Study of the matrix effect of table and wine grapes using GC-QqQ-MS

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The matrix effect in analytics is known as the variation in the response of the analytical system, induced by the presence of some components of the matrix (coextractives) in which the analyte is found.

This effect occurs throughout the entire analytical determination. In separative techniques, the most common case is the coelution of the analyte with the matrix components. In other cases, the characteristics of the analytical system also participate in this effect. In gas chromatography, these two aspects are involved: how the matrix influences the degradation of compounds at the injection port and their ability throughout the chromatographic run. The study of it is contemplated in the validation of analytical methodologies.

There are different ways of approaching the study of the matrix effect, ranging from statistical methods to methods based on instrumental determinations. According to the SANTE document, the matrix effect can be studied by analyzing the analytical sensitivity through the quotient of the slopes of the calibration curves prepared in the matrix and solvent, respectively.

Using the equation below, complementary information is obtained when its sign and module are analyzed, classifying the effect as low, moderate, and high and, in turn, signal suppression/increase.

EM (%) = ((matrix matched calibration slope)/(solvent calibration slope)-1) ×100

The present work studies the matrix effect that occurs using gas chromatography coupled with tandem mass spectrometry taking a table and wine grapes as a case study.

As expected, the differences between the two cases not only lay in their morphological characteristics, such as size, the shape of the bunches, and thickness of the skin, nor in their cultivation method but also the profile of co-extractives for each case.,When the information of the matrix effect is not taken into account or the correspondence between the matrix selected as the target and the one being analyzed, the consequemce is changes in the result of quantification of the pesticide residues either, under or over quantifying it.

Different calibration curves with table grapes (muscatel and white) and wine grapes (Chardonnay, Tannat, Merlot, and Albariño) were prepared, and the responses were compared for a representative group of compounds analyzable by GC-MS/MS, which mainly comprised organophosphates, pyrethroids, organochlorines, azoles, and strobilurins. The matrix effect was generally high in most cases, regardless of the type of grape, but the analyte quantification varied from matrix to matrix

In turn, the coextractives profile was evaluated by gas chromatography (Q3-Scan mode) and thin layer chromatography using UV absorption and universal developer to relate the information qualitatively, detecting significant differences in the coextractives profile. Depending on whether they are wine or table grapes, white or red.

[1]- D. R. Erney et al. *"Explanation of the matrix-induced chromatographic response enhancement of organophosphorus pesticides during open tubular column gas chromatography with splitless or hot on-column injection and flame photometric detection.* Journal of Chromatography A 638:57-63 (1993).