Addressing challenges
in individual atom Electron Energy Loss Spectroscopy

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The latest generation of STEM microscopes based on many instrumental developments (C_s corrector focusing lens delivering atomic resolution at lower primary voltages, EELS and EDX detector improvements,...) offers the ability to track in a spectrum-image mode, several signals generated simultaneously by individual atoms [1,2,3] and to rekindle the STEM-EELS spectro-microscopy of single atoms.

A Nion UltraSTEM microscope (USTEM200) equipped with a C_s corrector and with a home-made fast EELS detector, has been used to record a few typical cases illustrating the present situation in individual atom spectroscopy. The ProEM camera (Princeton Instruments) used in the EELS detection chain can be operated in two modes: a Low Noise mode and an Electron Multiplying mode providing a high CCD sensitivity but with a higher read-out noise level. With this new spectroscopic hardware, we can acquire EELS spectrum images (SI) of typically 100x100 pixels and covering a range of 1600 channels at an acquisition rate of 3000 spectra/s. Furthermore, the representation, exploitation and analysis of such data require some specific algorithms. The most widely used technique is the Principal Component Analysis (PCA) which performs dimensionality reduction [4][5] and, as a filtering technique, offers an improvement of the signal to noise ratio. However, for high noise levels, a bias is introduced by PCA as signal bearing components are discarded with the removal of components considered as noise [6]. We have tested some algorithms based on non-local methods for denoising. The non-local means (NL-means) perform denoising by exploiting the natural redundancy of patterns inside an image; they deliver a weighted average of pixels whose neighbourhoods (patches) are close to each other. This significantly reduces the noise while preserving most of the image content.

The first case is the determination of the position of Sm interstitial/substitutional dopants in ceria nanoparticles together with their valence changes in accordance with the variation of the ferromagnetic properties measured as a function of the nominal doping level [7]. The spectrum image has a high noise level and Sm doping could not be identified with usual PCA denoising. The second one addresses the challenge of identifying the characteristic EELS signals from heavy (Tb, Th) atoms in rapid motion on a thin carbon layer, in particular the signal from an individual atom, which imposes a compromise between time acquisition and detection limit (Figure1).

We have first tested Non-Local Sparse PCA (NLSPCA) [8] which produces interesting results: the filtered spectra display fine structures of edges and both spatial and spectral resolutions are preserved. The first good results obtained with NLSPCA encourage us to test this new algorithm on more complex examples to better understand the limitations of such data processing.

This contribution emphasizes the possibilities currently offered by a tiny electron probe, a suitable efficient detector strategy and a well chosen signal analysis tool for single atom spectroscopy.
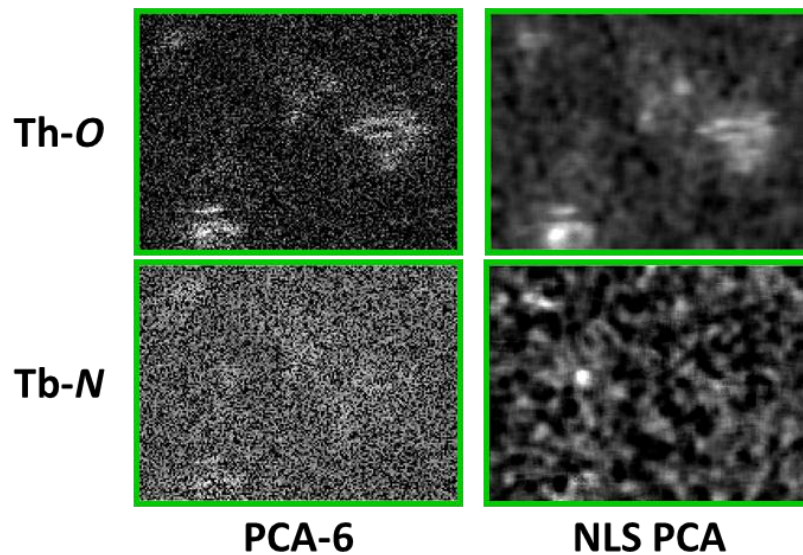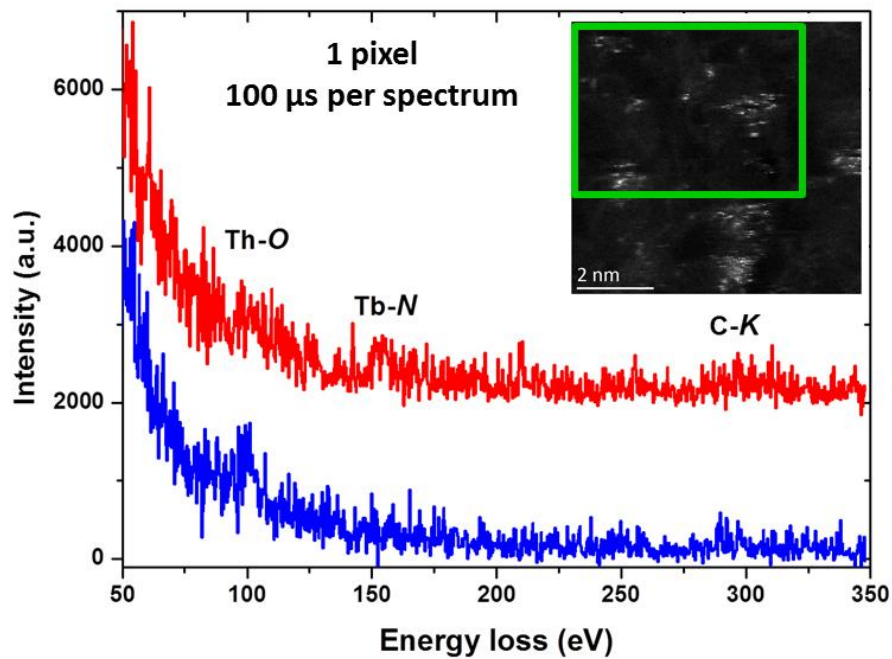
Figure 1: Imaging and spectroscopy of a small area of a DNA filament deposition, stained with 0.1% of Th and 2% of Tb, on a thin carbon foil. Most of the Th and Tb atoms are in motion at the surface under the electron beam (60 kV). Raw EELS spectra extracted from the SI at two different positions (blue and red) – acquisition time: 100 μs per spectrum, in insert: HAADF image at 100 μs per pixel. Comparison of Th and Tb maps from PCA and NLS PCA.

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