

Separation of chiral pesticides by applying supercritical fluid chromatography coupled to tandem mass spectrometry

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INTRODUCTION

Supercritical fluid chromatography (SFC) is a well-known technique used for enantioseparation in the pharmaceutical industry but its application in pesticides field has not been well studied yet. In this work 21 pesticides were separated using SFC-MS/MS with a polysaccharide-based chiral stationary phase column. Supercritical fluid chromatography allows the separation of isomers in a short run time because high flow rates can be applied without losing chromatographic efficiency. A change of the mobile phase used for the multiresidue method is not necessary, in addition, the absence of water and the low flow that reaches the source increase the sampling efficiency. This research focuses on those compounds whose isomers have a different toxicological nature like Lambda-Cyhalothrin.

EXPERIMENTAL

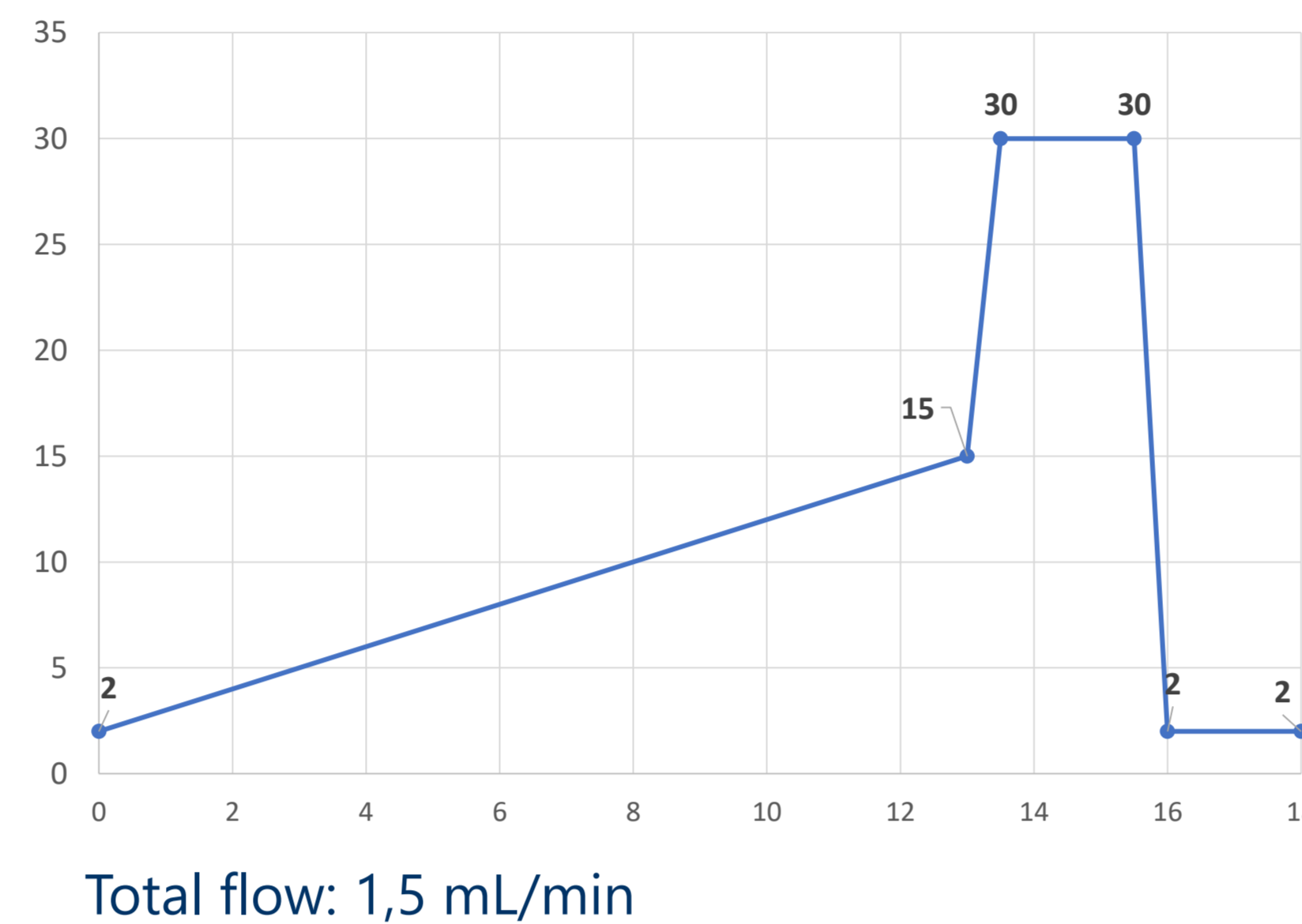
System: Shimadzu Nexera UC coupled to LC-MS 8060

SFC parameters:

- Injection volume: 2 µL
- Flow rate: 1,5 mL/min
- Make up flow: 0,08 mL/min
- Oven temperature: 40°C
- BPR pressure: 150 bar
- BPR Temperature: 50°C
- Mobile Phases:
Modifier: MeOH 1mM HCOONH₄
Make up: MeOH 5mM HCOONH₄ 0.1% HCOOH

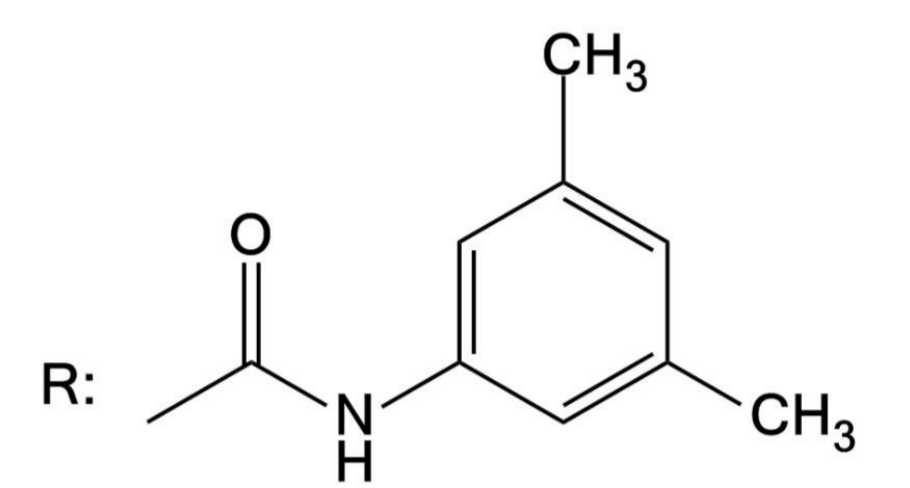
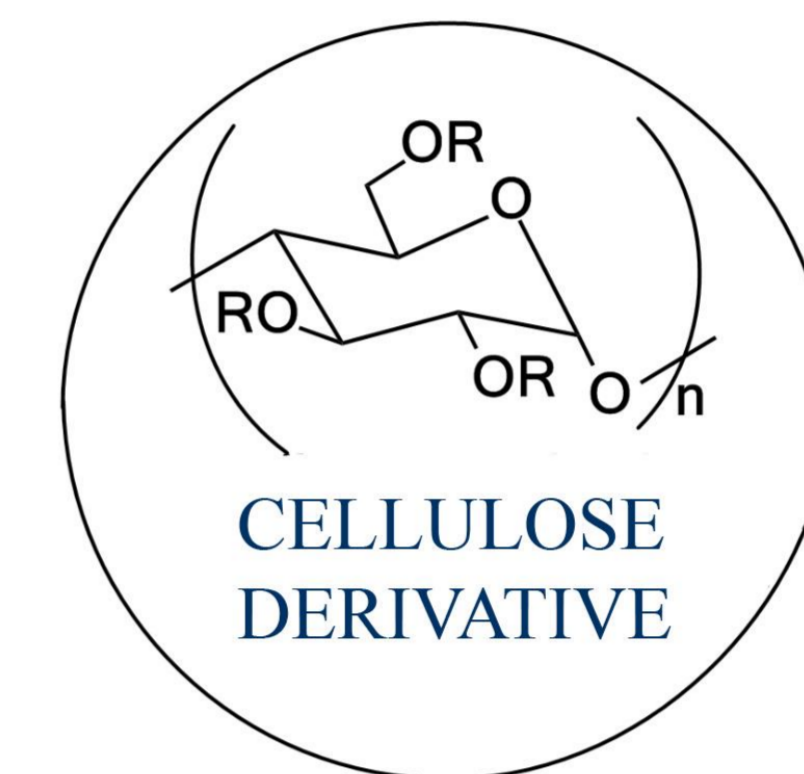
MS parameters:

- Ion source: ESI
- Polarity: Positive and negative
- Schedule MRM software features
- Dwell time: 5 ms



Column: Lux Cellulose-1

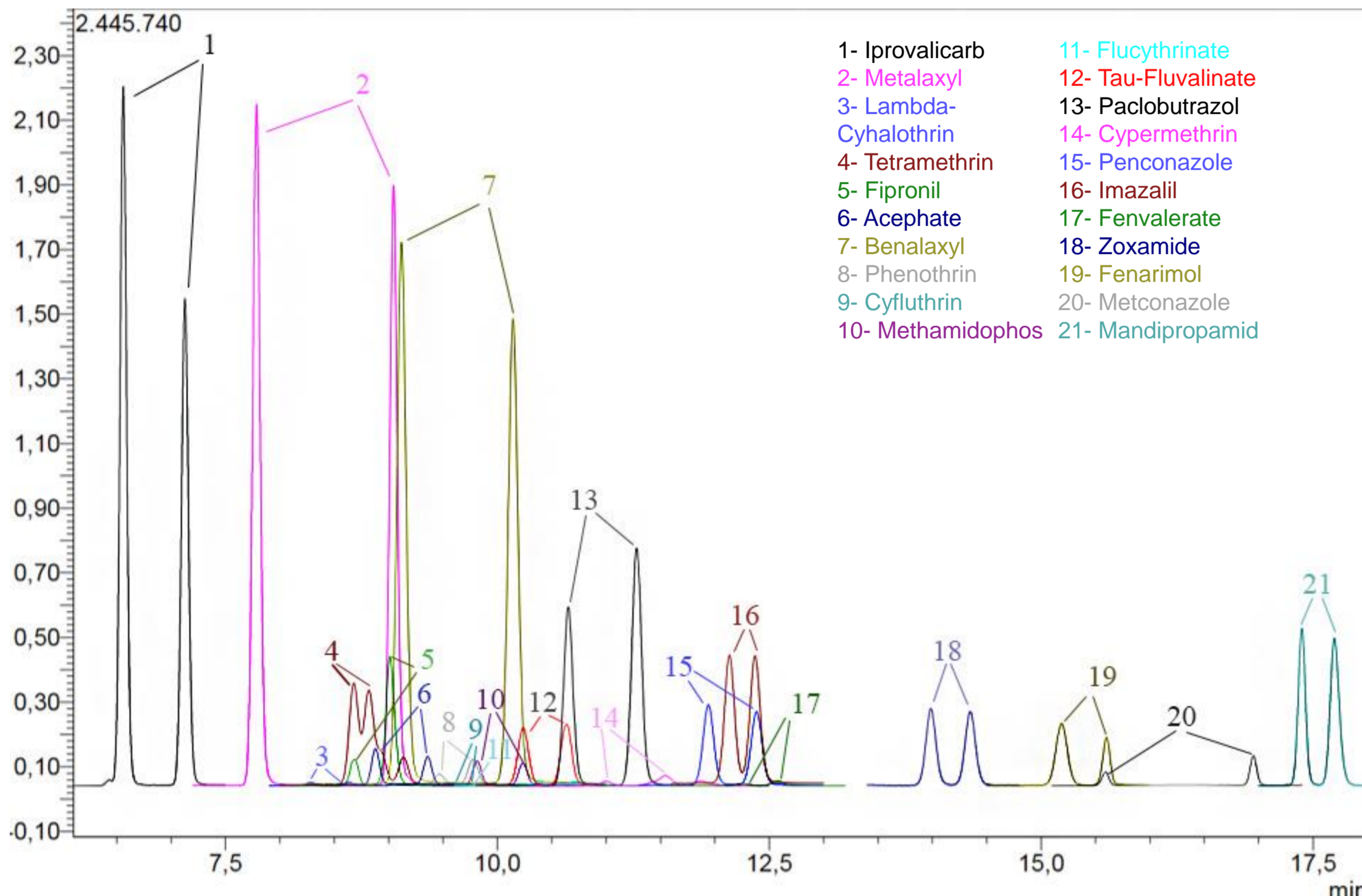
- Stationary phase: Cellulose tris(3,5-dimethylphenylcarbamate)
- Length: 250x4.6 mm
- Particle size: 5 µm



RESULTS AND DISCUSSION

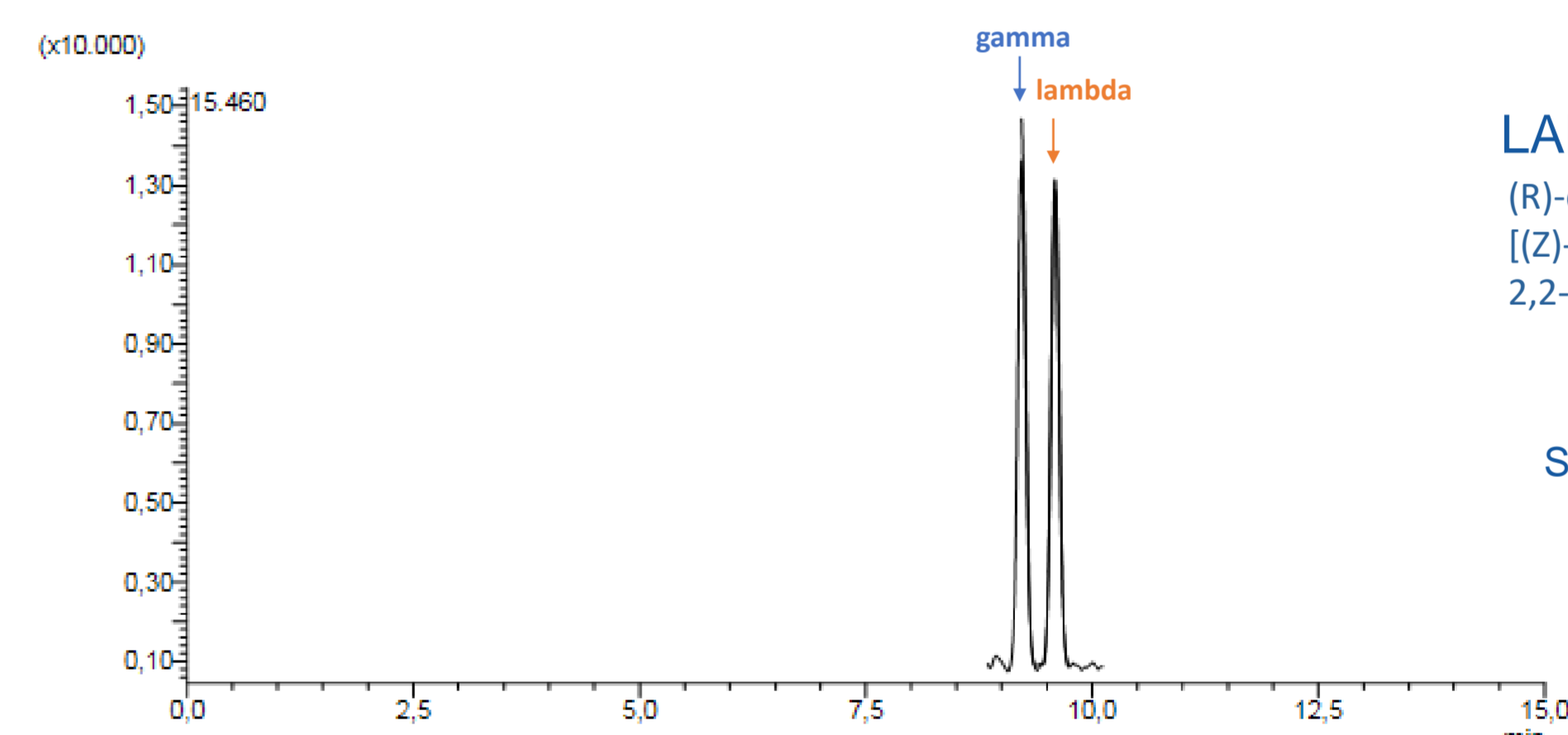
Chiral compounds separated

Injection of our chiral pesticides mix at 100 µg/kg in tomato matrix



Lambda-Cyhalothrin isomers

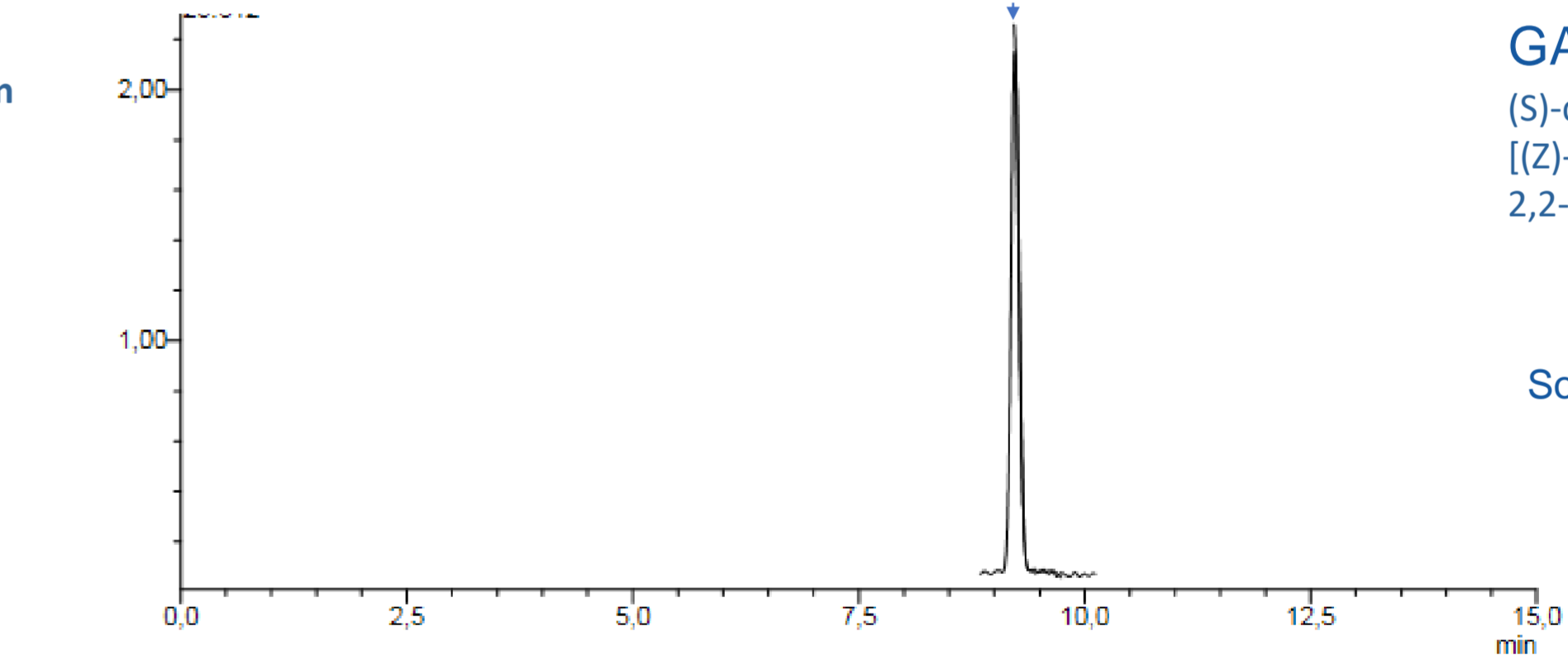
Standard
Lambda + gamma
cyhalothrin
Tomato
10 µg/kg
Price: 92€



LAMBDA- CYHALOTHRIN
(R)-α-cyano-3-phenoxybenzyl (1S)-cis-3-[(Z)-2-chloro-3,3,3-trifluoropropenyl]-2,2-dimethylcyclopropanecarboxylate

ARfD: 0.005
Source: Reg. (EU) No 1334/2014

Standard
Gamma cyhalothrin
Tomato
10 µg/kg
Price: 226€

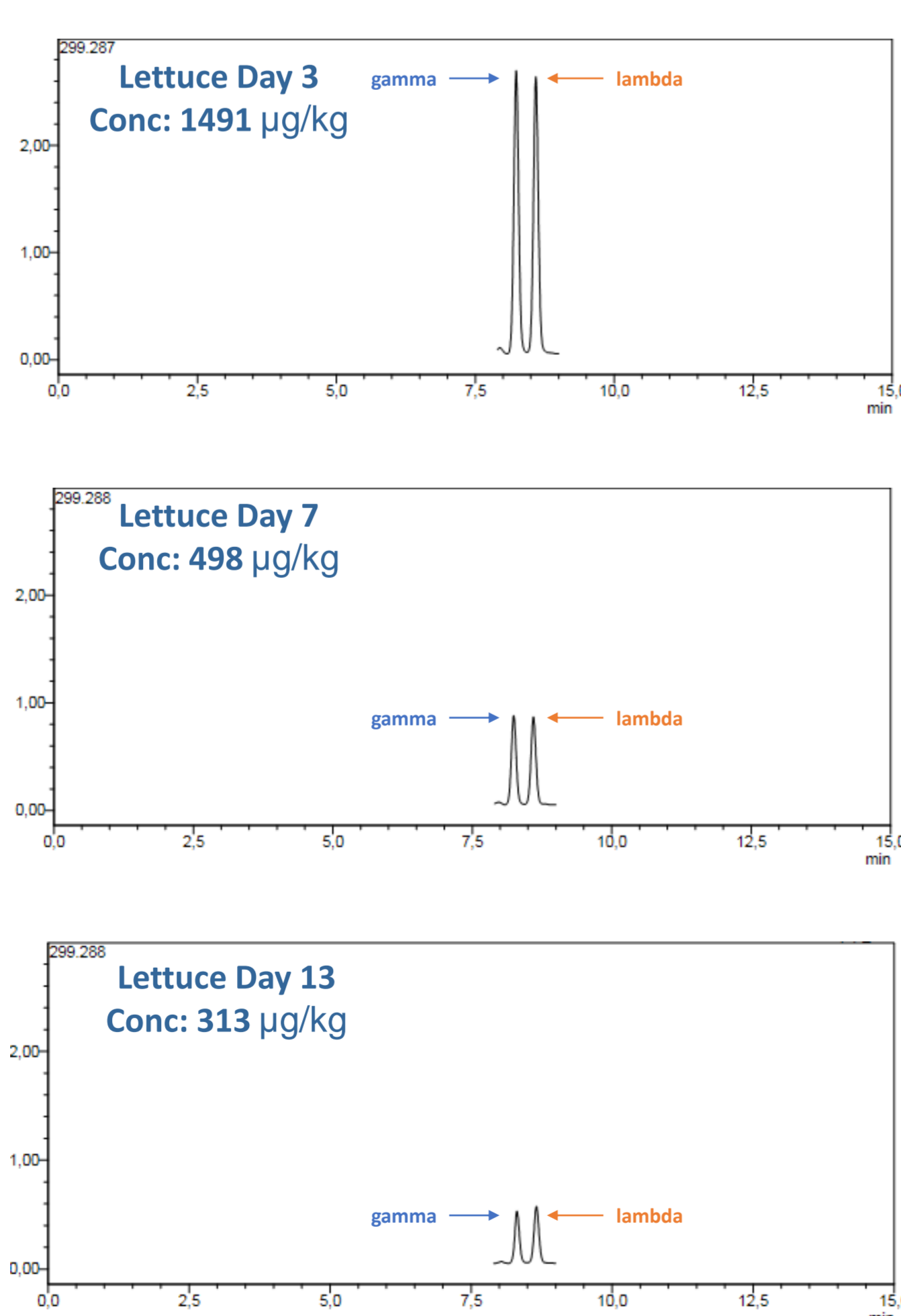


GAMMA- CYHALOTHRIN
(S)-α-cyano-3-phenoxybenzyl (1R)-cis-3-[(Z)-2-chloro-3,3,3-trifluoropropenyl]-2,2-dimethylcyclopropanecarboxylate

ARfD: 0.0025
Source: Reg. (EU) No 1334/2014

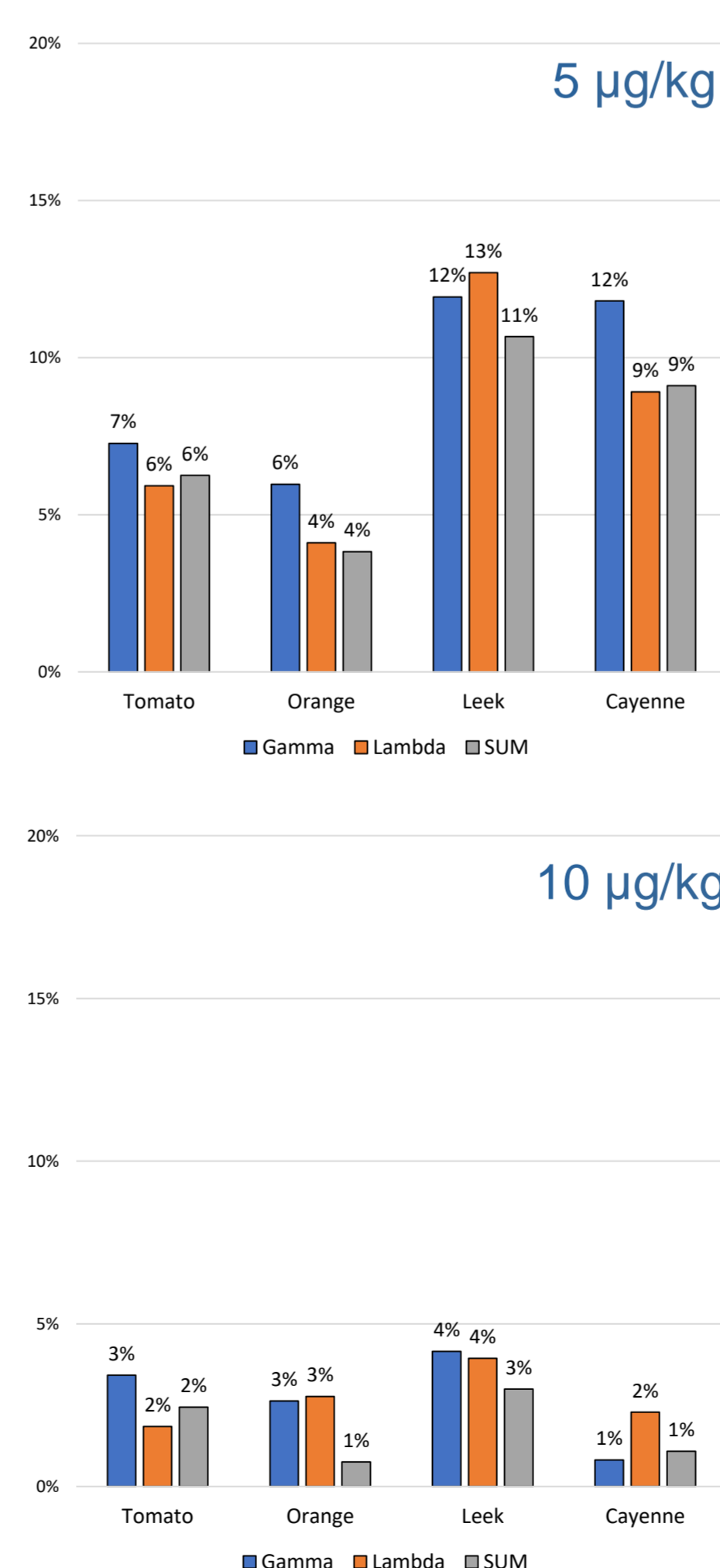
Incurred lambda-cyhalothrin

Lambda-Cyhalothrin was applied in lettuce under greenhouse conditions. Collections were made at different stages and analyzed to identify if there is any change in the isomers proportion



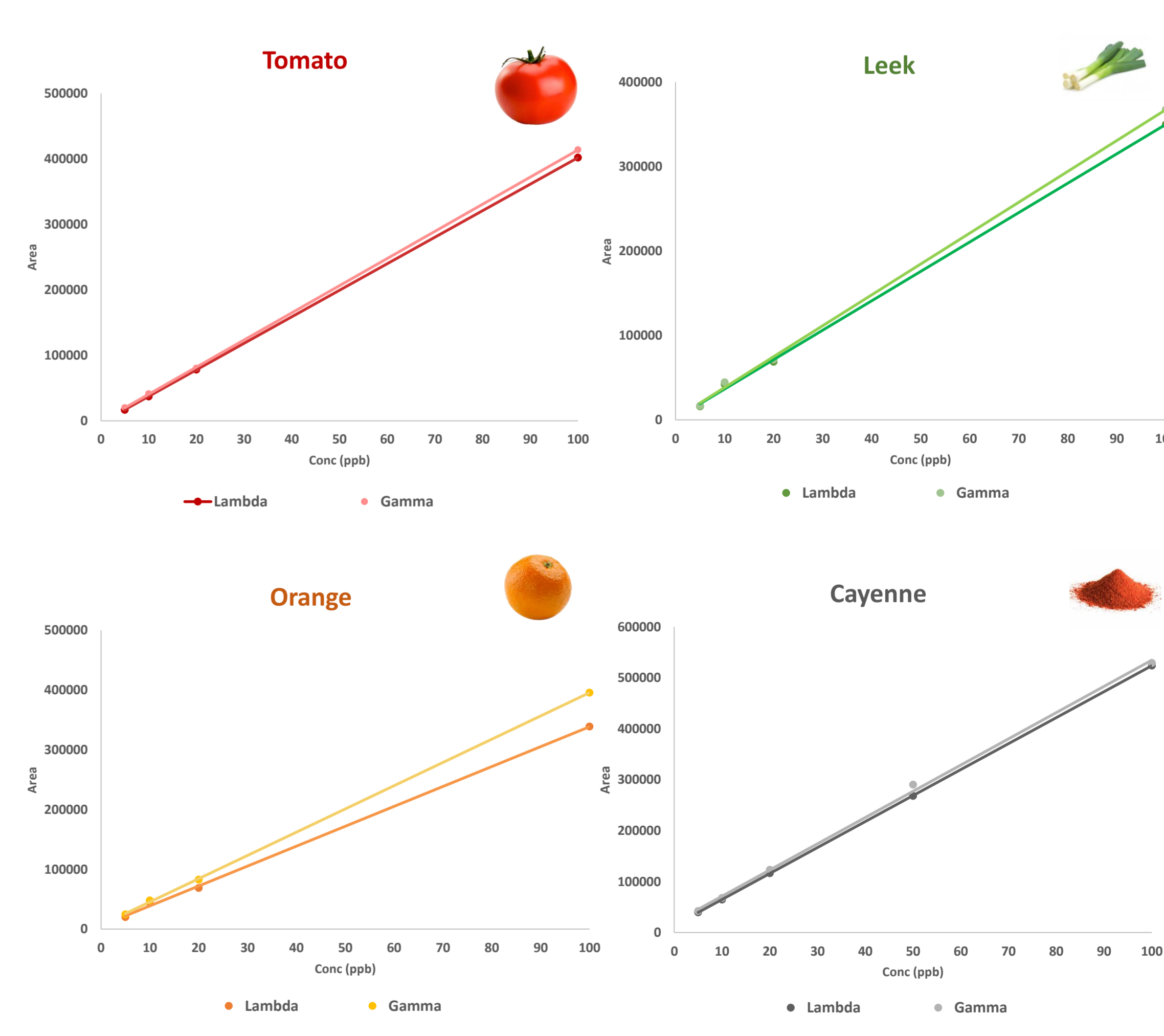
Reproducibility

For identified compounds at 5 and 10 µg/kg



Matrix effect

Calibration curves (5,10,20,100 µg/kg) for each isomer in four different matrices



CONCLUSIONS

- A fast enantioseparation of 21 different pesticides was performed using SFC-MS/MS
- Both isomers of lambda-cyhalothrin were identified at 5 µg/kg-1 in tomato, orange, leek, and cayenne.
- No significant matrix effect was observed in the 4 four matrices studied and both isomers did not show huge differences between them.
- The degradation of gamma and lambda-cyhalothrin seems to be proportional for both isomers at least in lettuce matrix.