Investigations into Pesticide Charge State Isomers with Ion Mobility and High-Resolution Mass Spectrometry

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OVERVIEW

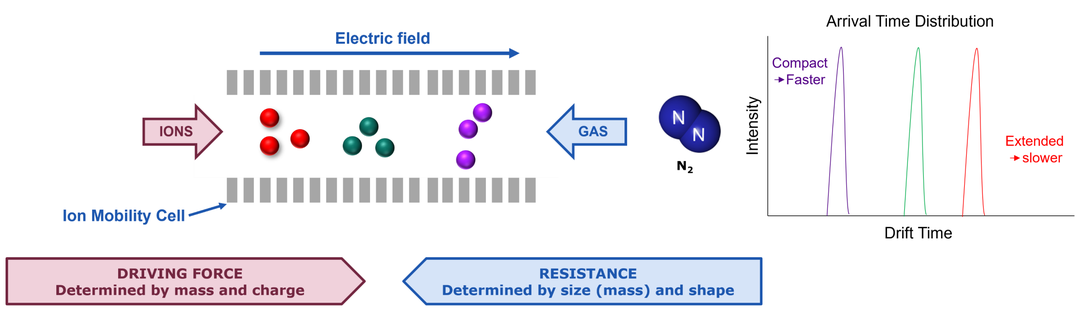
- **Exploring the use of ion mobility to reveal charge site isomer and conformer formation**
- **Understand the potential impact of charge site isomer formation on MRM ion ratios**
- **Using collision cross section (CCS) data of charge site isomers to provide a higher degree of specificity**

INTRODUCTION

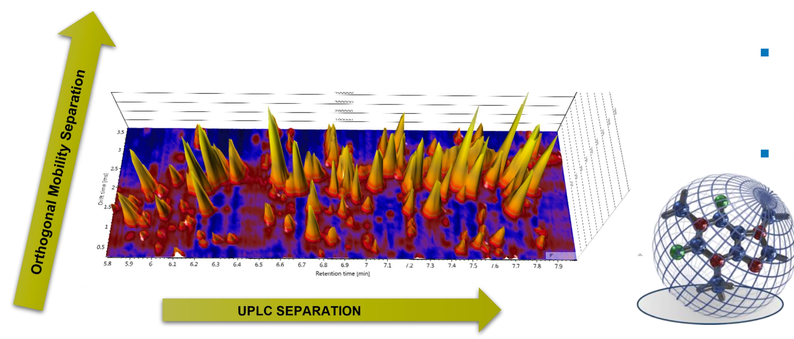
The testing for pesticides in food and other commodities is an important step in guaranteeing consumer safety. Typical analytical methodology for pesticide testing includes liquid chromatography-mass spectrometry (LC-MS) to detect ions based on retention time, mass/charge ratios, and the relative abundance of characteristic product ions (ion ratios). In particular, the ion ratios can be variable and has led to wide tolerances in regulatory methods. One source of this variability is the formation of different charge site isomers (protomers, sodimer, and potassimers) that yield different product ions and can be influenced by matrix, solution, and ion source conditions. In this study, we explored the use of ion mobility with high resolution mass spectrometry to gain a greater understanding of the charge site isomers and their influence on observed ion ratios. Using the IMS dimension, different charge-site isomers can be resolved based on their shape and the difference in their collisional cross section (CCS).[1] For some residues, separation of different charge site isomers required the use of a high-resolution cyclic IM device (Figure 1). This device was used to resolve and determine CCS values for isomer species of indoxacarb, spinosad, fenpyroximate, epoxiconazole, metaflumizone, and avermectin.[2]

Figure 1. (Top) Schematic of the SELECT SERIES™ Cyclic™ IMS Instrumentation. (Bottom) The cyclic ion optics (right) and a zoom in of the traveling wave array that enables the control of ions in the cyclic device (left).

ION MOBILITY



Ions separated based on their mass, charge and **shape**



IMS can be readily incorporated into an LC-IM-MS arrangement to add an extra dimension of separation and characterization.

- Ion mobility separation allows for measurement of collision cross section (CCS)
- CCS is an additional identification point
  - Not affected by changes to chromatography (mobile phase, column, etc.)
  - Not affected by matrix effects
  - Potential to identify isomers/conformers

RESULTS

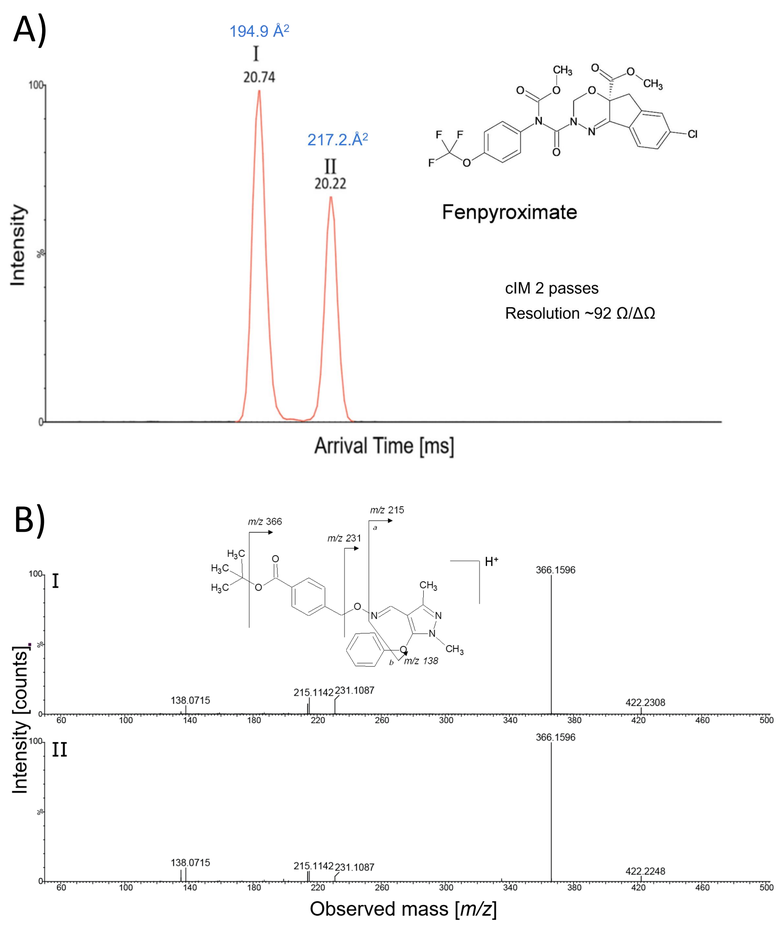


Figure 2. Ion mobility separation of fenpyroximate. A) Fenpyroximate consists of two components (likely a compact configuration (I) and elongated configuration(II)) that can be baseline-resolved after 2 passes in the cyclic ion mobility device. B) The two species produce equivalent product ion spectra.

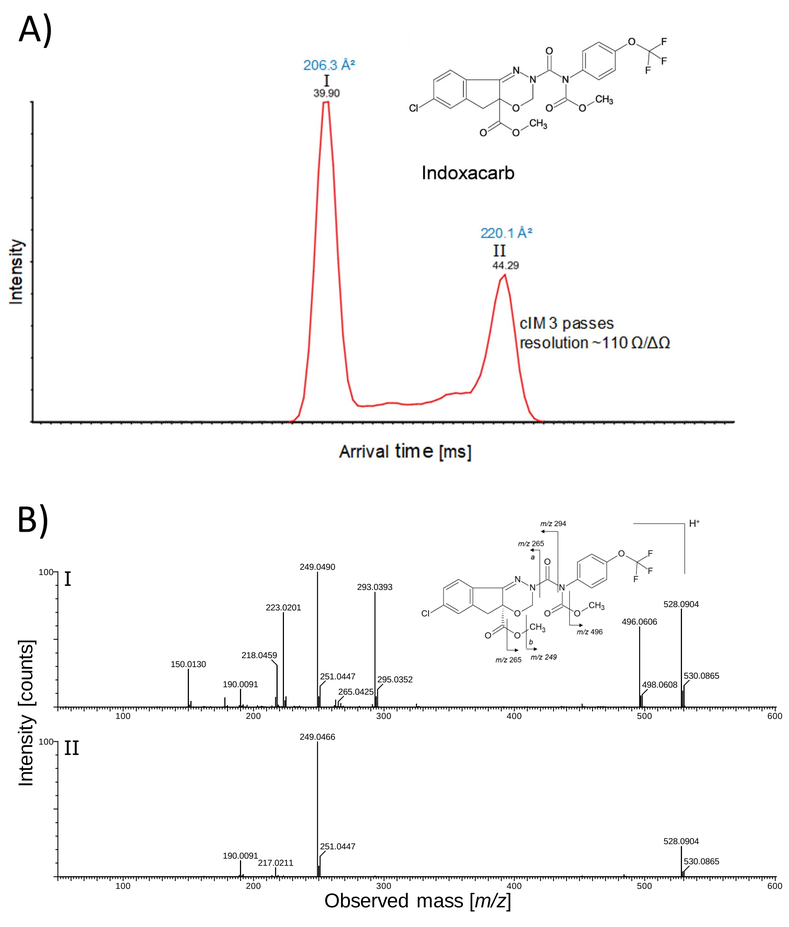


Figure 3. Ion mobility separation of indoxacarb. A) Using 3 passes around the cIM, the charged isomer species are resolved. B) The two components have non-identical product ion spectra, consistent with the different configurations having different protonation sites.

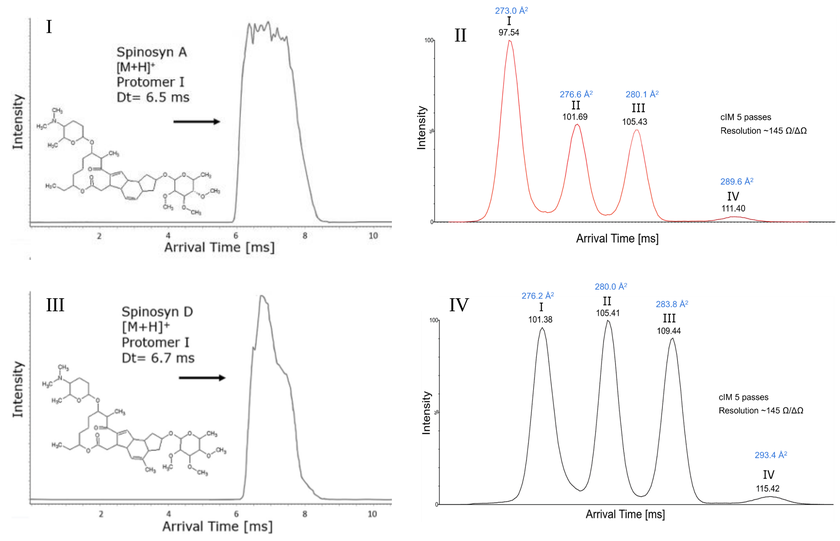


Figure 4. Ion mobility separation of spinosad conformers. I) Ion mobility separation of spinosyn A [M+H]+ *m/z* 732.468 on a linear ion mobility device. II) Using 5 passes around the cIM, four charged isomer species of spinosyn A are resolved. III) Ion mobility separation of spinosyn D [M+H]+ *m/z* 746.484 on a linear ion mobility device. II) Using 5 passes around the cIM, four charged isomer species of spinosyn D are resolved.

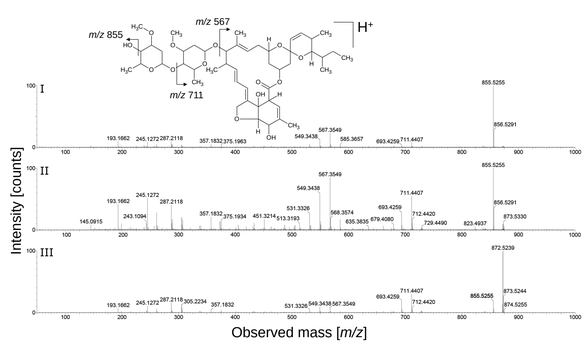


Figure 5. Avermectin B1a cIM resolved isomerising species product ion spectra. Using 5 passes around the cIM, three charged isomer species of avermectin B1a are resolved.

CONCLUSIONS

- **Ion mobility has enabled a unique insight into the process of ionization and fragmentation of pesticides in the gas phase**
- **The enhanced cIM separation facilitated separation of conformer species that were previously un-resolved with a linear ion mobility device. The extra separation enabled investigations into the individual charged isomer and conformer dissociation spectra, where single component fragmentation spectra were obtained.**
- **CCS of charged isomers can provide enhanced specificity and potentially be added into mass spectrometry databases to aid in identification**

REFERENCES

1.. Discovery of pesticide protomers using routine ion mobility screening. M McCullagh and S Goscinny. *Waters Appl. Note* 2014, *720005028E*.

2. McCullagh, M., Goscinny, S., Palmer, M., Ujma, J. Investigations into pesticide charge site isomers using conventional IM and cIM systems. Talanta 234 (2021) 122604.