

03-02: Raman spectroscopy combined with AFM reveals complexity of carotenoid samples

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The paper shows a potential of Raman spectroscopy for analysis of carotenoids in a form of crystals and in the solution as aggregates. Spectroscopic measurements of carotenoid crystals are combined with Atomic Force Microscopy (AFM) and Scanning Near-Field Optical Microscopy (SNOM), whereas aggregates are investigated with the use of Raman Optical Activity (ROA) spectroscopy.

Spectroscopic and microscopic scanning probe measurements were applied to the released crystals or to crystals accumulated in a unique, carotenoids rich callus tissue growing *in vitro*. Three distinct morphological crystal types of various carotenoid composition were identified, a needle-like, rhomboidal and helical. Raman imaging provided evidence that the needle-like and rhomboidal crystals had similar carotenoid composition and that they were composed mainly of β -carotene accompanied by α -carotene. AFM measurements of crystals revealed the crystal topography and showed the needle-like and rhomboidal crystals were planar but they differed in all three dimensions. Combining SNOM and Raman imaging enabled indication of carotenoid rich structures and visualised their distribution in the cell.

In the second part, a stereochemistry of carotenoids is investigated. Carotenoids dissolved in organic-water media can form two types of aggregates: H (card-packed) and J (head-to-tail) that exhibit hypsochromic and bathochromic shift of chromophore absorption, respectively. With the help of (resonance) ROA spectroscopy detailed information about the structure and configuration of chiral, supramolecular carotenoid assemblies is obtained.

References

- [1] RYGULA, R., OLESZKIEWICZ, T., GRZEBELUS, E., PACIA, M.Z., BARANSKA, M., and R. BARANSKI, 2018: Spectrochimica Acta A, **197**, 47-552.