

MELANIN GRANULES IN THE HUMAN HAIR SHAFT SHOWN WITH MULTI-ISOTOPES IMAGING MASS SPECTROMETRY (MIMS)

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Melanin in the epidermis plays an important role in photo protection and the prevention of skin cancers. While it is extremely important to study mammalian melanin granules *in situ* to understand their photochemical properties, their insolubility poses special problems. We used MIMS to study the chemical composition of melanin granules and other components of the human hair shaft at the surface of a cross section. Cryo-sections of hair samples 3 mm thick were prepared according to Hallegot and Corcuff (1993) and deposited on silicon support. They were analyzed with MIMS at a maximum resolution of 35 nm. We recorded in parallel quantitative images at mass ³²S and ³⁴S or at mass ¹⁶O, as ¹²C¹⁴N, and ³²S. The measured ³⁴S/³²S ratio (mean = 4.53% ± 0.28% SD; n = 10) was not significantly different from the terrestrial abundance ratio of 4.52%. The ¹²C¹⁴N map reveals mainly protein distribution and gives the histology of the scanned area. In a mosaic of 20 μm x 20 μm ³²S scans of a cross section of a caucasian hair, the cortex and the layered cuticle are clearly visible. The dark spots represent sulfur-poor eumelanin granules. The ³²S maps show the distribution of high-sulfur proteins in the various regions of the hair shaft. High-sulfur proteins are predominant in the cortex, but are excluded from zones of high CN content, such as the melanin granules. A high resolution image (8 μm x 8 μm; 256 x 256 pixels) reveals a complex distribution of high sulfur and high nitrogen regions in the cuticle and striking aggregates of eumelanin and pheomelanin granules. Finally, we found an inhomogeneous chemical composition of the melanin granules, which exhibit an oxygen-rich pole. An explanation for this asymmetry may be related to the formation of oxygen radicals through photoactivation of the melanin chromophores.

[1] P. Hallégot, P. Corcuff. High-spatial-resolution maps of sulphur from human hair sections: an EELS study. *J. Microsc.* 172 (1993), p.31-136.

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