SEMIQUANTITATIVE ESI/MS ANALYSIS OF METABOLITES IN BIOLOGICAL MATRICES MADE FEASIBLE VIA PREDICTION OF IONIZATION EFFICIENCIES

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Ionization efficiency in ESI/MS depends on the structure of the compound as well as on the solvent and on the setup used. Here, we demonstrate that ionization efficiencies in biological matrices in negative ESI mode can be predicted based on the charge delocalization parameter *WAPS*, ionization degree α, and a set of calibration compounds. This approach improves the prediction accuracy by more than an order of magnitude.

Ionization efficiencies (expressed in logarithmic units, log*IE*) of 10, predominantly pharmaceutical, compounds were measured in the biological matrices as well as in acetonitrile/0.1% ammonia aqueous solution 80/20 in negative ESI/MS. All the obtained results in matrices were correlated to the log*IE* values obtained in a solvent. In each matrix, the log*IE* prediction model was fitted.

Good correlation between matrices and solvent log*IE* values suggests that ionization efficiencies can be predicted in the matrices similarly to the procedure previously proposed for the solvent. The correlation between measured and predicted log*IE* values over all matrices is high, R^2 = 0.83 and s_{RMSE} = 0.86 log*IE* units. This value shows that on average the mismatch between the predicted and measured ionization efficiencies is lower than 8 times. Up to date, in the absence of authentic standards, equal ionization efficiencies are assumed in all matrices. For the compounds used in this study, this would lead to a mismatch of 660 times with reality. This means, that the proposed approach improves predicting ionization efficiency by more than an order of magnitude.

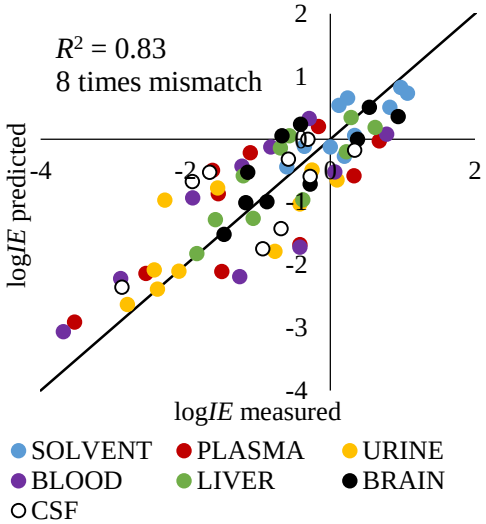

Fig. 1 Correlation of all the measured logIE values and predicted logIE values in different matrices.

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