Multivariate Curve Resolution with Alternating Least Square Fitting: An optimized algorithm for providing chemical speciation from time-resolved XAS data with a high time frame

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With the advent of 3rd generation synchrotron radiation facilities allowing high time frame for the monitoring of kinetics by X-ray Absorption Spectroscopy (XAS), the experimentalist can now access to a deeper and more accurate temporal description of the chemical species involved in such processes provided that the bottleneck of the data analysis has been overcome. Indeed, users at the time-resolved XAS beamlines have to face with a huge amount of data in a couple of minutes making the common strategy of data evaluation, reduction and analysis quite inefficient. New tools must be proposed to the users to interactively optimize the outcome of an experiment carried out at the beamline. In this framework, chemometric tools such as Multivariate Curve Resolution with Alternating Least Square fitting (MCR-ALS), developed by R. Tauler's group [1], are emerging as a powerful method for getting more information from XAS spectra of evolving mixtures upon catalytic [2,3] or electrochemical reactions [4].

MCR-ALS is a curve resolution method based on a bilinear model, fully verified for spectroscopies obeying to the Beer-Lambert law, which traduces that the measured spectra are a combination of the spectra of the pure species in the system weighted by their respective concentrations. The method includes the determination of the number of components by Principal Component Analysis (PCA), initial estimates for the concentration profile and/or spectra and finally iterative optimization. The MCR-ALS method benefits to the use of physical-chemical constraints, such as non-negativity of concentrations and spectra, closure of concentrations and eventually unimodality to obtain meaningful solutions, including concentration profiles and spectra of unknown intermediates. The XAS spectra of the pure species so-determined by MCR-ALS analysis can be further used in standard EXAFS analysis software for elucidating their local structures.

This presentation will give a brief description of the MCR-ALS method. Examples of its application to time-resolved XAS data acquired upon monitoring reactions will illustrate the strength and limitations of the methodology. The importance of the initial estimates and solutions to solve the problem of correlations between species concentrations will be discussed.

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