

## INTRODUCTION

Parathion is an organophosphate compound used as a potent insecticide. As a pesticide, parathion is often sprayed on cotton, rice, and fruit trees. Although the general public is not exposed to parathion, its use on farm crops is of concern and in many countries the use of parathion on food crops is banned because it is highly toxic to humans. Exposure can affect the central nervous system resulting in symptoms such as headaches, poor vision, vomiting, or abdominal pain. To avoid exposure, end users must wear appropriate protective gear. If contact is made with parathion, immediate decontamination procedures should be followed.

This application note demonstrates the capability of the Griffin 450 Gas Chromatograph/Mass Spectrometer (GC/MS) to identify parathion through MS/MS analysis (or multi-dimensional MS). MS/MS gives end users accurate information that allows them to make quick decisions regarding decontamination efforts and other precautionary procedures at the site of concern.

Mass spectrometry (MS) is the standard laboratory technology for detecting, differentiating and identifying trace levels of chemical compounds in complex chemical environments. Mass spectrometers are uniquely sensitive and accurate. They extract chemical signatures from test samples much more quickly and accurately than is possible with alternative technologies. They eliminate false positives. However, most conventionally designed units are too big and cumbersome to be deployed outside of a laboratory.

ICx mass spectrometers incorporate a Cylindrical Ion Trap (CIT). This significant advancement in MS capability allows for direct utilization in the field. Such technology was previously available in laboratories only. By incorporating the CIT, vacuum requirements normally associated with laboratory units have been reduced, power requirements minimized, and all achieved with analytical performance equivalent to traditional laboratory ion traps and quadrupoles.

The CIT provides unparalleled selectivity through the use of multi-dimensional mass spectrometry. MS/MS provides both a first-stage mass analysis to determine if a particular analyte of interest is present in a test sample, and, within minutes, a second-stage confirmation of the analyte's identity. ICx Analytical Instruments has been supplying this field-based technology since 2003.



Figure 1: The Griffin 450 – Mobile GC/MS/MS

## INSTRUMENTATION

- Griffin 450 GC/MS system
- Griffin System Software – GSS 3.7

## Gas Chromatograph and Conditions

Temperature Program: 80°C hold for 1 min, then increase at 25°C per minute to 290°C, hold for 1 min.	
Column	Rtx-5ms, 30 m x 0.25 mm x 0.25 µm
Injections	200°C
Carrier Gas	Helium, 1 mL/minute
Sample	1 µL of 10 ng/µL of parathion in methylene chloride

## Mass Spectrometer and Conditions

Automatic Level Control (ALC) enabled with maximum ionization time at 150 ms	
Mass Scan Range	m/z 40-425
Detector Temperature	150°C

## METHOD DEVELOPMENT AND RESULTS

### OPTIMIZATION OF ISOLATION METHOD

Figure 1 shows the chromatogram of 10 ng parathion using a full scan MS. Parathion was detected at a retention time of 8.26 min. The first step of MS/MS method development is to select the precursor ion. For parathion, m/z 292 was selected. Once the precursor ion is selected, the software will automatically load the default MS/MS method parameters. Figure 2 shows the default parameters after m/z 292 is selected as the precursor ion. The second step is to optimize the Isolation Adjust parameters. The Dissociation voltage was set to 0 for the isolation of the precursor ion. Figure 3 shows the isolation result with isolation method 1. Some dissociation from m/z 292 was observed (m/z 277, 189, 191). In order to minimize the dissociation of m/z 292 in the isolation step, the Upper Boundary m/z was set to 4. Figure 4 shows the isolation result with isolation method 2. Isolation method 3 further optimized the isolation parameters by lowering the Upper Boundary Amplitude to 3 v and changing the End m/z to 298. Figure 5 shows the result with isolation method 3.

### OPTIMIZATION OF DISSOCIATION METHOD

After optimizing the isolation, the next step is to optimize the dissociation parameters (voltage, frequency, and time). Dissociation voltage was varied in 0.5-volt increments from 0.5 to 2.5 volts, dissociation frequency was varied in 0.5-Hz increments from 170 to 180 kHz., and dissociation time was varied in 10-ms increments from 30 to 200 ms. We anticipate an optimum value for each of these parameters, with low values having too little energy to effect dissociation, and high values imparting so much energy that the target ions either dissociate further or escape the trap entirely. The results for voltage optimization (figure 6) illustrate this: at 0.5 V there were few fragments produced; an optimum was reached at 2 V, and at 2.5 V many fragments were produced, but total ion count was reduced. The combination of 174 kHz, 30 ms, and 2 V produced good dissociation (figure 7 shows these parameters entered in the MS-Method tab of Griffin System Software). Results are in good agreement with NIST MS/MS data, which show m/z 264 and 236 as major fragments.

## CONCLUSION

Phosphorous pesticide parathion was analyzed to demonstrate the tandem MS/MS capability of the Griffin™ 450 GC/MS/MS system. The MS/MS method development includes the optimization of isolation parameters and dissociation parameters. For parathion, m/z 292 was isolated and dissociated after optimizing the MS/MS method. The Griffin 450 is a fieldable MS/MS system utilized in numerous non-laboratory based applications. These results with parathion provide further confirmation of the utility provided by the Griffin 450 for on-site chemical analysis.

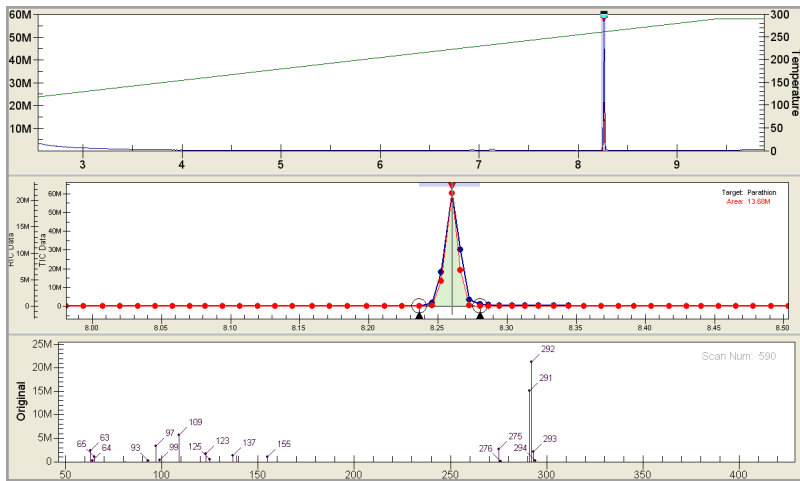


Figure 2: Chromatogram and full MS scan of Parathion

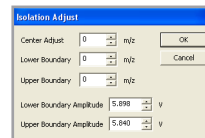
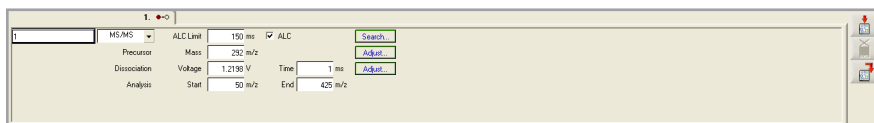


Figure 3: GSS default MS/MS method for precursor m/z 292

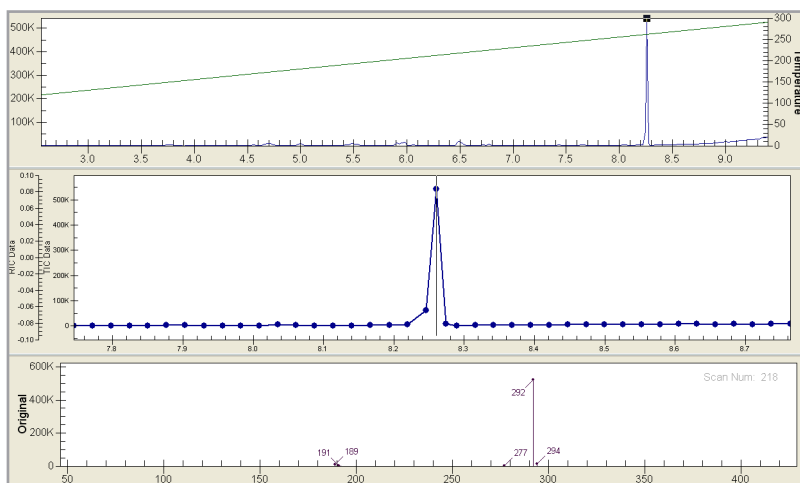
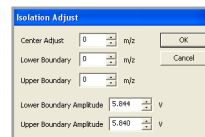
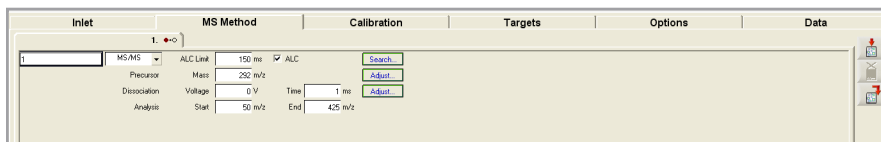


Figure 4: Isolation of m/z 292 with isolation method 1



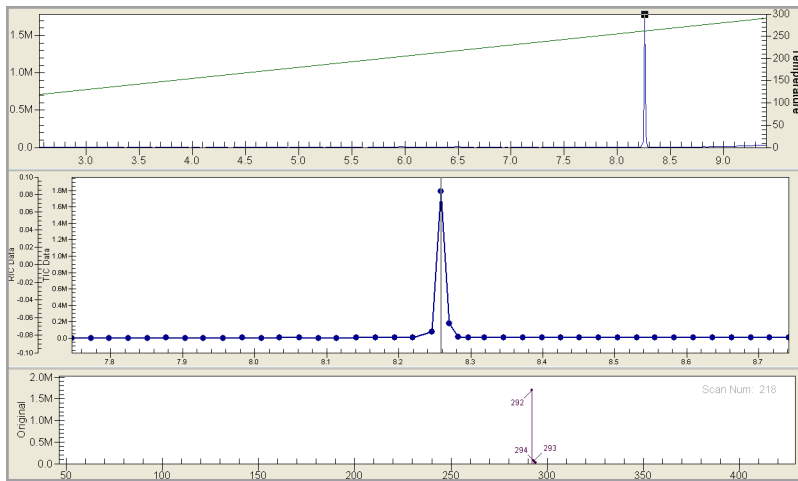


Figure 5: Isolation of m/z 292 with isolation method 2

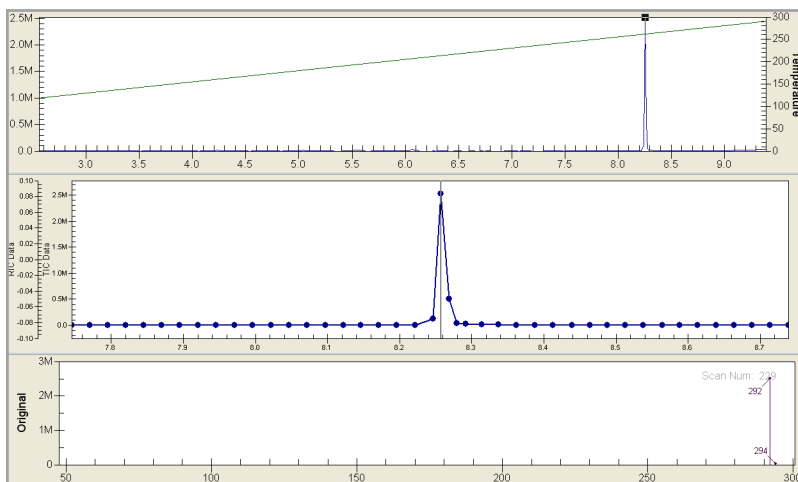
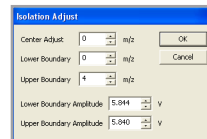
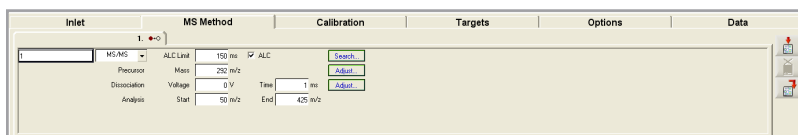
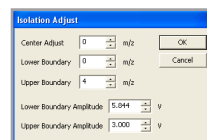
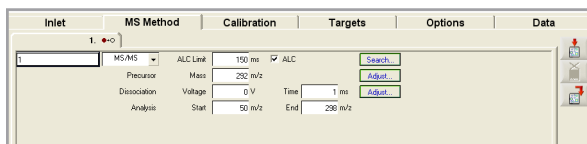
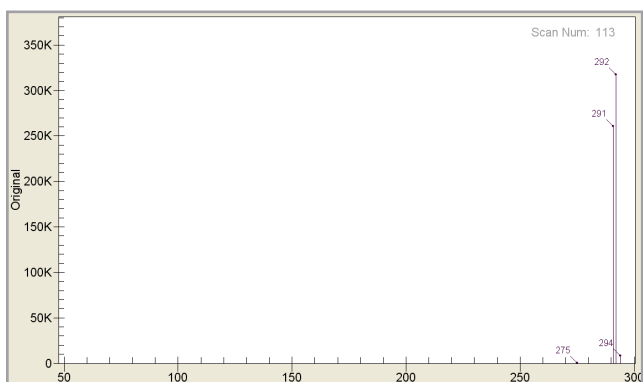


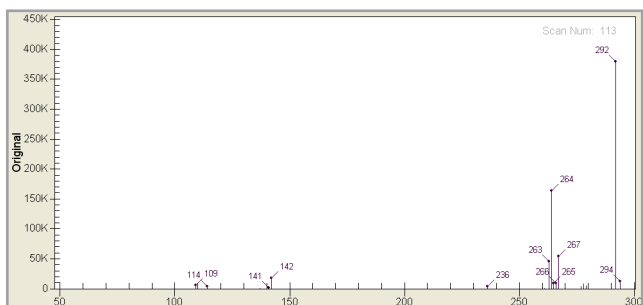
Figure 6: Isolation of m/z 292 with isolation method 3



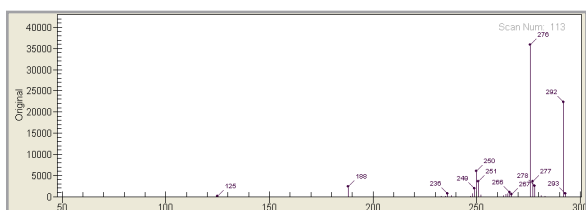
**Figure 7:** Ion production at 0.5V (top), 2 V (middle), and 2.5 V (bottom), with dissociation frequency held constant at 174 kHz. and dissociation time held at 30 ms.



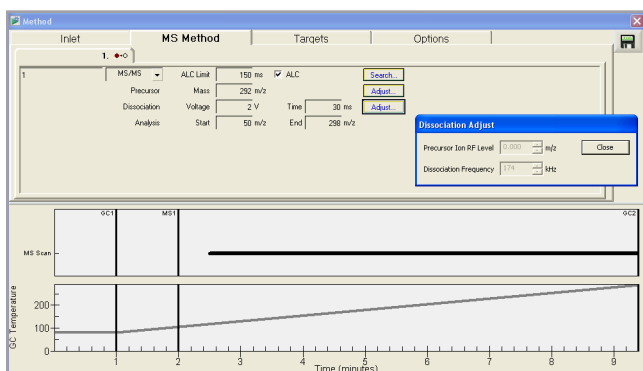
Parathion 174 kHz 30 ms 0.5 V



Parathion 174 kHz 30 ms 2 V



Parathion 174 kHz 30 ms 2.5 V



**Figure 8:** Optimized dissociation parameters

#### References

- (1) Wells, J.M.; Badman, E.R.; Cooks, R.G. *Anal. Chem.* 1998, 70, 438-444.
- (2) Patterson, G.E.; Guymon, A.J.; Riter, L.S.; Everly, M.; Griep-Raming, J.; Laughlin, B.C.; Ouyang, Z.; Cooks, R.G. *Anal. Chem.* 2002, 74, 6145-6153.

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