

Comparison between two chromatography conditions by LC-MS/MS for 150 pesticides

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Introduction

The pesticide analysis is a dynamic sector where methods are developed to quantify the largest number of pesticides with a minimum of methods involved. That is the reason why the choice of the chromatography conditions (buffer, solvent and gradient) is crucial in HPLC.

Experimental methods

The experimentations were carried out using a 2.8 μm , 50*2 mm C18 column. A mass spectrometer API 3200TM (AB Sciex) triple quadrupole in positive mode was used for detection. The injection volume and the oven temperature are the same for both methods and are respectively $V=10\mu\text{L}$ and $T=35^\circ\text{C}$.

Case 1 : A: $\text{H}_2\text{O} + 0.01\%$ formic acid
B: 95/5 v/v $\text{CH}_3\text{CN}/\text{H}_2\text{O} + 5\text{mM}$ ammonium acetate
+ 0.01% formic acid

Gradient 1				
Time (min)	0	15	20	23
% B	6	95	6	6

F = 150 $\mu\text{L}/\text{min}$

Case 2 : A: $\text{H}_2\text{O} + 5\text{mM}$ ammonium acetate + 0.1% formic acid
B: $\text{MeOH} + 5\text{mM}$ ammonium acetate + 0.1% formic acid

Gradient 2							
Time (min)	0	5	6	8	12	13	16
% B	5	70	70	90	90	5	5

F = 250 $\mu\text{L}/\text{min}$

A mixture composed of 150 pesticides at $500\mu\text{g}/\text{kg}$ in 1mL of acetonitrile and 2 μL of 5% formic acid has been prepared for the injection.

Results and discussion

For both methods, all the pesticides are eluted at the end of the run. Comparing the signal to noise of 26 transitions, the median value of ratio between case 2 and case 1 is equal to 0.9. Thus, case 1 generates a better sensitivity.

Nevertheless, all the pesticides have a good peak shape with gradient 2 whereas few pesticides like the cycluron (fig1) are too wide (more than 2 min) with gradient 1.

That can be due to the presence of acetonitrile which by changing the interactions with the molecules and the stationary phase makes wider peaks. It can also be due to the slope of the gradient which is inappropriate here. No experiments have yet been made with another slope to try to get thinner peaks.

Besides too wide peaks do not allow working with a scheduled MRMTM and would lead to a lower sensitivity.

Finally, the duration of gradient 2 is faster than the other. At production level, such method would allow to gain time compared with gradient 1.

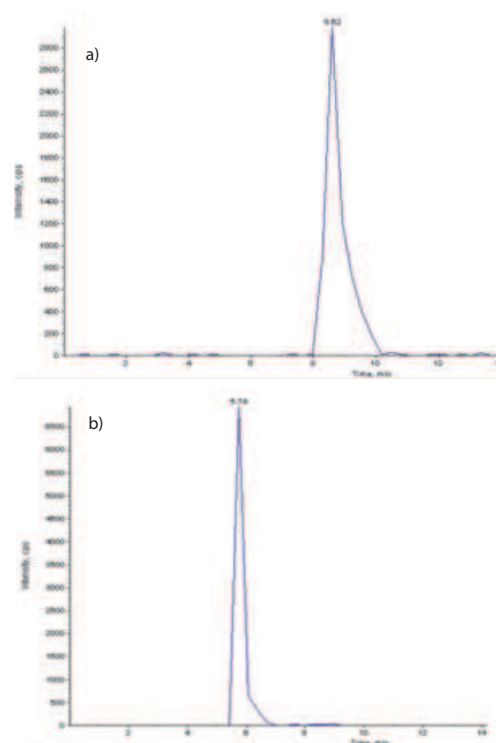


Figure 1 – Peak shape of cycluron in case 1 (a) and case 2 (b)

Conclusion

The case 2 is the most promising. First of all because all the pesticides injected give a thin Gaussian peak and also because we obtain an almost similar sensitivity with a shorter run time. So an optimization work could be led from this method to determine the best settings in terms of the buffer concentration, the percentage of formic acid and the gradient to develop a sensitive ($\text{LOQ} \approx 10\mu\text{g}/\text{kg}$) and robust method.



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