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Analysis of Multiclass Pesticide Residues in Dried Parsley Sample Using LC-MS and GC-MS

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Introduction

Abstract

Assessing multiclass pesticides in high chlorophyll samples is a challenging task. Here we propose a methodology for analysis of 346 pesticides at residue level with LOQ lower than EU-MRL values in parsley. Analytes common to LC-MS and GC-MS were reported at similar concentrations when detected. High recovery (>70%) of the method was obtained for more than 80% of pesticides.

Introduction

Dried parsley is a common ingredient for seasoning in Europe and the US. However, a complete solution for quantitation of pesticide residues using mass spectrometry is required of exporters from, e.g., India.

Quantitative and confirmative data were generated using both Agilent LC-MS (1290-6470 LC/TQ) and GC-MS (7000D GC/TQ) systems. Sample preparation involving QuEChERS and dSPE was common between both methods. Triple Quadrupole analytical methods ensured data and Ion ratio as per SANTE/11312/2021 guidelines[1].

Figure 1: 1290-6470 LC/TQ and 7000D GC/TQ

Experimental

Mass Spectrometry Parameters

The LC/TQ parameters were as per Agilent Application note[2].The GC/TQ parameters were as seen in Table 1.

Parameter	Value
MMI injection mode	Splitless, 2 µL
Inlet Temperature	280°C
Oven Temperature Program	60°C for 1 min 40°C/min to 120°C, 0 min 10°C/min to 310°C, 3 min
Total Run Time	20.75 min
Locking compound and RT	Chlorpyrifos methyl locked to 9.143 min
MS transfer line temperature	300°C
Collision flow	1.5 ml/min
Quench Flow	2.25 ml/min
GC Ion Source temperature	300°C
LC Ion Source temperature	150°C
Quad temperature (Q1 and Q2)	20.75 min

Table 1: GC/TQ method parameters

RT locking as per P&EP MRM database:

Chlorpyrifos methyl was locked at 9.143 min, to obtain the RTs as per P&EP MRM database in GC-MS. dMRM based method for 96 compounds was created using P&EP MRM database. All compounds were resolved with in 20.75 min. A backflush of 3 min was given in order to remove high boiler matrix in reverse direction.

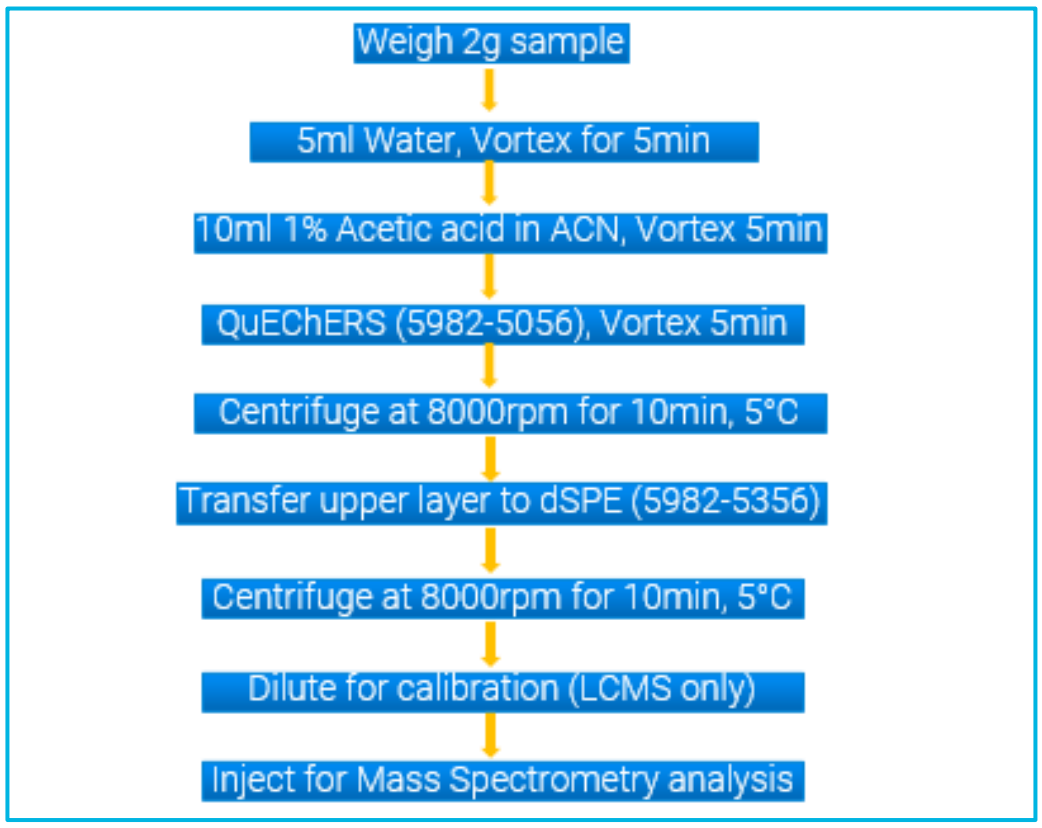

Figure 2: Sample Preparation Method

Matrix Calibration:

For GC/TQ the blank parsley was processed, and the final extract was used for preparing calibration from 1–100 ppb. For LC/TQ the blank parsley was diluted, and the final extract was used to prepare calibration between 0.5-100 ppb. For both the techniques, the r2 values as obtained were ≥0.995. For recovery calculations individual parsley sample was spiked at 10ppb followed by sample preparation as per Fig 3. A recovery factor was applied to while reporting the concentration of residual pesticides individually.

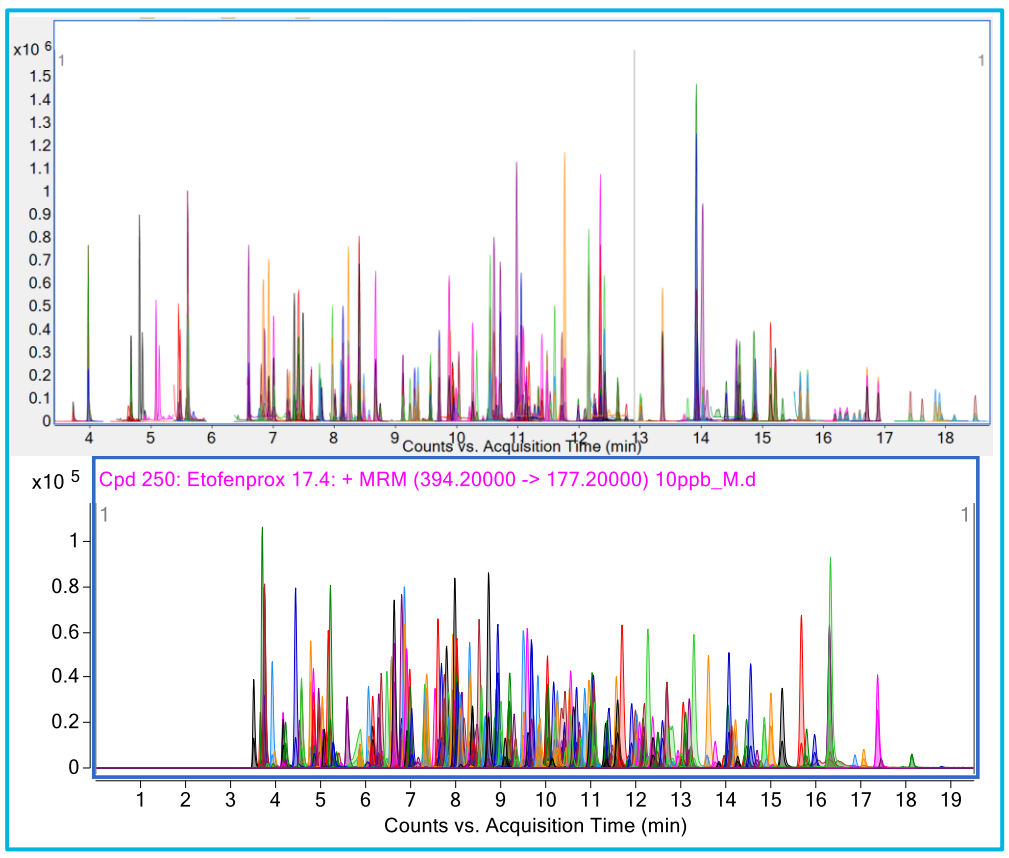

Figure 3: MRM plot of 96 Pesticides on GC/TQ at 0.1 µg/ml and 250 Pesticides on LC/TQ at 0.01 µg/ml

Figure 5: GC/TQ calibration plots few pesticides in matrix

Recovery data:

For GC/TQ, 96 pesticides were spiked in dried parsley sample at 0.05 mg/kg level. For 85% of the compounds recovery was found to be in range of 70% – 100%, as seen in Fig 6. In case of LC/TQ every sample was spiked with pesticides standards at 0.01 mg/kg level. Recovery was between 70% - 100% for more than 78% of compounds. Individual recovery factor was applied to pesticides having >70% recovery, while reporting.

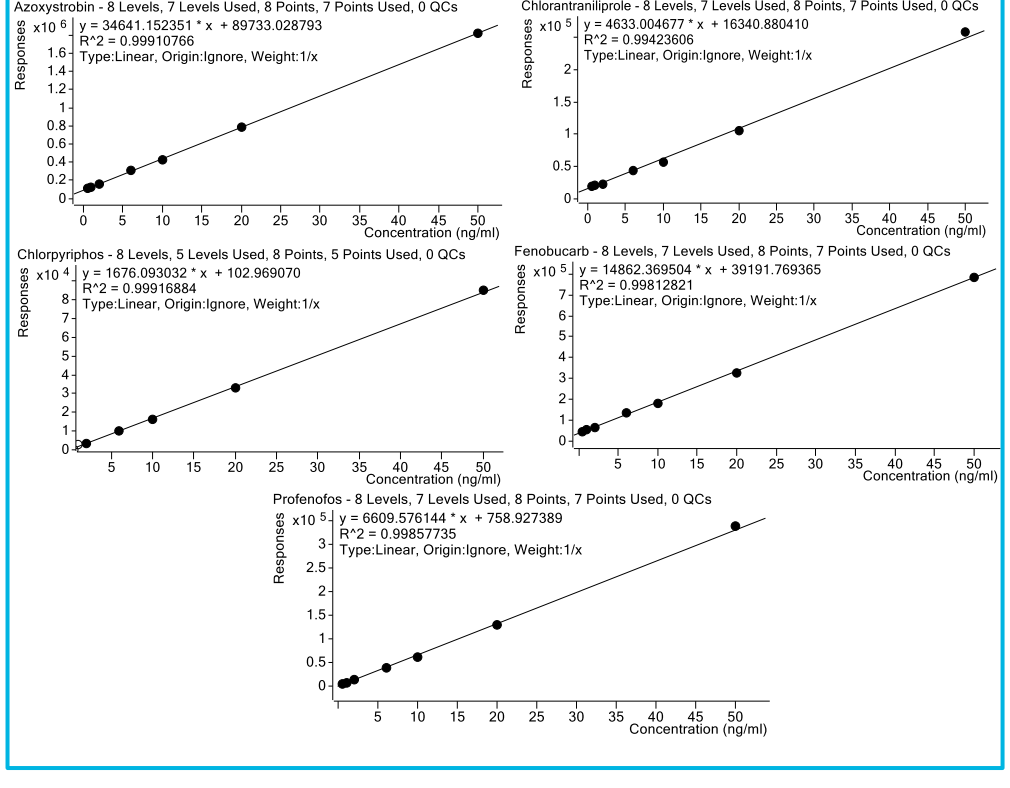

Figure 4: LC/TQ calibration plot of reported pesticides in matrix

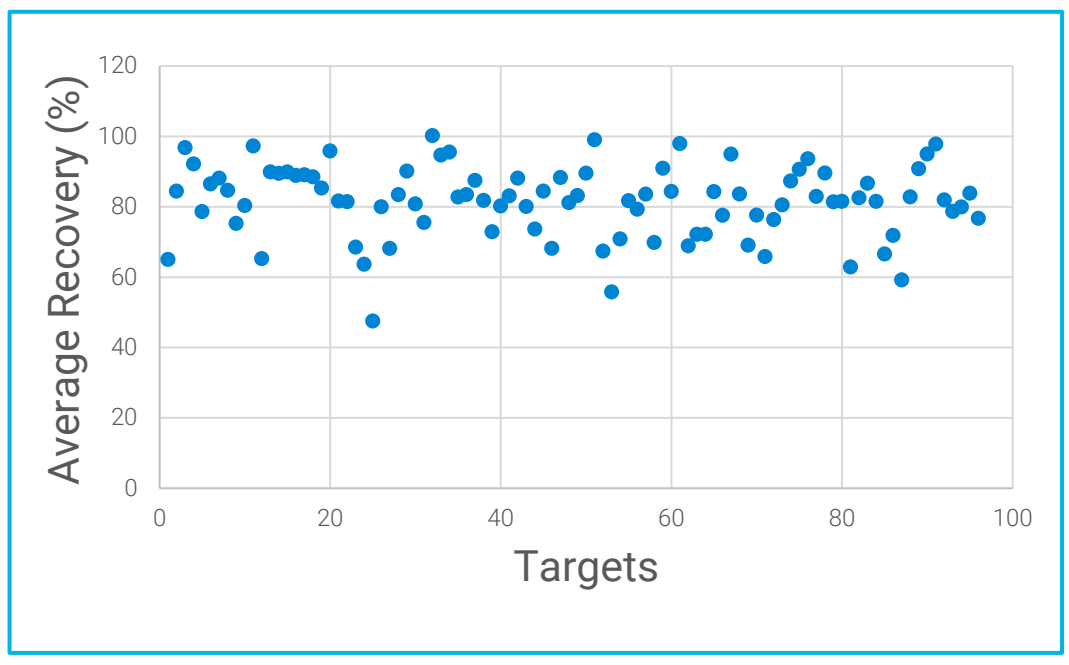

Figure 6: Target recoveries in Dried parsley sample spiked at 0.05 mg/kg for GC/TQ

Results and Discussion

Quantitative results:

Matrix calibration and usage of recovery factor in every sample were considered in final calculations. Among 346 pesticides, 96 analytes were found to be common among LC/MS and GC/MS (Fig 7). Azoxystrobin, Chlorpyrifos, Chlorantriniprole, p,p'-DDT, Fenobucarb and Profenofos were present in 3 Parsley samples. Chlorpyrifos and Profenofos were the common pesticides that were reported by both LC/TQ and GC/TQ in 3 different samples of dried parsley (Fig. 8). The pesticides which are above EU-MRL are reported, as seen in table 2.

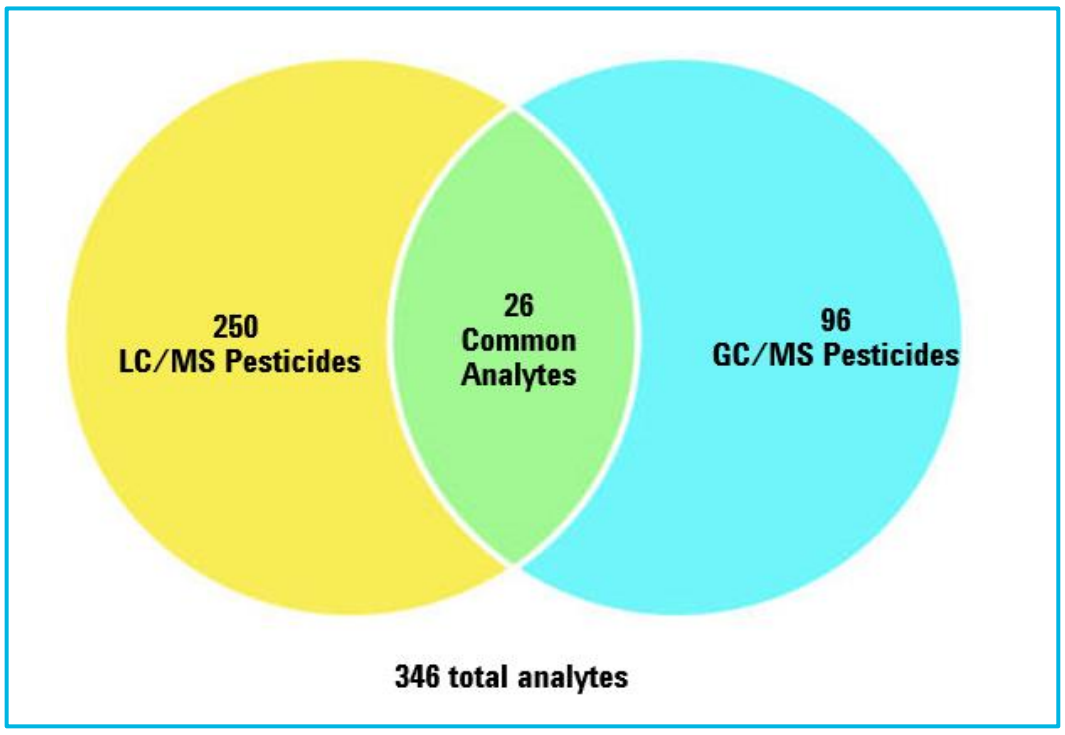

Figure 7: Analyte distribution among LC/MS and GC/MS

Pesticide / Sample	Sample 9	Sample 11	Sample 34
Azoxystrobin (LC/TQ)	728.9	337.09	196.9
Chlorpyrifos (LC/TQ)	39.33	37.47	23.62
Chlorpyriphos (GC/TQ)	40.75	37.85	22.63
Chlorantriniprole (LC/TQ)	1151.0	369.94	567.0
p,p'-DDT (GC/TQ)	15.60	15.09	16.48
Fenobucarb (LC/TQ)	604.5	293.7	417.8
Profenofos (LC/TQ)	11.90	11.43	50.05
Profenofos (GC/TQ)	10.51	13.56	43.73

Table 2: Pesticides and their concentration in µg/kg

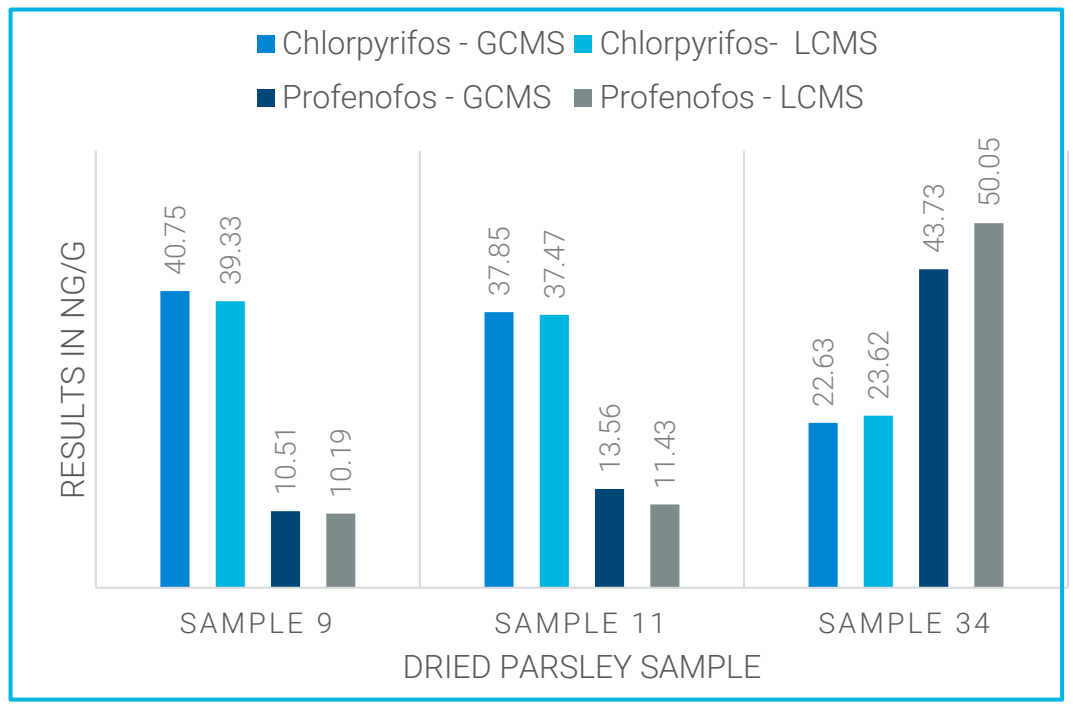

Figure 8: Comparison of Pesticides Reported as Common residues by GC/TQ and LC/TQ

Conclusions

- Pesticide residue analysis for high chlorophyll content samples is established using LC-MS and GC-MS.
- A common sample preparation method is followed for multiclass residual pesticide analysis.
- Excellent recoveries were obtained by GC-TQ for 96 pesticides that were spiked in dried parsley samples
- For common residual pesticides among LC/TQ and GC/TQ, the reported vales in parsley samples were also similar, suggesting high ruggedness of methodologies.

References

1. https://ec.europa.eu/food/system/files/2022-02/pesticides_mrl_guidelines_wrkdoc_2021-11312.pdf
2. Agilent Application Note : 5991-8154EN.
3. Agilent Application Note : 5994-0496EN.
4. Levels of pesticide residues in fruits and vegetables in the Turkish domestic markets, Toptanci et al, *Environ Sci Pollu Res* 28, 39451-57 (2021). https://doi.org/10.1007/s11356-021-13538-w

https://explore.agilent.com/asms
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