Minimizing Degradation of the Pesticides Captan and Iprodione by Using Fast Gas Chromatography—Time-of-Flight Mass Spectrometry

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Key Words: GC-TOFMS, Pesticides

1. Introduction

The United States Environmental Protection Agency (EPA) regulates the residual concentrations of the fungicides Captan and Iprodione that are commonly used on fruits. For example, the current EPA Tolerance Levels for fresh strawberries are 25 and 15 parts-per-million (ppm) for Captan and Iprodione, respectively. Typically, these pesticides are monitored, after extraction of fruit, by gas chromatography (GC) with a selective detector such as the nitrogen phosphorus detector (NPD), or electron capture detector (ECD). Unfortunately they tend to degrade both in the injector and on the GC column, which complicates their quantitative (and maybe even their qualitative) measurement.

One of the ways to verify that the parent compound is being measured for Captan and Iprodione, as opposed to a degradation compound, is to use mass spectrometry (MS). Additionally, to increase the chance to measure the parent pesticides it is desirable to use fast GC, which may prevent on-column degradation of components by minimizing the time they spend in the GC. When fast GC is used, chromatographic peak widths are on the order of 2 seconds, and a fast MS is necessary to accurately define the peaks. Because of its fast acquisition capability (up to hundreds of spectra per second), time-of-flight mass spectrometry (TOFMS) is the ideal mass spectrometer for fast GC.

This application note describes the different results obtained for Captan and Iprodione under two sets of GC-TOFMS conditions, one that gives a run time of 20 minutes, and the other faster at 13 minutes.

2. Experimental Conditions

Standards

Captan was obtained from Chem Service and Restek. Iprodione was from Chem Service.

Gas Chromatography:
LECO Pegasus® III GC-TOFMS
Column:
30 m x 0.25 mm x 0.25 µm Rtx-PCB (Restek)
Carrier:
Helium at 1.0 mL/minute, constant flow
Injection:
1 µL splitless at 250°C, 60 second valve
Liner:
4 mm Siltek gooseneck splitless with Carbofrit (Restek)
Oven Program:
60°C (1 minute), 30°/minute to 120°, 15°/minute to 360° (1 minute)
Total Run Time:
20 minutes

Mass Spectrometry

Ionization:	Electron ionization at 70eV
Source Temperature:	225°C
Stored Mass Range:	45 to 520 u
Acquisition Rate:	10 spectra/second

Fast Gas Chromatography
Column:
20 m x 0.18 mm x 0.14 µm CLPII (Restek)
Carrier:
Helium at 1.0 mL/minute, constant flow
Injection:
1 µL splitless at 250°C, 60 second valve
Liner:
4 mm Siltek gooseneck splitless with Carbofrit (Restek)
Oven Program:
40°C (1 minute), 40°/minute to 120°, 20°/minute to 320°
Total Run Time:
13 minutes

Mass Spectrometry

Ionization:	Electron ionization at 70eV
Source Temperature:	225°C
Stored Mass Range:	45 to 550 u
Acquisition rate:	20 spectra/second

Data Processing

LECO ChromaTOF® software with automatic Peak Find and Deconvolution.

Extraction of Strawberries

The Florida-modified California Department of Food and Agriculture method was used to prepare an extract from fresh strawberries obtained from a local grocery store.

Defining Chromatographic Peaks with TOFMS

Both GC methods produced relatively narrow chromatographic peaks (2 to 4 sec wide at the base), as illustrated for Tetrahydrophthalimide (THPI), the chief degradation product for Captan (Figures 1 and 2). The typical quadrupole, ion trap, or magnetic sector MS at an acquisition rate of 1 to 2 spectra/second would only be able to acquire about 4 to 8 spectra across these peaks, but TOFMS easily defines them with approximately 40 spectra at the experimental acquisition rates.

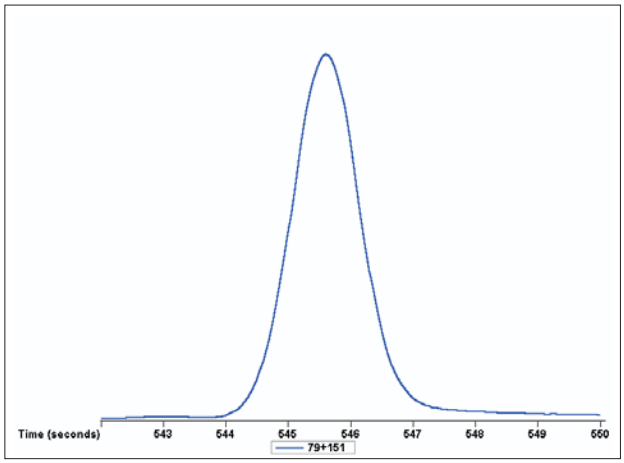

Figure 1. Extracted ion chromatogram for tetrahydrophthalimide (THPI) under the slower GC temperature program. The peak width is approximately 4 sec. The acquisition rate of 10 spectra/seondc gives about 40 spectra across the peak.

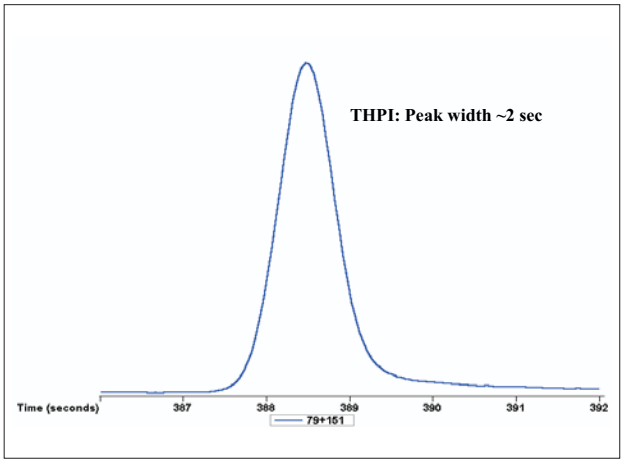

Figure 2. Extracted ion chromatogram for tetrahydrophthalimide (THPI) under the faster GC temperature program. The peak width is approximately 2 seconds. The acquisition rate of 20 spectra/second gives about 40 spectra across the peak.

3. Results

Analysis of Captan Standards Using the Two GC-TOFMS Methods

Figures 3 and 4 illustrate the different ratios of Captan to THPI using the two different GC temperature programs. In Figure 3, the Captan is small compared to the THPI, suggesting substantial degradation during the GC analysis, most likely during the injection. The reverse is seen in Figure 4, where the Captan peak is larger than the THPI peak. Interestingly, these results are contradictory when theorizing that injector degradation appears to be the cause, when only the ratios of Captan to THPI are considered. Since liner type and injector temperature are the same, residence time in the injector might be considered as a possible factor in Captan degradation. Figure 3 GC conditions yield an injector flow of 1.2 mL/min at the initial GC oven temperature, but Figure 4 GC conditions, the faster analysis, only show a 0.82 mL/min flow in the injector at the initial GC oven temperature.

Obviously there is another cause for the differing Captan/THPI ratios. One possibility might be that, in addition to the injector degradation, the Captan is degrading on-column during the slower analysis. This type of breakdown would not result in an increase to the THPI peak. Whether the analysis time (or perhaps the elution temperature) can cause the differences seen needs additional exploration. One thing is certain though, the faster analysis made it possible to calibrate for Captan from 10 pg/µL to 2 ng/µL (Figure 5). The slower analysis did not produce the sensitivity necessary for monitoring Captan as the parent compound.

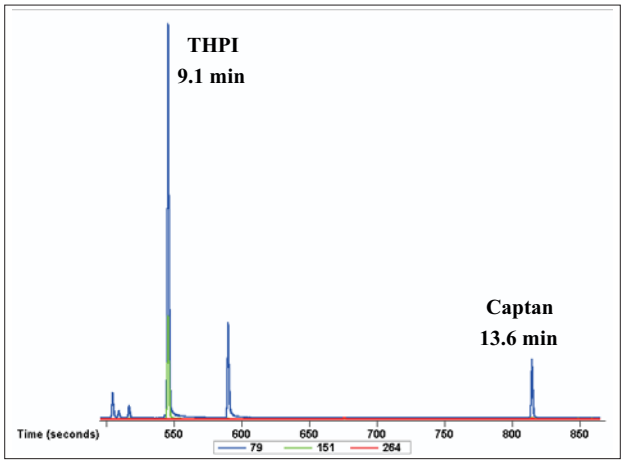

Figure 3. Extracted ion chromatograms for tetrahydrophthalimide (THPI) and Captan showing prominence for THPI, suggesting degradation of Captan standard during GC analysis (slower GC oven program).

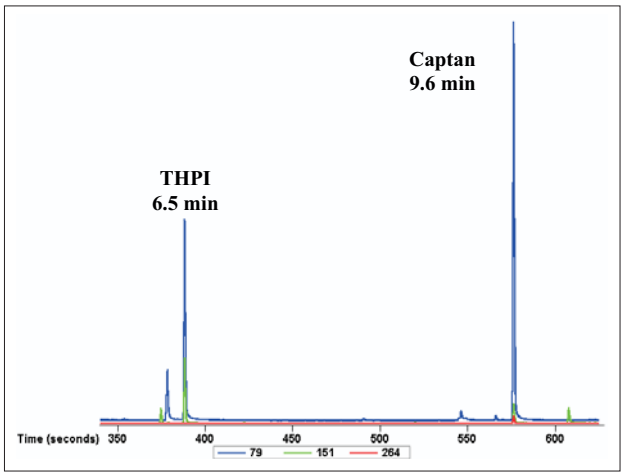

Figure 4. Extracted ion chromatograms for tetrahydrophthalimide (THPI) and Captan showing prominence for Captan, suggesting less degradation of Captan standard during faster GC analysis versus Figure 3 GC conditions.

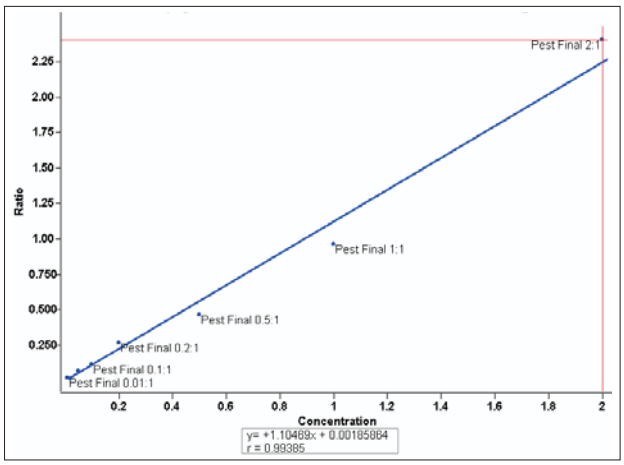

Figure 5. Calibration curve for Captan using faster GC conditions. The range is from 10 pg/µL to 2 ng/µL. Quantification masses are 79+117+149.

Analysis of Iprodione Standards Using the Two GC-TOFMS Methods

For Iprodione, the differences are more distinct, including the obvious degradation of Iprodione on-column for both slower and faster GC conditions (Figures 6 and 7). Using the slower GC conditions, monitoring of the Iprodione as a parent compound is not possible. With a faster analysis and careful selection of the quantification masses (314+316), calibration for Iprodione is easily accomplished, even at low pg levels (Figure 8).

The reason that selection of quantification masses is important is seen by again referring to Figure 7, where masses 187 and 189, which are possible quantification ions for Iprodione (Figure 9), are noticeably distorted as Iprodione degrades on-column to another compound. Masses 314 and 316, representative of Iprodione that has not degraded, show good chromatographic profiles (Figure 10), which makes them better as quantification masses. Another strong case for using mass spectrometry for measuring Iprodione is that exclusion of interfering peaks (masses) is not available with selective detectors (e.g. NPD). The peak shape for Iprodione when using a selective detector is going to reflect the degradation situation if it occurs. This distorted peak shape will result in imprecise integration.

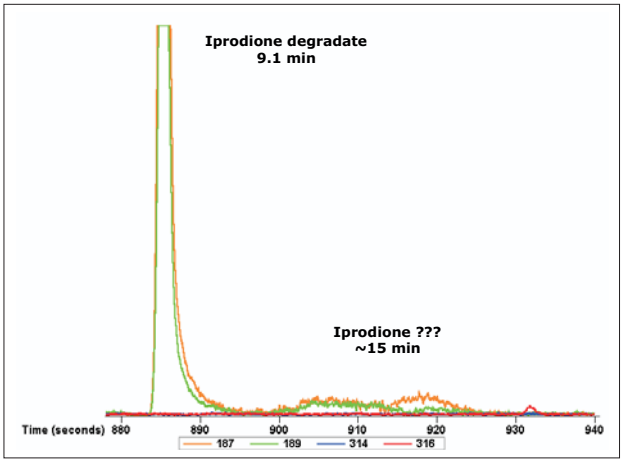

Figure 6. Extracted ion chromatograms for Iprodione and its degradation compound under the slower GC conditions. Iprodione, if it is even present, is a smear across the baseline from about 900 to 925 sec. This "smear" is representative of on-column degradation. The Iprodione degradate was plotted off scale so the possible Iprodione peak could be seen.

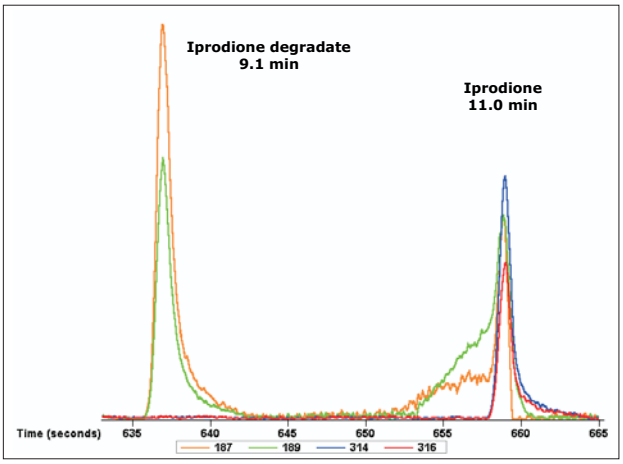

Figure 7. Extracted ion chromatograms for Iprodione and its degradation compound under the faster GC conditions. Iprodione is starting to break down on-column as illustrated by the peak fronting for ions 187 and 189 in the retention time range of 650 to 660 sec, but the chromatographic profile of the Iprodione only, as represented by the 314 and 316 ions, is very good.

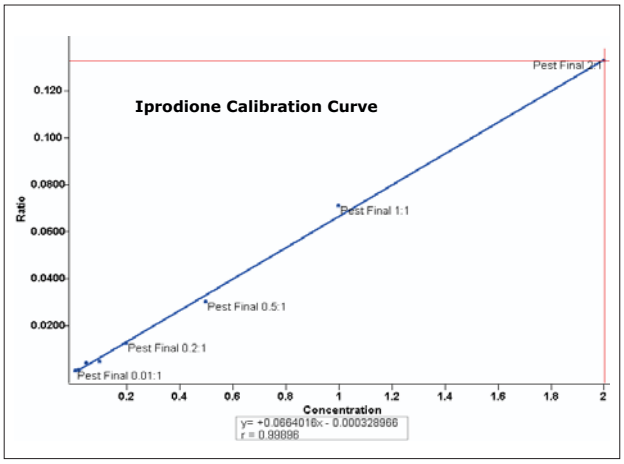

Figure 8. Calibration curve for Iprodione using faster GC conditions. The range is from 10 pg/µL to 2 ng/µL. Quantification masses are 314+316.

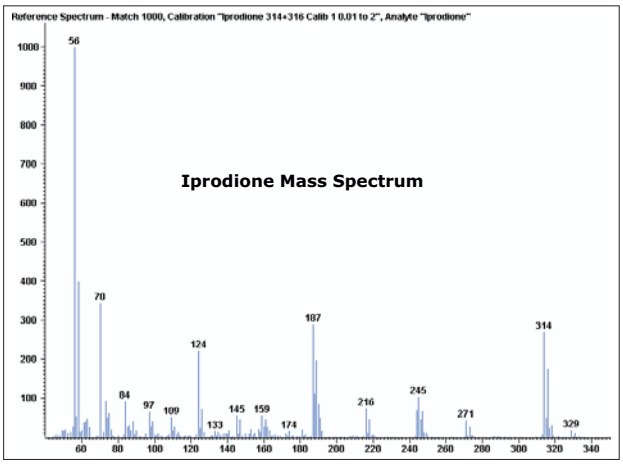

Figure 9. A mass spectrum for Iprodione. Note the presence of higher m/z ions 187, 189, 314, and 316, which would all make good choices for quantification masses if Iprodione did not degrade on the GC column. Ions 187 and 189 are present in the degradation products.

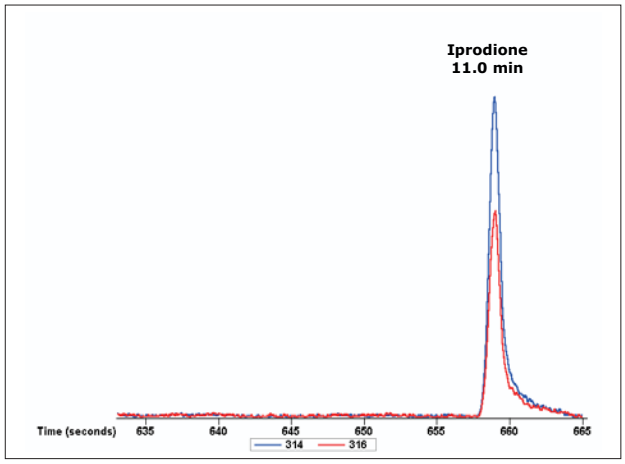

Figure 10. Extracted ion chromatograms 314 and 316 for Iprodione. Compare the good peak shape for these ions to 187 and 189 in Figure 7.

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Quantification of Captan and Iprodione in Strawberries

Using the faster GC conditions, it was possible to measure parent pesticide concentrations for Captan and Iprodione in strawberries. The concentration of Captan in the strawberries was 1.5 ppm, well below the EPA Tolerance of 25 ppm. Iprodione was not detected in the strawberries. The possibility that the matrix presented by the extract led to problems with Iprodione detection was explored by spiking the extract with 0.05 and 0.5 ng/µL concentrations of Iprodione (which calculates to 0.027 and 0.27 ppm in the fruit). Quantification of the spikes gave 0.06 and 0.50 ng/µL results, very close to the spiked amounts, and the Iprodione was automatically located in the matrix without user intervention. The mass spectra for Iprodione in the strawberry extracts are compared against reference spectra in Figures 11 and 12.

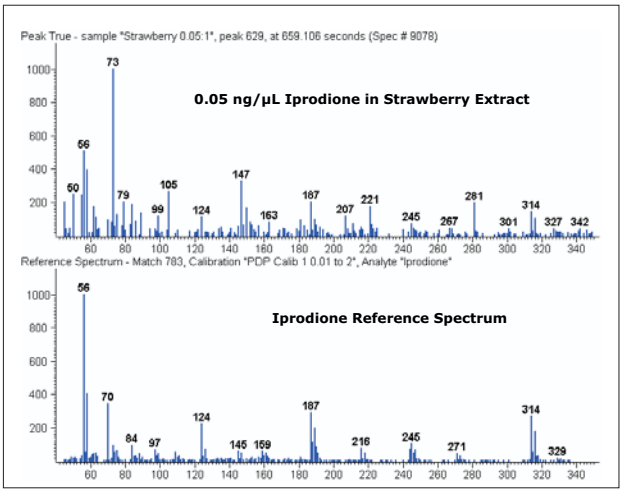

Figure 11. Comparing the mass spectrum from a 0.05 ng/µL spike of Iprodione in strawberry extract and an Iprodione reference mass spectrum. The sample mass spectrum (top) contains some matrix ions from strawberry, but the important ions for Iprodione (e.g. 187, 189, 314, 316) are easily visible and the match is 783 (out of 1000).

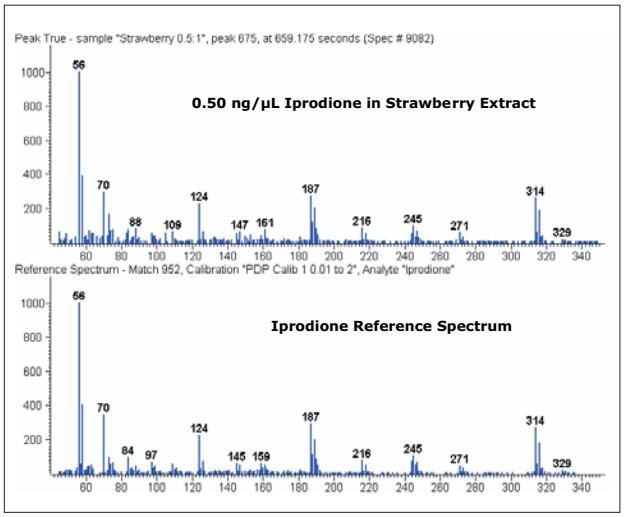

Figure 12. Comparing the mass spectrum from a 0.50 ng/µL spike of Iprodione in strawberry extract and an Iprodione reference mass spectrum. The match is excellent at 952 out of 1000.

4. Conclusions

Captan and Iprodione can be successfully analyzed as the parent pesticides by using fast GC conditions. To define the narrow peaks generated by fast GC, a TOFMS is necessary. Calibration and quantification can be accomplished to the low pg/µl range.

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