Non-Destructive XAS Analysis of Pigments Using High-Throughput Gas-Flow Total Electron-Yield Detection

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Over the last decade X-ray absorption spectroscopy (XAS) has become an almost mainstream synchrotron radiation X-ray technique that provides deep chemical analysis of inorganic pigments and other chemical components in works of art, with applications ranging from prehistoric artefacts, via mediaeval works of art, to classic oil and modern acrylic paintings. The standard modes of XAS acquisition are (i) transmission measurements, where X-rays are allowed to pass through the sample of interest and (ii) fluorescence-yield detection, where an X-ray fluorescence detector is placed opposite the spot sampled by the X-ray beam and the spectrum recorded by monitoring the intensity of the characteristic fluorescence form the element of interest.

Non-destructive application of both techniques is restricted, as transmission measurements require samples thin enough to let a significant fraction of the X-ray beam pass through, while fluorescence-yield spectra are accurate representations of the absorption spectrum only when the element of interest is present in dilute concentrations. Many of these limitations in non-destructive sampling can be overcome by total electron-yield detection, which is simply the measurement of the X-ray induced electron/ion current generated by a sample in its surrounding gas. This signal is almost quantitatively proportional to the X-ray absorption coefficient, easy to detect with a biased electrode and a picoammeter, and there are no sample preparation or dilution requirements.

To demonstrate the usefulness of this techniques we have constructed a miniature gas-flow system with a 9-fold sample array. Samples can be mounted on metal tips (diameter: 0.5 mm) of Al stubs that can be quickly removed and inserted into a support block. The block itself is mounted on a computer controlled XYZ-positioning system. The total electron-yield detection chamber is fixed in space and has windows for the incoming X-rays as well as simultaneous transmission (useful for alignment) and fluorescence-yield detection.

1/16” tubing supplies gas into the chamber. The gas-outlet is also a 1/16” tube that is coupled to a quadrupole mass spectrometer for analysis of the headspace composition over the sample. Sample changeover with this system is quick: exchanging a full set of 9 samples can be achieved in approximately 90 s. Gas purging of the sample environment at 100 ml/min completes to >99% purity within 60 s. After initial alignment, automated alignment of samples in the X-ray beam remains better than approximately ±20 µm from the optimum position. This cell array system has been tested with the analysis of an array of historic pigments. Analysable Fe K-edge, Zn K-edge and Cu K-edge electron-yield XAFS data were measured up to $k = 14 \text{ Å}^{-1}$, with about ~15 min acquisition time per absorption edge.