## SERS methodologies and practical considerations for analyses in cultural heritage

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The history of SERS in the field of cultural heritage spans 30 years having emerged suitable for the detection and identification of trace organic colorants and pigments in objects of artistic and archaeological importance. The added advantages over conventional Raman spectroscopy afforded by the physical and chemical processes occurring in the vicinity of nanoscale metal surfaces permits simultaneous fluorescence quenching and signal amplification<sup>1-2</sup>. This ultimately assists in tackling the challenges when investigating irreplaceable antique and contemporary artifact through the combined application of further complementary techniques, which together are capable of answering the different historical and conservation questions. Supplying a high molecular selectivity, specificity and sensitivity on sample sizes comparable to other instrumental methods makes SERS an increasingly go-to, quasi-routine technique in this field. Dedicated research over the years has permitted the efficient performance of metal substrates to coincide with advancing instrumental set-ups and microscopic sample pre-treatment methods that undergo ad-hoc optimization for the characterization of the numerous natural and synthetic classes of colorants most commonly encountered<sup>3-4</sup>. This work has led to the construction of comprehensive databases, which are necessary for a better understanding of features pertaining to heterogeneous mixtures of colorants and degradation phenomena<sup>5</sup>. Although still very much of a microdestructive nature here, SERS shows potential for in-situ applications, very much the next milestone for cultural heritage artefacts. This contribution intends to provide a practical resource by addressing the main SERS analytical methodologies while outlining current advantages, challenges and ultimate limitations through the presentation of significant case studies within different types of works of art and archaeological artefacts.

[1] H. G. M. Edwards, J. M., Chalmers in Raman Spectroscopy in Archaeology and Art History Royal, Society of Chemistry (GB) 2005.

[2] E. Le Ru, P., *Etchegoin in Principles of Surface-Enhanced Raman Spectroscopy: and Related Plasmonic Effects*, Elsevier, 2009.
[3] B. Doherty, M. Vagnini, K. Dufourmantelle, A. Sgamellotti, B. Brunetti, C. Miliani, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 121, 5, (2014) 292-305.

[4] K. Kato, B. Doherty, I. Degano, F. Sabatini, C. Miliani, A. Romani, K. Ito, B. G. Brunetti, Journal of Raman Spectroscopy 2020, <u>https://doi.org/10.1002/jrs.5856</u>.

[5] F. Pozzi, M- Leona, Journal of Raman Spectroscopy, 47, 1, (2016) 67-77.