Berry-based products classification by FIA−HRMS fingerprinting and chemometric analysis

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In recent years, nutraceuticals prepared with cranberry (*Vaccinium macrocarpon*) have gained special attention because of their beneficial effects on human health (*e.g.*, antioxidant activity and antimicrobial activity against bacteria involved in a wide range of diseases), which are mainly attributed to the high content of specific polyphenols in cranberry. However, these products present a risk of fraud consisting of the total or partial substitution of cranberry extracts with cheaper and more abundant fruit extracts.

Therefore, in this study, flow injection analysis coupled to high-resolution mass spectrometry (FIA−HRMS) fingerprinting was proposed as a rapid high-throughput analytical approach to address the classification of berry-based products through chemometrics, focusing on cranberry-based products authentication. Thus, several berry-based natural products (including 18 based on blueberry, 25 on grape, 12 on raspberry, and 28 on cranberry) and 21 cranberry-based nutraceuticals were analysed. Sample treatment consisted of a simple solid-liquid extraction method, using acetone:water:hydrochloric acid (70:29.9:0.1, *v/v/v*) as the extracting mix. After both negative and positive electrospray ionisation FIA−HRMS sample analysis, raw data were processed with mzMine 2.53 software to obtain the corresponding fingerprints. In this line, four different data matrices —including negative, positive, low-level data fusion (LLDF), and mid-level data fusion (MLDF) FIA−HRMS fingerprints— were then subjected to principal component analysis (PCA) and partial least squares regression-discriminant analysis (PLS-DA) using Solo 8.6 chemometrics software.

PCA results allowed the identification of specific sample groups and trends. Subsequently, the complete sample classification was segregated through a classification decision tree —consecutive two-input class PLS-DA models—, leading to excellent assignment accuracies after external validation according to sample botanical origin (independently of the employed data matrix).