

# The inherent matrix properties of lichen metabolites in MALDI-TOF MS

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**RATIONALE:**

Light-absorbing secondary metabolites from lichens were recently reported to exhibit promising Laser Desorption Ionization (LDI) properties, enabling their direct detection from crude lichen extracts. In addition, many of them display close structural homologies to commercial Matrix Assisted Laser Desorption Ionization (MALDI) matrices, which is incentive for the evaluation of their matrical properties. The current study systematically evaluated the matrix effects of several structural classes of lichen metabolites: monoaromatic compounds, quinone derivatives, dibenzofuran-related molecules and the shikimate-derived vulpinic acid. Their matrical properties were tested against a wide range of structurally diverse analytes including alkaloids, coumarins, flavonoids and peptides.

**METHODS:**

Triplicate automatic positive-ion mode MALDI analyses were carried out and ionization efficiencies were compared with those of structurally related reference matrices (i.e DHB, HCCA, dithranol and usnic acid) in terms of (i) analyte absolute intensities and (ii) Matrix Suppressing Effect (MSE) scores.

**RESULTS:**

Monoaromatic lichen metabolites revealed matrical properties similar to those of DHB under similar experimental conditions. Likewise, anthraquinone metabolites triggered ionization of tested analytes in a similar way to the structurally related dithranol.

Finally, dibenzofuran derivatives displayed a broad ionization profile, reminiscent of that of (+)-usnic acid.

**CONCLUSIONS:**

Lichen metabolites exhibit interesting matrix properties, especially for MALDI of medium and low molecular weight analytes. For many of the tested molecules, matrix ion formation was very limited. This proof-of-concept study paves the way for follow-up investigations to assess the matrix properties of lichen metabolites against a wider array of analytes as well as adapting experimental settings to individually optimize the performance of successfully tested candidates.

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