Development of Searchable Pesticide MS and MS-MS Libraries

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Each year laboratories worldwide conduct more than 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 of these pesticides 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 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.

We are acquiring both MS and MS-MS data for GC compatible pesticides. Spectra are collected on three 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. All MS data are acquired under standard conditions while the MS-MS data are collected for a variety of instrumental conditions. Up to three 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) utilize standard GC injection.

The variations in the MS and MS-MS data were explored under different instrumental conditions. We have varied the following parameters: precursor ion, trap temperature, GC flow rate, ion trap q-value, collision induced dissociation (CID) energy, analyte concentration, resonant or non-resonant ionization, and electron impact ionization (EI) or positive chemical ionization (PCI). Analyte concentration and ion trap temperature can affect relative ion intensities. The concentration in the ion trap can affect both MS and MS-MS data. Increasing the ion trap temperature increases the degree of dissociation that occurs (see figure 1). The precursor ions are chosen by the uniqueness of the precursors and their signal levels. The CID voltage and ion trap q-value should be chosen to produce sufficient dissociation products. The CID voltage affects the degree of dissociation (see figure 2) and is molecule dependent. Library search requirements for resonant vs. non-resonant and EI vs. CI need to be explored further.

Additional efforts 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.

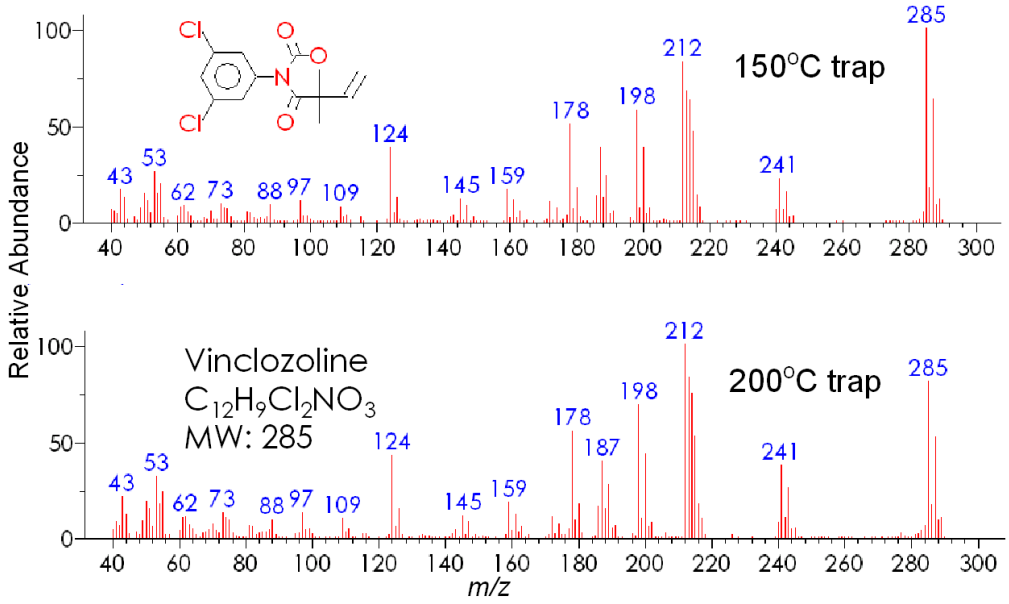

Figure 1. Ion Ratios change with trap temperature.

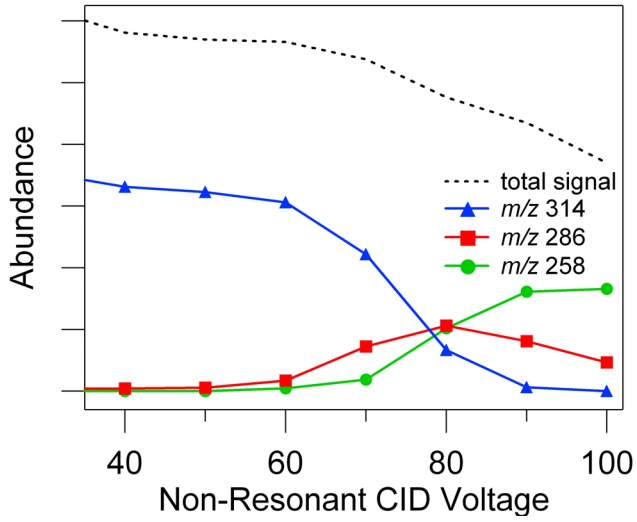

Figure 2. Effect of Collision Induced Dissociation energy on the degree of dissociation. This data is for Chlorpyrifos. The precursor ion is 314 *m/z*.