Development of Searchable Pesticide MS and MS-MS Libraries

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Overview

Goal: Evaluate the effects of different MS-MS conditions and instruments in order to develop a searchable MS-MS library of pesticides.

Requirement: Library must be searchable by different end users --must accommodate instrument differences and a variety of ion trap conditions.

Approach: Acquire data for pesticides on multiple ion trap instruments (two manufacturers) at a variety of ion trap conditions.

Main Conclusion: The MS-MS searching library is feasible --a modified library search algorithm can accommodate the spectral variations produced by different ion trap conditions.

Future Work: Continue to collect MS-MS data for more pesticides and work on development and optimization of search algorithms.

Introduction

Each year, laboratories worldwide conduct >200,000 analyses of pesticide residues in food and environmental samples. Of the approximately 800 pesticides registered for use in agricultural applications, more than half are thermally stable and amenable for gas chromatographic (GC) analysis. Ideally, pesticides targeted for detection should be confirmed by mass spectrometric (MS) analytical methods. However, matrix interferences from food and environmental samples frequently thwart detection using GC/MS. The added selectivity of MS-MS often improves the confirmation capability and lowers detection limits of targeted analytes in complex matrices. Currently, MS-MS libraries are not available to help the analyst choose instrumental conditions or identify unknown sample constituents.

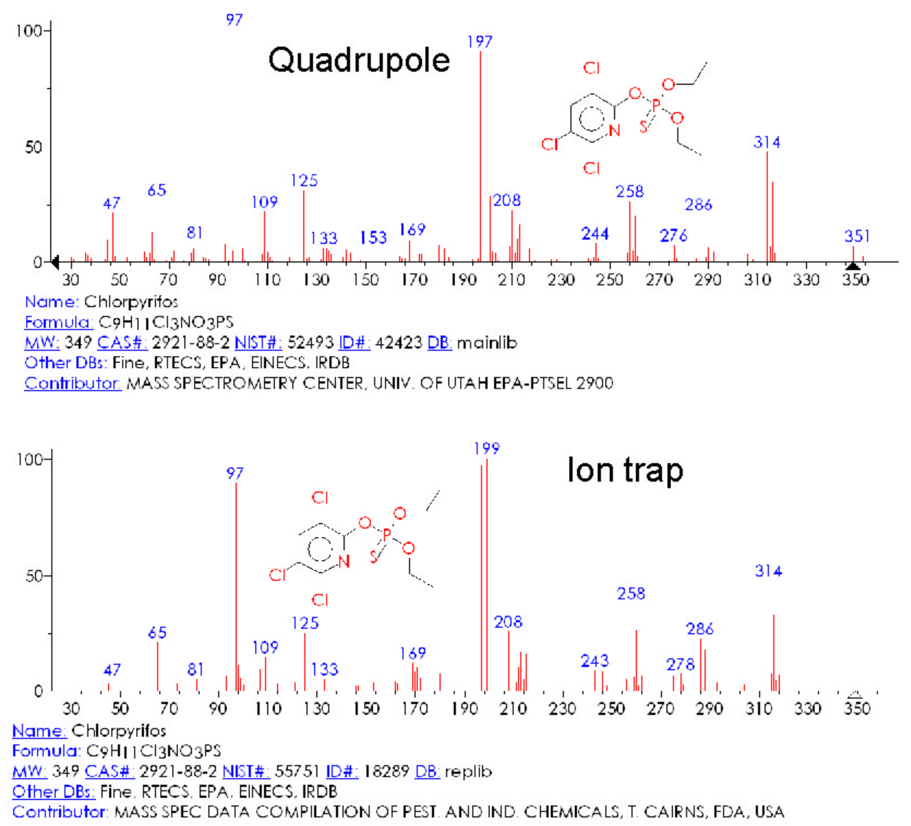
The goal of this ongoing work is to evaluate and determine optimal MS-MS parameters and to provide a searchable MS-MS library for use in pesticide monitoring. The library under construction focuses on about 300 of the GC stable pesticides and will be searchable as both an MS and an MS-MS database.

Methods

We are acquiring both MS and MS-MS data for GC compatible pesticides. Spectra are collected on 3 GC/MS instruments from different manufacturers. Two instruments are ion trap mass spectrometers for the MS and MS-MS data collection. The third instrument is a quadrupole mass spectrometer used for MS confirmation and comparison. Up to 3 precursor ions are selected for MS-MS data collection depending on the quantity and intensity of the MS ions for the pesticide. One ion trap instrument (Varian Saturn) has been equipped with a modified direct inlet (Chromatoprobe) for ease of data collection, whereas the other two instruments (Finnigan GCQ and Agilent 5973) utilized standard GC injection.

Comparison of Quadrupole and Ion Trap Mass Spectral Data

Figure 1: Quadrupole vs. Ion Trap Mass Spectra



- Example of quadrupole and ion trap mass spectra from NIST 98 Mass Spectral Library. See also ion trap MS in Figure 2 for more examples.

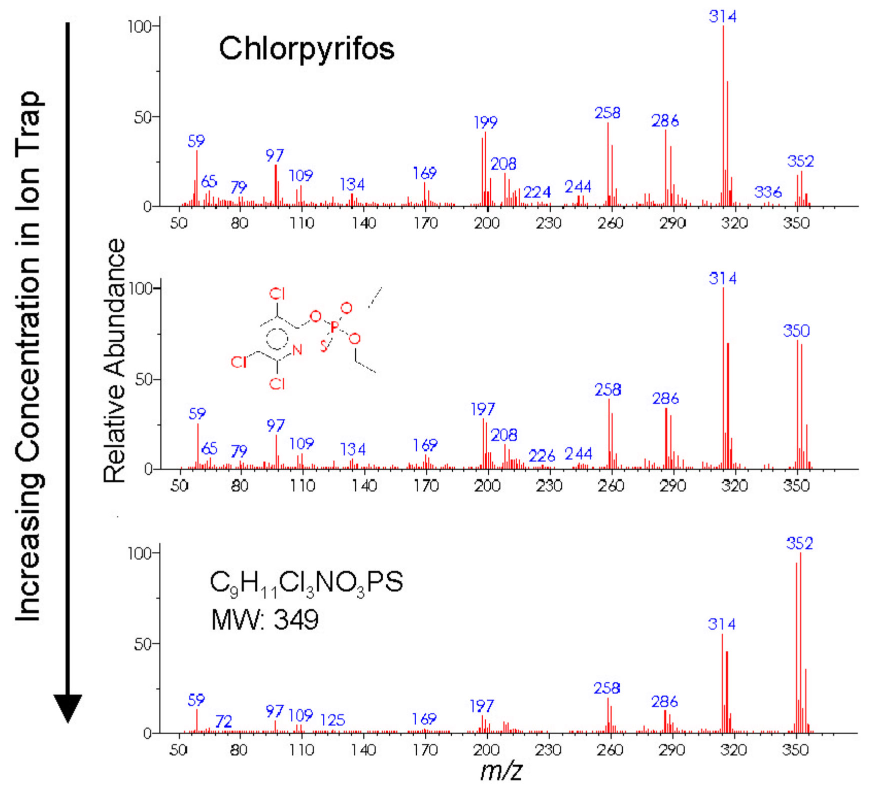
Library Search Results with Ion Trap and Quadrupole Data

CAS#	Compound Name	Net Match Factor: Quadrupole	Net Match Factor: Ion Trap
1719-06-8	Anthracene-d10	87	87
57-74-9	Chlordane	78	87
1897-45-6	Chlorothalonil	95	92
101-21-3	Chlorpropham	95	94
1719-03-5	Chrysene-d12	87	79
60-51-5	Dimethoate	83	72
122-39-4	Diphenylamine	99	93
959-98-8	Endosulfan	84	88
563-12-2	Ethion	76	79
950-37-8	Methidathion	95	82
52645-53-1	Permethrin	91	75
90-43-7	o-Phenylphenol	100	96
732-11-6	Phosmet	65	66
29232-93-7	Pirimiphos methyl	98	90
13071-79-9	Terbufos	98	85
1582-09-8	Trifluralin	94	90

- Example of matrix sample GC/MS analysis with MS Library match factors between NIST 98 and Ion Trap and Quadrupole Data.

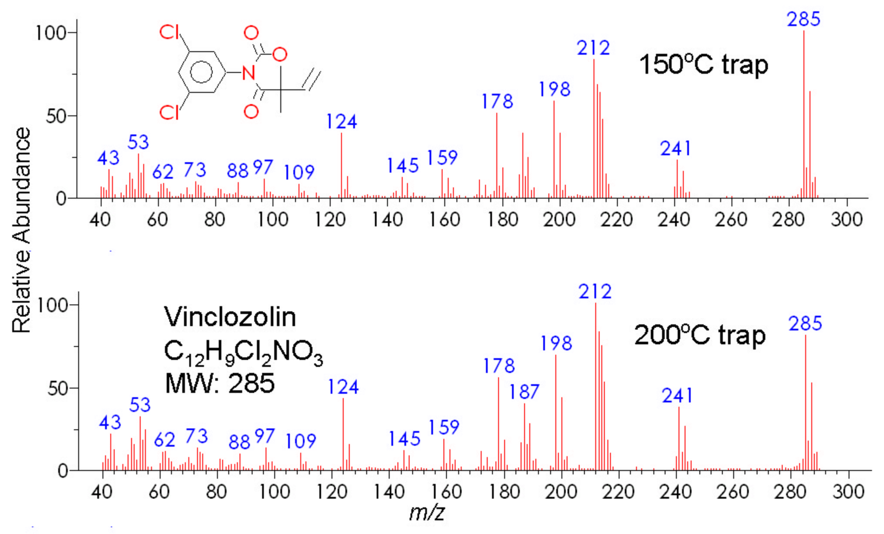
Effect of Ion Trap Variables on Mass Spectra

Figure 2. Concentration in Ion Trap



- Data taken with Chromatoprobe. No background subtraction.

Figure 3. Ion Trap Temperature



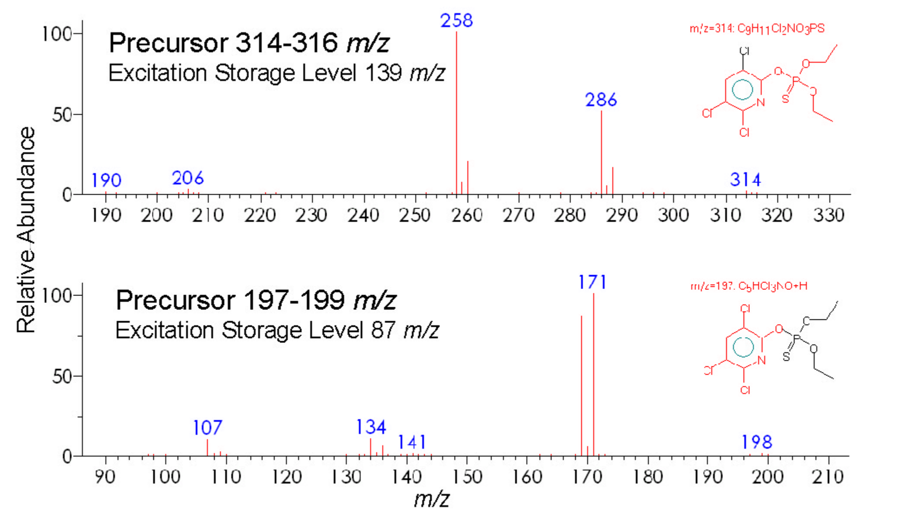
- Molecular ion intensity increases as concentration increases and temperature decreases.
- Changes are small enough that library search is still effective.

MS-MS Parameters Varied:

- Precursor Ion
- Temperature
- EI or PCI (MeOH)
- GC Flow Rate
- Ion Trap q-value
- CID Energy
- Analyte Concentration
- Resonant or Non-resonant Ionization

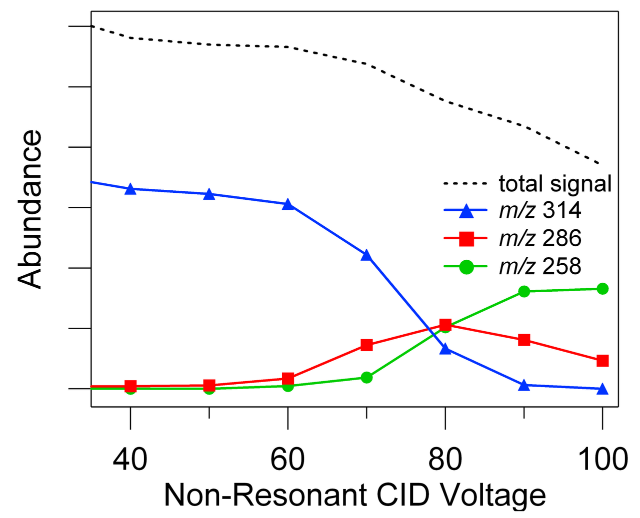
Effect of Ion Trap Variables on MS-MS

Figure 4. Precursor Ion



Ion Trap conditions for chlorpyrifos
top panel: 150°C, non-resonant 90 V CID, q-value = 0.4
bottom panel: 175°C, non-resonant 90 V CID, q-value = 0.4

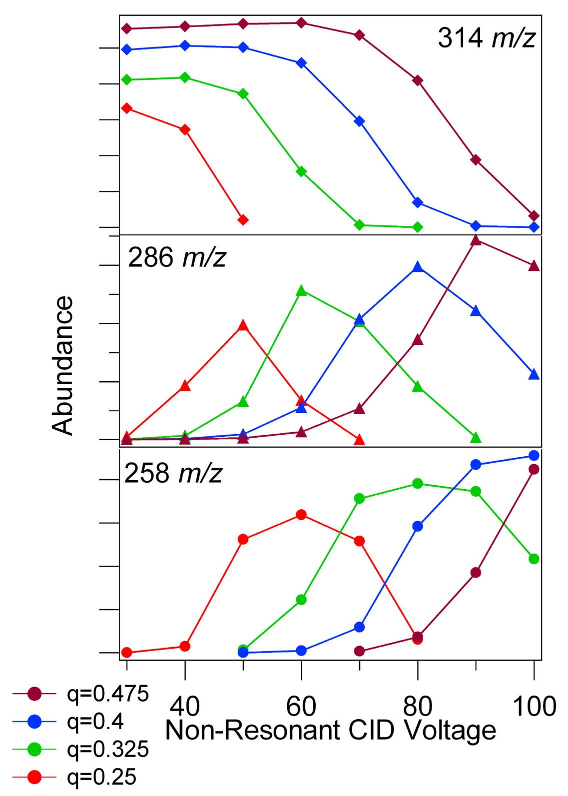
Figure 5. Collision Induced Dissociation (CID) Voltage



Chlorpyrifos, precursor 314 m/z, q=0.4, trap temp 150°C

- At a given q-value total signal decreased as CID energy increased, but more products were generated for identification.

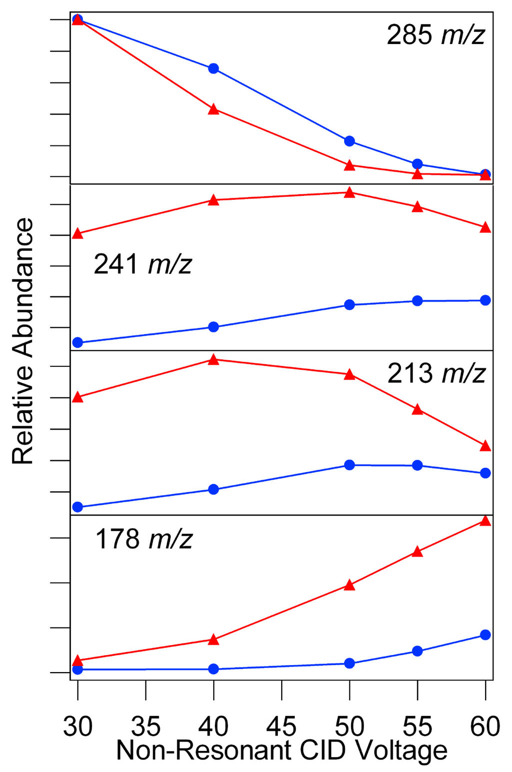
Figure 6. "q" Value



Chlorpyrifos
precursor 314 m/z
trap temp 150°C

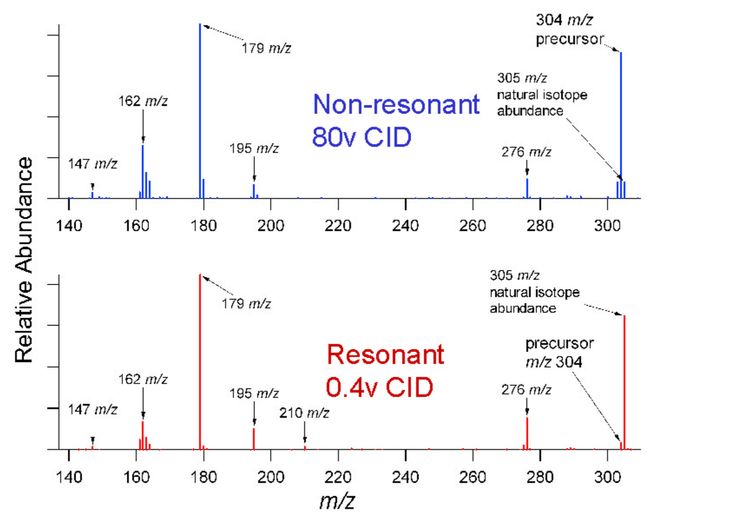
- Higher CID energy was required to dissociate the precursor ion as the q-value was increased.
- The molecule dissociated similarly independent of q-value.

Figure 7. Trap Temperature



- Vinclozolin at trap temperatures of 150°C and 200°C. Changes in response to CID voltage vary with temperature. More fragmentation occurs at higher trap temperatures.

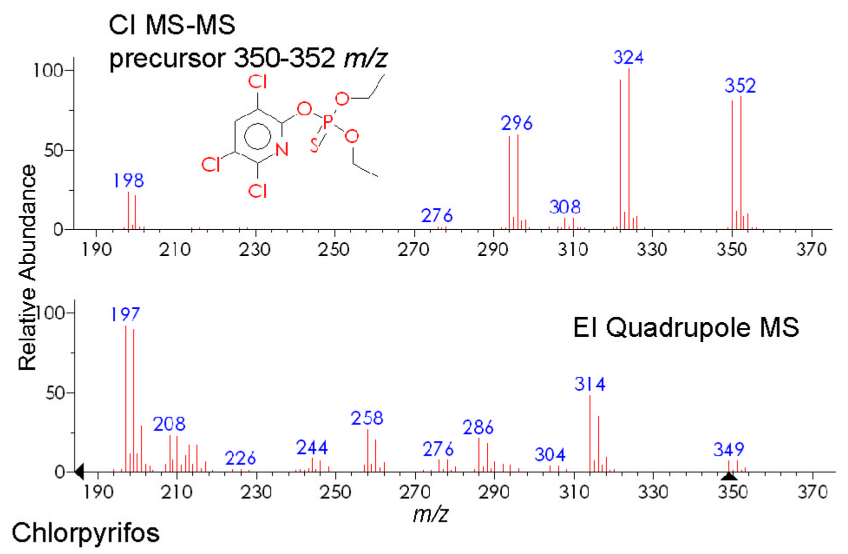
Figure 8. Non-resonant vs. Resonant Dissociation



Diazinon, trap 150°C, q=0.4, precursor 304 m/z

- The same products appear with both resonant and non-resonant dissociation in this case, but we expect to find some exceptions to this. Resonant dissociation is more selective requiring much lower CID voltages.

Figure 9. Electron Impact Ionization (EI) vs. Chemical Ionizaion (CI)



Chlorpyrifos

- EI MS-MS usually produces products that are also seen in MS. CI can produce a very different set of products.

Conclusions

- No major discrepancies were found between the ion trap mass spectra and the quadrupole mass spectra of the pesticides evaluated.
- Using ion trap pesticide MS to search a quadrupole MS library give satisfactory results.
- The variation in MS-MS data was explored at different MS-MS conditions.
  - Analyte **concentration** and **ion trap temperature** can affect relative ion intensities.
  - **Precursor ion** is chosen by the uniqueness of the ion and it's ability to produce at least one (more is better) product.
  - **CID voltage** and **ion trap q-value** should be chosen to produce sufficient dissociation products.
  - Library search requirements for **resonant** vs. **non-resonant** and **EI** vs. **CI** need to be explored further.
- Additional efforts will involve analyzing both the MS-MS data under various instrument conditions and the MS-MS search algorithm accuracy in order to allow library users complete flexibility when acquiring their own data for searching against the library.

Acknowledgment

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