

## Targeted HPLC-UV-FLD polyphenolics to assess paprika geographical origin

Xavi Collado<sup>a</sup>, Guillem Campmajó<sup>a,b</sup>, Sònia Sentellas<sup>a</sup>, Javier Saurina<sup>a,b</sup>, Oscar Núñez<sup>a,b</sup>

<sup>a</sup> Department of Chemical Engineering and Analytical Chemistry, University of Barcelona, Martí i Franquès 1-11, E08028 Barcelona, Spain.

<sup>b</sup> Research Institute in Food Nutrition and Food Safety, University of Barcelona, Av. Prat de la Riba 171, Edifici Recerca (Gaudí), E08921 Santa Coloma de Gramenet, Spain.

Paprika is a red powder seasoning with a characteristic flavour obtained from the drying and grinding of red pepper fruits of the genus *Capsicum* (Solanaceae family). In Europe, seven paprika products are distinguished with the protected designation of origin (PDO) label, which ensures a high-quality product by strict requirements, leading to higher retail prices than not-labelled paprika and making them susceptible to fraudulent practices.

Contents of polyphenol and phenolic compounds depend on several factors, such as the environmental conditions of the production area. Thus, in the present study, a simple and feasible high-performance liquid chromatography with ultraviolet and fluorescent detection (HPLC-UV-FLD) method was developed to determine 17 polyphenols in paprika samples, aiming at their authentication through chemometrics. A reversed-phase chromatographic separation was optimised, using a C<sub>18</sub> column and 0.1% formic acid aqueous solution and acetonitrile as the mobile phase components. The proposed methodology exhibited limits of detection below 0.9 mg L<sup>-1</sup>, as well as good linearity ( $R^2 \geq 0.984$ ), precision (RSD day-to-day values below 24%), and trueness (relative errors below 14%). Moreover, compound confirmation was carried out by high-performance liquid chromatography coupled to mass spectrometry (HPLC-MS).

The proposed methodology was applied to 109 paprika samples, including samples from Spain (*La Vera* PDO, *Murcia* PDO and *Mallorca* PDO), Hungary, and the Czech Republic. The obtained HPLC-UV-FLD polyphenolic profiles were employed as sample chemical descriptors to authenticate paprika geographical origin by a classification decision tree constructed by partial least squares regression-discriminant analysis (PLS-DA) models. As a result, a sample classification rate of 87.8% was reached after external validation. Moreover, two different paprika geographical origin blend scenarios (*La Vera* vs. *Murcia* and the Czech Republic vs. *Murcia*) were evaluated through partial least squares (PLS) regression, allowing blend percentage prediction with errors below 10.8% after external validation.