Compositional features of zooplankton species as studied by laser-based analytical techniques

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Laser-based techniques are advantageous for the analysis of vast variety of samples. Laser ablation sampling provides the basis for analytical techniques like laser-induced breakdown spectroscopy (LIBS) and inductively coupled plasma mass spectrometry with laser ablation (LA-ICP-MS). These are direct micro-destructive techniques, the former yielding information-rich atomic emission spectra, the latter making possible high sensitivity determination of trace elements. Raman spectroscopy, also based on laser interrogation, gives vibrational spectra characteristic of molecules comprising the sample. We used these techniques together to explore the untrivial compositional features of marine zooplankton, some species of which are known to accumulate Li, As and U. Our goal was to explore correlations between the elemental and molecular composition of these animals.

LIBS and LA-ICP-MS experiments were carried out using the Applied Spectra J200 Tandem LA-LIBS spectrometer (266 nm laser, detection within 186–1049 nm) and Agilent 7700 Series ICP-MS spectrometer. The signals of ^{7}Li, ^{11}B, ^{27}Al, ^{28}Si, ^{34}S, ^{35}Cl, ^{44}Ca, ^{56}Fe, ^{63}Cu, ^{66}Zn, ^{75}As, ^{88}Sr, ^{137}Ba, ^{238}U, ^{23}Na, ^{24}Mg, ^{31}P, and ^{39}K were recorded in the time-resolved mode. Raman measurements were done using the Thermo Scientific DXR Raman Microscope (780 nm laser) in the range of 45–3500 cm^{-1}. In all spectra, baseline was removed, prominent peaks selected and integrated. The resulting matrix of emission, mass, and scattering signals of 29 samples belonging to four biological taxa was analysed using PCA and non-negative matrix factorisation (NMF).

The PCA score plots allowed for a reasonably good discrimination of the animals, especially for two major taxa of *Calanoida* and *Euphasiaceae*. The loadings suggested that the classification was mainly driven by two latent vectors. One of them (more characteristic of *Calanoida*) contained the prominent signals of Li, Al, Cl, Fe, U and carotenoid pigments. The other included the signals of P, K, Ca, Cu, As, Sr, Ba and some Raman peaks. Thus, the accumulation patterns of Li and U are correlated, while As probably follows a different biochemical pathway (e.g. as a companion of P).

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