

GC/MS/MS Analysis of Dinitroaniline Based Herbicides In Fish

GC/MS

Varian Application Note

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Mike Cost and Bert Lynn
Mississippi State University

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Introduction

Dinitroaniline based herbicides are in use as preplant protection for agricultural products such as soybeans, cotton and rice. These herbicides control the unwanted growth of certain broadleaf weeds that would otherwise reduce the yields of these products. These herbicides are widely used (approximately 30 million lbs. annually) and the runoff from fields where these chemicals are applied contaminates streams, lakes and groundwater. The exposure of fish to these herbicides will result in greater human exposures. The LD₅₀ is 3380 to 3700 mg/kg in rats for the various herbicides of the dinitroaniline class. The analysis of fish samples for trace level herbicides is difficult due to the heavy matrix interference caused by fish oil and tissue. GC/MS/MS is a logical candidate as an analytical technique due to its extraordinary selectivity.

Discussion

Figure 1 shows the signal obtained for Trifluralin in fish sample #4676 (7 pg on column) when analyzed by GC/MS/MS. The analysis conditions can be optimized quickly using either a simplex optimization or the Toolkit software, which allows the changing of CID conditions on a scan by scan basis. In either case, ideal conditions for each target analyte can be developed in a minimum time for the analyst. The collision induced dissociation (CID) process can be achieved by either resonant or non-resonant excitation. This can be important as certain compounds favor a particular excitation process for best sensitivity.

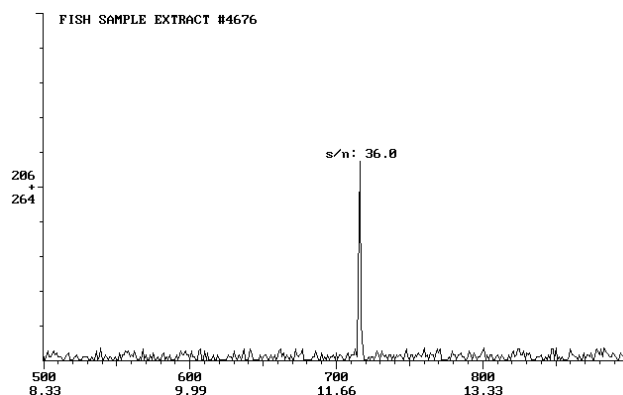


Figure 1: GC/MS/MS analysis of fish sample #4676 for Trifluralin (7 pg on column).

Table 1 shows the optimized conditions based on sensitivity of the product ions. All quantitation is based on external standards with calibration curves ranging from 20 pg to 1200 pg on column.

Table 1: Non-resonant MS/MS conditions for herbicides

| Compound | Parent Ion | RF | Amplitude |
|---------------|------------|-----|-----------|
| Benefin | 292 | 557 | 59 |
| Butralin | 266 | 587 | 58 |
| Fluchloralin | 306 | 550 | 55 |
| Pendimethalin | 252 | 886 | 89 |
| Prodiamine | 290 | 411 | 45 |
| Profluralin | 318 | 510 | 58 |
| Trifluralin | 306 | 857 | 83 |



Instrument Conditions

Gas Chromatograph

Column: 5% phenyl/95% methyl Arylene modified PDMS, Varian Equivalent: CP-Sil 8 CB Low-Bleed/MS, # 30m x 0.25 mm x 0.25 μ , # CP5860

Flow rate: 1 mL/min.

Oven program: 40°C for 1 min.; 20°C/min. to 200°C; then 4°C/min to 280°C; hold 5 min.

Injection temp.: 280°C

Transfer line: 280°C

Mode: splitless

Injection volume: 1 μ L

Mass Spectrometer

Mass range: 50-390 u

Scans/second: 1

Multiplier delay: 6 min.

RF level: 48

Threshold: 0

Ion Trap temperature: 250°C

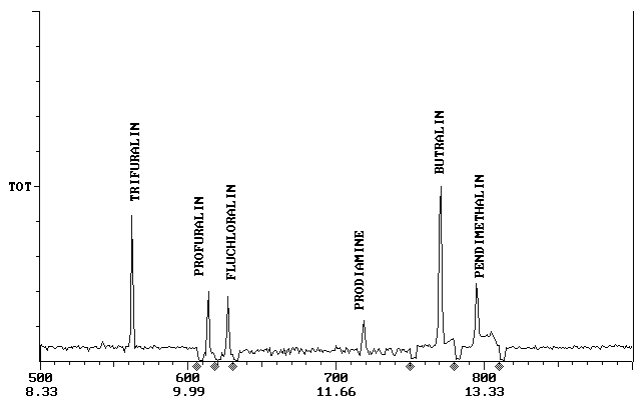


Figure 2: Total ion Chromatogram of herbicide standards using GC/MS/MS.

Conclusion

We have developed a GC/MS/MS method to analyze seven dinitroaniline based herbicides in a variety of matrices. A simplex optimization technique provided a simple and efficient way to optimize the MS/MS parameters. Using these optimized parameters resulted in average detection limits of 5 pg with a signal to noise ratio in excess of 10 for the analytes. Analysis of environmental samples, including fish tissue, demonstrated the utility of the MS/MS technique at removing matrix interferences.

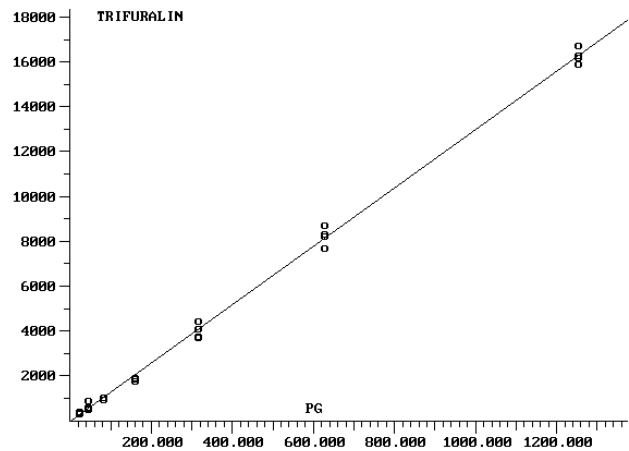


Figure 3: External standard calibration curve for Trifuralin (20 pg to 1200 pg) using GC/MS/MS.



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*These data represent typical results.
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