EXPERIMENTAL

The extracts of green plants of soybean, poppy, alfalfa and millet were prepared using a modified Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) method [1,2]. Briefly, a 5 g sample was extracted with 5 mL water and 10 mL acetonitrile for 10 min. This was followed by a salting out step with MgSO4 (4 g), NaCl (1 g) and citrate buffer pH 4.5 (5.5), and centrifugation. An aliquot of the supernatant was cleaned-up by dispersive solid phase extraction (d-SPE) in two sequential steps:

1) PSA/ChloroFiltr and MgSO4 (50, 25 and 150 mg per 1 mL extract)
2) Second step of d-SPE:
   a) GCB/C18 (7.5 and 50 mg per 1 mL extract)
   b) Z-Sep+ (50 mg per 1 mL extract)
   c) Z-Sep+C (20 mg per 1 mL extract)

An aliquot of the purified extract in acetonitrile was injected into the GC-MS/MS using the PTV-LVI technique (Fig. 1).

RESULTS AND DISCUSSION

- Zirconium dioxide-based sorbents (especially Z-Sep+) provided efficient removal of pigments and other co-extractives leaving nearly colourless extracts but, unfortunately, they also retained some pesticides of great importance for us, among others, triazole fungicides and pyrethroid insecticides (Fig. 2).
- The use of GCB/C18 at the second step of d-SPE provided the highest pesticide coverage with the recoveries in the acceptable range of 70–120%. The overall recoveries at the three spiking levels of 0.01, 0.05 and 0.2 mg/kg were 96±15, 93±13 and 92±13% with RSDs 10±7, 9±5 and 11±5%, respectively.
- The optimized method provided matrix effect <20% for 77% of the target analytes, which may be considered as negligible because such variability is closed to the accepted repeatability. For the rest of 8 and 15% of the target analytes, the matrix effects were 20–30% and >30%, respectively (Fig. 3).

CONCLUSIONS

- For highly complex chlorophyll-containing matrices, the proposed approach can be considered as an improvement over classical QuEChERS if single-step d-SPE is not 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 proposed 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) for both steps of d-SPE cleanup.

REFERENCES