Application Note: 10263

Fast Multi-Residue Pesticide Analysis Using Triple Quadrupole GC-MS/MS

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Key Words

- QuanLab Forms Software
- TSQ Quantum GC
- Fast GC
- Food Safety
- Maximum Residue Levels (MRL)
- Selected Reaction Monitoring SRM
- Target Compound Analysis

Introduction

International regulations on the maximum residue levels of pesticides in food (MRLs) cover hundreds of individual components at very low maximum residue limits – in the range of 10 ppb or lower.[1] Currently, more than 300 regulated pesticides can be analyzed by gas chromatography/mass spectrometry (GC/MS) while a large group of highly polar pesticides is covered by liquid chromatography/mass spectrometry (LC/MS) methods.[2] GC/MS analysis of that many pesticides at the MRL becomes an increasing challenge for quality and governmental control strategies. This application note provides the analytical methodology for a fast multi-residue pesticide determination using the unique capabilities of the Thermo Scientific TSQ Quantum™ GC triple quadrupole mass spectrometer for quantitation and confirmation of positive results.

A particular challenge in the detection and quantification of a large number of pesticides in one run derives from the complex elution situation. Because many compounds partially or completely coelute, a high speed analyzer is required to generate a sufficient number of data points. This ensures reliable integration of overlapping chromatographic peaks.

By taking advantage of the unique fast acquisition rate provided by the TSQ Quantum GC, the rapid analysis of multi-pesticide residues becomes routine in modern food safety testing labs and addresses the main challenges for this type of analysis:

a. Narrow GC peaks require fast MS acquisition rate to give sufficient data points for qualitative and quantitative analysis.

b. With multi-component methods the partial or complete coelution of components needs to be considered. The SRM transition speed needs to be fast enough to monitor many coeluting components while providing enough data points for reliable peak integration.

c. The multi-component method should include as many substances as possible, which requires the MS be capable of acquiring several hundred SRM transitions in single run.

d. The MS method should require as few acquisition segments as possible for multiple targets due to the small changes in retention time that may occur in heavy matrix samples. This means the MS must be able to measure as many transitions as possible in one segment window without losing sensitivity.

e. Under these conditions, it is necessary to use short SRM dwell times and a very short interscan time.

f. When using short dwell and interscan times for targets generating the same product ions, “cross talk” must be safely prevented. “Cross talk” can lead to false positive results in sample analyses.

Experimental Conditions

The purpose of this multi-residue target compound method is to improve analytical productivity in terms of increased sample throughput and through reduction in the time required to review and report for multiple pesticides analysis. Despite the large number of pesticides covered in this method a short capillary column was used to speed up the chromatography for high sample throughput. The data acquisition method includes a total of 175 SRM transitions in a single 20-minute run using the TSQ Quantum GC. The run was divided into 11 retention time windows (acquisition segments) with up to 25 SRM transitions in each. Dwell times of 25 ms were used to obtain good sensitivity and data rate for the quantification of the targets. Cross talk was not observed even in the window containing 25 SRM transitions.

The Thermo Scientific TRACE GC Ultra™ gas chromatograph was used to provide fast chromatography, and the Thermo Scientific TriPlus™ autosampler configured for liquid injection was used for automated, productive sample introduction. A Thermo Scientific TRACE™ TR-5MS analytical column was used for chromatographic separation. The short column length (15 m) contributed to the fast GC run time and improved sample throughput. Table 1 lists selected instrument parameters for the GC, autosampler and mass spectrometer.

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GC Parameters – TRACE GC Ultra	
Injector	Split/splitless injector, 220 °C
Injection	Splitless, 1 min
Carrier Gas	He, 1.0 mL/min, constant flow
Column	TRACE TR-5MS, 15 m x 0.25 mm x 0.25 µm
Oven Temp. Program	70 °C, 1 min 25 °C/min to 130 °C 15 °C/min to 160 °C 5 °C/min to 210 °C 25 °C/min to 280 °C, 5 min
MS Transfer Line Temp.	280 °C
Autosampler Parameters – TriPlus AS	
Sample Volume	1.0 µL
Injection Mode	Hot needle
Viscous Sample	Yes
MS Parameters – TSQ Quantum GC	
Ionization	EI, positive ion
Source Temp (°C)	220
Emission Current	50 µA
Scan Type	SRM (Selective Reaction Monitoring), H-SRM mode (Highly-Selective Reaction Monitoring)
Collision Gas Pressure	1.5 mTorr
Segment Windows	11
Segment (3-5.97min)	10 transitions
Segment (-8.27min)	25 transitions
Segment (-10.17min)	24 transitions
Segment (-11.27min)	17 transitions
Segment (-13min)	24 transitions
Segment (-14.6min)	22 transitions
Segment (-15.6min)	8 transitions
Segment (-16.8min)	16 transitions
Segment (-17.95min)	17 transitions
Segment (-19.2min)	7 transitions
Segment (-22min)	5 transitions
Scan Width	0.002 amu
Scan Time	0.025 s

Table 1: Selected instrument conditions for the TRACE GC Ultra, TriPlus Autosampler and TSQ Quantum GC mass spectrometer

To streamline the data review and reporting process for multiple pesticides analysis, Thermo Scientific QuanLab™ Forms 2.5 software was used to provide productivity enhancements tailored to the workflow demands of the pesticides analysis laboratory. QuanLab Forms includes an integrated user interface for the management of the total list of pesticides, automated data review, customizable views, and versatile reporting formats.

Results and Discussion

A complete chromatogram demonstrating the complexity of the elution profile of 170 pesticides at 50 pg/µL is shown in Figure 1. The last peak elutes at 20 minutes. The pesticides cover multiple compound classes; organochlorine, organophosphorus, carbamates, pyrethroids as well as triazine pesticides were analyzed using 175 corresponding SRM transitions.

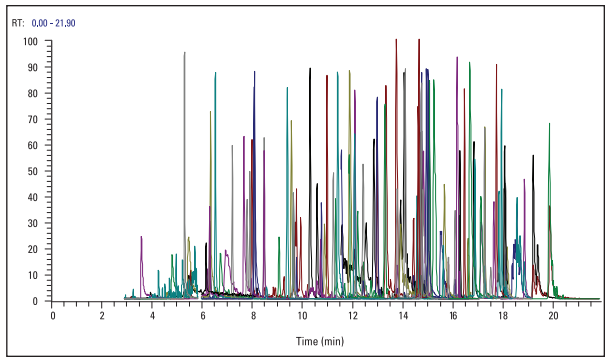

Figure 1: Total ion chromatogram of 170 pesticides under GC-MS/MS

The SRM acquisition segments were primarily chosen to ensure that each window provided a comfortable setup of the compound list, with each component having a transition dwell time of 25 ms. Table 2 uses the retention time window from 5.97 to 8.27 min as an example, with a total of 25 SRM transitions for 27 pesticides.

Pesticide	RT (min)	Precusor Ion	Product Ion	CID (V)	Dwell Time (ms)
Omethoate	6.16	156	110	10	25
Fenobucarb	6.31	121	93	15	25
Propachlor	6.33	120	92	15	25
Propoxur	6.33	152	110	10	25
Demeton-S-methyl	6.4	142	79	10	25
Diphenylamine	6.41	169	141	20	25
Ethorprofos	6.52	200	158	8	25
Chlorpropham	6.71	127	65	20	25
Methabenzthiazuron	6.91	164	136	12	25
Trifluralin	7.01	306	264	15	25
Cadusafos	7.05	213	185	15	25
Monocrotophos	7.06	127	109	20	25
Phorate	7.11	260	231	8	25
α-BHC	7.18	219	183	15	25
Hexachlorobenzene	7.31	284	249	20	25
Dichloran	7.5	176	148	15	25
Dimethoate	7.54	125	79	10	25
Carbofuran	7.68	164	149	8	25
β-BHC	7.74	219	183	15	25
γ-BHC	7.88	219	183	15	25
Quintozene	7.99	237	143	25	25
Phenanthrene-D10	8.02	188	160	20	25
Terbufos	8.04	231	203	10	25
Fonofos	8.09	137	109	10	25
Propyzamide	8.14	254	226	15	25
Pyrimethanil	8.25	198	183	20	25
Diazinon*	8.40	304	179	8	25

Table 2: A total of 27 pesticide target compounds (out of the total number of 170 compounds) with SRM transitions covered in a single segment covering the retention time window from 5.97 to 8.27 min. *Diazinon included in this segment and that from 8.27-10.17 due to overlap in RT windows.

Zero "Cross Talk"

"Cross talk" is described as a memory effect of the collision cell in a triple quadrupole mass spectrometer. In cases of cross talk, a signal for a pesticide compound not actually present in the sample would be seen as a false positive. With a total of 25 SRM transitions in the segment window from 5.97 to 8.27 min, the dwell times and interscan times are very short, which requires a fast scanning sequence with active cleaning of the collision cell before acquiring the next data set. Zero cross talk on the TSQ Quantum GC was demonstrated by acquiring two different SRM transitions of Monocrotophos (*m/z* 127→109) and Fonofos (*m/z* 137→109) which yields the same product ion of *m/z* 109 in same the segment window (Figure 2). A similar situation appears in the case of BHC (*m/z* 219→183) and pyrimethanil (*m/z* 198→183). The TSQ Quantum GC shows the clear absence of cross talk, providing absolute certainty in the data with no false positive results.

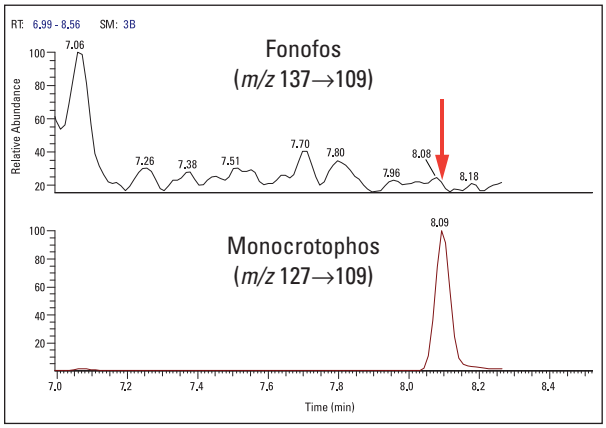

Figure 2: Cross talk is absent in the fast SRM acquisition sequence from Monocrotophos (*m/z* 127→109) at 8.09 min (bottom trace) to Fonofos (*m/z* 137→109) (upper trace) even at high concentration

Data Review and Reporting

For target compound quantitation, the QuanLab Forms software package provides a natural workflow orientation from method and sequence set-up to data reviewing and reporting. The total list of pesticide components in the multi-component method is maintained with the results of the peak integration and quantitative calibration (Figure 3). In this example, a chive sample was spiked with 10 ppb of a pesticides cocktail. The integrated peak is displayed at the maximum residue level (MRL). QuanLab Forms provides quick data review for samples, standards, quality controls (QCs), blanks and % of recovery. Figure 4 shows an example of a high density quantification report from QuanLab Forms. This type of report is useful for reporting long lists of compounds on fewer sheets of paper.

Figure 3: QuanLab Forms Data Review of a chive sample spiked with 10 ppb pesticides at the MRL level

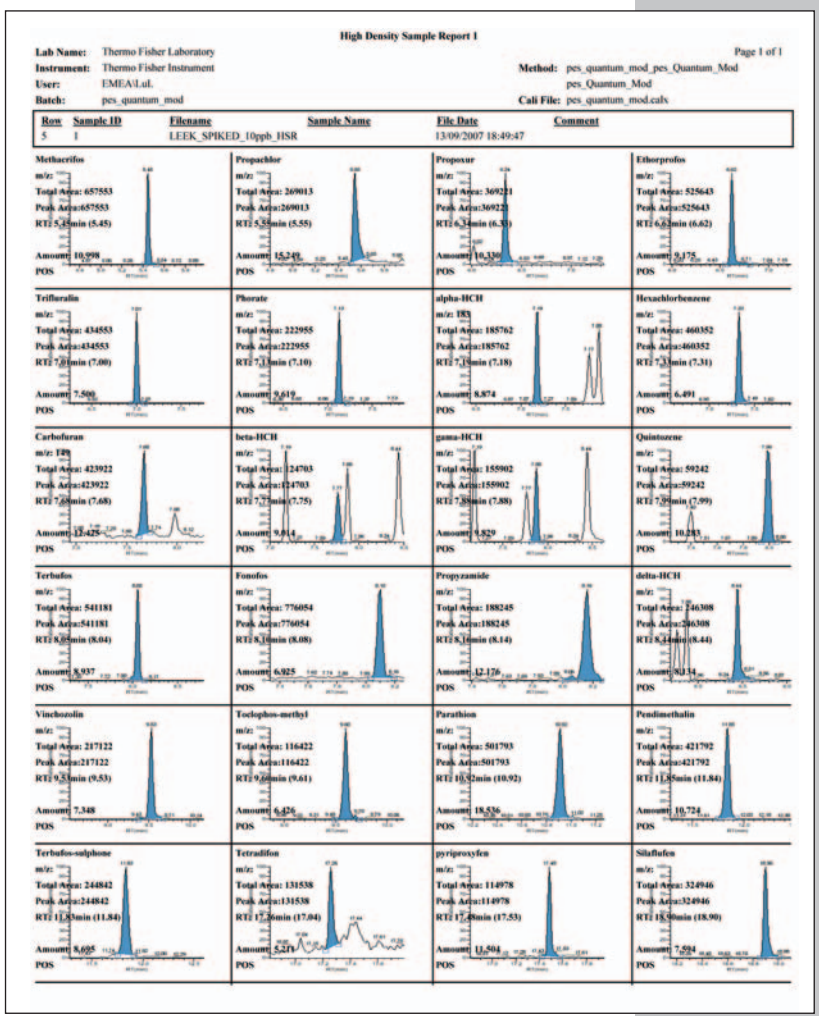

Figure 4: An example of a high-density peak integration report generated by QuanLab Forms. These are results at the 10 ppb MRL level for pesticides spiked into a chive sample and analyzed using TSQ Quantum GC in H-SRM mode.

Conclusions

The Thermo Scientific TSQ Quantum GC provides highest productivity for multi-residue pesticide analysis for effective control at the international MRL levels.

High sample throughput is demonstrated using a fast GC method. A total of 170 pesticide components were screened with high sensitivity on a TSQ Quantum GC in a single injection with an analysis time of only 20 minutes. Excellent sensitivity, selectivity and flexibility were given by using up to 25 transitions in 11 retention time windows. False positive results due to cross talk were safely excluded even under fast acquisition cycles. The TSQ Quantum GC offers the potential to even further reduce dwell times without sacrificing the overall sensitivity, which would then allow the addition of more target pesticides as necessary. QuanLab Forms software provides a workflow-oriented format that allows analysts to easily create and manage methods, acquire samples, review results and print reports.

References

1. EU Commission Directives 91/414/EEC, 86/362/EEC, 86/363/EEC, 90/642/EEC, Regulation (EC) N. 396/2005 and subsequent amendments.
2. Ministry of Health, Labour and Welfare Japan, Department of Food Safety, The Positive List System for Agricultural Chemical Residues in Foods, June 2006, see: http://www.mhlw.go.jp

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