

NEW APPROACHES FOR THREE-DIMENSIONAL MICROANALYSIS OF ENVIRONMENTAL AND CULTURAL HERITAGE MATERIALS

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Recently developed methods of non-destructive analysis, based on the use of synchrotron X-ray (micro) beams allow to employ various alternative procedures for obtaining information on the three-dimensional structure of materials. X-ray fluorescence (XRF) and X-ray diffraction (XRD) analysis are frequently used to examine cultural heritage objects and environmental materials in a complete non-destructive manner. X-ray absorption spectroscopy (XAS) is another X-ray based method capable of providing information on the oxidation state and the chemical environment of specific elements. However, due to the penetrative nature of the primary X-rays, the analysis of heterogeneous or multilayered materials by means of these methods have their limitations, since material at different depths within the sample is simultaneously irradiated and analysed. On the other hand, it is exactly this penetrative nature that is being exploited by X-ray microtomography, a powerful method for non-destructive 3D density mapping

A significant improvement in depth resolution of micro-XRF and micro-XAS can be realised by performing measurements in a confocal excitation/detection geometry, where in optimal conditions, currently depth resolutions of the order of 10 μm can be realised. This achievement can largely be ascribed to the gradual improvement of the performance of the polycapillary optical elements that are used in the confocal detection geometry. Nevertheless, an important limitation of the confocal method of depth profiling is that the depth profiles are strongly affected by the absorption of the incoming and exciting radiation inside the heterogeneous sample being examined and by the complexity of and the uncertainties associated with correcting for this type of secondary effects.

Another method, of which we recently have been exploring the possibilities in the context of paint multilayer characterization is tomographic micro-XRD, a three-dimensional variant of the more conventional scanning micro-XRD method. This method has the advantage that primary radiation of relatively high energy (e.g., 30 to 40 keV) can be employed, which is less affected by absorption effects within the sample itself, thus offering a more linear response. On the other hand, the tomographic data collection procedure imposes limitations of its own in terms of the size and shape of sample fragment that can be examined.

To illustrate the advantages and limitations of both above-mentioned methods, a number of case studies from the cultural heritage and environmental analysis field will be discussed, viz.:

- the characterization of Fe, As and U-rich sediment layers by means of a combination of confocal XAS and scanning micro-XRD, indicating the presence of a reduced As-species at the surface of pyrite microcrystals;
- the analysis of 15th C oil painting and of modern car paint multilayer samples by means of a combination of XRD tomography, confocal XRF and other forms of microscopy, revealing a complex stratigraphy, sometimes composed of more than 10 individual paint layers;
- the elucidation of the internal structure of U-rich spherical particles formed during nuclear explosions by means of a combination of X-ray microtomography and confocal XRF, showing these particles to be composed of at least two phases of different physico-chemical nature, composition and formation history.