



## Abstract **Targeted HPLC-UV-FLD Polyphenolics to Assess Paprika Geographical Origin**<sup>†</sup>

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Abstract: 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 through strict requirements, leading to higher retail prices than unlabelled 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 to authenticate them through chemometrics. Reversedphase chromatographic separation was optimised, using a C18 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 ( $R^2 \ge 0.984$ ), precision (RSD day-to-day values below 24%), and trueness (relative errors below 14%). Moreover, compound confirmation was carried out via 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 using a classification decision tree constructed via 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.

Keywords: paprika; HPLC; polyphenols; food authentication; chemometrics

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/Foods2021-10923/s1, Poster: Targeted HPLC-UV-FLD Polyphenolics to Assess Paprika Geographical Origin.

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