Discrimination of organic compounds in ancient and historical materials with *in situ* synchrotron-based X -Ray Raman scattering

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Carbon compounds are ubiquitous and occur in a diversity of chemical forms in many systems including ancient materials, ranging from cultural heritage to paleontology. Determining their speciation cannot only provide unique information on their origin, but may also elucidate degradation processes. Synchrotron-based X-ray absorption near-edge structure (XANES) spectroscopy at the carbon K-edge (280–320 eV) is a very powerful method to probe carbon speciation [1–3]. However, the short penetration depth of soft X-rays imposes stringent constraints on sample type, preparation and analytical environment. A hard X-ray probe can overcome many of these difficulties, and here we report the first use of X-ray Raman Scattering (XRS) based carbon K-edge XANES at 6 keV incident energy [4–6] to characterize the speciation of organic carbon in several specimens relevant to cultural and natural history. Using the backscattering geometry at large photon momentum transfer maximizes the XRS signal at the given X-ray energy and enhances non-dipole contributions compared to conventional XANES, thereby enhancing the speciation sensitivity. We report on experiments carried out at three synchrotron facilities (SOLEIL, SSRL and the ESRF) and show that despite its small cross section the XRS method allows a satisfactory signal to be collected on systems from cultural heritage and paleontology in realistic analytical time frames. It can thus be used as a powerful complement to FT-IR, Raman and conventional XANES spectroscopy, overcoming some of the limitations specifically imposed by these techniques [7].

[1] J. Stohr, NEXAFS spectroscopy; Springer-Verlag Berlin, 1992; Vol. 25.
[2] C. Jacobsen, S. Wirick, G. Flynn, C. Zimba, Journal of Microscopy 197, 2000, 173–184.

[3] H. Bluhm, K. Andersson, T. Araki, K. Benzerara, G. E. Brown, J. J. Dynes, S. Ghosal, M. K. Gilles, H.-C. Hansen, J. Hemminger, et al. Journal of Electron Spectroscopy and Related Phenomena, 150, 2006, 86–104.
[4] U. Bergmann, P. Glatzel, S. P. Cramer, Microchemical Journal, 71, 2002, 221–230.
[5] U. Bergmann, H. Groenzin, O. C. Mullins, P. Glatzel, J. Fetzer, S. Cramer, Chemical Physics Letters, 369, 2003, 184–191.
[6] M. Krisch, F. Sette, C. Masciovecchio, R. Verbeni, Physical Review Letters, 78, 1997, 2843.
[7] L. Bertrand, S. Bernard, F. Marone, M. Thoury, I. Reiche, A. Gourrier, P. Sciau, U. Bergmann, Topics in Current Chemistry, 374, 2016, 1–39.