoyi, Zimbabwe; [e]Department of Engineering 'Enzo Ferrari', University of Modena and Reggio Emilia, Via Vivarelli 10, 41125 Modena, Italy; [f]Center for Colloid and Surface Science (CSGI), Via della Lastruccia 3, 50019 Sesto Fiorentino, Italy; [g]Insititute of Chemistry of Organometallic Compounds (ICCOM) – National Research Council (CNR), via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy*

Poster	P2	**Validation of Methods and Analysis of Metals in Food Matrices by ICP-MS** *M. Borelli[a], A. Bergomi[a], V. Comite[a], S. Bottino[a], S. Vitaliti[b], M. Rizzi[b], M. Bornatici[b], G. Notaro[b], G. Amato[b], P. Fermo[a]* *[a]Dipartimento di Chimica, Università degli Studi di Milano, 20133 Milano, Italy; [b]ATS-Milan Laboratorio di prevenzione, Via Juvara 22, 20129, Milan, Italy*
Poster	P3	**Biomarkers in human saliva via vibrational spectroscopy in tandem with chemometrics: role of the preanalytical step** *B. Campanella[a], S. Legnaioli[a], M. Onor[a], E. Benedetti[b], E. Bramanti[a]* *[a]National Research Council of Italy, C.N.R., Institute of Chemistry of Organometallic Compounds-ICCOM, 56124, Pisa, Italy; [b] Hematology Unit, Department of Oncology, University of Pisa, 56100 Pisa, Italy*
Orale	O5	**Aqueous derivatization by ethyloxonium salts extended to the analysis of methionine and selenomethione in foods** *C. Malvestio[a], M. Onor[b], E. Bramanti[b], E. Pagliano[c], B. Campanella[b]* *[a]Department of Chemistry and Industrial Chemistry, University of Pisa, via Giuseppe Moruzzi 13, 56124, Pisa, Italy; [b]Institute of Chemistry of Organometallic Compounds, National Research Council, via Giuseppe Moruzzi 1, 56124, Pisa, Italy; [c]National Research Council of Canada, 1200 Montreal Road, K1A0R6 Ottawa, Ontario, Canada.*
Orale	O6	**Growth and Characterization by ARXPS of (3-mercaptopropyl) trimethoxysilane (MPTMS) films on Gold and Food-Grade PVC** *G. Casula[a], M. Fantauzzi[a], B. Elsener[a], A. Rossi[a]* *[a]Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Cagliari, ss 554-bivio per Sestu, 09042 Monserrato (CA)*
Poster	P4	**Experimentation in accelerated ageing chambers to evaluate the action of catalysts in the sulphation process** *V. Comite[a], C. A. Lombardi[a,b], C. Castellano[a], A. Bergomi[a], M. Borelli[a] M. Formenti[a], C. Cavaterra[c], P. Fermo[a], C. Della Pina[a]* *[a]Dipartimento di Chimica, Università degli Studi di Milano, 20133 Milan, Italy; [b]Dipartimento di Scienze dell'Antichità, Sapienza Università di Roma, 00185 Rome, Italy; [c]Dipartimento di Matematica 'Federigo Enriques' Università degli Studi di Milano, 20133 Milan, Italy*

Poster	P5	**Multispectral 3D models for monitoring in conservation of wooden statues** *S. Croci[a], L. Es Sebar[a], P. Buscaglia[a,b], S. Grassini[a], C. Ricci[b]* *[a] Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, Turin, Italy; [b] Centro Conservazione e Restauro "La Venaria Reale", Venaria Reale, Italy*
Orale	O7	**Advances in Diagnostics using Plasmonic-based Imaging Sensor and liquid biopsy approaches** *R. D'Agata[a,b], N. Bellassai[a,b], G. Spoto[a,b]* *[a]Department of Chemical Sciences, University of Catania, Viale Andrea Doria, 6, 95125, Catania, Italy; [b]INBB, Istituto Nazionale di Biostrutture e Biosistemi, Viale Delle Medaglie D'Oro, 305, 00136, Roma, Italy*
Orale	O8	**Correlation between surface chemical composition and catalytic activity of MnO_2-based catalysts** *N. Ditaranto[a,b,c], F. Nocito[a,b], D. Linsalata[a], M. Naschetti[a,b], M. Aresta[b,d], A. Dibenedetto[a,b,d]* *[a]Dipartimento di Chimica, Università degli Studi di Bari Aldo Moro, Via Orabona, 4 – 70125 Bari; [b]CIRCC, Interuniversity Consortium on Chemical Reactivity and Catalysis, Bari, Via Celso Ulpiani, 27 – 70126 Bari; [c]CSGI - Centre for Colloid and Surface Science, Bari Unit, Bari; [d]IC2R, srl - Tecnopolis, 70010 Valenzano (BA)*
Orale	O9	**Surface enhanced Raman scattering of crevicular fluid in periodontics and implantology** *S. Fornasaro[a], A. Rapani[b], F. Berton[b], C. Stacchi[b], V. Sergo[c], A. Bonifacio[c]* *[a]University of Trieste, Dept. of Chemical and Pharmaceutical Sciences, via L. Giorgeri 1, 34127 Trieste, Italy; [b]Maxillofacial and Dental Surgical Clinic, Dept. of Medical, Surgical and Health Sciences, University of Trieste, Piazza dell'Ospitale 1, 34125, Trieste, Italy; [c]Raman Spectroscopy Lab, Dept. of Engineering and Architecture, University of Trieste, via A. Valerio 6a, 34127 Trieste, Italy*
Poster	P6	**Reconsidering the value of the information from the OH stretching band in FT-IR spectroscopy** *L. Geminiani[a], C. Corti[b], L. Rampazzi[b]* *[a] Dipartimento di Scienza e Alta Tecnologia, Università degli Studi dell'Insubria, Via Valleggio 11, 22100 Como, Italy; [b] Dipartimento di Scienze Umane e dell'Innovazione per il Territorio, Università degli Studi dell'Insubria, Via Sant'Abbondio 12, 22100 Como, Italy*

Poster	P7	**Electrodeposition of manganese arsenides (Mn_xAs) and its compositional optimization assisted by microanalysis spectroscopy** *W. Giurlani[a,b], G. Pappaianni[a], M. Bonechi[a], C. Bazzicalupi[a], C. Fontanesi[b,c], M. Innocenti[a,b,d,e]* *[a] Department of Chemistry “Ugo Schiff”, University of Florence, Via della Lastruccia 3, 50019 Sesto Fiorentino (FI), Italy; [b] National Interuniversity Consortium of Materials Science and Technology (INSTM), Via G. Giusti 9, 50121 Firenze (FI), Italy; [c] Department of Engineering ‘Enzo Ferrari’, University of Modena and Reggio Emilia, Via Vivarelli 10, 41125 Modena, Italy; [d] National Research Council-Organometallic Compounds Chemistry Institute (CNR-ICCOM), Via Madonna del Piano 10, 50019 Sesto F.no (FI), Italy; [e] 5 Center for Colloid and Surface Science (CSGI), Via della Lastruccia 3, 50019 Sesto F.no (FI), Italy*
Orale	O10	**A new process control tool based on ATR-FT-IR spectroscopy and dissimilarity index to identify anomalies in wine alcoholic fermentation** *B. Giussani[a], D. Schorn-García[b], J. Ezenarro[b], O. Busto[b], L. Aceña[b], R. Boqué[b], M. Mestres[b]* *[a]DISAT, Università Degli Studi Dell’Insubria, Como, Italy; [b]QAQO Dpt, Universitat Rovira i Virgili, Tarragona, Spain*
Orale	O11	**How explore raw data characteristics and sources of uncertainty could be a crucial step for spectroscopic method development** *G. Gorla[a], C. Alamprese[c], S. Grassi[c], R. Boqué[b], J. Riu[b], B. Giussani[a]* *[a]Department of Science and High Technology, University of Insubria, Via Valleggio 9, 22100 Como, Italy; [b]Chemometrics, Qualimetrics and Nanosensors Group, Department of Analytical Chemistry and Organic Chemistry, Universitat Rovira i Virgili, Campus Sescelades, 43007 Tarragona, Spain; [c]Department of Food, Environmental and Nutritional Sciences, Università degli Studi di Milano, Via Giovanni Celoria 2, 20133 Milan, Italy*
Orale	O12	**The Identification of Pigments through Non-Invasive Spectroscopic Analyses: the Bernardino Luini Frescoes of Santuario della Beata Vergine dei Miracoli in Saronno (Italy) as a Case Study** *V. Guglielmi[a], V. Comite[a], G. Fiocco[b,c], M. Albano[b,c], C. Merlo[b,d], T. Rovetta[b], C. Lee[b,e], F. Volpi[b,c], A. Bergomi[a], C. A. Pini[a], C. A. Lombardi[a], C. Mariani[f], M. Malagodi[b,c], P. Fermo[a]* *[a]Department of Chemistry, Università degli Studi di Milano, Via Golgi 19, 20124 Milano, Italy; [b]Arvedi Laboratory of Non-Invasive Diagnostics, CISRiC, Università di Pavia, Via Bell’Aspa 3, 26100 Cremona, Italy, [c]Department of Musicology and Cultural Heritage, Università degli Studi di Pavia, Corso Garibaldi 178, 26100 Cremona, Italy,* *[d]Laboratorio di Diagnostica applicata ai Beni Culturali, Scuola di Restauro Cr.Forma, C.so Matteotti 17, 26100 Cremona, Italy, [e]Department of Chemistry, University of Pavia, Via Torquato Taramelli 12, 27100 Pavia, Italy;* *[f]Freelance architect*

Poster	P8	**Analytical Spectroscopy in Electroplating industry** *M. Innocenti[a,b*], M. Bonechi[a,b], W. Giurlani[a,b], A. De Luca[a,b], A. Comparini[a,c], M. Verrucchi[a], M. Pagliai[a], S. Martinuzzi[a,b], A. Caneschi[b,d]* *[a] Dipartimento di Chimica "Ugo Schiff", University of Florence;* *[b]INSTM, via Giuseppe Giusti, 9, 50121, Florence, Italy;* *[c] Valmet Plating S.r.l. Calenzano, via Erbosa 5, Firenze - Italy;* *[d]Department of Engineering, DIEF, University of Modena and Reggio Emilia, 41125 Modena, Italy*
Poster	P9	**Electrochemical impedance spectroscopy (EIS) as a valuable technique for the quantification of additives in electroplating baths** *A. Comparini[a], M. Verrucchi[a], W. Giurlani[a], A. De Luca[a], A. Meoli[a], M. Voroboya[a,b], M. Innocenti[a,b,c,d]* *[a]Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 3, 50019 Sesto Fiorentino (FI), Italy; [b]National Interuniversity Consortium of Materials Science and Technology (INSTM), Via G. Giusti 9, 50121 Firenze (FI), Italy; [c]National Research Council-Organometallic Compounds Chemistry Institute (CNR-ICCOM), Via Madonna del Piano 10, 50019 Sesto F.no (FI), Italy; [d]Center for Colloid and Surface Science (CSGI), Via della Lastruccia 3, 50019 Sesto F.no (FI), Italy.*
Orale	O13	**Probing the interaction of antimicrobial metal nanoparticles with lipid membranes by fluorescent probes** *M. Izzi[a], M. Oliver[b], M. Miró[b], N. Cioffi[a]* *[a]Department of Chemistry, University of Bari Aldo Moro, via Orabona 4, 70126 Bari, Italy* *[b]Department of Chemistry, University of the Balearic Islands, Carretera de Valldemossa km 7.5, E-07122 Palma de Mallorca, Spain*
Poster	P10	**Spectroscopic characterization of bioactive coatings for food packaging applications** *M. Izzi[a], M. C. Sportelli[a], A. V. Montefusco[a,b], D. D'Agostino[a], R. A. Picca[a], N. Cioffi[a]* *[a] Department of Chemistry, University of Bari Aldo Moro, via Orabona 4, 70126 Bari, Italy;* *[b] Department of Electrical and Information Engineering, Polytechnic of Bari, Bari, Italy*
Poster	P11	**Combined Reflectance and Fluorescence VNIR imaging for the Study of Coloured Textiles: the role of chemometric strategies in the processing of multiblock hyperspectral data** *Z. Li[a], G. Sciutto[a], A. Candeo[b], M. Ghirardello[b], S. Prati[a], E. Catelli[a], P. Oliveri[c], R. Mazzeo[a], D. Comelli[b]* *[a] Dept. of Chemistry, Università di Bologna – Ravenna Campus, Via Guaccimanni 42, 48121, Ravenna, Italy;* *[b] Dept. of Physics, Politecnico di Milano, P.zza Leonardo da Vinci 32, Milano, Italy;* *[c] Dept. of Pharmacy, Università di Genova, via Cembrano, 4, 16148, Genova, Italy*

Orale	O14	**Preliminary results on archaeological materials from Miaswan Project (Mummies Investigations Anthropological and Scientific West Aswan Necropolis)** *C. A. Lombardi*[a,b], *V. Comite*[b], *V. Guglielmi*[b], *A. D'Amato*[c], *A. Tomaino*[d] *P. Piacentini*[d], *P. Fermo*[b] *[a]Dipartimento di Scienze dell'Antichità, Università La Sapienza, 00185 Roma, Italy; [b]Dipartimento di Chimica, Università degli Studi di Milano, 20133 Milano, Italy; [c]Dipartimento di Scienza Farmaceutiche, Università degli Studi di Milano, 20133 Milano, Italy; [d]Dipartimento di Studi Letterari, Filologici e Linguistici, Università degli Studi di Milano, 20133 Milano, Italy*
Orale	O15	**Spectroscopic characterization of corrosion processes on galvanic coatings** *I. Maccioni*[a,b], *F. Pizzetti*[b], *G. Pappaianni*[a], *A. Meoli*[a], *E. Mariani*[a], *C. Giovani*[a,c], *R. Emanuele*[d], *M. Innocenti*[a,c,e,f] *[a]Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 3, 50019 Sesto Fiorentino (FI), Italy; [b]Rubinetterie 3M S.r.l, Via E. Mattei 10, 53041 Asciano (SI), Italy; [c]National Interuniversity Consortium of Materials Science and Technology (INSTM), Via G. Giusti 9, 50121 Firenze, Italy; [d]Valmet Plating S.r.l. Via Erbosa, 5, 50041 Calenzano (FI), Italy; [e]Institute of Chemistry of Organometallic Compounds (ICCOM) – National Research Council (CNR), Via Madonna del Piano 10, 50019 Sesto Fiorentino (FI), Italy; [f]Center for Colloid and Surface Science (CSGI) Via della Lastruccia 3, 50019 Sesto Fiorentino (FI), Italy*
Orale	O16	**Cerium oxide Nanoparticles stabilized by PLGA micelles and englobed in gelatine and starch films** *V. Marchianò*[a], *M. Matos*[b], *G. Gutierrez*[b], *M. C. Blanco-Lopez*[c], *N. Cioffi*[a,d], *N. Ditarant*[a,d] *[a]CSGI – Centre for Colloid and Surface Science, Bari Unit, Bari, Italy; [b]Department of Chemical and Environmental Engineering, University of Oviedo, Julián Clavería 8, 33006 Oviedo, Spain; [c]Department of Physical and Analytical Chemistry, University of Oviedo, Julián Clavería 8, 33006 Oviedo, Spain; [d]Department of Chemistry, Università degli Studi di Bari Aldo Moro, via Orabona 4, 70125 Bari, Italy*
Poster	P12	**Morphological and Spectroscopic Characterization of Self-Templated Highly Porous Gold (h-PG) as D-(-)-Fructose Amperometric Biosensor** *V. Marchianò*[a], *A. Tricase*[bc], *N. Ditaranto*[bc,], *E. Macchia*[b,cd,], *K. Sowa*[ef], *C. Di Franco*[f], *L. Torsi*[a,c,d] ,*P. Bollella*[b,c] *[a] CSGI - Centre for Colloid and Surface Science, -Bari Unit, Bari (Italy; [b]Dipartimento di Chimica, Università degli Studi di Bari Aldo Moro, 70125 Bari , via Orabona 4,Italy; [c]Dipartimento di Farmacia-Scienze del Farmaco, Università degli Studi di Bari Aldo Moro,via Orabona 4 70125 Bari,Italy .[d]Faculty of Science and Engineering, Åbo Akademi University, 20500 Turku Finland; [e]Division of Applied Life Sciences, Graduate School of Agriculture, Kyoto University, Kitashirakawa Oiwake-cho, Sakyo-ku, Kyoto, 606-8502, Japan;[f] Istituto di Fotonica e Nanotecnologie CNR, c/o Dipartimento Interateneo di Fisica, Università degli Studi di Bari Aldo Moro,via Orabona 4, Bari, 70125 Italy.*

Orale	O17	**Colour evaluation via everyday tools: cameras and smartphone** *A. Meoli[a,b], F. Biffoli[a], I. Maccioni[a], E. Mariani[a], E. Carretti[a,c], W. Giurlani[a,d], M. Innocenti[a,c,d,e]* *[a]Department of Chemistry "Ugo Schiff", University of Florence, via della Lastruccia 3, 50019 Sesto Fiorentino, Italy; [b]Creazioni Lorenza Srl, via Fiorentina 18, 50063 Figline Valdarno; [c]Center for Colloid and Surface Science (CSGI), via della Lastruccia 3, 50019 Sesto Fiorentino, Italy; [d]National Interuniversity Consortium of Materials Science and Technology (INSTM), via G. Giusti 9, 50121 Firenze, Italy; [e]Institute of Chemistry of Organometallic Compounds (ICCOM)-National Research Council (CNR), via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy*
Orale	O18	**Electrosynthesis and analytical characterization of antimicrobial mixed oxides for cultural heritage applications** *M. Izzi[a], M. C. Sportelli[a], D. Quarato[a], N. Cioffi[a], R. A. Picca[a]* *[a]Chemistry Department, University of Bari Aldo Moro, via E. Orabona 4, 70125 Bari, Italy*
Poster	P13	**Development and characterization of antimicrobial composites for food packaging containing bioactive species** *R. A. Picca[a], M. C. Sportelli[a], S. M. Sanzani[b], F. Caponio[b], G. Difonzo, L. Gentile[a], G. Palazzo[a], A. Ippolito[b], N. Cioffi[a]* *[a]Dipartimento di Chimica, Università degli Studi di Bari Aldo Moro, Bari; [b]Dipartimento di Scienze del Suolo della Pianta e degli Alimenti, Università degli Studi di Bari Aldo Moro, Bari*
Orale	O19	**Overcoming beam damage in In-situ XAS: study of Ni-$SrTiO_3$ deactivation during overall photocatalytic water splitting** *M. Pinna[a,b], M. T. Abudukade[b], D. Spanu[a], A. Minguzzi[c], P. Ghigna[d], S. Recchia[a], G. Mul[b], M. Altomare[b]* *[a]Dipartimento di Scienza e Alta Tecnologia, Università degli studi dell'Insubria, Via Valleggio 9, Como 22100, Italy; [b]Faculty of Science and Technology, University of Twente, Drienerloaan 5, Enschede 7522 NB, The Netherlands; [c]Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, Milan 20133, Italy; [d]Dipartimento di Chimica, Università degli Studi di Pavia, Via Taramelli 16, Pavia 27100, Italy*
Orale	O20	**New advances in the application of NIR hyperspectral based methods for the non destructive characterization of artistic multilayered artefacts and archeological remains** *S. Prati[a], G. Sciutto[a], R. Alberti[b], S. Benazzi[c], E. Catelli[a], T. Frizzi[b], L. Gatti[a], Z. Li[a], C. Malegori[d], M. Occhipinti[b], P. Oliveri[d], S. Talamo[e], A. Tocchio[b], R. Mazzeo[a]* *[a]University of Bologna, Department of Chemistry "G. Ciamician", Ravenna Campus, Via Guaccimanni, 42, 48121, Ravenna, Italy; [b]XGLab SRL - Bruker Nano Analytics, Via Conte Rosso 23, I-20134 Milano, Italy; [c]Department of Cultural Heritage, University of Bologna, Via degli Ariani 1, 48121, Ravenna, Italy; [d]University of Genova, Department of Pharmacy, Viale Cembrano 4, I-16148, Genova, Italy; [e]Department of Chemistry G. Ciamician, Alma Mater Studiorum, University of Bologna Via Selmi 2, Bologna, 40126, Italy*

Orale	O21	**Characterization of unknown animal glues from artwork samples by structural, rheological and thermal analysis** *E. Pulidori[a], E. Crisci[a], M. R. Tinè[a], L. Birolo[b], G. Ntasi[b], E. Bramanti[c], I. Bonaduce[a], C. Duce[a]* *[a]Department of Chemistry and Industrial Chemistry, University of Pisa, Via G. Moruzzi 13, Italy; [b]Department of Chemical Sciences, University of Naples Federico II, Complesso monte Sant' Angelo Via Cinthia 21, Italy; [c]Institute of Chemistry of Organometallic Compounds, National Research Council, Via G. Moruzzi 1, Italy*
Orale	O22	**Analytical investigation of SAMs-modified gold electrodes** *A. Tricase[a,b], V. Marchianò[b], N. Ditaranto[a], R. A. Picca[a,b], E. Macchia[c,c], G. Scamarcio[e], D. Blasi[a], P. Bollella[a], L. Torsi[a,d,e]* *[a]Dipartimento di Chimica, Università degli Studi di Bari "Aldo Moro", 70125 Bari (Italy); [b]CSGI (Centre for Colloid and Surface Science), 70125 Bari (Italy); [c]Dipartimento di Farmacia – Scienze del Farmaco, Università degli Studi di Bari Aldo Moro, 70125 Bari; [d]The Faculty of Science and Engineering,Åbo Akademi University, 20500 Turku (Finland); [e]Dipartimento Interateneo di Fisica "M. Merlin",Università degli Studi di Bari "Aldo Moro", 70125 Bari (Italy)*
Poster	P14	**Electrochemical pH-controlled apo-Ferritin Bionanoreactors for CdSe nanoparticles synthesis** *A. Tricase[a,b], V. Marchianò[b], N. Ditaranto[a,b], E. Macchia[c,d], R. Gupta[e], L. Torsi[a,b,d], P. Bollella[a,b]* *[a]Dipartimento di Chimica, Università degli Studi di Bari Aldo Moro, 70125 Bari (Italy), [b]Centre for Colloid and Surface Science - Università degli Studi di Bari Aldo Moro 70125, Bari (Italy), [c]Dipartimento di Farmacia – Scienze del Farmaco, Università degli Studi di Bari "Aldo Moro", Bari, 70125 Italy, [d]Faculty of Science and Engineering, Åbo Akademi University, 20500 Turku (Finland), [e]School of Chemistry, University of Birmingham, Birmingham (UK)*
Orale	O23	**Spectroscopic characterization of PVD coatings for decorative applications** *M. Vorobyova[a,b], L. Donati[b], D. Bettoni[a,b], E. Cioppi[b], W. Giurlani[a,b], M. Linser[d], M. Innocenti[a,b], A. Caneschi[c]* *[a]INSTM, via Giuseppe Giusti, 9, 50121, Florence, Italy; [b]Dipartimento di Chimica "Ugo Schiff", University of Florence; [c]Department of Industrial Engineering, University of Florence, Via di S. Marta 3, 50139 Firenze, Italy; [d]LEM INDUSTRIES S.P.A,Via Leo Valiani, 45/47, 52021 Bucine AR*

Presentazione Contributi

Functional antifouling coating on plasmonic platform for Lysozyme aptamer-based detection in food sample

N. Bellassai[a,b], *R. D'Agata*[a,b], *G. Spoto*[a,b]

[a]*Dipartimento di Scienze Chimiche, Università degli Studi di Catania, Viale Andrea Doria, 6 – 95125 Catania;* [b]*Istituto Nazionale di Biostrutture e Biosistemi (I.N.B.B.), Viale delle Medaglie d'Oro, 305 – 00136 Roma*
noemi.bellassai@unict.it

Antifouling coatings are strictly required in optical biosensors for many analytical application fields, from medical diagnostics to foodborne pathogens, to prevent the non-specific protein/cell adhesion and capture the analytes directly in the complex media [1]. Over the past three decades, the advances in non-fouling plasmonic surfaces have been mainly focused on the detection of ultrasensitive clinical biomarkers in real biofluids [1,2]; while the development of antifouling coatings for direct analysis of complex media for food quality control and safety has been scarcely investigated [3]. In this context, lysozyme is a small protein with interesting antimicrobial activity exploited in food industry, such as cheesemaking and winemaking process. Lysozyme also shows allergic activity, and it triggers immune-mediated adverse reactions in sensitive individuals with a possible severe outcome even in trace amounts [4]. Therefore, the detection of lysozyme in food samples to prevent its allergic effect is required.

Herein, we propose a new low-fouling poly-L-lysine (PLL)-based polymer for the detection of lysozyme directly in food matrix by using Surface Plasmon Resonance technology. The PLL-based polymer contains densely immobilized anionic oligopeptide side-chains to create a charge-balanced layer, able to repel the non-specific adsorption of undesired molecules on the biosensor surface. Also, PLL-based polymer includes sparsely attached aptamer probes with high affinity and specificity for lysozyme capturing directly in milk samples with no sample manipulation. The sensitivity and affinity of lysozyme's aptamer have been deeply explored by changing the ionic strength, ions, and type of buffer, ~~to obtain a label-free~~ protein detection at the nanomolar level directly in food samples. The work here described highlights the versatility of the antifouling aptasensor, which can be applied for the sensitive detection of lysozyme in different complex media, such as food or biological matrices, with minimal pre-analytical sample treatments.

Acknowledgments to Research and innovation programme 2014-2020 "PON REACT-EU project" and MUR Prin 2017 project (n. 2017RHX2E4).

References:
[1] N. Bellassai, R. D'Agata, A. Marti, A. Rozzi, S. Volpi, M. Allegretti, R. Corradini, P. Giacomini, J. Huskens, G. Spoto, ACS Sensors 6 (2021) 2307–2319.
[2] R. D'Agata, N. Bellassai, M.C. Giuffrida, A.M. Aura, C. Petri, P. Kögler, G. Vecchio, U. Jonas, G. Spoto, Talanta (221) 2021 121483.
[3] R. D'Agata, N. Bellassai, V. Jungbluth, G. Spoto, Polymers (13) 2021 1929.
[4] G. Melinte, O. Hosu, G. Ștefan, D. Bogdan, C. Cristea, G. Marrazza, Electrochimica Acta (403) 2022 139718.

Characterization of black crusts from the Monumental Cemetery (Milan) using a combined LIBS and Raman approach

A. Bergomi[a], V. Comite[a], C. Della Pina[a], P.M. Carmona-Quiroga[b], L. Maestro-Guijarro[b], M. Oujja[b], A. Crespo[c], C.A. Lombardi[a], M. Borelli[a], M. Castillejo[b] and P. Fermo[a]

[a]Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133 Milano, Italy; [b]Instituto de Quimica Fisica Rocasolano, IQFR-CSIC, C/Serrano 119, 28006 Madrid, Spain; [c]Instituto de Estructura de la Materia, IEM-CSIC, C/Serrano 121, 28006 Madrid, Spain
andrea.bergomi@unimi.it

Black crusts represent one of the most dangerous degradation phenomena affecting stone materials of calcareous nature, which are very common substrates in architectural cultural heritage [1-2]. These layers of decay are generated from the interaction of the limestone substrate with atmospheric pollutants (SO_2 and particulate matter), which induces the chemical transformation of the substrate into gypsum in a process known as “sulphation”. The numerous studies conducted on the sulphation process in the last decades were able to unveil the chemical reactions responsible for the degradation, highlighting the catalytic role of carbonaceous particles incorporating several metal species commonly found in particulate matter (Fe, Mn, V, etc.). However, the mechanism of this process is not fully understood and the role of each metal in promoting the sulphation process is still unclear.

In the present study, black crust samples were taken from the Monumental Cemetery of Milan and characterized using Laser-Induced Breakdown Spectroscopy (LIBS) and Raman Spectroscopy [3]. The Monumental Cemetery of Milan is one of the largest and most renowned cemeteries in the city. It is known for its large number of tombs and monuments, which make it one of the symbols of the city and a popular tourist attraction. The site was officially opened in 1866 and therefore hosts hundred-year-old monuments which have been exposed through the years to a series of environmental pollutants that pose a threat to the conservation of cultural heritage. Indeed, Milan is one of the most polluted cities in Italy and the cemetery is in proximity to a very busy road, exposed to all the pollutants deriving from vehicular traffic. Black crust formation was abundant in many of the sampled monuments and thanks to the use of the LIBS and Raman techniques it was possible to evaluate more than one-hundred years of pollutant accumulation. Specifically, the former technique was employed to evaluate the elemental superficial distribution and the in-depth metallic concentration profile from the outer part of the black crust to the substrate. Raman analyses were also carried out on different parts of the surface to highlight mineralogical transformations and the presence of organic substances. Moreover, thin sections of the black crusts were obtained and Raman mapping was performed to evaluate compositional differences between the different layers.

The results obtained from LIBS and Raman spectroscopies were compared to the ones from other analytical techniques (IC, SEM-EDX, TOT) and the combined data allowed for a complete characterization of the crusts’ composition. This enabled to obtain a temporal registry of the crusts’ formation that will be useful in the implementation of new protocols for the conservation of the architectural heritage of the Monumental Cemetery.

References:
[1] Comite V., et al., The impact of atmospheric pollution on outdoor cultural heritage: an analytic methodology for the characterization of the carbonaceous fraction in black crusts present on stone surfaces, in Environ. Res., 201, 2021, art. no. 111565, DOI: 10.1016/j.envres.2021.111565.
[2] Fermo P., et al., Study and characterization of environmental deposition on marble and surrogate substrates at a monumental heritage site, in Geosciences (Switzerland), 8 (9), 2018, art. no. 349. DOI:10.3390/geosciences8090349.
[3] Martínez-Hernández A. et al. Analysis of heritage stones and model waal paintings by pulsed laser excitation of Raman, laser-induced fluorescence and laser-induced breakdown spectroscopy signals with a hybrid system, in Journal of Cultural Heritage, 32, 2018, 1-8.

Unravelling the composition of surface films formed on Ni-free DIN 1.4456 stainless steel for orthodontics by XPS

D. Biggio[a], B. Elsener[a], G. Usai[a], M. Fantauzzi[a], A. Rossi[a]

[a]Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari, Cittadella Universitaria, 09042, Monserrato, Cagliari, Italy
deborah.biggio@gmail.com

Materials for orthodontics must fulfill severe requirements of corrosion resistance and biocompatibility. The relevant corrosion studies are performed *in vitro* using model saliva solutions, that simulates the real human saliva [1] such as the saliva formulation known as Tani-Zucchi (T-Z) that consist of inorganic salts, such as chlorides, phosphates, thiocyanates and only urea as organic component.[1-3] As an example, the corrosion resistance of the Ni-Fee DIN 1.4456 stainless steel in contact with Tani-Zucchi (T-Z) formulation was studied by electrochemical techniques [3].As organic compounds present in saliva might play an important role in the stability of surface films and in the dangerous release of metal ions as reported for brass [4,5], there is an increasing need relating electrochemical results with the corrosion products formed at their surface when in contact with saliva. The aim of this work was the development of an analytical method for identifying the chemical state of the elements and the composition of the surface films on Ni-free films following the contact with model saliva solutions, that differ for the organic compounds content: Darvell (D) [6], Carter-Brugurard (C-B) [7] and SALMO [8], that better simulate the real human saliva. D solution contains urea, trisodium citrate, uric acid and lactic acid, SALMO solution contains urea and glycine, and C-B solution contains only urea. The same approach as in [3] was followed in this work and it appears that the results are similar to those measured in T-Z [3], thus the corrosion rates of DIN 1.4456 stainless steels are scarcely influenced by the presence of organic compounds in saliva. On the other hand, the composition of the passive film is strongly affected by the presence of lactic acid, uric acid, and sodium citrate: the film formed on the stainless steel exposed 1 h to D solution is strongly enriched in chromium and depleted in iron (Figure 1). The iron depletion might be due to the complexation of iron ions by organic compounds, not being reflected in the overall corrosion rate. Ni-free DIN 1.4456 stainless steels are suitable materials for orthodontic applications even in the presence of a more complex saliva formulation.

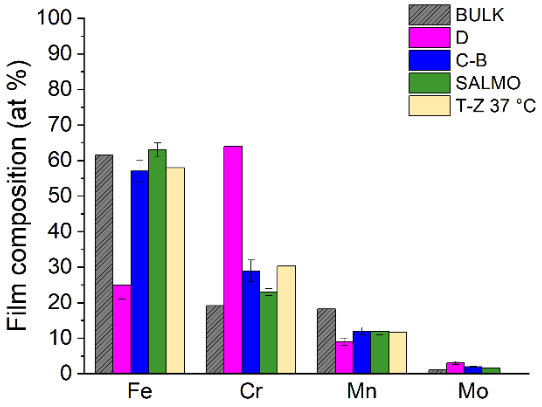


Figure 1: Film composition (at %) at the surface of the Ni-free 1.4456 stainless exposed for 1 to D, C-B and SALMO formulations. The composition of the bulk and the composition of the passive film grown upon exposure to T-Z [3] are reported for comparison.

References:
[1] A. Kocijan, D. K. Merl, M. Jenko, *Corrosion Science*. 2011, *53*, 776–783.
[2] J.-I. Gal, Y. Fovet, M. Adib-Yadzi, *Talanta*. 2001, *53*, 1103–1115.
[3] B. Elsener, M. Pisu, M. Fantauzzi, D. Addari, A. Rossi, *Materials and Corrosion*. 2016, *67*, 591–599.
[4] B. W. Darvell, *J. of Oral Rehab.* 1978, *5*, 41–49.
[5] M. Andrei, B. Galateanu, A. Hudita, M. Costache, P. Osiceanu, J. M. Calderon Moreno, S. I. Drob, I. Demetrescu, *Mater. Sci. Eng. C*. 2016, *59*, 346–355.
[6] F. Crea, C. De Stefano, D. Milea, A. Pettignano, S. Sammartano, *Bioinorg. Chem. Appl.* 2015, Article ID 267985
[7] D. Biggio, B. Elsener, D. Atzei, A. Rossi, M. Fantauzzi, *Materials and Corrosion*. 2023, *74* (*2*), 269–276.
[8] D. Biggio, M. Fantauzzi, B. Elsener, D. Atzei, A. Rossi, *Surface and Interface Analysis*. 2022.

A spectroscopic investigation of palladium recovery from electroplating solutions using carbon materials and electrochemical reduction

M. Bonechi[a], I. Maggini[a], W. Giurlani[a,b], M. Savastano[a], A. Meoli[a], A. Bianchi[a], M. Innocenti[a,b,c,d]

[a]Department of Chemistry "Ugo Schiff", University of Florence, via della Lastruccia 3, 50019 Sesto Fiorentino, Italy; [b]National Interuniversity Consortium of Materials Science and Technology (INSTM), Via G. Giusti 9, 50121 Firenze, Italy; [c]Center for Colloid and Surface Science (CSGI), Via della Lastruccia 3, 50019 Sesto Fiorentino, Italy; [d]Insititute of Chemistry of Organometallic Compounds (ICCOM) – National Research Council (CNR), via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy
marco.bonechi@unifi.it

Increasing demand and resource depletion have focused attention on the recovery of precious metals to reduce industrial waste and promote the development of a circular economy. Large quantities of wastewater are produced in electroplating industries, because of electroplating processes. This wastewater not only has to be properly processed before it is released into the environment, but also contains large quantities of precious metals like palladium [1]. In this work, we propose the study of two possible methods for recovering palladium from electroplating industry wastewater. The first way consists in the electrochemical reduction of palladium on a copper mesh. The second method involves the use of carbon materials: carbon black (CB), and two different types of graphene named as (G4) and (G7). In addition, the two most promising materials CB and G4 were functionalized with a pyrimidine tren derivative capable of complexing Pd(II) [2].

The amount of Pd recovered was assessed using UV-Vis spectrophotometric methods and Microwave Plasma Atomic Emission Spectroscopy (MP-AES). In the case of UV-Vis method an optimization study of the analytical procedure, using xylenol orange indicator [3] was carried out.

The best conditions for electrochemical recovery of Pd were investigated through cyclic voltammetry carried out in a three-electrode cell consisting of a working electrode, an Ag/AgCl reference electrode and a Pt counter electrode. We performed chrono-amperometric measurements at different potentials and times using a copper mesh as working electrode, and we found that the electrochemical process allows more than 99% of the palladium to be recovered by applying a potential of -1.0 V for one hour.

The Pd recovery using the second method was performed by dispersing carbon materials in a Pd solutions and keeping them under stirring. It was found that CB, G4 and functionalized materials can recover up to 97% palladium. Results show that functionalization of CB and G4 dramatically increases the recovery rate. We can conclude that electrochemical method allows recovery to be achieved in a very short time but the further palladium removal from the copper mesh and its purification to obtain metallic palladium could make the recovery expensive. The use of carbon materials, on the other hand, requires a longer recovery time but allows for easier further purification through incineration methods. It must also be noted that the use of carbon materials leads to hybrid materials containing palladium that could be promising candidates for use as catalysts for the Oxygen Reduction Reaction (ORR) in alkaline fuel cells [4].

References:
[1] E. De Beni, W. Giurlani, L. Fabbri, R. Emanuele, S. Santini, C. Sarti, T. Martellini, E. Piciollo, A. Cincinelli, M. Innocenti, Chemosphere 2022, 292, 133448
[2] M. Otomo, BCSJ 1963, 36, 889–892.
[3] M. Savastano, P. Arranz-Mascarós, C. Bazzicalupi, A. Bianchi, C. Giorgi, M. L. Godino-Salido, M. D. Gutiérrez-Valero, R. López-Garzón, RSC Adv. 2014, 4, 58505–58513.
[4] M. Bonechi, W. Giurlani, M. Vizza, M. Savastano, A. Stefani, A. Bianchi, C. Fontanesi, M. Innocenti, Catalysts 2021, 11, 764.

Chiral "doped" MOFs: an electrochemical and spectroscopic study

M. Bonechi[a], *D. Bettoni*[a], *I. Maccioni*[a], *W. Giurlani*[a,b], *T. Salzillo*[c], *R. Kawondera*[d], *C. Fontanesi*[e], *W. Mtangi*[d], *M. Innocenti*[a,b,f,g]

[a]*Department of Chemistry "Ugo Schiff", University of Florence, via della Lastruccia 3, 50019 Sesto Fiorentino, Italy;* [b]*National Interuniversity Consortium of Materials Science and Technology (INSTM), Via G. Giusti 9, 50121 Firenze, Italy;* [c]*Department of Industrial Chemistry "Toso Montanari", University of Bologna, Viale del Risorgimento, 4, 40136, Bologna, Italy;* [d]*Institute of Materials Science, Processing and Engineering Technology, Chinhoyi University of Technology, P Bag 7724, Chirundu Road, Chinhoyi, Zimbabwe;* [e]*Department of Engineering 'Enzo Ferrari', University of Modena and Reggio Emilia, Via Vivarelli 10, 41125 Modena, Italy;* [f]*Center for Colloid and Surface Science (CSGI), Via della Lastruccia 3, 50019 Sesto Fiorentino, Italy;* [g]*Insititute of Chemistry of Organometallic Compounds (ICCOM) – National Research Council (CNR), via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy*
marco.bonechi@unifi.it

Metal-organic frameworks (MOFs) have unique features including exceptional porosity, high specific surface areas, and tunable pore size. These features make MOFs suitable candidate for solid-state materials. Among the many types of MOFs existing nowadays, we can find chiral MOFs. The attractiveness of chiral MOFs is due to their specific application including chiral enantioselective recognition, enantioselective separation, asymmetric catalysis, and sensing [1]. Fe-based and Zn-based MOFs are two different stable and nontoxic types of MOF. MIL-53(Fe) is the most common iron-based MOF. This class of compound is obtained by a combination between Fe(III) cations and terephthalic acid consists of a three-dimensional networks which contain FeO_6 hexagonal chains [2]. On the other hand, Zn-MOF have a network consisting of Zn(II) cations tetrahedrally coordinated by two molecules of 1,4-dicarboxylic acid and two molecules of N,N'-bis(pyridin-4-methyl)cyclohexane-1,4-diamine [3].

In this work, we doped Fe and Zn based metal-organic framework (MOF) compounds with chiral molecules (cysteine and camphor sulfonic acid). Doped MOF were investigated performing "solid-state" electrochemical measurements, using an "ad-hoc" tailored experimental set-up and cyclic voltammetry (CV) experiments. We used elemental analysis (X-ray fluorescence), phase analysis (X-ray diffraction), morphology and elemental analysis (scanning electron microscopy combined with energy-dispersive X-ray spectroscopy), infrared (IR) spectroscopy and UV-Vis spectroscopy for the study of structural and electronic properties. The experimental results were integrated and related to the properties obtained using DFT based quantum mechanical calculations.

References:
[1] Z. Sharifzadeh, K. Berijani, A. Morsali, *Coordination Chemistry Reviews* 2021, *445*, 214083.
[2] C. Scherb, A. Schödel, T. Bein, Angew. Chem. Int. Ed. 2008, 47, 5777–5779..
[3] M. Altaf, M. Sohail, M. Mansha, N. Iqbal, M. Sher, A. Fazal, N. Ullah, A. A. Isab, ChemSus-Chem 2018, 11, 542–546.

Validation of Methods and Analysis of Metals in Food Matrices by ICP-MS

M. Borelli[a], *A. Bergomi*[a], *V. Comite*[a], *S. Bottino*[a], *S. Vitaliti*[b], *M. Rizzi*[b], *M. Bornatici*[b], *G. Notaro*[b], *G. Amato*[b], *P.Fermo*[a]

[a]*Dipartimento di Chimica, Università degli Studi di Milano, 20133 Milano, Italy;* [b]*ATS-Milan Laboratorio di prevenzione, Via Juvara 22, 20129, Milan, Italy*
mattia.borelli@unimi.it

The problem of heavy metals and human exposure to them is a widely addressed issue in the field of environmental chemistry, particularly with regard to their distribution and effects on human health. Due to their ability to bioaccumulate within tissues, they can lead to serious problems in exposed individuals, even in the case of very low concentrations. Based on these considerations, it is therefore important to prevent and carefully control the concentrations of these metals within the matrices that humans are likely to come into contact with on a daily basis and in particular foodstuffs.

In the present study, the content of metals such as mercury, cadmium and lead within food matrices was analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) . In particular, with regard to mercury, the method was validated. The validation procedure was made necessary following an update of EC Regulation number 1881/2006.

The regulation and its subsequent additions in fact set maximum permitted values for certain contaminants in foodstuffs and provide limits for cadmium, lead, mercury, inorganic arsenic and inorganic tin in certain types of foodstuffs. The document is continuously updated, and in April 2022 it was updated with regard to the legal limits for mercury, introducing table salt as a new matrix of concern. The concentration of mercury was determined in a laboratory standard consisting of NaCl and a commercial iodized salt. In both cases, the values were 1/10 of the prescribed limit.

Strawberries, blond oranges, apricots, two types of bitter cocoa, cherries, chocolate and vegetable oil were also analysed as concerns metals concentrations. In all cases, the values found were below the legal threshold limits. Therefore, these products can be considered non-hazardous for human health.

Biomarkers in human saliva via vibrational spectroscopy in tandem with chemometrics: role of the preanalytical step

B. Campanella[a], S. Legnaioli[a], M.Onor[a], E. Benedetti[b], E. Bramanti[a]

[a]*National Research Council of Italy, C.N.R., Institute of Chemistry of Organometallic Compounds-ICCOM, 56124, Pisa, Italy;* [b] *Hematology Unit, Department of Oncology, University of Pisa, 56100 Pisa, Italy*
emilia.bramanti@pi.iccom.cnr.it

Saliva is an easily sampled matrix containing a variety of biochemical information, which can be correlated to the individual health status. The fast, straightforward analysis of saliva by vibrational (ATR-FTIR and Raman) spectroscopy is a good premises for large scale pre-clinical studies to aid translation into clinics. In this work, the effects of saliva collection (spitting/swab) and processing (two different deproteinization procedures) have been explored by principal component analysis (PCA) of ATR-FTIR and Raman data, and by investigating the effects on the main saliva metabolites by reversed phase chromatography (RPC-HPLC-DAD). Despite saliva collection by cotton swabs is not invasive, the spitting/drooling method is even easier, minimizes patient hassle, and it is cost effective in repeated "personal monitoring" when the dynamics of salivary metabolites would be required. As for the other spectrochemical approaches, FTIR is in fact advantageous for providing a holistic information, but the extraction of information from the spectra is a key point to make this information useful for clinical purposes. In tandem with chemometrics vibrational spectroscopy of saliva is potentially a straightforward technique for pathology biomarker research and for personalized medicine screening, to facilitate the diagnosis and follow up of patient during pharmacological therapies once biomarkers have been identified.

We found that both Raman and FTIR spectral patterns are not affected by saliva collection method (spitting or swab). The deproteinization method, instead, may affects the results of saliva-based vibrational spectroscopy, most of all because saliva contains non proteic nitrogen that precipitates in ethanol [1]. Thus, the collection-processing protocol should be based on the biochemical component suitable to get differential diagnoses or to extract info on specific biomarkers [2]. Raman analysis before and after proteins removal with cut-off filters allows to get information complementary to FTIR. Lastly, the saliva deposition onto low-cost polypropilene sheets and the acquisition of spectra on "printed" micro amounts of sample dried spots transferred onto ATR diamond window is novel, and it allows to get reproducible conditions and spectra.

The development of methods based on vibrational spectroscopies, coupled with easy pre-analytical steps (sampling/processing) and portable infrared and Raman spectrophotometers would in principle favorite bed-side applications. The application of these methods to saliva analysis of patients for the discovery of specific, "fast" biomarkers during oral glucose tolerance test and acute and chronic inflammation, in collaboration with clinicians is in progress.

References:
[1] Araki, Y. Nitrogenous substances in saliva. I. Protein and non-protein nitrogens. Jpn. J. Physiol. 1951, 2, 69–78.
[2] Paschotto, D.R.; PUPIN, B.; Bhattacharjee, T.T.; Soares, L.E.S. Saliva Preparation Method Exploration for ATR-FTIR Spectroscopy: Towards Bio-fluid Based Disease Diagnosis. Anal. Sci. 2020, 36, 1059–1064.
[3] Campanella, B.; Legnaioli, S.; Onor, M.; Benedetti, E.; Bramanti, E. The Role of the Preanalytical Step for Human Saliva Analysis via Vibrational Spectroscopy. Metabolites 2023, 13, 393.

Aqueous derivatization by ethyloxonium salts extended to the analysis of methionine and selenomethionine in foods

C. Malvestio[a], *M. Onor*[b], *E. Bramanti*[b], *E. Pagliano*[c], *B. Campanella*[b]

[a]*Department of Chemistry and Industrial Chemistry, University of Pisa, via Giuseppe Moruzzi 13, 56124, Pisa, Italy;* [b]*Institute of Chemistry of Organometallic Compounds, National Research Council, via Giuseppe Moruzzi 1, 56124, Pisa, Italy;* [c]*National Research Council of Canada, 1200 Montreal Road, K1A0R6 Ottawa, Ontario, Canada*.
beatrice.campanella@cnr.it

The assessment of the amino acidic composition of food products is of crucial importance, both from a clinical and an industrial perspective. Particular attention is reserved for sulfur-containing amino acids, i.e. methionine and cysteine, or the main source of selenium dietary intake, selenomethionine [1].

A novel method for the simultaneous gas chromatography – mass spectrometry (GC-MS) determination of methionine (Met) and selenomethionine (SeMet) in food samples is therefore herein proposed for the first time. A single step derivatization in aqueous medium employing triethyloxonium tetrafluoroborate has been optimized for the conversion of the analytes to their ethyl derivatives, followed by their extraction with hexane and GC-MS analysis. Low ng/g quantification limits were achieved for both compounds (1 ng/g for Met and 10 ng/g for SeMet). The method was validated by the analysis of a selenized yeast certified reference material (SELM-1) after microwave assisted acid digestion with methanesulfonic acid and using isotopic internal standards for quantification.

The main goal of this work was to offer a clean and simple derivatization procedure as a valid alternative to the traditional alkyl chloroformate method.

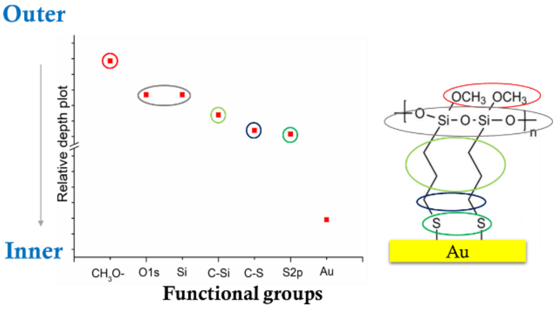
References:
[1] Schrauzer, G. N. The nutritional significance, metabolism and toxicology of selenomethionine. Adv Food Nutr Res, 47, (2003) 73-112.

Growth and Characterization by ARXPS of (3-mercaptopropyl) trimethoxysilane (MPTMS) films on Gold and Food-Grade PVC

G. Casula[a], *M. Fantauzzi*[a], *B. Elsener*[a], *A. Rossi*[a]

[a]*Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Cagliari, ss 554-bivio per Sestu, 09042*
Monserrato (CA)
giulio.casula@unica.it

In this work fresh-cleaved gold and food-grade polyvinyl chloride (PVC) functionalized with (3-mercaptopropyl) trimethoxysilane (MPTMS) was investigated by means of angle-resolved X-ray photoelectron spectroscopy (ARXPS). While this approach was applied to SiO_2 wafer used as substrate [1], the literature on gold samples functionalized with MPTMS characterized by this technique is scarce despite many investigations were carried out on thiols on gold so far. Even more challenging is the characterization of silane films on PVC. Due to the presence of carbon atoms both in the substrate (PVC) and in the silane, it is difficult to distinguish the C 1s components ascribable to the MPTMS from those ascribed to the PVC. In this context, a carbon-free substrate such as fresh cleaved gold samples have been functionalized with MPTMS and analyzed by ARXPS to determine the best parameters for XPS data analysis (i.e. curve fitting parameters for the C 1s signal, inelastic mean free path calculation and models for the calculation of the monolayer thickness). Gold samples were dipped in a 10% ethanol (3-mercaptopropyl) trimethoxy silane (MPTMS) solution for one hour. The presence of the silane film was confirmed: the binding energy values indicated a strong covalent bond to the gold surface in agreement with [2, 3]. The use of the small-area XPS allowed assessing the formation of a laterally homogeneous self-assembled monolayer onto the gold surface. The quantitative analysis results, obtained using the IMFP calculated according to Tanuma, Powell and Penn-2 model (TPP-2M), resulted to be in agreement with the stoichiometry being the S:Si:O ratio equal to 1:1:2.5. The relative depth plot (Figure 1) provides evidence that the $-OCH_3$ is in the outer part of the film followed by the Si-O-Si while S is at the film – gold interface. The film thickness was also calculated and it was found to be 1.9 ± 0.5 nm, the formation of a single layer of MPTMS on the gold surface could be assessed. This analytical method, validated on gold, was thus applied to the characterization of MPTMS-functionalized food-grade PVC. ARXPS results showed the formation of a monolayer thick film by a nucleophilic substitution reaction. The quantitative analysis was in good agreement with the stoichiometry of the molecule and the film thickness resulted to be 2.2 ± 0.2 nm [4] due to the presence of a contamination layer.



References:
[1] A. Penna, M. Careri, N.D. Spencer, A. Rossi, Effects of Tailored Surface Chemistry on Desorption Electrospray Ionization Mass Spectrometry: a Surface-Analytical Study by XPS and AFM, J. Am. Soc. Mass Spectrom. 26 (2015) 1311–1319. https://doi.org/10.1007/s13361-015-1135-9.
[2] I. Piwoński, J. Grobelny, M. Cichomski, G. Celichowski, J. Rogowski, Investigation of 3 - mercaptopropyltrimethoxysilane self-assembled monolayers on Au(111) surface, Applied Surface Science. 242 (2005) 147–153. https://doi.org/10.1016/j.apsusc.2004.08.009.
[3] P.K. Gothe, D. Gaur, V.G. Achanta, MPTMS self-assembled monolayer deposition for ultra-thin gold films for plasmonics, J. Phys. Commun. 2 (2018) 035005. https://doi.org/10.1088/2399-6528/aaaedd.
[4] G. Casula, M. Fantauzzi, B. Elsener, A. Rossi, Surface modification of food-Grade PVC by angle-resolved mode to be published.

Experimentation in accelerated ageing chambers to evaluate the action of catalysts in the sulphation process

V. Comite[a], C. A. Lombardi[a,b], C. Castellano[a], A. Bergomi[a], M. Borelli[a] M. Formenti[a],
C. Cavaterra[c], P. Fermo[a], C. Della Pina[a]

[a]Dipartimento di Chimica, Università degli Studi di Milano, 20133 Milan, Italy; [b]Dipartimento di Scienze dell'Antichità, Sapienza Università di Roma, 00185 Rome, Italy; [c]Dipartimento di Matematica 'Federigo Enriques' Università degli Studi di Milano, 20133 Milan, Italy
valeria.comite@unimi.it

Research conducted on the degradation of cultural and architectural heritage caused by the deposition of air pollutants indicates that both sulphur dioxide and particulate matter produced by the combustion of fossil fuels are the main agents responsible for the deterioration of carbonate materials. The main chemical degradation process is the sulphation of the substrate and consists in the initial conversion of sulphur dioxide (SO_2) into sulphuric acid (H_2SO_4) and the subsequent reaction of sulphuric acid with calcium carbonate which forms the black crusts. The sulphation process takes place only thanks to the presence of heavy metals which catalyze the reaction.

Despite the presence of numerous studies related to black crusts formation [1,2], a specific role of the single metals is still unclear. Aiming to unveil the catalytic action of different metals, a series of experimental tests was carried out in specific climatic chambers for accelerated aging.

This research work concerns with a second exposure test in accelerated aging chambers following the first experimental phase [3] which did not allow to discriminate the catalytic action of the metals. More specifically, two climatic chambers were employed: a "corrosion chamber" providing a source of SO_2 and humidity at determined concentration and temperature, and a "light-irradiation chamber" to simulate the sunlight irradiation naturally falling on monumental stone during the day. This second monitoring campaign was carried out at different experimental conditions inside the "corrosion chamber" with respect to the first campaign. Accordingly, upon lowering the concentration of SO_2 by 20 times, the reactions took place more slowly thus decelerating the phenomenon and, hence, better highlighting the catalytic role of individual metals.

After the preparation and exposure of the marble samples inside the climatic chambers (carried out as in the first campaign), the physico-chemical characterization was carried out by means of a multi-analytical approach involving different techniques. Colorimetric analysis was used to define the variation of the chromatic coordinate L (brightness), which is related to the formation of gypsum on the surface. SEM-EDX was employed to study the elemental composition and morphology of the surface and degradation products. Moreover, XRPD was used to identify the mineralogical composition of the degradation layer and IC was performed to identify and quantify soluble salts (in particular sulphate ions).

All the experimental data collected will be processed in the next step of the project to create a predictive mathematical model. This will help to predict the formation of black crusts on carbonate surfaces based on the outdoor pollution present in a given site. Actually, this research work is part of the interdepartmental SEED 2019 project of the University of Milan entitled SciCult (mathematical modelling and Scientific analysis for Cultural heritage: prediction and prevention of chemical and mechanical degradation of monumental stones in outdoor environments).

References:
[1] Grgic I., et al., Aqueous S(IV) oxidation-I. Catalytic effects of some metal ions. Atmos. Environ., 25A (1991), 1591-1597.
[2] Grgic I., et al.,1992. Aqueous S(IV) oxidation-II. Synergistic effects of some metal ions. Atmos. Environ., 26, 4 (1992) 571-577.
[3] Comite V., et al., Climatic chamber tests to evaluate the catalytic action of heavy metals in the sulphation process, IMEKO TC-4 International Conference on Metrology for Archaeology and Cultural Heritage University of Calabria, Italy, (2022).

Multispectral 3D models for monitoring in conservation of wooden statues

S. Croci[a], *L. Es Sebar*[a], *P. Buscaglia*[a,b], *S. Grassini*[a], *C. Ricci*[b]

[a] *Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, Turin, Italy;*
[b] *Centro Conservazione e Restauro "La Venaria Reale", Venaria Reale, Italy*
sara.croci@polito.it

Digitalization techniques, such as photogrammetry, are attracting the interest of experts in the field of cultural heritage. Photogrammetry allows the creation of three-dimensional virtual replicas of historical artifacts acquiring data about the overall appearance of an item, its geometry, and texture by using 2D digital images. Among several image-based techniques exploited for the conservation of artifacts, multispectral imaging (MSI) is useful for the non-invasive investigation of the materials employed for the creation of historical items. MSI finds great application in the study of pigments, binders, varnishes, and other materials since it may aid their characterization by taking advantage of their different response when exposed to specific wavelengths of the electromagnetic spectrum [1]. Nevertheless, MSI techniques are traditionally applied only at a 2D level photogrammetry. Despite the combination of geometric and radiometric information in a 3D model could represent a powerful tool in the field of conservation of cultural heritage, MSI techniques and photogrammetry are often used as separate tools. The possibility of integrating data coming from MSI and photogrammetry can notably expand the information carried by a 3D model. 3D models can represent virtual documentation useful for study, preservation, and research aims, preventing the acquisition of incorrect dimensional and metrical data is of paramount importance. In spite of this, nowadays there is no unique way to assess the dimensional accuracy of 3D models in the Cultural Heritage field [2]. Therefore, this paper presents the integration of geometrical and spatial information coming from photogrammetry and radiometric data of multispectral imaging in a unique 3D model.

A novel research methodology and experimental setup, that enable the acquisition of multispectral 3D models, combining the outcomes of photogrammetry and multispectral imaging in a single coordinate system, is presented [3].

To verify its application in the cultural heritage field, this approach has been developed on a case study and combined with diagnostic analyses aimed at the characterization of the artifact's materials. In particular, a multispectral imaging campaign and the creation of a 3D model have been exploited for the study of the state of preservation of a wooden sculpture belonging to the collection of the Museo di Arte Orientale (MAO) di Torino. The artifact is one of a group of seven Chinese Buddhas studied and restored at the Centro Conservazione e Restauro "La Venaria Reale". The creation of a multispectral 3D model was performed to investigate and locate the materials present on the surface, both the original ones and the ones applied in previous treatments.

For the characterization of pictorial materials, the model so obtained was also functional to identify the most interesting areas to be investigated with X-ray fluorescence (XRF) and Fourier-transform infrared spectroscopy (FTIR).

References:
[1] Dyer J., Verri G., and Cupitt J., Multispectral imaging in reflectance and photo-induced luminescence modes: a user manual, British Museum London, (2013).
[2] Beraldin J.A., Rioux M., Cournoyer L., Blais F., Picard M., and Pekelsky J., Traceable 3D imaging metrology, in Videometrics IX, 6491 (2007) 64910B.
[3] Es Sebar L., Lombardo L., Parvis M., Angelini E., Re A., and Grassini S., A metrological approach for multispectral photogrammetry, Acta IMEKO, 10 (2021), 111–116.

Advances in Diagnostics using Plasmonic-based Imaging Sensor and liquid biopsy approaches

R. D'Agata[a,b], *N. Bellassai*[a,b], *G. Spoto*[a,b]

[a]*Department of Chemical Sciences, University of Catania, Viale Andrea Doria, 6, 95125, Catania, Italy;*
[b]*INBB, Istituto Nazionale di Biostrutture e Biosistemi, Viale Delle Medaglie D'Oro, 305, 00136, Roma, Italy*
dagata.r@unict.it

High-quality diagnostic technologies could be designed by making an early and non-invasive diagnosis with devices based on Surface Plasmon Resonance (SPR) Imaging sensors. The success of SPR sensing in molecular diagnostics is motivated by the benefits that it can bring in improving the low-fouling sensing, minimizing the non-specific adsorptions from biofluids, the sensitivity enhancement (in the fM range or below), the multiplexing capability, and real-life sample analysis [1]. More, the above features explain the attractiveness of the SPRI sensor in the development of diagnostic tests based on liquid biopsy approaches [2]. Here, we will present some examples of strategies capable to detect, directly in a clinical sample, diagnostic biomarkers (i.e. tumor DNAs, cell-free DNA, proteins, and microRNAs) circulating at low concentrations in body fluids.

By implementing a sandwich assay, it was possible to reveal ~1 attomolar KRAS mutated DNA circulating in 40 µL of plasma from cancer patients, greatly simplifying the liquid biopsy workflow [3]. Firstly, by using genomic DNA from tissues, we showed that our assay easily differentiates the most frequent RAS colon rectal cancer (CRC) mutations from the wild-type. For the eleven tested RAS point mutations, the method exhibited 100% sensitivity and 83% specificity. The feasibility of the assay was then investigated by running spike-in experiments with KRAS DNA sequences in plasma from healthy donors. Finally, the plasmonic assay was efficiently applied to detect KRAS mutations in circulating DNAs from the plasma of CRC patients.

A similar approach is envisaged to be applied for non-invasive prenatal fetal sex determination based on the detection of a Y-chromosome specific sequence (single-gene SRY) in cell-free fetal DNA from maternal plasma, even at the earliest gestational age [4].

A new anti-fouling PEG-pentrimer carboxybetaine-based surface has demonstrated its applicability in plasma for the SPRI biosensing of human Arginase [5].

Possibilities offered in the quantification of microRNAs [6] as cancer biomarkers circulating in the serum of glioma patients will be also discussed.

We acknowledge support from the European Union's Horizon 2020 research and innovation programme under grant agreement No 633937 project ULTRAPLACAD, from the European Union's European Innovation Council under grant agreement No 101046217 project VERSILIB and from Università degli Studi di Catania, STARTING GRANT 2020, project PATmiREC.

References:
[1] Usha, S.P.; Manoharan, H.; Deshmukh, R.; Álvarez-Diduk, R.; Calucho, E.; Sai, V.V.R.; Merkoçi, A. Chemical Society Reviews 2021, 50, 13012 – 13089.
[2] Alix-Panabières, C. Nature, 2020, 579, S9.
[3] D'Agata, R.; Bellassai, N.; Allegretti M.;Rozzi, A.; Korom, S.; Manicardi, A.; Melucci, E.: Pescarmona, E.; Corradini, R.; Giacomini, P.; Spoto, G. Biosensors and Bioelectronics 2020, 170, 112648.
[4] Calcagno, M.; D'Agata, R.; Breveglieri, G.; Borgatti, M.; Bellassai, N.; Gambari, R.; Spoto, G. Analytical Chemistry 2022, 94, 1118 – 1125.
[5] D'Agata, R.; Bellassai, Giuffrida, M.C.; Aura, A.M.; C. Petri, C.; Kogler, P.; Vecchio, G.; Jonas, U.; Spoto, G. Talanta 2021, 221, 121483.
[6] D'Agata, R.; Spoto G., Analytical and Bioanalytical Chemistry 2019, 411, 4425 – 4444.

Correlation between surface chemical composition and catalytic activity of MnO_2-based catalysts

N. Ditaranto[a,b,c], F. Nocito[a,b], D. Linsalata[a], M. Naschetti[a,b], M. Aresta[b,d], A. Dibenedetto[a,b,d]

[a]Dipartimento di Chimica, Università degli Studi di Bari Aldo Moro, Via Orabona, 4 – 70125 Bari; [b]CIRCC, Interuniversity Consortium on Chemical Reactivity and Catalysis, Bari, Via Celso Ulpiani, 27 – 70126 Bari; [c]CSGI - Centre for Colloid and Surface Science, Bari Unit, Bari; [d]IC2R, srl - Tecnopolis, 70010 Valenzano (BA)
nicoletta.ditaranto@uniba.it

In this study, we report on the analytical characterization of different MnO_2 – based catalysts and the correlation between the surface properties and their catalytic activity. High Energy Milling (HEM) was used to prepare MnO_2/CeO_2, MnO_2/CuO, and $MnO_2/CuO/CeO_2$ mixed oxides. A second route using Microwave-Assisted Hydrothermal (MWHT) was also employed to prepare $MnO_2@CeO_2$, obtaining a core-shell catalyst.

All the oxides were tested in the selective aerobic oxidation of furfural into furoic acid. X-ray photoelectron spectroscopy (XPS) analyses showed that both commercial MnO_2 and HEM prepared mixed oxides, present on the surface a certain abundance of Mn(III) species, which is less active in the furfural oxidation. Noteworthy, calcination of the samples in air led to an increased amount of manganese in lower oxidation states [Mn(III) and Mn(II)], highlighting the MnO2 instability at high temperature [1,2]. This behaviour was well correlated with low performance in the catalytic tests.

XPS on MWHT prepared $MnO_2@CeO_2$ revealed only Mn(IV) species on the surface, highlighting its excellent catalytic properties [3].

In conclusion, XPS, along with EDX and TPD analyses performed on all the catalysts, were used to explain the different behaviour of the catalytic materials, in terms of activity, recoverability, and reusability.

References:
[1] D.M. Tinsley, J.H. Sharp, *J. Therm. Anal.* 3 (1971) 43–48.
[2] F.A. Deorsola, S. Andreoli, M. Armandi, B. Bonelli, R. Pirone, *Appl. Catal. A Gen.* 522 (2016) 120–129.
[3] F. Nocito, N. Ditaranto, D. Linsalata, M. Naschetti, R. Comparelli, M. Aresta, A. Dibenedetto, *ACS Sustainable Chemistry & Engineering*, 10 (2022) 8615–8623.

Surface enhanced Raman scattering of crevicular fluid in periodontics and implantology

S. Fornasaro[a]*, A. Rapani*[b]*, F. Berton*[b]*, C. Stacchi*[b]*, V. Sergo*[c]*, A. Bonifacio*[c]

[a]*University of Trieste, Dept. of Chemical and Pharmaceutical Sciences, via L. Giorgeri 1, 34127 Trieste, Italy;* [b]*Maxillofacial and Dental Surgical Clinic, Dept. of Medical, Surgical and Health Sciences, University of Trieste, Piazza dell'Ospitale 1, 34125, Trieste, Italy;* [c]*Raman Spectroscopy Lab, Dept. of Engineering and Architecture, University of Trieste, via A. Valerio 6a, 34127 Trieste, Italy*
sfornasaro@units.it

Periodontal disease is one of the most frequent diseases affecting dental elements, with periods of disease activity followed by periods of remission. Traditional clinical and radiological methods only capture pre-existing destruction rather than current disease activity, and metabolomic analysis of gingival crevicular fluid (GCF) and peri-implant crevicular fluid (PICF) has attracted attention as a valuable tool for periodontal disease prognosis and diagnosis [1].

Surface enhanced Raman scattering (SERS) is a spectroscopic technique that has various advantages over standard bioanalysis for the analysis of biological samples ranging from *in vitr*o cell culture models to *ex vivo* tissues and biofluids. SERS datasets derived from biofluids are rich in metabolic fingerprint information, but access to this information is not always simple. Bioanalytical SERS is a highly complicated field that necessitates a thorough understanding of the chemical and physical interactions that exist between photons, nanomaterials, and biological systems. Discovering meaningful information in the midst of this complication is a difficult task [2].

This communication will present a brief overview of several approaches to dealing with the handling, processing, and interpretation of SERS spectral data from biofluids. In addition, we will discuss how the SERS metabolic fingerprint of CFs can offer information about the periodontal health of teeth and dental implants, and we will present a successful and comprehensive deployment of chemometrics and machine learning strategies (including design of experiments, multivariate analysis, and data fusion) to support the use of SERS spectroscopy as a complementary metabolomic tool for the early diagnosis and treatment monitoring of the periodontal and peri-implant pathologies.

References:
[1]. Fornasaro S, Berton F, Stacchi C, Farina F, Esposito A, Sergo V, Di Lenarda R, Bonifacio A. (2021) Label-free analysis of gingival crevicular fluid (GCF) by surface enhanced Raman scattering (SERS). Analyst. 146(4):1464–1471.
[2] Fornasaro S, Beleites C, Sergo V, Bonifacio A (2022) Data analysis in SERS diagnostics, in SERS for Point-Of-care and Clinical Applications, ed.: Andrew Fales, Elsevier, 1-51.

Reconsidering the value of the information from the OH stretching band in FT-IR spectroscopy

L. Geminiani[a], *C. Corti*[b], *L. Rampazzi*[b]

[a] *Dipartimento di Scienza e Alta Tecnologia, Università degli Studi dell'Insubria, Via Valleggio 11, 22100 Como, Italy;* [b] *Dipartimento di Scienze Umane e dell'Innovazione per il Territorio, Università degli Studi dell'Insubria, Via Sant'Abbondio 12, 22100 Como, Italy*
lgeminiani@uninsubria.it

Water molecule shows some strong absorption peaks in the infrared region, which generally interfere with the detection of the molecular species of interest. Yet, it is difficult to completely remove humidity from the sample, as it can undergo morphological or chemical modifications when exposed to heat or vacuum. Instead of eliminating water molecules, it could be interesting to evaluate how water bonds the material under analysis and causes changes into its infrared spectrum. As shown in our study, some materials such as cellulosic fibres and silk show predictable modifications in their spectra when they are conditioned at different relative humidity (RH) levels [1]. Similarly, when different materials are stored at the same RH level, their water uptake can be inferred from the visual evaluation of the spectra or from the comparison of the gaussian curves obtained from peak fitting analysis [2].

This is the key for the discrimination of different materials which show a very similar spectrum. It is the case of soft and hard silk [3], which were both used in historical textiles. The unprocessed fibre is named hard in contrast to soft silk, which was subjected to degumming process to eliminate the sericin coating. The distinction between hard and soft silk gives both historical information and useful indications for informed conservation. With this aim, 32 samples of silk textiles from the Morigi Collection of traditional Japanese samurai armours (15th - 20th century) were characterized in a non-invasive way. An innovative analytical protocol based on external reflection FTIR (ER-FTIR) spectroscopy was employed, coupled with spectral deconvolution and multivariate data analysis. When samples are stored under the same conditions, the higher water content, which causes the broad absorption at around 3600 cm^{-1}, is linked to the presence of sericin and, indirectly, to the detection of hard silk. Cotton and viscose are another couple of materials which was easily differentiated through the proposed method [4]. In this case, Attenuated Total Reflectance FTIR (ATR-FTIR) spectroscopy was used to study 10 samples of different cellulosic materials coming from the same armours collection. Viscose is a modified fibre obtained when cotton waste is treated with CS_2 and aqueous NaOH and then extruded. Due to the different crystalline structures, which makes water molecules bind differently, there are some signals in the OH stretching band which can differentiate the two fibres [5]. The information is of a great help to find out past restoration materials and to reconstruct the history of the work of art.

The proposed approach exploits a "weakness" of FTIR spectroscopy – the strong absorption from water molecules – in order to indirectly obtain the results. While the OH stretching bands are generally considered "forbidden" regions, we showed that these bands are useful to study adsorbed water, by means of peak fitting analysis which appeared an interesting tool to evaluate the different contributes of OH stretching band.

References:
[1] Olsson AM, Salmén L. The association of water to cellulose and hemicellulose in paper examined by FTIR spectroscopy. *Carbohydr Res.* 2004; 339:813–8.
[2] Pellegrini, ... & Bramanti, E. (2016). Fourier transform infrared spectroscopic study of rabbit glue/inorganic pigments mixtures in fresh and aged reference paint reconstructions. *Microchemical Journal*, *124*, 31-35.
[3] Geminiani, ... & Rampazzi, L. (2023). Historical Silk: A Novel Method to Evaluate Degumming with Non-Invasive Infrared Spectroscopy and Spectral Deconvolution. *Materials*, *16*(5), 1819.
[4] Geminiani L, & Rampazzi L. Differentiating between Natural and Modified Cellulosic Fibres Using ATR-FTIR Spectroscopy. *Heritage* 2022; 5(4)
[5] Fengel, D. Characterization of Cellulose by Deconvoluting the OH Valency Range in FTIR Spectra. *Holzforschung* 1992, 46, 283–288

Electrodeposition of manganese arsenides (Mn_xAs) and its compositional optimization assisted by microanalysis spectroscopy

W. Giurlan[a,b], *G. Pappaianni*[a], *M. Bonechi*[a], *C. Bazzicalupi*[a], *C. Fontanesi*[b,c], *M. Innocenti*[a,b,d,e]

[a] Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 3, 50019 Sesto Fiorentino (FI), Italy; [b] National Interuniversity Consortium of Materials Science and Technology (INSTM), Via G. Giusti 9, 50121 Firenze (FI), Italy; [c] Department of Engineering 'Enzo Ferrari', University of Modena and Reggio Emilia, Via Vivarelli 10, 41125 Modena, Italy; [d] National Research Council-Organometallic Compounds Chemistry Institute (CNR-ICCOM), Via Madonna del Piano 10, 50019 Sesto F.no (FI), Italy; [e] 5 Center for Colloid and Surface Science (CSGI), Via della Lastruccia 3, 50019 Sesto F.no (FI), Italy
walter.giurlani@unifi.it

Spintronics is an emerging field of electronics that involves manipulating both the spin and charge of electrons to achieve specific outcomes. Spintronic devices hold great promise for applications in memory storage, magnetic sensors, and even quantum computing, where electron spin can serve as a unit of information. To make these devices more efficient and cost-effective, researchers have explored the use of molecular inorganic compounds and low-cost preparation methods [1].
Most of these materials are synthesized using physical or vapor-phase techniques, which can be complex to manage and expensive. To overcome these challenges, this study explores electrochemical deposition as a cheap, versatile, and easily scalable method for depositing a compound with promising spintronic properties in an aqueous medium. The Mn-As system was selected as the building block for spin valves due to its good magnetic and transport properties [2]. MnAs has potential applications in spintronics, including electrical spin injection into GaAs and Si-based devices, and DFT simulations predict that Mn_2As and Mn_3As have low magnetization saturation and high spin polarization at the Fermi level [3].

Deposits were obtained using MnSO4 and NaAsO2 precursor solutions with various concentrations, supporting electrolytes, and pH levels. Electrochemical behaviour was analysed using cyclic voltammetries, and both potentiostatic and galvanostatic deposition were carried out. The deposits were morphologically and compositionally characterized using scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS) and X-ray fluorescence spectroscopy (XRF). Furthermore, the chemical states were analysed using X-ray photoelectron spectroscopy (XPS), and the crystalline structure was investigated using X-ray diffraction measurements (XRD). The preliminary magnetic evidence the promising properties of this deposition process to provide spinfiltering materials.
In particular EDS analysis allowed for the optimization of the compound's composition through deposition under various conditions, further highlighting the potential of this electrochemical deposition process for producing spinfiltering materials. Overall, this study presents an innovative and cost-effective approach to developing spintronic materials with promising properties.

Project funded under the National Recovery and Resilience Plan (NRRP), Mission 4 Component 2 Investment 1.3 - Call for tender No. 341 of 15 March 2023 of Italian Ministry of University and Research (MUR) funded by the European Union - NextGenerationEU - Project code PE_00000004, CUP B83C22004890007, Project title "3A-ITALY - Made-in-Italy circolare e sostenibile".

References:
[1] M. Innocenti et al., Journal of Electroanalytical Chemistry 2020, 856, 113705, doi: 10.1016/j.jelechem.2019.113705
[2] T. Graf et al., Progress in Solid State Chemistry 2011, 39, 1-50, doi: 10.1016/j.progsolidstchem.2011.02.001
[3] C. Mocuta et al. Scientific Reports 2017, 7, 16970, doi: 10.1038/s41598-017-17251-y

A new process control tool based on ATR-FT-IR spectroscopy and dissimilarity index to identify anomalies in wine alcoholic fermentation

B. Giussani[a], D. Schorn-García[b], J. Ezenarro[b], O. Busto[b], L. Aceña[b], R. Boqué[b], M. Mestres[b]

[a]DISAT, Università Degli Studi Dell'Insubria, Como, Italy; [b]QAQO Dpt, Universitat Rovira i Virgili, Tarragona, Spain
barbara.giussani@uninsubria.it

The complexity of food processing arises from the presence of numerous species, including microorganisms that can engage in biochemical transformations. Therefore, quality control is essential throughout all phases of processing and production. While traditional quality control relies on daily univariate measurements and final product characterization, Process Analytical Technologies (PAT) are increasingly being used in the food and beverage sector to ensure quality throughout the production process [1]. Spectroscopic techniques, such as infrared, play a critical role in PAT by providing fast and non-destructive measurements of molecular composition [2]. Multivariate Statistical Process Control (MSPC) techniques are used to monitor and control the food processing process as spectroscopic techniques generate multivariate data.

The Dissimilarity Index (DI) is a multivariate statistical process control technique that can be used to monitor and control the fermentation process. It was originally proposed by Muncan et al. for monitoring yogurt fermentation using near-infrared spectroscopy [3]; it allowed to describe the progress of the process based on the first principal component (PC) loading. Changes in the process can be detected using a moving-window approach and the first PC loading of the fermentation.

In this study, a modified version of DI was proposed to monitor wine alcoholic fermentation by using an evolving window approach and calculating a reference loading from the first hours' spectra under Normal Operating Conditions (NOC). Infrared spectra from the beginning of the alcoholic fermentation to a given sampling point are then compared to the reference loading to monitor the process.

The proposed approach was successful in monitoring alcoholic fermentation and detecting deviations in the process using an MSPC control chart. Experiments were conducted by simulating temperature control problems and an initial deficit in assimilable nitrogen compounds that affect yeast metabolism. The effect of these deviations was studied with ANOVA–simultaneous component analysis (ASCA), showing that the initial nitrogen concentration has a greater impact on the evolution of the process compared to sudden changes in temperature.

References:
[1] FDA Official Document (2004) Guidance for Industry PAT — A Framework for Innovative Pharmaceutical Development, Manufacuring, and Quality Assurance 16.
[2] Cozzolino D (2022) Advantages, Opportunities, and Challenges of Vibrational Spectroscopy as Tool to Monitor Sustainable Food Systems, Food Anal Methods. 15 1390–1396.
[3] Muncan J, Tei K, Tsenkova R (2021) Real-time monitoring of yogurt fermentation process by aquaphotomics near-infrared spectroscopy, Sensors (Switzerland). 21 1–18.

How explore raw data characteristics and sources of uncertainty could be a crucial step for spectroscopic method development

G. Gorla[a]*, C. Alamprese*[c]*, S. Grassi*[c]*, R. Boqué*[b]*, J. Riu*[b]*, B. Giussani*[a]

[a]*Department of Science and High Technology, University of Insubria, Via Valleggio 9, 22100 Como, Italy;*
[b]*Chemometrics, Qualimetrics and Nanosensors Group, Department of Analytical Chemistry and Organic Chemistry, Universitat Rovira i Virgili, Campus Sescelades, 43007 Tarragona, Spain;* [c]*Department of Food, Environmental and Nutritional Sciences, Università degli Studi di Milano, Via Giovanni Celoria 2, 20133 Milan, Italy*
ggorla@uninsubria.it

Nowadays, handheld and miniaturized instruments have gained popularity due to their efficacy in various applications and orientation toward green analytical chemistry. An increased number of end-users is attracted by the low-cost and easy-to-use interfaces [1]. Alongside instrument portability, measurements are often subjected to multivariate data analysis to separate information from noise and extract information. In particular, handheld miniaturized NIR instruments are demonstrating increasing proof of efficacy for various applications [2,3]. However, despite the attention given to the analytical protocol, from sampling to data collection, up to the data processing, the significance of investigating error structure in raw data is often disregarded [4].

Within this context, the importance of evaluating sources of uncertainty in raw data when different acquisition parameters are set, types of replicates are considered, and acquisition configurations or instrumentations are involved has been studied [5,6]. The influences on the errors arising from sample compactness in external dispersive NIR reflectance spectra were also addressed.

This study serves multiple purposes. Firstly, it gives an excellent example of how understanding the sources of errors in raw data could improve the quality of measurements. Secondly, it furnishes a look into how the information on the uncertainties could be used to manage and treat the data suitably. In addition, it shows how identifying the error shape could help monitor instrumental performances. Overall, it proposes a practical and feasible methodology to investigate raw data uncertainties and enhance the need to evaluate measurements error before the optimization of every analytical method.

References:

[1] Crocombe, R.A. Portable Spectroscopy. Applied Spectroscopy. 2018, 72, 12.

[2] Wentzell, P.D. Measurement Errors in Multivariate Chemical Data. J. Braz. Chem. Soc. 2014, 25, 183–196.

[3] Giussani, B.; Gorla, G.; Riu, J. Analytical chemistry strategies in the use of miniaturised NIR Instruments: An overview. Crit. Rev. Anal. Chem. 2022, 1–33.

[4] Beć, K.B.; Grabska, J.; Huck, C.W. Principles and applications of miniaturized Near-Infrared (NIR) spectrometers. Chem.–A Eur. J. 2020, 27, 1514–1532.

[5] Gorla, G.; Taina, A. ; Boqué, R.; Bani, P; Gachiuta, O.; Giussani, B. Unravelling error sources in miniaturized NIR spectroscopic measurements: The case study of forages. Anal Chim Acta, 2022, 1211, 339900

[6] Gorla, G.; Taborelli, P.; Alamprese, C.; Grassi, S.; Giussani, B. On the Importance of Investigating Data Structure in Miniaturized NIR Spectroscopy Measurements of Food: The Case Study of Sugar. Foods 2023, 12, 493.

The Identification of Pigments through Non-Invasive Spectroscopic Analyses: the Bernardino Luini Frescoes of Santuario della Beata Vergine dei Miracoli in Saronno (Italy) as a Case Study

V. Guglielmi[a], V. Comite[a], G. Fiocco[b,c], M. Albano[b,c], C. Merlo[b,d], T. Rovetta[b], C. Lee[b,e], F. Volpi[b,c], A. Bergomi[a], C. A. Pini[a], C. A. Lombardi[a], C. Mariani[f], M. Malagodi[b,c], P. Fermo[a]

[a]Department of Chemistry, Università degli Studi di Milano, Via Golgi 19, 20124 Milano, Italy; [b]Arvedi Laboratory of Non-Invasive Diagnostics, CISRiC, Università di Pavia, Via Bell'Aspa 3, 26100 Cremona, Italy, [c]Department of Musicology and Cultural Heritage, Università degli Studi di Pavia, Corso Garibaldi 178, 26100 Cremona, Italy, [d]Laboratorio di Diagnostica applicata ai Beni Culturali, Scuola di Restauro Cr.Forma, C.so Matteotti 17, 26100 Cremona, Italy, [e]Department of Chemistry, University of Pavia, Via Torquato Taramelli 12, 27100 Pavia, Italy; [f]Freelance architect
vittoria.guglielmi@unimi.it

It is well known that the painting technique of the great Leonardo da Vinci heavily affected many notable artists of his age. Among them there was Bernardino Luini, who was one of the most important Italian masters that worked between the 15th and 16th centuries.

In this research paper, the first results of the analytical survey made on two of the numerous wall paintings present in the Santuario della Beata Vergine dei Miracoli in Saronno (Italy) are shown. In detail, the "Marriage of the Virgin and the Adoration of the Christ Childmade" by Luini (Figure 1) and the "Adoration of the Christ Child" (which is suspected to be a Luini as well) were analysed in a totally non-destructive manner in order to compare the colour palettes utilised for their creation and to possibly help with the attribution of the latter.

The multi-analytical spectroscopic study was performed by portable X-ray fluorescence (XRF), Fourier transform infrared reflection (R-FTIR) spectroscopy, Raman spectroscopy and visible reflectance spectroscopy. It permitted the identification of the majority of pigments of both paintings and the presence of some retouches and degradation products.

The research is ongoing and will be completed with the application of some imaging techniques, such as hyperspectral imaging, to obtain the distribution of the different colours and restoration areas on the two wide painted surfaces.

Figure 1 – The marriage of the Virgin and the Adoration of the Christ Childmade by Bernardino Luini

Analytical Spectroscopy in Electroplating industry

M. Innocenti[a,b], M. Bonechi[a,b], W. Giurlani[a,b], A. De Luca[a,b], A. Comparini[a,c], M. Verrucchi[a],*
M. Pagliai[a], S. Martinuzzi[a,b], A. Caneschi[b,d]

[a] *Dipartimento di Chimica "Ugo Schiff", University of Florence;*
[b]*INSTM, via Giuseppe Giusti, 9, 50121, Florence, Italy ;*
[c] *Valmet Plating S.r.l. Calenzano, via Erbosa 5, Firenze - Italy;*
[d]*Department of Engineering, DIEF, University of Modena and Reggio Emilia, 41125 Modena, Italy*
m.innocenti@unifi.it

The interest in scientific research within the metal finishing sector is growing. The demand for durable metals and adaptable manufacturing processes is increasing across a wide range of applications, from aerospace and automotive to machinery and jewelry. In that respect, alloy plating offers better answers in terms of economic growth and environmental sustainability due to fine-tuning composition, morphology, and crystallinity [1]. Here, current trends in alloy electrodeposition research are reviewed highlighting open challenges and process innovations from an industrial perspective. Combining basic electrochemical techniques with spectroscopic, microscopic, and structural techniques is crucial for characterizing the structure-activity relationship for many different technological devices. Particular attention is devoted to advances in industrial quality control and viable solutions for the reduction of precious metal content in electroplated accessories as well as the replacement of cyanide and nickel baths with non-toxic compounds.

The authors acknowledge Regione Toscana POR CreO FESR 2014-2020 – azione 1.1.5 sub-azione A1 – Bando 1 which made possible the project: "RAM-PVD" (CUP 3647.04032020. 157000057_1225), and PE11 Made in Italy Circolare e sostenibile – MICS - 3A-ITALY, Spoke n. 2.

Project funded under the National Recovery and Resilience Plan (NRRP), Mission 4 Component 2 Investment 1.3 - Call for tender No. 341 of 15 March 2023 of Italian Ministry of University and Research (MUR) funded by the European Union - NextGenerationEU - Project code PE_00000004, CUP B83C22004890007, Project title "3A-ITALY - Made-in-Italy circolare e sostenibile".

References:
[1] W. Giurlani, M. Innocenti et all. , Electroplating for Decorative Applications: Recent Trends in Research and Development, Review, Coatings 2018, 8(8), 260.

Electrochemical impedance spectroscopy (EIS) as a valuable technique for the quantification of additives in electroplating baths

A. Comparini[a], M. Verrucchi[a], W. Giurlani[a], A. De Luca[a], A. Meoli[a], M. Voroboya[a,b], M. Innocenti[a,b,c,d]

[a]Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 3, 50019 Sesto Fiorentino (FI), Italy; [b]National Interuniversity Consortium of Materials Science and Technology (INSTM), Via G. Giusti 9, 50121 Firenze (FI), Italy; [c]National Research Council-Organometallic Compounds Chemistry Institute (CNR-ICCOM), Via Madonna del Piano 10, 50019 Sesto F.no (FI), Italy; [d]Center for Colloid and Surface Science (CSGI), Via della Lastruccia 3, 50019 Sesto F.no (FI), Italy.
m.innocenti@unifi.it

Organic additives are commonly used in commercial plating baths to ensure high-quality metallic coatings. However, the concentration of these additives decreases over time due to degradation and drag-out, necessitating monitoring and dosing to maintain their concentration and preserve the technical and aesthetic properties of the deposits. The complex matrix of plating baths makes theoretical predictions of the effect of a single compound difficult, and the function of additives is the result of the interaction of one with another [1]. Consequently, conventional chromatographic methods are not typically used in industrial environments for the determination of these additives. Electrochemical methods represent a reliable alternative, enabling quantitative analyses that consider the effects of additives on the electrodeposition rate regardless of their chemical nature, while also providing useful information about the condition of the bath [2].

We conducted Cyclic Voltammetric Stripping (CVS) measurements, which correspond to the state of art, on a commercial acid copper plating bath to determine the concentrations of the three main additives generally used in these baths: suppressor, brightener, and leveller. Depending on the additive under investigation, various analytical methods, such as dilution titration and standard additions, were selected. Due to the complex nature of the baths and the need to consider the interaction between additives, reliable results are hard to obtain with this method.

We also conducted Electrochemical Impedance Spectroscopy (EIS) experiments to characterize the deposition process in terms of resistive and capacitive components. EIS provides a wealth of information about the system under study with minimal experimentation, making it of great interest in both industrial and academic settings. Its application in the galvanic field is particularly useful for achieving a detailed understanding of the function of each additive, their interactions, and the aging of plating baths.

Project funded under the National Recovery and Resilience Plan (NRRP), Mission 4 Component 2 Investment 1.3 - Call for tender No. 341 of 15 March 2023 of Italian Ministry of University and Research (MUR) funded by the European Union - NextGenerationEU - Project code PE_00000004, CUP B83C22004890007, Project title "3A-ITALY - Made-in-Italy circolare e sostenibile".

References:
[1] P. Taephaisitphonges et al., J. Electroche. Soc., 2001, 148, C492
[2] B. Xie et al., J. Electroche. Soc., 2007, 154, D516

Probing the interaction of antimicrobial metal nanoparticles with lipid membranes by fluorescent probes

M. Izzi[a], M. Oliver[b], M. Miró[b], N. Cioffi[a]

[a]*Department of Chemistry, University of Bari Aldo Moro, via Orabona 4, 70126 Bari, Italy*
[b]*Department of Chemistry, University of the Balearic Islands, Carretera de Valldemossa km 7.5, E-07122 Palma de Mallorca, Spain*
margherita.izzi@uniba.it

Copper nanoparticles (CuNPs) have been proposed worldwide as antimicrobial agents, providing a strategic approach to fight antimicrobial resistance and biofilm formation. Due to their increasing use in several real-life goods, significant concerns about their potential toxicity are arising and appropriate legislation is being issued in different countries. Particularly, the well-known health risks related to the NP size-controlled unprecedented reactivity should be considered. In this regard, metal nanoparticles should be investigated not only in terms of their direct biological effects, but also for the actual processes dictating their human bioavailability. The first step in investigating the toxicity mechanisms of nanoantimicrobials is the exploration of permeability and distribution of NPs in cell membranes. To this end, lipid nanoparticles, also known as liposomes, have been consolidated as an artificial biomembrane model to explore the potential *in vitro* supramolecular interactions of contaminants (e.g., inorganic nanostructures) with the phospholipids composing the membrane. In particular, NP-membrane interaction can induce membrane deformation, NP absorption or wrapping, depending on the size, composition and properties of the NP-membrane system [1]. This contribution presents an analytical chemistry holistic approach for the assessment of the interactions between ultra-small CuNPs and phospholipid membranes. Large unilamellar vesicles (LUVs) made of soybean phosphatidylcholine, with an average diameter of 100 nm, were used as biomimetic eukaryotic cell membranes. 4 nm-sized CuNPs were synthesized by means of a wet-chemical route that involves the glutathione (GSH) as stabilizer and characterized by UV–vis absorption spectroscopy, fluorescence spectroscopy, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared (FTIR) spectroscopy. Then, a fluorescence spectroscopic investigation of the interaction of CuNPs with liposomes was carried out to study their potential membranotropic effects. The individual incorporation of two fluorescent membrane probes bearing naphthalene moieties (namely, Laurdan and Prodan) was used to investigate the interactions with the biomembranes [2,3]. In particular, such probes are able to penetrate into the phospholipid bilayer at different depths. Laurdan, due to the lauryl acyl chain, is located inside the membrane at the level of glycerol backbone, whereas Prodan is placed closer to the lipid-aqueous interface ,at the polar group. Their fluorescent properties, which depend on the polarity of the microenvironment they are surrounded by, allow low resolution monitoring of changes in bilayer organization by generalized polarization (GP) measurements, providing specific information about alterations in lipid order, packing and hence membrane hydration and permeability. Specifically, the results demonstrated a fluorescence hypsochromic shift, which is attributed to the progressive membrane dehydration at the hydrophobic-hydrophilic interface region of the membrane in which probe's fluorophore is aligned. Furthermore, such results suggested an enhancement of lipid packing in the presence of CuNPs. The methodology will be extended to screen the potential risk of different antimicrobial MeNP systems.

References:

[1] C. Contini, M. Schneemilch, S. Gaisford and N. Quirke, Journal of Experimental Nanoscience, 2018, 13, 62–81.
[2] M. Oliver, A. Bauzá, A. Frontera and M. Miró, Environ. Sci. Technol., 2016, 50, 7135–7143.
[3] M. Oliver, M. Adrover, A. Frontera, J. Ortega-Castro and M. Miró, Science of The Total Environment, 2020, 738, 140096.

Spectroscopic characterization of bioactive coatings for food packaging applications

M. Izzi[a], *M. C. Sportelli*[a], *A. V. Montefusco*[a,b], *D. D'Agostino*[a], *R. A. Picca*[a], *N. Cioffi*[a]

[a] *Department of Chemistry, University of Bari Aldo Moro, via Orabona 4, 70126 Bari, Italy;*
[b] *Department of Electrical and Information Engineering, Polytechnic of Bari, Bari, Italy*
margherita.izzi@uniba.it

Bioactive nanomaterials can help in the fight against antibiotic resistance and biofilm formation. Antimicrobial ability can be conferred to polymeric matrices by embedding inorganic nanoparticles of suitable composition, such as silver, copper and zinc oxide. Stabilized nanostructures (NSs) are able to release active ions, under defined kinetics, that inhibit bacterial growth [1-2]. Antimicrobial materials have been already applied as active components for the development of food packaging coatings [3,4]. In this field, there has been a growing incentive to use sustainable materials with reduced harmfulness towards humans and the environment, which gradually have been replacing synthetic petroleum-based polymers. In this context, we aim at exploring the combination of naturally occurring compounds or biodegradable polymers with non-toxic metal-based nanostructures. The use of zinc oxide nanostructures (ZnONSs) is continuously growing, due to their biocompatibility and low toxicity. ZnONSs can be electrosynthesized by using a sacrificial Zn anode in an aqueous electrolytic bath [5] as alternative approach to conventional methods. Both anionic and cationic stabilizers can be dissolved in the electrolytic bath, resulting in different NS morphologies, ranging from spheroidal particles to rice-grain, rod-like or nano-sea-urchin structures. Flower-like NSs have been successfully tested against *Bacillus subtilis* as a Gram-positive model microorganism [6]. Besides them, green and sustainable syntheses of silver and copper nanoparticles have been investigated, in order to produce safe metal-based antimicrobials for the development of environmentally friendly coatings, based on natural-sourced compounds, such as zein, chitosan and alginate. In this contribution, the analytical characterization of the composite materials developed in our laboratories will be presented. X-ray Photoelectron Spectroscopy (XPS) provided quantitative information about metal surface availability, and its surface chemical state. Atomic or UV-Vis Absorption Spectroscopy allowed investigating metal ion release in aqueous contact media. The morphological features of the NPs as well as the potential release of entire nanoparticles from treated materials was studied by Transmission Electron Microscopy (TEM) on contact solutions. Conclusions will be drawn about the safety and efficiency of the mentioned composites.

References:
[1] M. Sportelli, M. Izzi, A. Volpe, V. Lacivita, M. Clemente, C. Di Franco, A. Conte, M. A. Del Nobile, A. Ancona, N. Cioffi, Food Packaging and Shelf Life 22 (2019) 100422.
[2] M. C. Sportelli, M. Izzi, A. Volpe, M. Clemente, R. A. Picca, A. Ancona, N. Cioffi, Applied Surface Science 507 (2020) 145156.
[3] D. Kışla, G. G. Gökmen, G. A. Evrendilek, T. Akan, T. Vlčko, P. Kulawik, A. R. Jambrak, F. Ozogul, Trends in Food Science & Technology, 135 (2023) 144.
[4] R. Singh, S. Dutt, P. Sharma, A. K. Sundramoorthy, A. Dubey, A. Singh, S. Arya, Global Challenges, 7,4 (2023), 2200209.
[5] M. Izzi, M.C. Sportelli, N. Ditaranto, R.A. Picca, M. Innocenti, L. Sabbatini, N. Cioffi, ChemElectroChem 2020, 7, 386.
[6] M.C. Sportelli, M. Izzi, E. A. Kukushkina, S. I. Hossain, R. A. Picca, N. Ditaranto and N. Cioffi, Nanomaterials, 2020, 10, 802.

Combined Reflectance and Fluorescence VNIR imaging for the Study of Coloured Textiles: the role of chemometric strategies in the processing of multiblock hyperspectral data

Z. Li[a], *G. Sciutto*[a], *A. Candeo*[b], *M. Ghirardello*[b], *S. Prati*[a], *E. Catelli*[a], *P. Oliveri*[c], *R. Mazzeo*[a], *D. Comelli*[b]

[a] *Dept. of Chemistry, Università di Bologna – Ravenna Campus, Via Guaccimanni 42, 48121, Ravenna, Italy;*
[b] *Dept. of Physics, Politecnico di Milano, P.zza Leonardo da Vinci 32, Milano, Italy;*
[c] *Dept. of Pharmacy, Università di Genova, via Cembrano, 4, 16148, Genova, Italy*
zelan.li2@unibo.it

Natural dyes have been used to colour textiles for centuries, and their preservation is vital for conservation and maintaining of the historical value of the cultural heritage objects. The identification and study of natural dyes and their aging are crucial to ensure effective conservation and planning the most adequate intervention. While micro-invasive techniques such as high-performance liquid chromatography[1][2], Raman-SERS[3], and FTIR spectroscopies[4] permit the precise identification of dyes (or their chemical classes), they require sample collection and often lengthy pre-treatment of the specimen. In recent years, advances in hyperspectral imaging technologies opened reliable possibilities for the straightforward, rapid and non-invasive characterization of dyes in textiles.

In this study, we propose a multimodal imaging approach for investigating dyed wool yarns *in situ* with a custom-made hyperspectral imaging system, without the need of sample collection. The approach combines the results of macroscopic hyperspectral reflectance (400-1000nm) and fluorescence (540-1000nm) imaging, taken with the same spatial dimension and pixel resolution and hence spatially correlated.

To analyse the data obtained from the multimodal imaging approach, a chemometric multi-block data processing method was applied to enhance the complementary information embedded in the reflectance and fluorescence hyperspectral datasets. The chemometric strategy, based on the combination of principal component analysis (PCA), proved to be highly efficient for the extraction and integration of the most useful information coming from the different spectroscopies, through an effective data visualization and inter-correlation assessment. The approach was applied to different dyed wools at different aging stages, revealing the presence of volumetric inhomogeneities in the wool yarn induced by aging. The results demonstrate that the proposed multimodal imaging approach, with the aid of data fusion, allows for a more comprehensive and nuanced analysis of the physical and chemical changes during the aging process of dyed wool samples, providing valuable information for the ageing assessment, monitoring and conservation management of the coloured textiles.

References:
[1] C. Mouri and R. Laursen, “Identification of anthraquinone markers for distinguishing Rubia species in madder-dyed textiles by HPLC,” Microchimica Acta, vol. 179, no. 1–2, pp. 105–113, Aug. 2012, doi: https://doi.org/10.1007/s00604-012-0868-4.
[2] M. Shahid, J. Wertz, I. Degano, M. Aceto, M. I. Khan, and A. Quye, “Analytical methods for determination of anthraquinone dyes in historical textiles: A review,” Analytica Chimica Acta, vol. 1083, pp. 58–87, Nov. 2019, doi: https://doi.org/10.1016/j.aca.2019.07.009.
[3] M. Leona, J. Stenger, and E. Ferloni, “Application of surface-enhanced Raman scattering techniques to the ultrasensitive identification of natural dyes in works of art,” Journal of Raman Spectroscopy, vol. 37, no. 10, pp. 981–992, 2006, doi: https://doi.org/10.1002/jrs.1582.
[4] S. Prati, M. Milosevic, G. Sciutto, I. Bonacini, S. G. Kazarian, and R. Mazzeo, “Analyses of trace amounts of dyes with a new enhanced sensitivity FTIR spectroscopic technique: MU-ATR (metal underlayer ATR spectroscopy),” Analytica Chimica Acta, vol. 941, pp. 67–79, Oct. 2016, doi: https://doi.org/10.1016/j.aca.2016.09.005.

Preliminary results on archaeological materials from Miaswan Project (Mummies Investigations Anthropological and Scientific West Aswan Necropolis)

C. A. Lombardi[a,b], *V. Comite*[b], *V. Guglielmi*[b], *A. D'Amato*[c], *A. Tomaino*[d]
P. Piacentini[d], *P. Fermo*[b]

[a]*Dipartimento di Scienze dell'Antichità, Università La Sapienza, 00185 Roma, Italy;* [b]*Dipartimento di Chimica, Università degli Studi di Milano, 20133 Milano, Italy;*[c]*Dipartimento di Scienza Farmaceutiche, Università degli Studi di Milano, 20133 Milano, Italy;* [d]*Dipartimento di Studi Letterari, Filologici e Linguistici, Università degli Studi di Milano, 20133 Milano, Italy*
chiara.lombardi@unimi.it

The identification of the compounds utilised in the creation of painted objects of artistic and historical meaning is important, since it can give vital information such as the painting technique and the availability of natural pigments and/or the capability of the production of pigments from raw materials and, consequently, information concerning the technological expertise in a particular historical period. Furthermore, the chemical-physical characterisation of materials can also permit the detection of possible previous restoration or conservation work. In some events, it can even supply information about the authenticity and/or dating of the artwork. Research studies conducted in this field were able to identify the array of colours the ancient Egyptians had at their disposal [1-8]. The following work aimed to investigate the nature and composition of the pictorial layers of four different Egyptian artefacts found in West Aswan, Egypt. In particular, spectroscopic analyses were performed on artefacts excavated in the area surrounding the Mausoleum of the Aga Khan, within the campaign of Miaswan Project and headed by Prof. Piacentini. The necropolis covers around 1000 years (6th cent. BCE-4th cent. CE). The analysed artefacts were three different cartonnages and one piece of pottery. Strict Egyptian laws prohibit the possibility of taking samples from artefacts and then transporting them to other countries, which is why the use of portable instrumentation was essential. The investigations were carried out by means of portable ATR/FTIR for in-situ analyses to highlight the nature of the pigments present on the samples. The artefacts analysed with this technique were then moved from their original location (the tombs) to a storage room where the measurements were carried out. In addition to FTIR, visible reflectance analyses were also performed by means of a portable spectrophotometer. In this case, it was possible to use the instrument directly on the artefacts at their place of discovery, so the colorimetric analyses were done on-site. The analyses performed by infrared spectroscopy revealed several pigments, including red ochre, yellow ochre and Egyptian blue. A particularly interesting pink pigment was made mixing hematite and calcium carbonate. By studying the data obtained by reflectance spectroscopy, it can be deduced that the pigments applied on the studied cartonnage are the same for each colour and the palette remains confined to a limited range of pigments.

References:

[1] Bonizzoni et al., 2016 Bonizzoni, L., Bruni, S., Guglielmi, V., Milazzo, M., & Neri, O. (2011). Field and laboratory multi-technique analysis of pigments and organic painting media from an Egyptian coffin (26th dynasty). *Archaeometry*, *53*(6).

[2] David, A. R., Edwards, H. G. M., Farwell, D. W., & De Faria, D. L. A. (2001). Raman spectroscopic analysis of ancient Egyptian pigments. *Archaeometry*, *43*(4)

[3] Hallmann, A., Rickerby, S., & Shekede, L. (2021). Blue and green in the decoration of a Kushite chapel in Karnak, Egypt: Technical evaluation using low-tech, non-invasive procedures. *Journal of Archaeological Science: Reports*, *39*

[4] Lombardi, C. A., Comite, V., Fermo, P., Bergomi, A., Trombino, L., & Guglielmi, V. (2023). A Multi-Analytical Approach for the Characterisation of Pigments from an Egyptian Sarcophagus Cover of the Late Dynastic Period: A Case Study. *Sustainability*, *15*(3)

[5] Pagès-Camagna, S., & Raue, D. (2016). Coloured materials used in Elephantine: Evolution and continuity from the Old Kingdom to the Roman Period. *Journal of Archaeological Science: Reports*, *7*

[6] Pozza, G., Ajò, D., Chiari, G., De Zuane, F., & Favaro, M. (2000). Photoluminescence of the inorganic pigments Egyptian blue, Han blue and Han purple. In *Journal of Cultural Heritage*, *1*

Spectroscopic characterization of corrosion processes on galvanic coatings

I. Maccioni[a,b], *F. Pizzetti*[b], *G. Pappaianni*[a], *A. Meoli*[a], *E. Mariani*[a], *C. Giovani*[a,c], *R. Emanuele*[d], *M. Innocenti*[a,c,e,f]

[a]Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 3, 50019 Sesto Fiorentino (FI), Italy; [b]Rubinetterie 3M S.r.l, Via E. Mattei 10, 53041 Asciano (SI), Italy; [c]National Interuniversity Consortium of Materials Science and Technology (INSTM), Via G. Giusti 9, 50121 Firenze, Italy; [d]Valmet Plating S.r.l. Via Erbosa, 5, 50041 Calenzano (FI), Italy; [e]Institute of Chemistry of Organometallic Compounds (ICCOM) – National Research Council (CNR), Via Madonna del Piano 10, 50019 Sesto Fiorentino (FI), Italy; [f]Center for Colloid and Surface Science (CSGI) Via della Lastruccia 3, 50019 Sesto Fiorentino (FI), Italy
irene.maccioni@unifi.it

The electrodeposition of metals and alloys is one of the most widely exploited techniques in the jewelry and faucet industry, in order to obtain coatings with specific aesthetic and mechanical characteristics.

Two of the most commonly electrodeposited metals are chromium, nickel and their alloys with other elements; these finishes, in addition to their decorative purpose, also have the important task of providing protection to substrates, generally made of nonnoble alloys such as brass and ZAMAK, against corrosive agents.

One of the major issues affecting galvanic deposits is corrosion resistance, which is dependent on the type of metal deposited, the thickness of the various layers that make up the coating and their quality [1].

Four finishes composed of different layers were investigated: (i) Bright Nickel; (ii) Nickel Phosphorus (NiP); (iii) White Chromium(VI); (iv) Black Chromium(III). Cr(III) was chosen because of its lower toxicity compared to Cr(VI), while NiP alloy was investigated because of its high corrosion resistance capabilities [2].

In this work we aim to evaluate some finishes by determining the colorimetric coordinates via spectrophotometry, surface composition through SEM-EDS analysis and the thickness determination of the layers by using XRF analysis [3].

In addition, to estimate the corrosion resistance of the coatings, the samples were subjected to two tests to simulate the aging process: Damp Heat test (ISO 4611:2010) and Neutral Salt Spray test (ISO 9227:2017).

Since the results of the aging tests are semi-qualitative, we performed a further characterization of the samples by performing SEM-EDS and colorimetric analysis also after subjecting the samples to Neutral Salt Spray and Damp Heat tests; the scope of these analysis was to obtain, in addition to the visual (subjective) evaluation, an objective estimation of the corrosion level by using colorimetric (ΔE) and compositional differences.

References:

[1] W. Giurlani *et al.*, "Electroplating for decorative applications: Recent trends in research and development," *Coatings*, vol. 8, no. 8. MDPI AG, Aug. 01, 2018. doi: 10.3390/coatings8080260.

[2] B. Elsener, M. Crobu, M. A. Scorciapino, and A. Rossi, "Electroless deposited Ni-P alloys: Corrosion resistance mechanism," *J Appl Electrochem*, vol. 38, no. 7, pp. 1053–1060, Jul. 2008, doi: 10.1007/s10800-008-9573-8.

[3] W. Giurlani, E. Berretti, M. Innocenti, and A. Lavacchi, "Measuring the thickness of metal coatings: A review of the methods," *Coatings*, vol. 10, no. 12. MDPI AG, pp. 1–36, Dec. 01, 2020. doi: 10.3390/coatings10121211.

Cerium oxide Nanoparticles stabilized by PLGA micelles and englobed in gelatine and starch films

V. Marchianò[a], M. Matos[b], G. Gutierrez[b], M. C. Blanco-Lopez[c], N. Cioffi[a,d], N. Ditarant[a,d]

[a]CSGI – Centre for Colloid and Surface Science, Bari Unit, Bari, Italy; [b]Department of Chemical and Environmental Engineering, University of Oviedo, Julián Clavería 8, 33006 Oviedo, Spain; [c]Department of Physical and Analytical Chemistry, University of Oviedo, Julián Clavería 8, 33006 Oviedo, Spain; [d]Department of Chemistry, Università degli Studi di Bari Aldo Moro, via Orabona 4, 70125 Bari, Italy
verdiana.marchiano@gmail.com

In the last years, cerium oxide nanoparticles (CeO_2NPs) have caught the attention in research world related to biomedical field. Particularly, antimicrobial and antibiofilm activity is being investigated [1]. In this work, a new system based on CeO_2NPs protected in a polymeric matrix formed by PLGA micelles was developed, to avoid the rapid oxidation of cerium oxide. The synthesis of CeO_2NPs was carried out following the W/O microemulsion method [2]. Subsequently CeO_2NPs were encapsulated in PLGA micelles. Encapsulation in micelles was performed according to the single emulsion/solvent method [3]. All formulations (free NPs, empty micelles and loaded micelles) were incorporated in two types of films for food packaging use, according to solvent casting method, equilibrating the right ratio between gelatine or starch and glycerol. The main components of these films were gelatine or maize starch, both in different ratio with glycerol. The chemical and physical characterization of the NPs and micelles solutions was carried out by Dynamic Light Scattering (DLS), to determine the size and zeta-potentials, Transmission Electron Microscopy (TEM), and X-ray Photoelectron Spectroscopy (XPS). The interactions among the film matrix compounds and the incorporated colloids (micelles and NPs) were investigated by Scanning Electron Microscopy (SEM) and XPS: blank films were compared with films incorporating micelles and NPs [4-5].

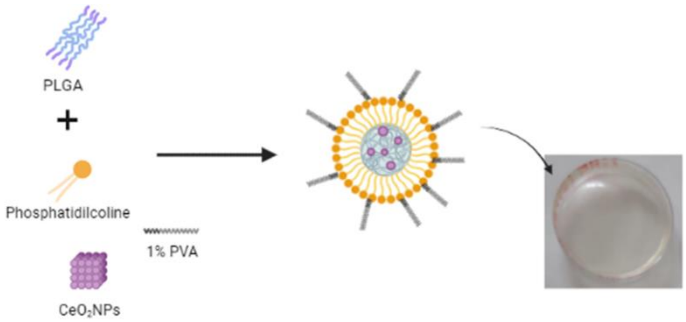


Figure 1- Synthesis and encapsulation of CeO_2NPs in PLGA micelles incorporated in films.

References:
[1] Thakur, N.; Manna, P.; Das, J. Synthesis and biomedical applications of nanoceria, a redox active nanoparticle. J. Nanobiotechnol. 2019, 17, 84.
[2] Salvador, M., Gutiérrez, G., Noriega, S., Moyano, A., Blanco-López, M. C., & Matos, M. (2021). Microemulsion synthesis of superparamagnetic nanoparticles for bioapplications. International Journal of Molecular Sciences, 22(1), 427.
[3]Bazsefidpar, S., Moyano, A., Gutiérrez, G., Matos, M., & Blanco-López, M. C. (2021). Lipid–Polymer Hybrids Encapsulating Iron-Oxide Nanoparticles as a Label for Lateral Flow Immunoassays. Biosensors, 11(7), 218.
[4]. M. Romeo, K. Bak, J. El Fallah, F. Le Normand, and L. Hilaire, "XPS Study of the reduction of cerium dioxide," Surf. Interface Anal., vol. 20, no. 6, pp. 508–512, 1993.
[5] J. El Fallah, L. Hilaire, M. Roméo, and F. Le Normand, "Effect of surface treatments, photon and electron impacts on the ceria 3d core level," J. Electron Spectros. Relat. Phenomena, vol. 73, no. 1, pp. 89–103, May 1995.

Morphological and Spectroscopic Characterization of Self-Templated Highly Porous Gold (h-PG) as D-(-)-Fructose Amperometric Biosensor

V. Marchianò[a], A. Tricase[bc], N. Ditaranto[bc,], E. Macchia[b,cd,], K. Sowa[ef] ,
C. Di Franco[f], L. Torsi[a,c,d] ,P. Bollella[b,c]

[a] CSGI - Centre for Colloid and Surface Science, -Bari Unit, Bari (Italy; [b]Dipartimento di Chimica, Università degli Studi di Bari Aldo Moro, 70125 Bari , via Orabona 4,Italy; [c]Dipartimento di Farmacia-Scienze del Farmaco, Università degli Studi di Bari Aldo Moro,via Orabona 4 70125 Bari,Italy .[d]Faculty of Science and Engineering, Åbo Akademi University, 20500 Turku Finland; [e]Division of Applied Life Sciences, Graduate School of Agriculture, Kyoto University, Kitashirakawa Oiwake-cho, Sakyo-ku, Kyoto, 606-8502, Japan;[f] Istituto di Fotonica e Nanotecnologie CNR, c/o Dipartimento Interateneo di Fisica, Università degli Studi di Bari Aldo Moro,via Orabona 4, Bari, 70125 Italy.
verdiana.marchiano@gmail.com

In the last decades, nanomaterials have shown great advantages in terms of functional properties for a wide range of technological applications [1]. Metal nanoparticles provide a lot of advantages compared to macroelectrodes, such as enhancement of mass transport, catalysis, high effective surface area and control on the electrode conductive microenvironment. Highly porous gold (h-PG) can be synthesized by using a chemical approach and electrodeposition. The main advantages of the electrodeposition method are the thickness, roughness and size control of the h-PG layer [2].

In this work h-PG was directly electrodeposited onto a gold electrode (AuE) by using a two-steps method: 1) sweeping the potential in a 10 mM HAuCl4 solution (supporting electrolyte 2.5 M NH4Cl); 2) applying a potential -3 V vs. Ag|AgClsat [3,4]. Initially we optimized the different parameters that can affect the electrodeposition process, such as scan numbers, concentration of precursor solution, etc.

Afterwards, the nanostructured electrodes were characterized by scanning electron microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS). The so modified electrodes were further characterized with Fe(CN)63-/4- by cyclic voltammetry and electrochemical impedance spectroscopy, and compared to the naked gold electrode (AuE) in order to determine the electroactive area (AEA), electron transfer rate constant (k0), real surface area (Areal) and the roughness factor (ρ) [5].

Finally, the electrodes were modified with FDH and poly(vinyl alcohol), N-methyl-4(4'-formylstyryl)pyridinium methosulfate acetal (PVA-SbQ) to detect D-(-)-fructose in fruit juice samples as potential on-line biosensor for food industrial production processes [6].

References:
[1] S.D. Minteer, Top. Catal. 55 (2012) 1157-1161.
[2] J. Zhang, M. Oyama, Anal. Chim. Acta 540 (2005) 299-306.
[3] X. Dai, R.G. Compton, Anal. Sciences 22 (2006) 567-570
[4] G. Sanzó, I. Taurino, R. Antiochia, L. Gorton, G. Favero, F. Mazzei, G. De Micheli, S. Carrara, Bioelectrochemistry 112 (2016) 125-131.
[5] I. Lavagnini, R. Antiochia and F. Magno, Electroanalysis 16 (2004) 505-506.
[6] R. Antiochia, I. Lavagnini, F. Magno, Anal. Letters 37 (2004) 1657-1669.

Colour evaluation via everyday tools: cameras and smartphone

A. Meoli[a,b], F. Biffoli[a], I. Maccioni[a], E. Mariani[a], E. Carretti[a,c], W. Giurlani[a,d], M. Innocenti[a,c,d,e]

[a]Department of Chemistry "Ugo Schiff", University of Florence, via della Lastruccia 3, 50019 Sesto Fiorentino, Italy; [b]Creazioni Lorenza Srl, via Fiorentina 18, 50063 Figline Valdarno; [c]Center for Colloid and Surface Science (CSGI), via della Lastruccia 3, 50019 Sesto Fiorentino, Italy; [d]National Interuniversity Consortium of Materials Science and Technology (INSTM), via G. Giusti 9, 50121 Firenze, Italy; [e]Institute of Chemistry of Organometallic Compounds (ICCOM)-National Research Council (CNR), via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy
arianna.meoli@unifi.it

Colour evaluation is an important aspect for industrial applications, especially for electroplating processes involving decorative applications. Colour, indeed, is used as quality control of the surface deposits of manufactured goods, which have to be conform to required colorimetric characteristics [1].

The evaluation of colorimetric coordinates can be performed with UV-Vis spectrophotometry or, more commonly and rapidly, with a portable spectrophotometer. The colour information are extracted by exploiting the CIELAB color space via the measurement of three parameters, L*, a* and b*, which indicate, respectively: the brightness, the red-green component and the yellow-blue component [2].

In addition to classic techniques, colorimetric coordinates could be measured by using images captured by a digital camera or smartphone using a colorimetric references and dedicated software for image processing. The reference is used during image processing to rework the images and obtain accurate colors of the image ; this step is done to ensure that the information obtained is evaluable and represents the color of the object being studied as realistically as possible, regardless of the lighting conditions [3].

At the end of reprocessing, the colorimetric coordinates L*, a* and b*, described above can be obtained.

This project aims to perform and compare colorimetric measurements obtained with UV-Vis spectrophotometer, a portable spectrophotometer, a digital camera and a smartphone. Sample composed of different finishes made by galvanic deposits of gold, palladium, rhodium and/or their alloys were measured.

The colorimetric coordinates obtained for each instrument described above were compared to assess the possibility of making colorimetric determination more accessible, especially in situations such as industry, where often advanced instruments (e.g., spectrophotometer) are not available.

References:
[1] Giurlani, W., Giambinossi, F.; Salvietti, E.; Passaponti, M.; Innocenti, M. "Color Measurements In Electroplating Industry: Implication For Product Quality Control" *ECS Transactions*, 2017, 80, 757-766.
[2] Ibraheem, N. A.; Hasan, M.M.; Khan, R.Z.; Mishra, P.K. "Understanding Color Models: A Review"*ARPN Journal of Science and Technology*, VOL.2, NO. 3, April 2012, pp. 265-275.
[3] Vitorino, T.; Casini, A.; Cucci, C.; Gebejes, A.; Hiltunen, J.; Hauta-Kasari, M.; Picollo, M.; Stefani, L. "Accuracy in Colour Reproduction: Using a ColorChecker Chart to Assess the Usefulness and Comparability of Data Acquired with Two Hyper-Spectral System" *Springer International Publishing Switzerland*, 2015, pp. 225–235, DOI: 10.1007/978-3-319-15979-9_21.

Electrosynthesis and analytical characterization of antimicrobial mixed oxides for cultural heritage applications

M. Izzi[a]*, M. C. Sportelli*[a]*, D. Quarato*[a]*, N. Cioffi*[a]*, R. A. Picca*[a]

[a]*Chemistry Department, University of Bari Aldo Moro, via E. Orabona 4, 70125 Bari, Italy*
rosaria.picca@uniba.it

Nanomaterials are receiving attention as alternative or complementary tools for stone consolidation or against biodeterioration in the field of cultural heritage [1,2]. For example, $Ca(OH)_2$ nanostructures (NSs) are consolidating agents for carbonatic stones [3], whereas ZnO NSs have excellent antimicrobial properties [4]. Novel multifunctional approaches combining different properties in a single treatment are then particularly appealing. Moreover, there is an increasing demand to implement sustainable strategies with low environmental and health impact also in this field. With this aim, we have developed a novel synthetic approach for the preparation of synergistic nanomaterials combining the antimicrobial activity of ZnO NSs with the consolidating properties of nanolime as suitable treatments designed for carbonatic stones [5]. In this contribution, this green strategy based on the sacrificial anode electrolysis preparation of ZnO NSs and a precipitation method for $Ca(OH)_2$ NSs will be presented. Both nanomaterials grow simultaneously in the same medium using NaOH solution. The process is performed under deaerated conditions at 80°C, obtaining a precipitate that is washed and dried under vacuum. Results about the morphological (TEM) and spectroscopic (FTIR, XPS) characterizations of the as-synthesized nano-oxides will be shown. NSs with different morphology and composition were obtained by tuning the concentration of Ca precursor. Stable suspensions of the proposed hybrid NSs were prepared and brushed on suitable specimens to develop suitable coatings. Finally, contact angle measurements, Zn^{2+} ion release as well as their antimicrobial activity against *Bacillus subtilis* will be also reported.

References:
[1] I. Franco-Castillo, L. Hierro, J.M. de la Fuente, A. Seral-Ascaso, S.G. Mitchell, Perspectives for antimicrobial nanomaterials in cultural heritage conservation, Chem. 7 (2021) 629–669. https://doi.org/10.1016/j.chempr.2021.01.006.
[2] N. Ditaranto, I.D. van der Werf, R.A. Picca, M.C. Sportelli, L.C. Giannossa, E. Bonerba, G. Tantillo, L. Sabbatini, Characterization and behaviour of ZnO-based nanocomposites designed for the control of biodeterioration of patrimonial stoneworks, New J. Chem. 39 (2015) 6836–6843. https://doi.org/10.1039/C5NJ00527B.
[3] C. Rodriguez-Navarro, A. Suzuki, E. Ruiz-Agudo, Alcohol Dispersions of Calcium Hydroxide Nanoparticles for Stone Conservation, Langmuir. 29 (2013) 11457–11470. https://doi.org/10.1021/la4017728.
[4] M.C. Sportelli, R.A. Picca, M. Izzi, G. Palazzo, R. Gristina, M. Innocenti, L. Torsi, N. Cioffi, ZnO Nanostructures with Antibacterial Properties Prepared by a Green Electrochemical-Thermal Approach, Nanomaterials. 10 (2020) 473. https://doi.org/10.3390/nano10030473.
[5] M. Izzi, M. Chiara Sportelli, R. Anna Picca, N. Cioffi, Electrochemical Synthesis and Analytical Characterization of Hybrid Zinc/Calcium Antimicrobial Nano-Oxides for Cultural Heritage Applications, ChemElectroChem. 10 (2023) e202201132. https://doi.org/10.1002/celc.202201132.

Development and characterization of antimicrobial composites for food packaging containing bioactive species

R. A. Picca[a], M. C. Sportelli[a], S. M. Sanzani[b], F. Caponio[b], G. Difonzo, L. Gentile[a],
G. Palazzo[a], A. Ippolito[b], N. Cioffi[a]

[a]Dipartimento di Chimica, Università degli Studi di Bari Aldo Moro, Bari; [b]Dipartimento di Scienze del Suolo della Pianta e degli Alimenti, Università degli Studi di Bari Aldo Moro, Bari
rosaria.picca@uniba.it

This research aims at studying innovative and low environmental impact solutions to improve the biological safety and the sensory quality of perishable fruits and vegetables (strawberries, tomatoes, etc.) and extend their shelf life. In order to achieve a reduction in bacterial proliferation during primary and secondary shelf life, active food packaging materials have been here developed [1]. These materials are characterized by the presence of a biodegradable/recyclable polymer matrix, which is loaded with bioactive agents; the latter ensure the limitation of spoilage formation. Specifically, two different approaches were exploited. First, some soluble salts of bioactive metal ions of oligoelements (preferably Cu^{2+}, Ca^{2+} or Zn^{2+}) and active molecular agents have been exploited, also in combination with non-harmful ion exchangers like montmorillonite. Second, aqueous and green/low impact approaches were chosen for the production of colloidal metal or metal oxide nanoparticles (NPs) of Cu, Zn and Ca. These formulation were embedded in polymers already commonly used in food industry, like polyethylene oxide (PEO), polylactic acid (PLA), etc. [2]. This, along with the use of cardboard packaging boxes, helps reducing the use of highly pollutant petroleum-based plastics. Morphological and spectroscopic characterizations were performed on both bioactive formulations and polymeric composites. Infrared, UV-Vis, and X-ray photoelectron spectroscopies were used to this aim. Release kinetics of bioactive ions were assessed, in order to foresee the antimicrobial and/or antifungal properties of the prepared composites. Either spectrophotometric assays or atomic absorption spectroscopy were exploited.

Authors acknowledge the Project “Imballaggio Attivo Ortofrutticoli”, Grant n° J98H23000070008, from the “Ministero dell’Agricoltura, della Sovranità Alimentare e delle Foreste” for the finantial support to this research.

References:
[1]. Wikström, F., Verghese, K., Auras, R., Olsson, A., Williams, H., Wever, R., Grönman, K., Kvalvåg Pettersen, M., Møller, H. and Soukka, R. (2019), Packaging Strategies That Save Food: A Research Agenda for 2030. Journal of Industrial Ecology, 23: 532-540.
[2] Sportelli, M.C., Izzi, M., Volpe, A., Clemente, M., Picca, R.A., Ancona, A., Cioffi, N. (2020), Novel polyethylene oxide coatings implementing ultra-stable laser-ablated silver nanoparticles, Applied Surface Science, 507, 145156.

Overcoming beam damage in In-situ XAS: study of Ni-$SrTiO_3$ deactivation during overall photocatalytic water splitting

M. Pinna[a,b], *M. T. Abudukade*[b], *D. Spanu*[a], *A. Minguzzi*[c], *P. Ghigna*[d], *S. Recchia*[a], *G. Mul*[b], *M. Altomare*[b]

[a]Dipartimento di Scienza e Alta Tecnologia, Università degli studi dell'Insubria, Via Valleggio 9, Como 22100, Italy; [b]Faculty of Science and Technology, University of Twente, Drienerloaan 5, Enschede 7522 NB, The Netherlands; [c]Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, Milan 20133, Italy; [d]Dipartimento di Chimica, Università degli Studi di Pavia, Via Taramelli 16, Pavia 27100, Italy
mpinna@uninsubria.it

Spectroscopic measurements under in-situ conditions are a powerful tool to investigate catalytic systems as they help clarify the mechanism of reactions of interest. X-ray Absorption Spectroscopy (XAS) is element-specific and provides information on electronic structure and local geometry. Hence, it has been widely applied to study heterogenous catalysts. With the advent of high brilliance synchrotron however, the effect of beam damage cannot be ignored. In particular, reducing effects have been reported on both organic, inorganic, and biological systems [1-3]. Thus, a proper X-ray irradiation time must be chosen to avoid exposing the sample to an excessive photon flux. In the present case study, $SrTiO_3$ powders decorated with Ni@NiO_x core-shell nanoparticles were employed for photocatalytic overall water splitting under UV light (365 nm). Previous studies [4] suggested that UV illumination of the catalyst causes oxidation of the metallic Ni core to Ni(II) species (NiO/$Ni(OH)_2$) and of the NiO_x shell to NiOOH. Moreover, partial dissolution of the co-catalyst was confirmed by ex situ Inductive Coupled Plasma Mass Spectrometry (ICP-MS) measurements. In-situ X-ray Near Edge Spectroscopy (XANES) measurements in fluorescence mode were performed at DESY synchrotron (beam line P65, Hamburg, Germany) to understand how Ni oxidation states changes and its possible dissolution relates to the deactivation of photocatalyst (*Figure 1b*) proven by Gas Chromatography (GC). However, reproducing the experiment in the co-presence of the X-ray beam, leads to a different behavior: due to beam damage, no change in the relative composition of Ni oxidation is noticeable. For this reason, we decided to study in detail this effect by systematically changing the X-ray exposition time during UV illumination. The effect of different X-ray beam exposures can be noticed by looking at the relative composition of Ni oxidation state reported in *Figure 1a*. The lower the exposition to the probing beam, the more oxidized the co-catalyst. Combining the obtained XANES results with GC data (*Figure 1b*) it can be seen that the increase in Ni oxidation coincides with a reduced photocatalytic H_2 production, at the same time the H_2:O_2 ratio (<<2) confirms that the photogenerated holes (h^+) are used to oxidize Ni and not for photocatalytic O_2 production. The oral presentation will provide a rationale of the beam damage processes and how to minimize them.

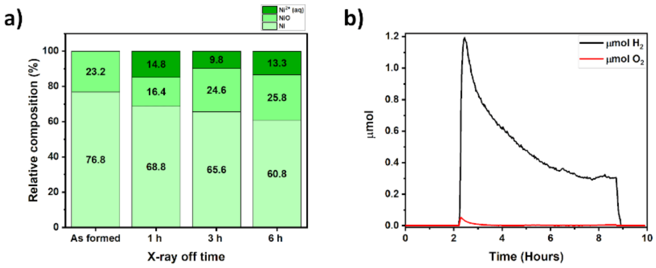


Figure 1: In a) relative composition of the Ni co-catalyst after 7h long UV illumination with different X-ray exposition, in b) kinetic test for overall water splitting reporting µmoles for produced H_2 and O_2

References:
[1] Phys. Chem. Chem. Phys., 2022,24, 21916-21926
[2] J. Phys. Chem. B 2005, 109, 9, 4042–4047
[3] X-Ray Spectrom 2022, 51(3), 294.
[4] ACS Catal. 2017, 7, 3, 1610–1614

New advances in the application of NIR hyperspectral based methods for the non destructive characterization of artistic multilayered artefacts and archeological remains

S. Prati[a], G. Sciutto[a], R. Alberti[b], S. Benazzi[c], E. Catelli[a], T. Frizzi[b], L. Gatti[a], Z. Li[a], C. Malegori[d], M. Occhipinti[b], P. Oliveri[d], S. Talamo[e], A. Tocchio[b], R. Mazzeo[a]

[a]University of Bologna, Department of Chemistry "G. Ciamician", Ravenna Campus, Via Guaccimanni, 42, 48121, Ravenna, Italy; [b]XGLab SRL - Bruker Nano Analytics, Via Conte Rosso 23, I-20134 Milano, Italy; [c]Department of Cultural Heritage, University of Bologna, Via degli Ariani 1, 48121, Ravenna, Italy; [d]University of Genova, Department of Pharmacy, Viale Cembrano 4, I-16148, Genova, Italy; [e]Department of Chemistry G. Ciamician, Alma Mater Studiorum, University of Bologna Via Selmi 2, Bologna, 40126, Italy
s.prati@unibo.it

Near-infrared hyperspectral techniques have been employed in the study of cultural heritage thanks to the penetration of the NIR radiation, which may reach up to hundreds of microns inside the surface of the artifacts, depending on the energy of the source, the incident angle, and the material physical properties. Infrared reflectography techniques, for instance, allows to reach the preparation drawing of a painting discovering repaintings and pentimenti.

When hyperspectral techniques are employed a distribution of the compounds active in the NIR range can be non-invasively achieved, obtaining information also from the inner layers.

In this contribution two recent applications of NIR hyperspectral (NIR-HIS) method for the non-destructive characterisation of multi-layered artefacts and for the pre-screening of archaeological bones prior to their sampling for further micro-destructive analyses [1-2] are presented.

A recently commercialized analytical set up (IRIS XGLAB, an analytical instrument developed in the framework of the project "MOBARTECH", co-financed by Regione Lombardia POR FESR 2014 – 2020) which is able to co-register simultaneously VNIR, SWIR and XRF spectral data, has been exploited in combination with a tailored data processing method for the analyses of multi-layered painting layers [1]. NIR and XRF spectroscopies have the advantage to go in-depth inside the sample up to several microns and to provide elemental and molecular information. The chemometric strategy adopted, based on principal component analysis and correlation maps, allowed to obtain useful information for the reconstruction of the paint stratigraphy without the need to take any sample.
NIR-HSI was also used to build a multivariate regression model for the prediction of collagen content and distribution in ancient bones [2], as a prescreening approach to choice the most collagen rich areas to be sampled for further micro-destructive investigations, such as radiocarbon dating.
This approach is extremely promising since archaeological remains can be extremely precious and are considered a cultural and historical patrimony.

References:
[1] Catelli, E., Li, Z., Sciutto, G., Oliveri, P., Prati, S., Occhipinti, M., Tocchio, A., Alberti, R., Frizzi, T., Malegori, C., Mazzeo, R. Towards the non-destructive analysis of multilayered samples: A novel XRF-VNIR-SWIR hyperspectral imaging system combined with multiblock data processing(2023) Analytica Chimica Acta, 1239, art. no. 340710,
[2] Malegori C., Sciutto G., Oliveri P., Prati S., Gatti L., Catelli E., Benazzi S., Cercatillo S., Palecek D., Mazzeo R., Talamo S., Near-infrared hyperspectral imaging to map collagen content in prehistoric bones for radiocarbon dating (2023) Communications Chemistry, in press.

Characterization of unknown animal glues from artwork samples by structural, rheological and thermal analysis

E. Pulidori[a]*, E. Crisci*[a]*, M. R. Tinè*[a]*, L. Birolo*[b]*, G. Ntasi*[b]*, E. Bramanti*[c]*, I. Bonaduce*[a]*, C. Duce*[a]

[a]*Department of Chemistry and Industrial Chemistry, University of Pisa, Via G. Moruzzi 13, Italy;* [b]*Department of Chemical Sciences, University of Naples Federico II, Complesso monte Sant' Angelo Via Cinthia 21, Italy;* [c]*Institute of Chemistry of Organometallic Compounds, National Research Council, Via G. Moruzzi 1, Italy*
elena.pulidori@unipi.it

Animal glues have been widely used as adhesives and binders in various fields [1]. The earliest uses date back to ancient Egypt, where animal glues were used to fix wood inlays with ebony and ivory, to anchor faience to pyramid walls, or as a binder in pigments [1]. Animal glues are produced by hydrolysis of animal tissues such as bone, skin, cartilage, and connective tissue and during the production process, collagen, the major protein component of animal tissues, is partially hydrolyzed [2,3]. In this study, samples of animal glue obtained from artworks and provided by Museo Nacional del Prado (Madrid) and Restoration Workshop of the University Suor Orsola Benincasa (Naples) were characterized from a structural, thermal, and rheological point of view to determine possible correlations between macroscopic properties and the molecular structure of collagen. ATR-FTIR analysis was carried out to investigate the collagen structure, while thermal analysis was performed to study the thermal degradation and the degree of denaturation of collagen by using thermogravimetric analysis and differential scanning calorimetry (DSC), respectively. Modulated-DSC was used for the first time to study the physical ageing of a fibrous protein, collagen, by determining the enthalpy relaxation value. Overall, the results obtained allowed the identification of two main groups of glues, namely strong glues and weak glues, characterized by different degrees of hydrolysis of collagen and consequently different viscoelastic properties, temperature range of thermal decomposition and decomposition rates.

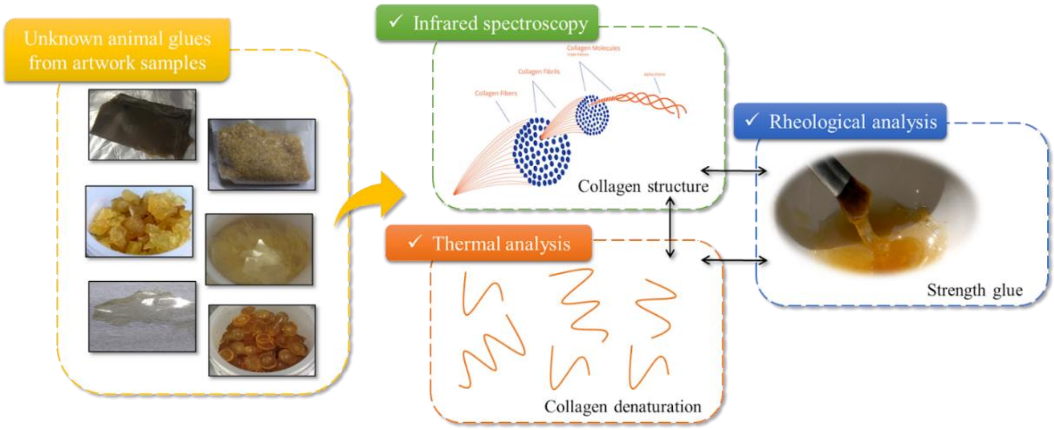


Figure 1. Schematic representation of the characterization carried out on animal glue samples from artworks.

References:
[1] Schellmann N. C. Animal Glues: A Review of Their Key Properties Relevant to Conservation. Stud. Conserv. 2007; 52:55–66.
[2] Ebnesajjad S.Characteristics of Adhesive Materials. In Handbook of Adhesives and Surface Preparation, William Andrew Publishing: Oxford, 2011; pp 137–183.
[3] Fay P. A. A History of Adhesive Bonding. In Adhesive Bonding. 2nd ed. Woodhead Publishing; 2021;3–40.

Electrochemical pH-controlled apo-Ferritin Bionanoreactors for CdSe nanoparticles synthesis

A. Tricase[a,b], *V. Marchianò*[b], *N. Ditaranto*[a,b], *E. Macchia*[c,d], *R. Gupta*[e], *L. Torsi*[a,b,d], *P. Bollella*[a,b]

[a]Dipartimento di Chimica, Università degli Studi di Bari Aldo Moro, 70125 Bari (Italy), [b]Centre for Colloid and Surface Science - Università degli Studi di Bari Aldo Moro 70125, Bari (Italy), [c]Dipartimento di Farmacia – Scienze del Farmaco, Università degli Studi di Bari "Aldo Moro", Bari, 70125 Italy, [d]Faculty of Science and Engineering, Åbo Akademi University, 20500 Turku (Finland), [e]School of Chemistry, University of Birmingham, Birmingham (UK)
angelo.tricase@uniba.it

Semiconducting nanoparticles (SNPs) have applications ranging from sensing to medical imaging [1]. Fluorescent and other properties of nanoparticles are size dependent [2]. Current methods used to make nanoparticles result in large variations in their size, which is far from ideal. Furthermore, current methods are not green, requiring organic solvents. Nature has provided proteins that have uniform size cavities in their centers. These cavities can act as reaction vessels to make uniformly sized nanoparticles in aqueous conditions. A challenge is to be able to recycle these proteins so that each protein can make many nanoparticles. This in turn requires triggering and monitoring of multiple cycles of synthesis and release of nanoparticles to achieve a sustainable process [3,4].

In this wok, size-controlled synthesis of Cadmium-Selenide (CdSe)NPs were carried out using aproferritin/ferritin nanoreactors as exemplars. We designed an electrode comprising substrate, noble metal film, hydrogel, and covalently attached laccase-aproferritin. Voltage was applied to increase the local pH, resulting in apoferritin to fold and act as nanoreactors and synthesis of (CdSe)NPs to start. Similarly, local pH was decreased to release synthesized (CdSe)NPs. The hydrogel film on top of metal film acted as broadband LW i.e., partially confined white light. This partially confined light interacted with immobilized apoferritin, allowing measurement of optical absorption and refractive index of the protein, related to the concentration of (CdSe)NPs in its core. Moreover, several spectroscopic (e.g., XPS, IR etc.) and morphological characterizations were performed to analyze (CdSe)NPs. Finally, we were able to monitor the nanoparticles formation by measuring the variation of refractive index at the interface by using an optical sensor [5]. The approaches described in this work will be adaptable to diverse SNPs and protein nanoreactors [6,7].

References:
[1] Bai et al. J. Mater. Chem. B 2022, 10, 6248-6262
[2] Deka et al. Carbon Lett. 2022, 32, 1131-1149
[3] Duan et al., Chem. Soc. Rev. 2015, 44, 5778-5792
[4] Shah et al., Materials 2015, 8, 7278-7308
[5] R. Gupta et al., Anal. Chem. 2019, 9, 7366-7372
[6] P. Bollella et al., ChemElectroChem 2020, 7, 3386-3403
[7] P. Bollella et al., ChemElectroChem 2021, 8, 3923-3935

Analytical investigation of SAMs-modified gold electrodes

A. Tricase[a,b]*, V. Marchianò*[b]*, N. Ditaranto*[a]*, R. A. Picca*[a,b]*, E. Macchia*[c,d]*, G. Scamarcio*[e]*, D. Blasi*[a]*, P. Bollella*[a]*, L. Torsi*[a,d,e]

[a]*Dipartimento di Chimica, Università degli Studi di Bari "Aldo Moro", 70125 Bari (Italy)*; [b]*CSGI (Centre for Colloid and Surface Science), 70125 Bari (Italy);* [c]*Dipartimento di Farmacia – Scienze del Farmaco, Università degli Studi di Bari Aldo Moro, 70125 Bari;* [d]*The Faculty of Science and Engineering,Åbo Akademi University, 20500 Turku (Finland);* [e]*Dipartimento Interateneo di Fisica "M. Merlin",Università degli Studi di Bari "Aldo Moro", 70125 Bari (Italy)*
angelo.tricase@uniba.it

Self-assembled monolayers (SAMs) were widely studied in the last decades, gaining an increasing interest thanks to their implementation in different bioelectronic devices as surface plasmon resonance (SPR) and field-effect transistors (FETs) [1,2]. SAMs growth for biosensor application typically consists in a mixed SAM, where a longer chain is used to anchor the biorecognition element and a shorter one as spacer, increasing both the functionalization yield and the performance of the final devices. Mixed SAMs were exploited in the gate electrode development for biosensors based on electrolyte gated organic field-effect transistors (EGOFETs), able to reach the physical limit of detection [3]. In similar devices SAMs are typically used to efficiently immobilize the biorecognition element [4], but Macchia et al. hypothesized a role in improving device performance thanks to the formation of a diffuse hydrogen bonding network between chains [3]. In this regard, a combined strategy of electrochemical, X-ray photoelectron spectroscopy (XPS) and Grazing Angle – Attenuated Total Reflectance (GA-ATR) Infrared Spectroscopy experiments was carried out. This approach was used to investigate of SAMs conformational reorganization onto an electrode surface due to the application of an electrical field [5]. In particular, 3-mercaptopriopionic acid SAM (3MPA SAM)-modified gold electrodes were activated with a 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) and N-hydroxysulfosuccinimide (NHSS) (EDC/NHSS) by shortening the activation time, from 2 h to 20 min, labelled as Protocol-A, -B and -C, respectively. In fact, this step plays a key role in the reaction yields (formation of N-(2-hydroxyethyl)-3-mercaptopropanamide, NMPA) but also in the conformational rearrangement observed during the application of the electrical field [6,7]. Moreover, differential pulse voltammetry (DPV) in NaOH 0.1 M was used to estimate the reductive desorption of functionalized SAMs. These results were compared with well-known trend available for other SAM structures for correlating supramolecular behaviour of the SAM due to the electric field application with performance of EGOFETs biosensors.

References:
[1] K. V. Gobi, K. Matsumoto, K. Toko, H. Ikezaki, and N. Miura, "Enhanced sensitivity of self-assembled-monolayer-based SPR immunosensor for detection of benzaldehyde using a single-step multi-sandwich immunoassay", Anal. Bioanal. Chem, 387, 8, 2727–2735 (2007);
[2] S. Casalini, C. A. Bortolotti, F. Leonardi, and F. Biscarini, "Self-assembled monolayers in organic electronics," Chem. Soc. Rev., 46, 1, 40–71, (2017);
[3] E. Macchia et al., "Single-molecule detection with a millimetre-sized transistor," Nat. Commun., 9, 1, (2018);
[4] F. Leonardi, A. Tamayo, S. Casalini, and M. Mas-Torrent, "Modification of the gate electrode by self-assembled monolayers in flexible electrolyte-gated organic field effect transistors: Work function: Vs. capacitance effects," RSC Adv., 8, 48, 27509–27515, (2018);
[5] A. Tricase et al., "Electrochemical and X-ray Photoelectron Spectroscopy Surface Characterization of Interchain-Driven Self-Assembled Monolayer (SAM) Reorganization," Nanomaterials , 12, 5. (2022);
[6] S. Sam et al., "Semiquantitative study of the EDC/NHS activation of acid terminal groups at modified porous silicon surfaces," Langmuir, 26, 2, 809–814, (2010);
[7] A. Tricase et al., "Surface composition of mixed self-assembled monolayers on Au by infrared attenuated total reflection spectroscopy," Appl. Surf. Sci., 559, 149883 (2021)

Spectroscopic characterization of PVD coatings for decorative applications

M. Vorobyova[a,b], L. Donati[b], D. Bettoni[a,b], E. Cioppi[b], W. Giurlani[a,b], M. Linser[d], M. Innocenti[a,b], A. Caneschi[c]

[a]INSTM, via Giuseppe Giusti, 9, 50121, Florence, Italy; [b]Dipartimento di Chimica "Ugo Schiff", University of Florence; [c]Department of Industrial Engineering, University of Florence, Via di S. Marta 3, 50139 Firenze, Italy; [d]LEM INDUSTRIES S.P.A,Via Leo Valiani, 45/47, 52021 Bucine AR
mariya.vorobyova93@gmail.com

Physical vapor deposition (PVD) coatings are widely used for decorative applications due to their durability, wear and corrosion resistance, and ability to provide a range of colours. Characterization of these coatings is critical for understanding their structure and composition, and several spectroscopic techniques are available for this purpose. In this study, we focus on the application of energy-dispersive X-ray spectroscopy (EDX) in scanning electron microscopy (SEM), X-ray fluorescence (XRF), electrochemical impedance spectroscopy (EIS), and colorimetric spectroscopy to evaluate and develop new protective and eco-friendly systems in PVD, applied directly on the brass substrate bypassing the standard procedure that involves an electroplated nickel layer.

Brass substrates are commonly used in the manufacturing industry due to their desirable properties, but their inadequate corrosion resistance negatively affects the final products' quality. The following investigation was on the applications of Cr/CrN coatings on brass substrate using spectroscopic techniques such as EDS-SEM, SEM, and XRF [1]. Specifically, we prepared five thin films of Cr/CrN with different N_2/Ar ratios and analysed their homogeneity, chemical composition, colour coordinates, thickness, and structure. Colorimetric measurements with Vis-Spectrophotometer were also carried on. From these analyses, we selected the 0.4 N_2/Ar ratio for CrNx layers and created a multilayer film of Cr/CrN. Furthermore, we performed electrochemical tests such as free corrosion test OCP, Electrochemical Impedance Spectroscopy (EIS), and neutral salt spray (NSS) test (ISO 9227:2017) to compare the performance of different combinations of engineered multilayer films and optimize their suitability for protective applications. Working on the modification of pressure conditions in the vacuum chamber, we can explore new design possibilities for the application of Cr/CrN coatings on brass substrates. The results achieved contribute to the development of coatings that improve the corrosion resistance of brass while maintaining a desirable appearance.

Spectroscopic techniques provided valuable information on the elemental composition, thickness, surface morphology, electrochemical behaviour, and colour of the coatings, respectively. We discussed the advantages and limitations of these techniques and their applications in the characterization of various PVD coatings. Overall, these spectroscopic techniques provide a comprehensive understanding of the structural and compositional properties of PVD coatings for decorative applications.

The authors acknowledge Regione Toscana POR CreO FESR 2014-2020 – azione 1.1.5 sub-azione A1 – Bando 1 "Progetti Strategici di ricerca e sviluppo" which made possible the project: "RAM-PVD" (CUP 3647.04032020.157000057_1225).

References:
[1] Giurlani et al. Coatings 2018, 8, 84.

Sponsors

Ringraziamo le ditte per la sponsorizzazione dell'Incontro Spettroscopia Analitica ISA 2023 a Milano

nanoVision	Società Chimica Italiana Sezione Lombardia
MADAtec	DIPCHI DIPARTIMENTO DI CHIMICA
ThermoFisher SCIENTIFIC	JEOL

PROGRAMMA MERCOLEDÌ 14/06/2023

Ore 14.00-15.00

REGISTRAZIONE

Ore 15.00-16.00

Saluto delle autorità Maria Pia Abbracchio - Prorettrice dell'Università degli studi di Milano.

Premiazione e Relazione del vincitore Premio Mazzucotelli conferito da Alice Mazzucotelli

GIURLANI W. Application of computational methods to analytical spectroscopy techniques for the characterization of films and metal alloys
Department of Chemistry "Ugo Schiff", University of Florence
National Interuniversity Consortium of Materials Science and Technology (INSTM)

Sessione 1

Ore 16.00-16.15

IZZI M. Probing the interaction of antimicrobial metal nanoparticles with lipid membranes by fluorescent probes
Department of Chemistry, University of Bari Aldo Moro

Ore 16.15-16.30

CASULA G. Growth and Characterization by ARXPS of (3-mercaptopropyl) trimethoxysilane (MPTMS) films on Gold and Food-Grade PVC
Department of Chemical and Geological Sciences, University of Cagliari

Ore 16.30-16.45

VOROBYOVA M. Spectroscopic characterization of PVD coatings for decorative applications
National Interuniversity Consortium of Materials Science and Technology (INSTM)
Department of Chemistry "Ugo Schiff", University of Florence

Ore 16.45-17.00

BIGGIO D. Unravelling the composition of surface films formed on Ni-free DIN 1.4456 stainless steel for orthodontics by XPS
Department of Chemical and Geological Sciences, University of Cagliari

Ore 17.00-17.15 **SPONSOR THERMO FISHER**

Sessione 2

Ore 17.15-17.30

MACCIONI I. Spectroscopic characterization of corrosion processes on galvanic coatings

Department of Chemistry "Ugo Schiff", University of Florence

Rubinetterie 3M S.r.l

Ore 17.30-17.45

MARCHIANÒ V. Cerium oxide Nanoparticles stabilized by PLGA micelles and englobed in gelatine and starch films

CSGI-Centre for Colloid and Surface Science, Bari Unit

Ore 17.45-18.00

PICCA R.A. Electrosynthesis and analytical characterization of antimicrobial mixed oxides for cultural heritage applications

Department of Chemistry, University of Bari Aldo Moro

Ore 18.00 **Aperitivo di benvenuto**

PROGRAMMA GIOVEDÌ 15/06/2023

Ore 9.00-9.30 **Invited lecture**

FELIPE CONZUELO - Instituto de Tecnologia Química e Biológica António Xavier, Universidade Nova de Lisboan, Oeiras, Portugal

Scanning Photoelectrochemical Microscopy for the Study of Light-Dependent (Bio)electrochemical Reactions

Sessione 3

Ore 9.30-9.45

BONECHI M. A spectroscopic investigation of palladium recovery from electroplating solutions using carbon materials and electrochemical reduction

Department of Chemistry "Ugo Schiff", University of Florence

Ore 9.45-10.00

DITARANTO N. Correlation between surface chemical composition and catalytic activity of MnO_2- based catalysts

Department of Chemistry, University of Bari Aldo Moro
CIRC, Interuniversity Consortium on Chemical Reactivity and Catalysis, Bari
CSGI-Centre for Colloid and Surface Science, Bari Unit

Ore 10.00-10.15

PINNA M. Overcoming beam damage in In-situ XAS: study of Ni-$SrTiO_3$ deactivation during overall photocatalytic water splitting

Department of Science and High Technology, University of Insubria
Faculty of Science and Technology, University of Twente

Sessione 4

Ore 10.15-10.30

GORLA G. How explore raw data characteristics and sources of uncertainty could be a crucial step for spectroscopic method development-

Department of Science and High Technology, University of Insubria

Ore 10.30-10.50 **SPONSOR NANOVISION**

Ore 10.50-11.45 **Coffee Break e** **SESSIONE POSTER I**

Sessione 5

Ore 11.45-12.00
CAMPANELLA B. Aqueous derivatization by ethyloxonium salts extended to the analysis of methionine and selenomethionine in foods
Institute of Chemistry of Organometallic Compounds, National Research Council

Ore 12.15-12.30
BELLASSAI N. Functional antifouling coating on plasmonic platform for Lysozyme aptamer-based detection in food sample
Department of Chemical Sciences, University of Catania
Biostructures and Biosystems National Institute (INBB)

Ore 12.30-12.45
FORNASARO S. Surface enhanced Raman scattering of crevicular fluid in periodontics and implantology
Department of Chemical and Pharmaceutical Sciences, University of Trieste

Ore 12.45-13.00
GIUSSANI B. A new process control tool based on ATR-FT-IR spectroscopy and dissimilarity index to identify anomalies in wine alcoholic fermentation
DISAT, University of Insubria

Ore 13.00-14.30 **Pranzo libero**

Ore 14.30-14.45 **SPONSOR JEOL**

Sessione 6

Ora 14.45-15.00
TRICASE A Analytical investigation of SAMs-modified gold electrodes
Department of Chemistry, University of Bari Aldo Moro
CSGI-Centre for Colloid and Surface Science, Bari Unit

Ore 15.00-15.15
MEOLI A. Colour evaluation via everyday tools: cameras and smartphone
Department of Chemistry “Ugo Schiff”, University of Florence
Creazioni Lorenza S.r.l

Ore 15.15-15.30
D’AGATA R. Advances in Diagnostics using Plasmonic-based Imaging Sensor and liquid biopsy approaches
Department of Chemical Sciences, University of Catania
Biostructures and Biosystems National Institute (INBB)

Ore 16.00- 17.00 **Coffee Break e** **SESSIONE POSTER II**

Ore 17.00-18.00 **Gita Sociale**
Ore 18.30 **Aperitivo Sociale**

PROGRAMMA VENERDÌ 16/06/2023

Ore 9.00-9.30 **Invited lecture**

FEDERICA POZZI - Direttrice dei Laboratori Scientifici. Centro per la Conservazione ed il Restauro dei Beni Culturali "La Venaria Reale", Italia

The Visconti-Sforza tarocchi cards: unveiling court secrets through analytical spectroscopy

Sessione 7

Ore 9.30-9.45

PRATI S. New advances in the application of NIR hyperspectral based methods for the non destructive characterization of artistic multilayered artefacts and archeological remains

Department of Chemistry “G. Ciamician”, University of Bologna, Ravenna Campus

Ore 9.45-10.00

BERGOMI A. Characterization of black crusts from the Monumental Cemetery (Milan) using a combined LIBS and Raman approach

Department of Chemistry, University of Milan

Ore 10.00-10.15

GUGLIELMI V. The Identification of Pigments through Non-Invasive Spectroscopic Analyses: the Bernardino Luini Frescoes of Santuario della Beata Vergine dei Miracoli in Saronno (Italy) as a Case Study

Department of Chemistry, University of Milan

Ore 10.15 -10.30 **SPONSOR MADATEC**

Ore 10.30-11.30 **Coffee Break e SESSIONE POSTER III**

Sessione 8

Ore 11.30-11.45

PULIDORI E. Characterization of unknown animal glues from artwork samples by structural, rheological and thermal analysis

Department of Chemistry and Industrial Chemistry, University of Pisa

Ore 11.45-12.00

LOMBARDI C.A. Preliminary results on archaeological materials from Miaswan Project (Mummies Investigations Anthropological and Scientific West Aswan Necropolis)

Department of Sciences of Antiquity, University “La Sapienza”
Department of Chemistry, University of Milan

Ore 12.00-13.00 **Riunione del gruppo di spettroscopia analitica**

Ore 13.00-13.15 **Conclusioni finali**