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Innovation Development of Comprehensive Dimensional and Lossless Profiling Technology (CDLPT) of the Multi-Residue Pesticides Analysis in Traditional Chinese Medicine using LC/TQ System

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Introduction

Pesticides are widely applied for the control of pests, including insects, rodents, weeds, bacteria, mold, and fungus. Analysis of pesticides and sample cleanup in Traditional Chinese Medicine (TCM) is challenging because TCM is a complex matrix. A simple, fast, and fully automated multi-dimensional LC-MS/MS method was developed for the determination of 30 pesticides cited in the Chinese Pharmacopoeia drug code using an innovative technology called: Comprehensive Dimensional and Lossless Profiling Technology (CDLPT). This next generation full automated analysis platform delivers sensitivity, versatility, robustness, and intelligence.

- Two 1290 UHPLC
- Two 2-position/4-port Duo-valves
- 6470B TQ system, combined with Study Manager and Masshunter automatic quantitation software

Experimental

1290 UHPLC Loading & Trap System

1D Column: Agilent Zorbax HILIC-plus, 2.1X100, 3.5 μm

Multi-trap columns: Agilent Cartridges with Zorbax SB-C8 (4.6X12.5 mm, 5 μm) connect with PLRP-S (4.6X12.5 mm)

Mobile phase A: 5mM $\text{NH}_4\text{CO}_2\text{H}$ in water

Mobile phase B: 5mM $\text{NH}_4\text{CO}_2\text{H}$ in acetonitrile/water=90/10

Injection volume: 10 μL

Column Oven: 40 $^\circ\text{C}$

Gradient program: (Flow rate: 0.2 mL min^{-1})

Time (min)	0	2.5	5.0	15	16	35
A (%)	0	0	50	50	0	0
B (%)	100	100	50	50	100	100

Experimental

1290 UHPLC Analytical System

2D Column: Agilent Poroshell EC-C18, 3.0X150 mm, 2.7 μm

Mobile phase A: 5mM $\text{NH}_4\text{CO}_2\text{H}$ and 0.1% formic acid in water

Mobile phase B: 5mM $\text{NH}_4\text{CO}_2\text{H}$ and 0.1% formic acid in methanol.

Column Oven: 40 $^\circ\text{C}$

Gradient program: (flow rate: 0.3 mL min^{-1})

Time (min)	0	1	1.2	2.2	2.21	5	7	27	29	30
A (%)	98	98	100	100	98	95	50	0	0	95
B (%)	2	2	0	0	2	5	50	100	100	5

6470B LC/TQ MS Conditions

Ion source: Agilent Jet Stream, fast polarity switch mode

Nebulizer gas: 30 psi

Dry gas: 8 L min^{-1}

Dry gas Temperature: 280 $^\circ\text{C}$

Sheath gas: 11 L min^{-1}

Sheath gas Temperature: 325 $^\circ\text{C}$

Nozzle voltage: 0 V (Positive); 1500 V (Negative)

Capillary voltage: 4000 V (Positive); 3000 V (Negative)

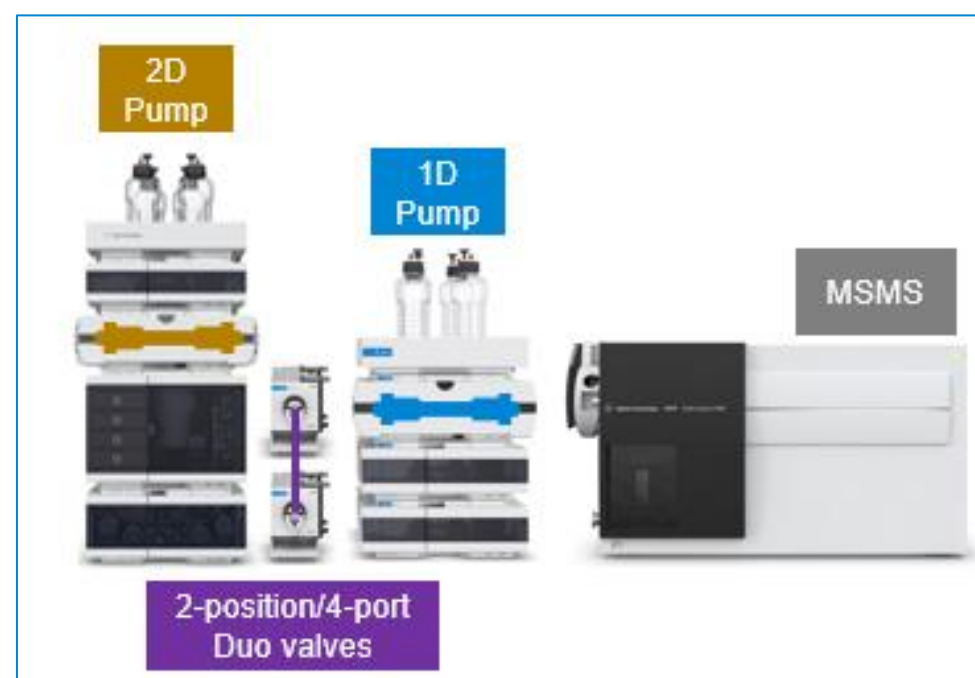


Figure 1. Agilent CDLPT 6470B LC/TQ System

The CDLPT LC/TQ technology for pesticide analysis of complex TCM samples is composed of three parts: 1) automatic multi-dimensional (MD) extraction, 2) Study manager software and 3) Masshunter automatic quantitation workflow (Figure 2). In a 1D system the pesticides are not retained and are separated with high interferences. The pesticides were separated by heart-cutting into multi-column trapping and retention using C8 and PLRP-S material with two 2-position/4-port Duo valve systems. After the system flush (two minutes), the pesticides were analyzed with the 2D system. (Figure 3). The Study Manager software and Masshunter automatic quantitation workflow were configured to inject and report a qualified result, automatically. The sample preparation of this system is simple and faster with traditional techniques like liquid-liquid extraction (LLE), filter extraction or QuEChERS.

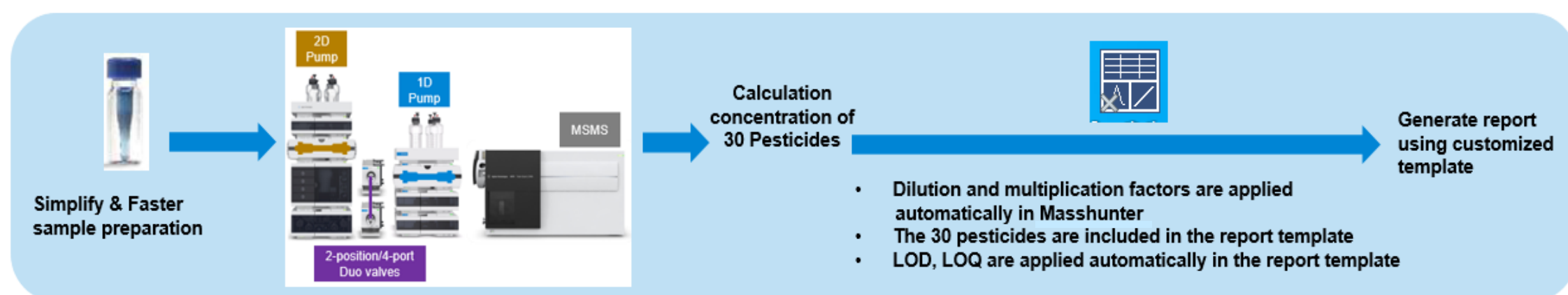


Figure 2. Automatic Workflow of CDPLT LC/TQ Analysis and Data Processing with Masshunter

The CDLPT LC/TQ technology is a lossless system. All 30 pesticides are eluted and analyzed including HILIC separation (3.0-5.0 min), C18 separation (5.0-35.0 min) or no separation (0-3.0 min). In this study, methamiphos was the most polar pesticide that could not be analyzed with HILIC and C18. Its retention time was at 2.0 min. (Figure 3).

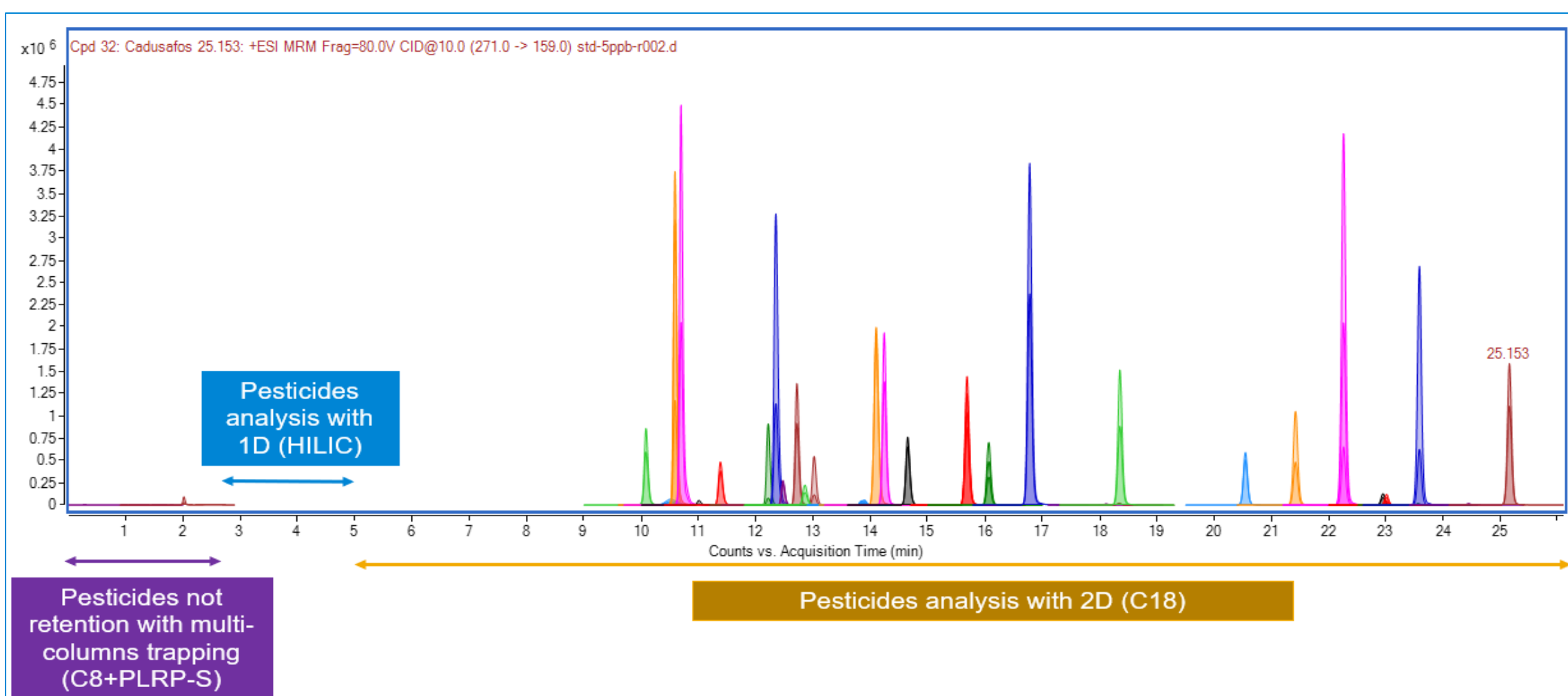


Figure 3. The 30 Pesticide Standards at a Concentration of 5 ng mL⁻¹ were analyzed with the CDLPT LC/TQ System.

Results and Discussion

30 pesticides were measured in two TCM matrices (malva nut tree and ginseng) by injecting a matrix-matched calibration curve at 5 concentrations ranging from 0.5 to 20 ng g⁻¹. As an example, good precision and linearity of three representative pesticides is shown for quantitative determination in Ginseng. (Figure 4). Precision was <20% and the R² value was better than 0.99.

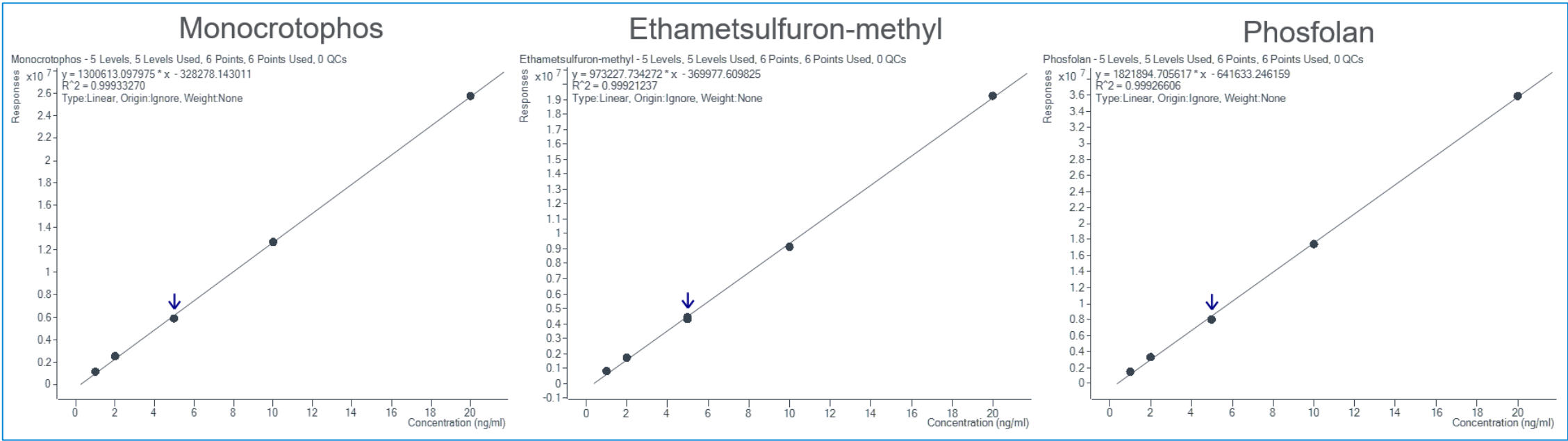


Figure 4. The Excellent Matrix-Match Calibration for Three Representative Pesticides.

Results and Discussion

The recovery testing used different injection volumes to evaluate the loading capacity of the system with 20 µL and 5 µL after the sample preparation with acetonitrile and filter extraction. The good total recovery of over 95% pesticides was found to be in the range of 70-120% and the detection limit (DL) was between 0.5-1.0 ng g⁻¹ for quantitation with matrix-match calibration. (Figure 5). Finally, the optimized injection volume was 10 µL for TCM samples.

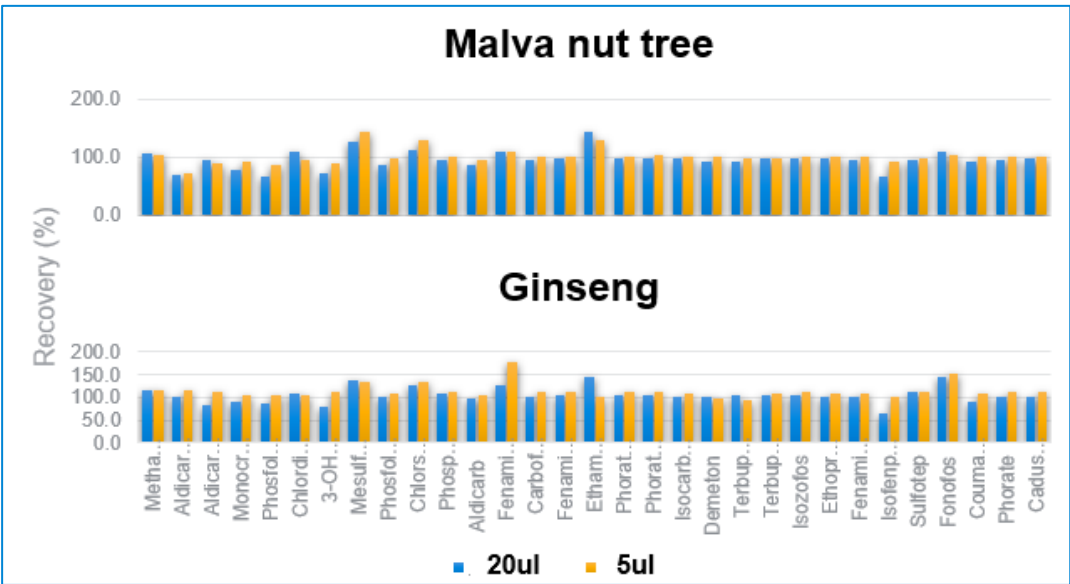


Figure 5. The Distribution of Recovery of 30 Pesticides Spiked 5 ng g⁻¹.

Conclusions

Gradient elution and Dynamic MRM with the innovative CDLPT LC/TQ technology were employed for simultaneous identification of 30 pesticides in TCM samples. The benefits were:

- Simple sample preparation.
- Wide polarity profiling analysis and multi-dimension separation with one injection.
- >50% time saving with automatic data processing.

References

- [1] Rapid Quantification of Polar and Semipolar Pesticide Metabolites with Combined Online SPE and Direct Injection., Agilent Application Note: 5994-0151EN
- [2] Development and validation of an efficient automated method for the analysis of 300 pesticides in foods using two-dimensional liquid chromatography-tandem mass spectrometry. Kittlaus, S., Schimanke J., Kempe G., & Speer, K. Journal of Chromatography A, 1283 (2013) 98-109.