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Analysis of Carbofuran (sum) via modified QuEChERS method

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Carbofuran (CF) is an insecticide, nematicide and acaricide of the carbamate group. Carbosulfan (CS), furathiocarb (FT) and benfuracarb (BF) are pro-pesticides that degrade to CF, which is the active substance. None of the four compounds is approved in the EU but there are still uses in other countries. A recent import-tolerance request for mushrooms was rejected.

CF exhibits a very high acute neurotoxicity and was thus allocated with very low ARfD and ADI figures. Following a toxicological re-evaluation of CF, very low MRLs were newly established. Originally the 4 compounds were regulated separately; however given the tendency of CS, BF and FT to degrade during laboratory analysis and food processing a new residue definition was introduced which includes CF, its three pro-pesticides and 3-OH-carbofuran (3 OH-CF) expressed as CF. 3 OH-CF is considered to exhibit similar toxicity as the parent. For products of animal origin the residue definition refers to 3 OH-CF (free and conjugated). Due to toxicological concerns the MRLs for this residue definition were set very low for all products with high short-term consumption figures (0.001 mg/kg for potatoes, apples and milk and 0.002 mg/kg for stone fruits, grapes, fruiting vegetables, brassica vegetables, salad plants and stem vegetables).

Given the very low MRLs a conversion of CS, BF and FT to CF, in the case of plant products, was considered crucial, as it reduces the number of compounds to be analytically determined from five to two (CF and 3-OH-CF). Apart of that, direct analysis of CS and BF is very challenging as these compounds are highly susceptible to degradation during sample milling and analysis. FT proved to be considerably more stable.

We have developed an acidic hydrolysis module, that can be applied to the final QuEChERS extracts, for the analysis of CF (sum) to convert CS, BF and FT to CF. Final analysis is sensitively and selectively accomplished via LC-MS/MS.

CS and BF are easily and quantitatively converted to CF in acidified QuEChERS extracts even at room temperature. FT, however, proved to be more challenging requiring heating at 80°C over 2-3 hours. Conversion yields were in all cases nearly quantitative. The method was validated at 0.001 mg/kg for CF and 3-OH-CF, as well as separately for CS, BF and FT, each spiked at 0.001 mg/kg and determined as CF (expected CF levels assuming quantitative conversion and considering MW-factors 0.00054-0.00058 mg/kg).

Prior to establishing the new residue definition, the EURL-SRM conducted experiments to study the impact of household processing on the fate of CS, BF and FT. Interestingly, FT, which was chemically more resistant than CS and BF when conducting hydrolysis on QuEChERS extracts, was found to be clearly more labile in crop homogenates than CS and BF, suggesting enzymatically assisted decomposition.