GC/MS/MS Analysis of Triazine Herbicide Residues Using Multiple Reaction Monitoring

GC/MS

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Introduction

Triazines are a class of herbicides commonly applied as pre-and-post-emergent weed control agents in agricultural fields containing corn, apple, grapes, wheat, etc. These herbicides have environmental half-lives of weeks to several months. Degradation products are typically more water-soluble, dealkylated compounds. According to various reports[1, 2], large amounts of triazines (approximately 100-150 million pounds) are applied annually and thus pose a major threat to the environment. Some triazine herbicides have been characterized as carcinogenic, mutagenic and teratogenic in animal studies[2]. The serious risks posed by these contaminants are reported to be additive and thus will have a greater impact on infants and small children. From the above discussion, it is clear that better methods for the analysis of triazine residues are required.

Triazine herbicides are referred to as s-triazines, meaning they are symmetrical in structure. This structural similarity makes identification and quantitation of residue levels of individual triazines difficult. In this study, a method was developed for the analysis of seven triazine herbicides using MS/MS and multiple reaction monitoring (MRM). The seven triazines studied include simazine, atrazine, propazine, cyanazine, ametryn, prometryn and prometon. With a 60M DB-5ms capillary column, six triazines in this study exhibit partial chromatographic resolution. Incomplete chromatographic separation does not pose a limitation to unique MS/MS conditions for each analyte due to the multiple reaction monitoring (MRM) feature of the MS/MS ToolKit. MRM allows the analysis of coeluting compounds in the MS/MS mode by analyzing each compound on alternate scans. Non-resonant collisionally induced dissociation (CID) MS/MS parameters were optimized for maximum sensitivity using the automated method development (AMD) ToolKit software. The AMD ToolKit software offers a quick and easy way to optimize the MS/MS parameters to achieve maximum sensitivity with a minimum number of experiments.

The optimized MS/MS parameters were used to construct the three ion preparation method (IPM) files used for the analysis of the seven triazines of interest. Each IPM file was constructed using the ToolKit software in the MRM mode. The first IPM file was composed of four individual microscans containing the MS/MS parameters for prometon, simazine, atrazine, and propazine. The second MRM IPM file contained two microscans with MS/MS parameters for ametryn, prometryn. The third MRM IPM file contained only one microscan with MS/MS parameters for cyanazine. Using the 3 MRM IPM files in time segmented acquisition, the seven triazines were analyzed at residue levels in a single chromatographic run as shown in Figure 1.

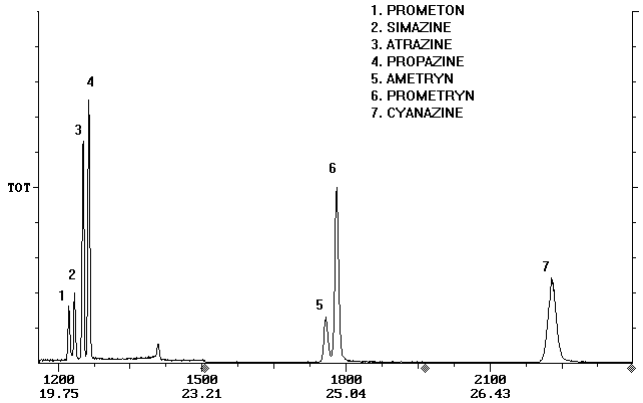

Figure 1: 1 ng/uL standard of triazines by MS/MS

Results

Figure 2 shows a typical herbicide formulation sample contaminated with prometryn by GC/MS/MS. The prometryn signal represents 48 pg on column.

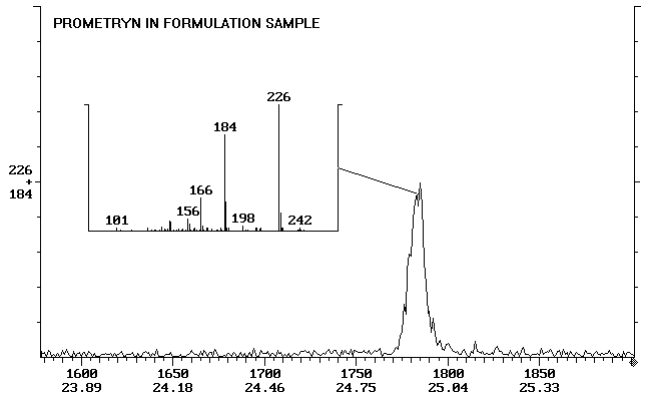

Figure 2: MS/MS analysis of Prometryn in a formulation sample with 48 pg on column

Instrument Conditions

Gas Chromatograph
Column: DB-5ms, 60M X 0.25mm X 0.25um
Oven Program: 50°C for 1 min., then 20°C/min. to 170°C with no hold time, 3°C/min. to 240°C and hold for 3 minutes.
Injector: 1078 270°C Splitless
Transfer Line: 300°C
Flow Rate: 1.5 ml/min.

Mass Spectrometer
Mass Range: 50-250 u
Multiplier Delay: 6 minutes
Filament: 20 μamps
Ion Trap Temperature: 250°C

MS/MS Conditions (Non-resonant)

Compound	Parent Ion	RF level	Voltage	Product Ion
Prometon	210	120	100	168
Simazine	201	99	73	138
Atrazine	215	143	98	200
Propazine	214	123	100	172
Ametryn	227	106	78	212
Prometryn	241	119	96	226
Cyanazine	225	94	83	189

Conclusion

A GC/MS/MS method was developed using the MRM ToolKit software to analyze mixtures of triazine herbicides in a single chromatographic run. This method has been applied to a variety of real world samples including residues found in complex pesticide formulations. Excellent sensitivities with high signal to noise ratios were routinely achieved. This application demonstrates the utility of the MRM ToolKit software for the analysis of compounds that are difficult to separate chromatographically such as the environmentally important triazine herbicides.

References

1. *Gianessi, L. P. A National Pesticide Usuage Data Base, Resources for the Future, Washington, DC, 1986, 1-14.*

2. *Long, J. Chemical & Engineering News, 1994, Oct 24, 8*