Two-step dispersive-solid phase extraction strategy for pesticide multiresidue analysis in highly complex matrices by gas chromatography-tandem mass spectrometry

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A new cleanup strategy for improving multiclass, multiresidue pesticide analysis in complex chlorophyll-containing matrices prior to GC-MS/MS determination will be presented. The proposed approach entails an application of two sequential steps of dispersive-solid phase extraction (d-SPE) to obtain sample extracts with less co-extractives. Several sorbents and sorbent mixtures were tested to find those providing efficient reduction of co-extractives while maintaining acceptable recoveries in the range of 70 – 120%. For the first d-SPE step, we employed a new type of sorbent, known as ChloroFiltr together with PSA, whereas for the second d-SPE step, we evaluated different sorbents including new types of zirconium-based sorbents (Z-Sep+ and Z-Sep/C18) as well as graphitized carbon black (GCB) and C18. Although Z-Sep+ provided excellent cleanup, it strongly retained some pesticides of importance to us, among others conazole fungicides and pyrethroid insecticides. Therefore, the method entailing the use of GCB/C18 at the second d-SPE step was selected as the most favourable option for chlorophyll-containing samples. The overall recoveries from green soybean, at three spiking levels of 0.01, 0.05 and 0.2 mg kg⁻¹, were 96 ± 15%, 93 ± 13% and 92 ± 13% with relative standard deviations of 10 ± 7%, 9 ± 5%, and 11 ± 5%, respectively. The proposed method provided matrix effect <20% for approximately 80% of the target compounds. For highly complex matrices, the proposed method can be considered as an improvement over classical QuEChERS when single step d-SPE will not be able to provide sufficient reduction of co-extractives. Also, injections of cleaner extracts will minimize the need for instrument maintenance with only a trade-off being modestly higher cost and somewhat longer time needed to carry out the two steps of d-SPE. The developed method was applied to analyze pesticide residues in samples, such as green soybean, poppy, alfalfa and millet, originating from field experiments in which new crop protection strategies were evaluated. The aforementioned crops are classified as minor crops in Poland, thereby the results obtained in our work helped establish safe and proper use of pesticides by extension of authorization on minor uses of pesticides already registered on other crops, i.e. major crops. However, the developed and validated method is clearly extendable to multiresidue pesticide analysis in other chlorophyll-containing matrices. Furthermore, the applied method development strategy has potential for extension to other types of highly complex matrices (e.g., fatty matrices) by optimization of the type and amount of sorbent(s) used for both steps of d-SPE cleanup.