METHOD DEVELOPMENT AND VALIDATION FOR MULTI-RESIDUE ANALYSIS OF PESTICIDES AND MYCOTOXINS BY UPLC-MS/MS (ESI+) AND GC-MS (ITD-EI) IN GRAPE JUICE

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The goal of this work was the development of a comprehensive and integrated method for both pesticides and mycotoxins in grape juice samples. Another aim was to optimize the sample preparation in such way to contain just fewer necessary steps, what makes this method very appropriate to be applied in routine analysis.

Samples were extracted using a modification of the QuEChERS method[1]. The extraction was carried out by shaking 10 g sample in a centrifuge tube with acetonitrile/ HAc 1%, followed by a partitioning step induced by the addition of 5.0 g magnesium sulphate. The extract was transferred, for mycotoxins analysis, to UPLC^{TM}-MS/MS. Posteriorly, 1.0 g sodium acetate was added and after centrifugation the extract was analyzed for LC amenable pesticide search. The extracts were then cleaned-up by dispersive solid phase extraction, 0.4 g of PSA in the presence of 1.2 g of magnesium sulfate and the GC amenable pesticides were quantified by GC-MS (ITD-EI).

To the group 1 of micotoxins (17 mycotoxins), all of them were spiked at 1, 2 and 10 μg kg^{-1} levels, the recoveries average were between 70-120% and the relative standard deviation (RSD) ≤ 20% for 65% of those mycotoxins. The group 2, with 19 mycotoxins, spiked at 50, 100 and 500 μg kg^{-1} levels, showed recoveries average between 70-120% for 96% of the mycotoxins and RSD ≤ 20% for 81% of them. No significant matrix effects were observed for all 36 compounds. For LC amenable pesticides, at three spiking levels 10, 20 and 50 μg kg^{-1}, the obtained recoveries average were between 70-120% for 84% of 149 pesticides. The RSD ≤ 20% for 83% of them. To the analysis by GC-MS (ITD-EI), pesticides were spiked at 20, 50 and 100 μg kg^{-1} levels, presenting recoveries average between 70-120% for 62% of the 89 GC amenable pesticides, RSD ≤ 20% for 69% of them.

The complete multi-residue method was successfully validated on the parameters selectivity, accuracy, repeatability (precision), linearity of detector response, limit of detection (LOD) and limit of quantification (LOQ). This method reduces considerably the sample throughput time and thereby the costs per sample/analysis.

[1] Pizzutti, I. R., De Kroon, M., Prestes, O. D., Rensen, P., De Kok, A., 7th European Pesticide Residue Workshop, Berlin, Book of Abstracts, 2008, 213.