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Automated Injection Solvent Modulation for Improved LC/MS Data Quality in the Measurement of Early Eluting Polar Pesticides

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Introduction

A general problem in LC/MS analysis of polar compounds is that their chromatographic separation suffers from the elution strength of the sample solvent. With increasing sample solvent elution strength in reversed-phase chromatography and increasing injection volume, the peak performance of early-eluting polar compounds is destroyed, even resulting in complete breakthrough with the solvent front.

This work demonstrates the application of a newly developed injection principle, Feed Injection (Figure 1)[1]. This injection mode enables solvent modulation by sample infusion for multiresidue LC/MS analysis of polar pesticides dissolved in solvents like acetonitrile, as is typical after QuEChERS sample preparation. The positive effect of solvent modulation by sample infusion on peak performance and maximum sensitivity by increasing injection volumes will be shown and discussed.

Experimental

Instrumentation

- Agilent 1260 Infinity II Hybrid Multisampler
- Agilent 1260 Infinity II Flexible pump
- Agilent 1290 Infinity II MCT
- Agilent Ultivo LC/TQ

Software

- MassHunter Acquisition Ultivo LC/TQ V1.1
- MassHunter Qualitative Analysis software V10.0
- MassHunter Quantitative Analysis software V10.0

Column

- ZORBAX SB C18, 2.1 x 100, 1.8 µm

Samples

QuEChERS extract from strawberries in acetonitrile spiked to a concentration of 10 ppb for all pesticides.

Pesticides

- 1) Methamidophos, 2) Acephate, 3) Omethoate, 4) Propamocarb 5) Aminocarb 6) Pymetrozine, 7) Dinotefuran, 8) Oxamyl.

Calibration

- Stock solutions of 1,000 ppb each pesticide. Concentrations for calibration: 100, 20, 10, 2, 1, and 0.2 ppb in acetonitrile.

Experimental

LC and MS Conditions	
Solvents	A) Water + 5 mM AmFormate + 0.1% FA, B) MeOH + 5 mM AmFormate + 0.1% FA
Flow rate	0.5 mL/min
Gradient	0 min - 5% B, 5 min – 30% B.
Column. Temp.	40°C
Injection Volumes	0.5, 1.0, 1.5 and 2.0 µL
Feed Injection	Feed Speed: 35 µL/min Flush out volume: 6 µL with Solvent B
Needle wash	3 sec. Water/AcN (50/50) + 0.1% FA
Agilent Jet Stream Source	
Gas temp.	120°C
Gas flow	12 L/min
Sheath gas temp.	325°C
Nebulizer pressure	45 psi
Capillary	positive: 3500 V
Nozzle	positive: 300 V
Time filter	0.02 min
MRM	Table 2

Table 1) LC and MS Conditions

Compound	Precursor [*m/z*]	Fragmentor [V]	Frag. [*m/z*]	CV [V]	Frag. [m/z]	CV [V]
Methamidophos	142.0	88	125.9	12	93.9	12
Acephate	184.0	60	143.0	4	49.1	20
Omethoate	214.0	88	155.0	12	125.0	20
Propamocarb	189.2	106	102.0	16	74.0	28
Aminocarb	209.1	101	137.0	24	122.0	48
Pymetrozine	218.1	106	105.1	24	78.0	48
Dinotefuran	203.1	78	157.0	4	129.1	8
Oxamyl	237.1	70	90.0	4	72.0	16

Table 2) MRM Conditions for Pesticide Selection

Results and Discussion

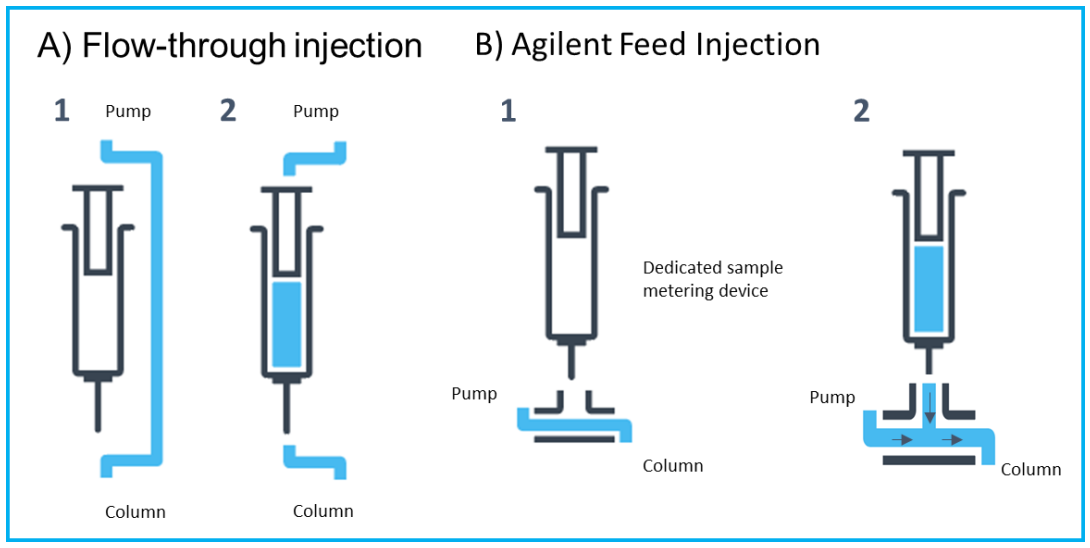


Figure 1) Schematic principle of flow-through injection and Feed Injection modes

To demonstrate the influence of the injection mode (i.e., either Feed Injection or Flow-through injection mode), a mixture of eight polar, early-eluting pesticides was dissolved in acetonitrile at a final concentration of 10 ppb for each compound.

The results, obtained for all eight pesticides acquired in both injection modes with injection volumes of 1.0 µL and 1.5 µL are shown for MRM quantifier and qualifier peaks in Figures 2 and 3.

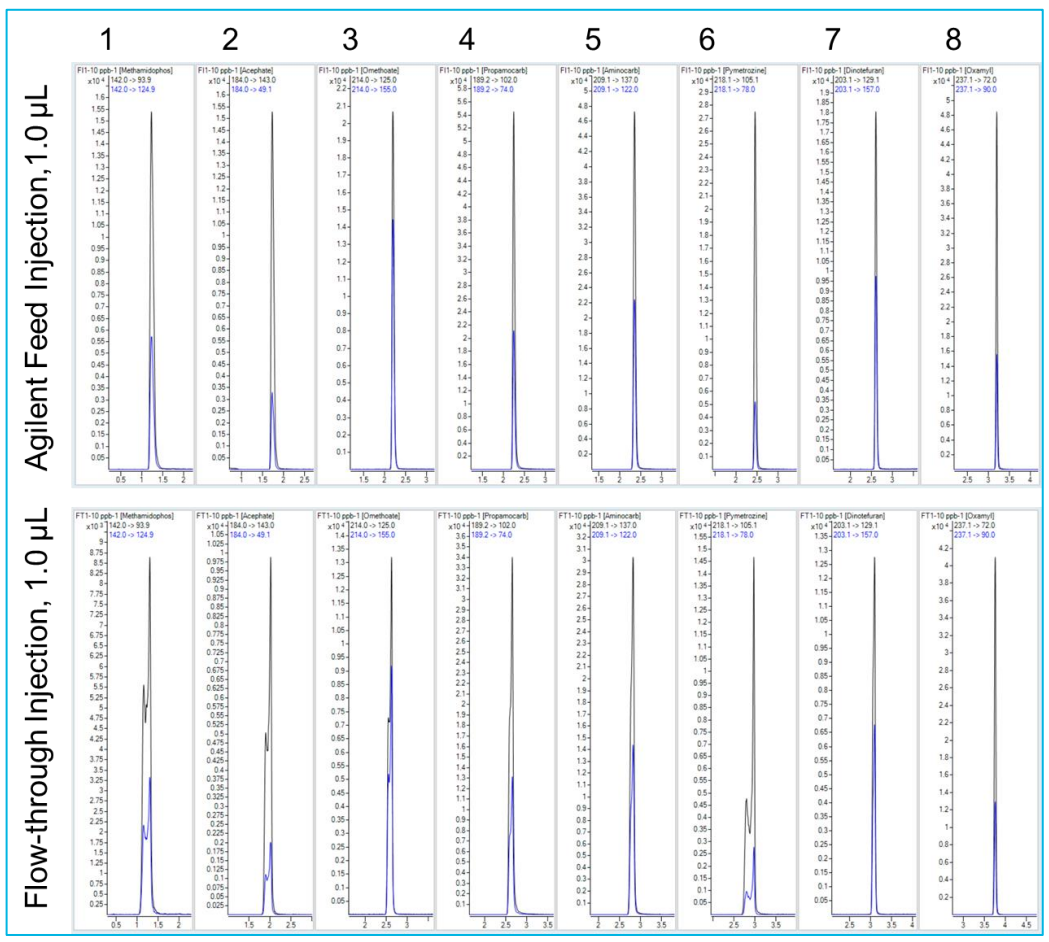


Figure 2) Injection of 1.0 µL of a mixture of eight polar pesticides by Feed Injection and by classical Flow-through injection. Used pesticides see experimental.

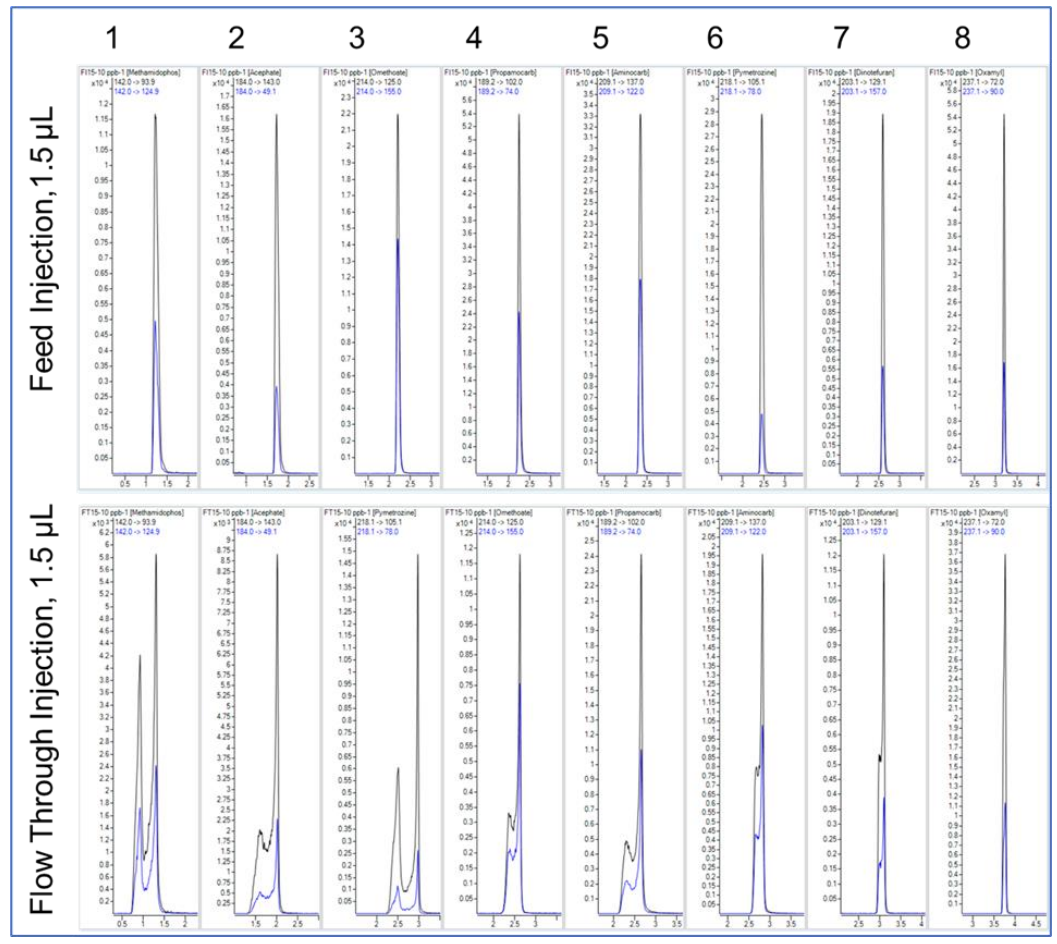


Figure 3) Injection of 1.5 µL of a mixture of eight polar pesticides by Feed Injection and by classical Flow-through injection. Used pesticides see experimental.

From all measured calibration curves, the obtained area RSDs were calculated (Figure 4), and linearity was compared in terms of the R^2 value (Figure 5). From the calibration curves created using Feed Injection, the obtained R2 values for all compounds were typically >0.999 at all applied injection volumes. In Flow-through injection mode, at injection volumes of 1.5 µL and upward, a decline of the R^2 value could be seen for all compounds.

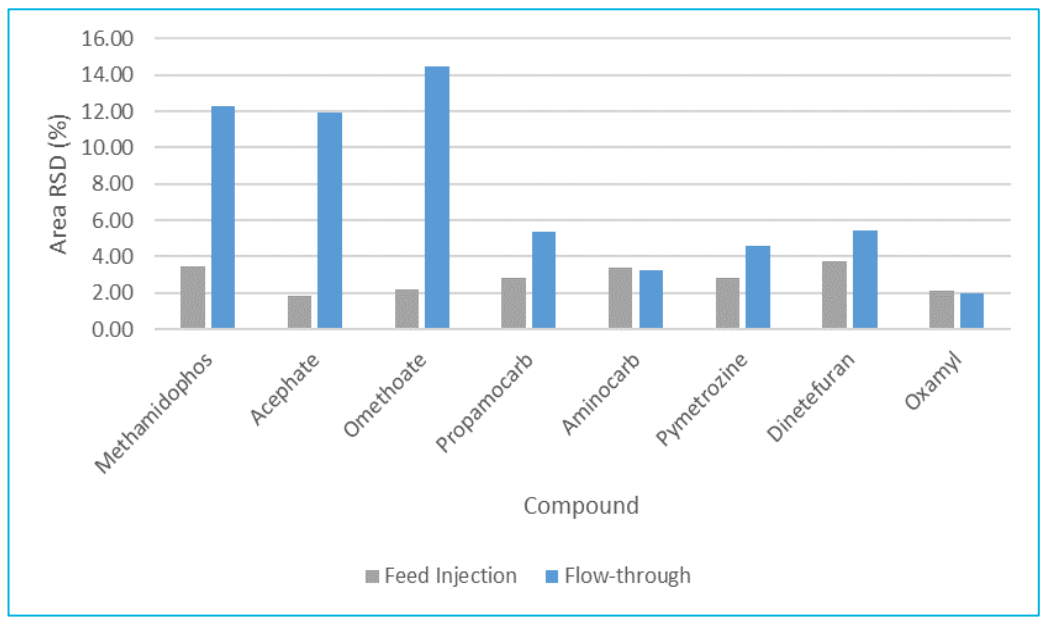
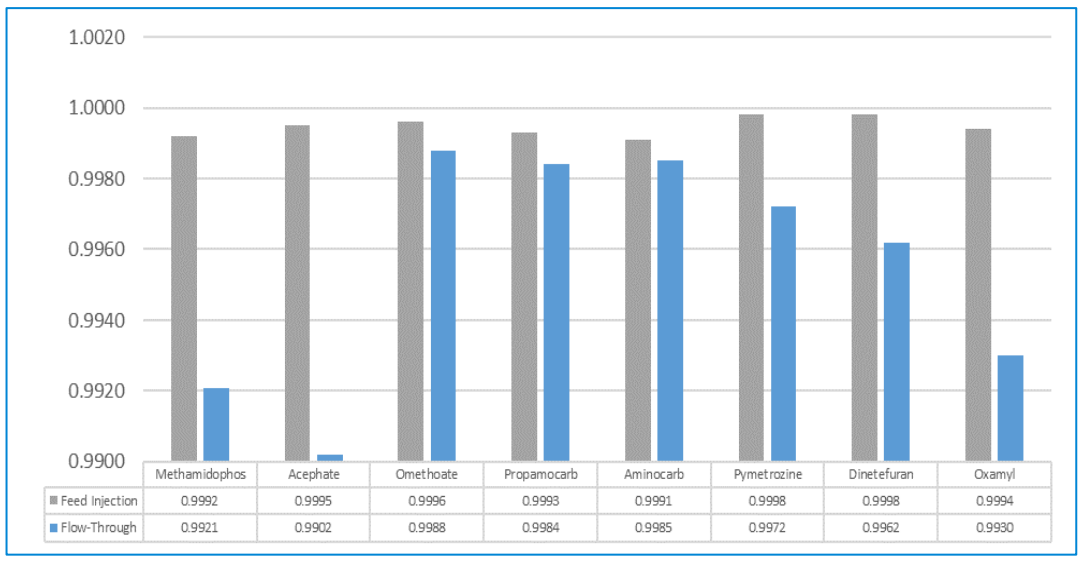


Figure 4) Influence of the injection mode on the peak area RSD depended on the compound (10 ppm each) at 1.5 µL injection volume.

Results and Discussion



	Methamidophos	Acephate	Omethoate	Propamocarb	Aminocarb	Pymetrozine	Dinetefuran	Oxamyl
Feed Injection	0.9992	0.9995	0.9996	0.9993	0.9991	0.9998	0.9998	0.9994
Flow-Through	0.9921	0.9902	0.9988	0.9984	0.9985	0.9972	0.9962	0.9930

Figure 5) Linearities obtained from calibration curves for all measured pesticides using Agilent Feed Injection and Flow-through injection at 1.5 µL injection volume.

Another difference between results obtained with Feed Injection or Flow-through injection for early-eluting pesticides dissolved in acetonitrile is the varying limits-of-quantification (LOQ). The LOQs (s/n = 10) were calculated from the lowest accessible calibration point. The achieved values were typically between 30 and 40 ppt with Feed Injection over the complete injection volume range. The LOQ was between 70 and 120 ppt with Flow-through injection at 1.5 µL injection volume (Figure 6).

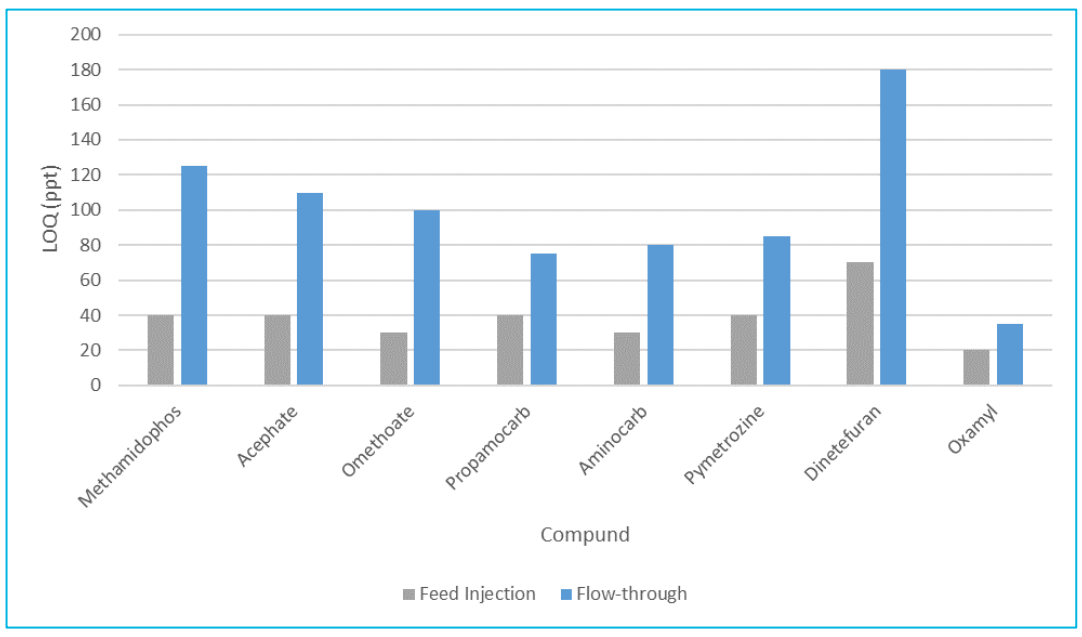


Figure 6) LOQ for Feed Injection versus Flow-through injection

In a test using real QuEChERS acetonitrile extraction conditions, the recovery was determined from a strawberry matrix spiked with 10 ppb of the eight pesticides. For all pesticides, a recovery between 85% and 105% could be measured in Feed Injection mode, which is within the required tolerance of 80 % to 120%[2].

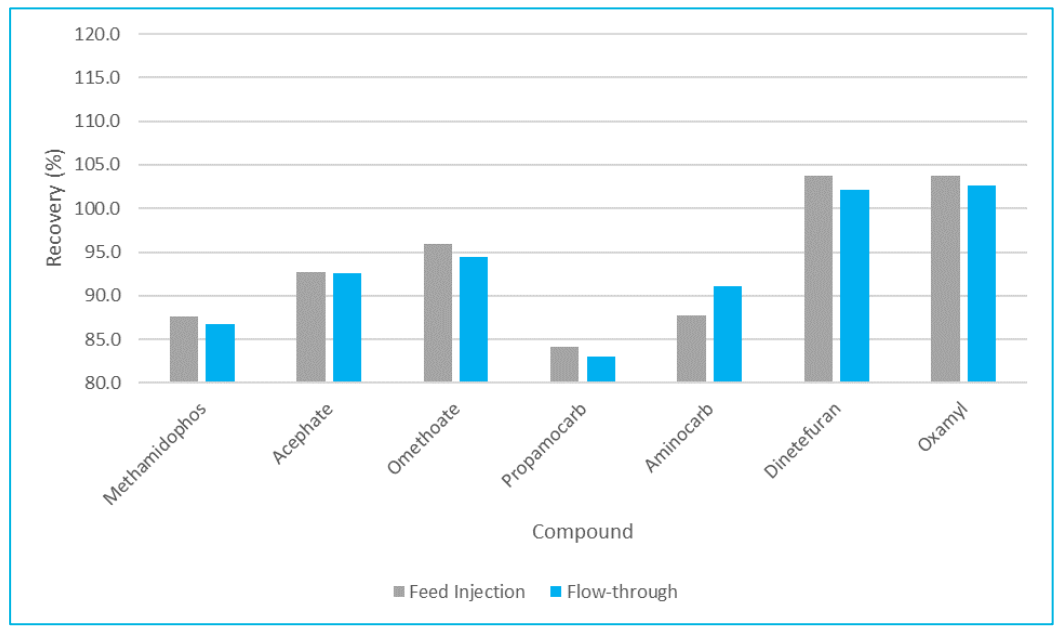


Figure 7) Recovery of pesticides (spiked at 10 ppb) from strawberry matrix in Feed Injection versus Flow-through injection at 1.5 µL injection volume

The recoveries of the three earliest eluting pesticides tended to be between 85% and 95%. The two pesticides that eluted last showed a recovery between 100% and 105% (Figure 7). The percentage recoveries achieved in Flow-through injection mode were within the same range, with an identical tendency to increase with the later-eluting pesticides.

Conclusions

- Feed Injection provides typically superior peak shapes for the early eluting polar pesticides from solution in acetonitrile.
- This also improves area RSDs, linearity of calibration curves and the achieved LOQs
- The recoveries obtained from QuEChERS extracts in acetonitrile meet the requirements to be between 80% and 120%.
- Due to the optimum peak shape time consuming data review can be reduced.

References

1. Herschbach, H.; Naegele, E. Performance Characteristics of the Agilent 1260 Infinity II Hybrid Multisampler. Agilent Technologies technical overview, publication number 5994-5952EN, 2023.
2. European Commission: Health & Consumer Protection Directorate – Method Validation and Quality Control Procedures for Pesticide Residues Analysis in Food and Feed, SANTE/12682/2019.

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