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Fast GC-MS/MS Analysis Of Multicomponent Pesticide Residues (360) In Food Matrix

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Introduction

Contamination of food products with pesticides is a growing concern because of recognized adverse health effects, increasing world-wide usage of pesticides, and increasing imports of raw foodstuffs from foreign sources. Consequently, the number of samples as well as monitored pesticides became significantly higher in the last decade. To handle this high sample load, a Quick, Easy and Cheap cleanup procedure called QuEChERS was established[1]. Unfortunately, samples prepared by this method contain large matrix signals which can complicate accurate pesticide quantification by MS alone. As a consequence of matrix effects in MS, tandem MS/MS instruments using multiple reaction mechanisms (MRM), have more frequently been adopted in recent years, as it increases selectivity and sensitivity. Besides matrix interference, short analysis times are more frequently needed when handling large sample numbers in routine work. The use of narrow bore capillary columns has been shown to be a powerful tool to dramatically reduce the analysis time while maintaining chromatographic resolution in different GCMS applications[2]. In fast GC experiments typically peak width at half height (FWHM) was reduced to ~1 sec therefore requiring ultra fast scanning and polarity switching. As a result of the ultra fast GC and selectivity of tandem MS increases in laboratory efficiency can be gained in addition to reduced working costs.
In this work ultra fast GC-MS/MS analysis was tested by analyzing 360 pesticides in apple QuEChERS extract in less than 10 minutes.

Methods and Materials

Sample preparation

Apple extract was used as test sample matrix. The sample matrix was extracted and subjected to cleanup using the well-established QuEChERS procedure. The calibration curve had 6-points (0.5 ppb to 100 ppb) by spiking the blank sample matrix using internal standard technique. The spiked solution contained overall 360 different pesticides and TPP as internal standard.

Table 1: GC Analytical Conditions

Instrument	: GCMS-TQ8040 (Shimadzu, Japan)
Software	: GCMSSolution 4.2 with SmartMRM and MRM Optimization Tool
Injector	: Optic-4, IP deactivated liner with glass insert
PTV Programme	: 70 °C, 15 °C/s to 280 °C, 1.2 min, 15 °C/s to 320 °C, 6 min
Split	: Splitless Injection (1.3 min)
Injection Volume	: 1 µL
Column	: 5 MS 20m, 0.18 mm, 0.18 µm
GC Oven	: 80 °C, 1 min, 35 °C/min to 210 °C, 25 °C/min to 320 °C, 2 min

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Table 2: MS Analytical Conditions (GCMS-TQ8040)

Transfer Line	: 300 °C
Ion Source	: 200 °C
Emission Current	: 100 µA
Ionization Mode	: EI, 70 eV
Mass Resolution	: Q1 0.8 Da, Q3 at 3.0 Da (FWHM)
CID Gas	: Argon (200 kPa)
Loop Time	: 0.18 s
Acquisition Mode	: MRM
Min Dwell time per MRM	: 3 ms
Processing Window	: ±0.1 min

Sample measurement

The Shimadzu GCMS-TQ8040 equipped with the GLScience multi-mode inlet Optic-4 and an AOC-5000 Plus was used for sample measurement. MRMs and collision energies (CE) were taken from Shimadzu´s SmartDB for pesticides. MRMs and CEs for pesticides missing in the database were determined by the fully automatic MRM Optimization Tool available in the latest version of GCMSSolution (version 4.3). SmartMRM was utilized for the measurement time optimization. The algorithm guaranteed a processing time window not less than 12 seconds for each compound and a dwell time per MRM of at least 3 msec. All compounds were measured with one quantifier and one qualifier. Tables 1 & 2 provide detailed summary of analytical conditions.

Results

Figure 1 shows the full chromatogram of the measured 360 pesticides in which all compounds elute in less than 10 minutes. Moreover, a strong tendency for co-elution is evident with an accelerated GC gradient. To enable meaningful data analysis in such a highly compressed time window, the use of tandem MS triple quadrupole technology is essential.

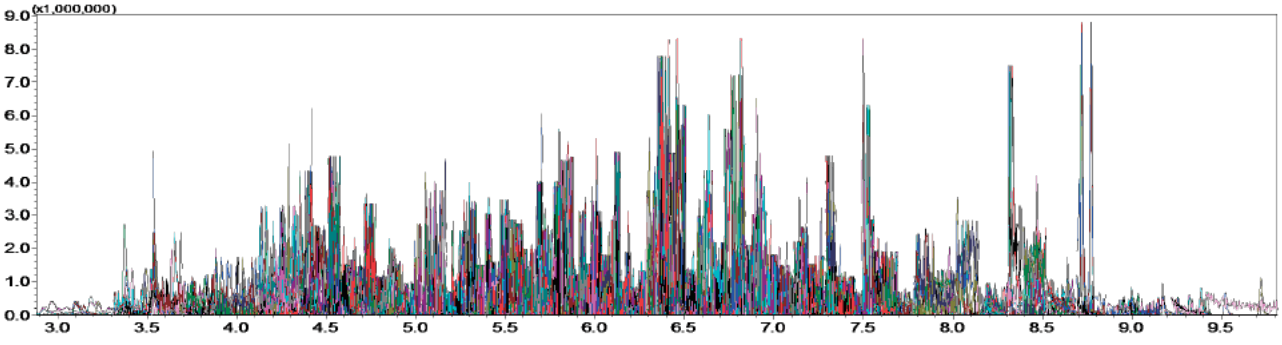

Figure 1: Chromatogram 360 Pesticides In Apple Matrix

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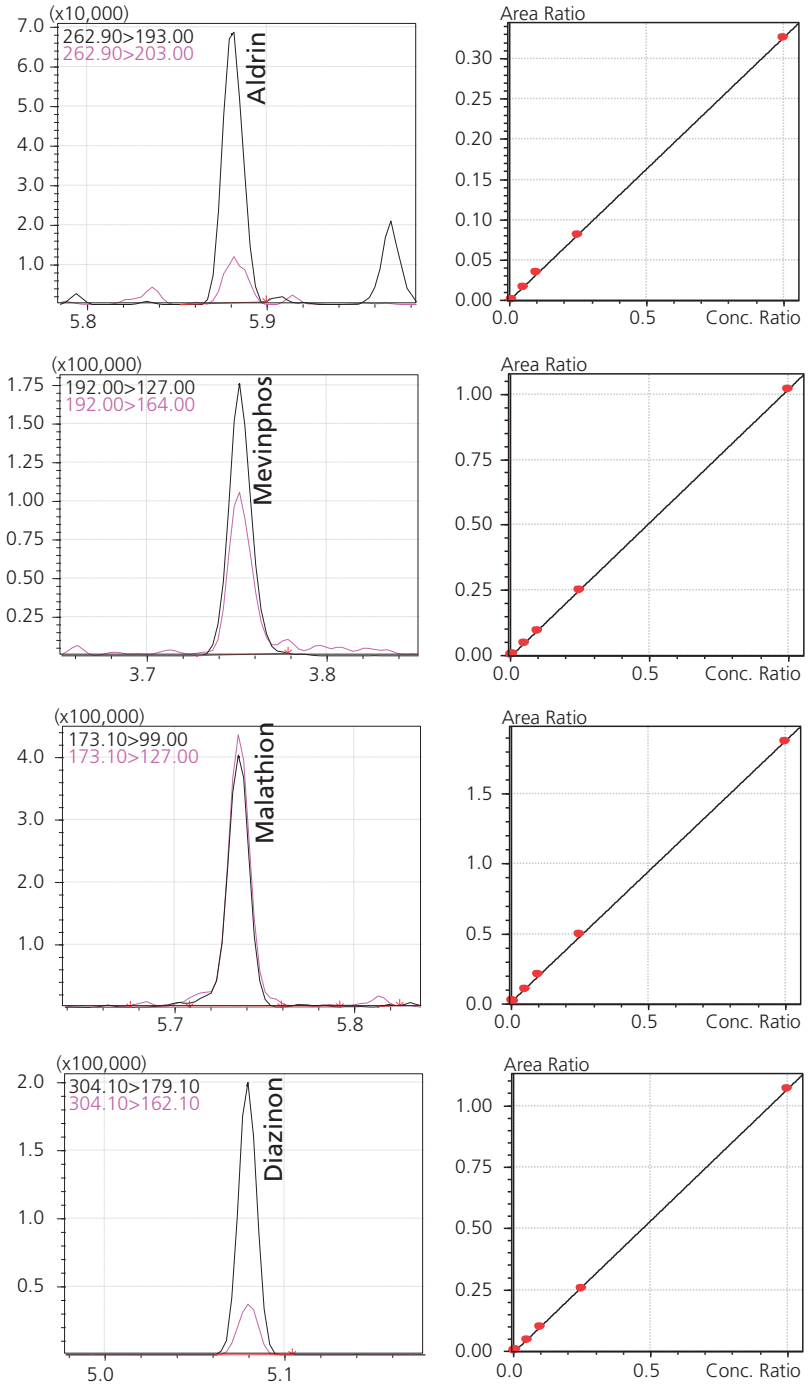

Figure 2: Calibration Curve (0.5 ppb – 100 ppb) and Peak Profile at 5 ppb (Aldrin, Malathion, Mevinphos and Diazinon)

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Results shown in figure 1 were obtained using a 5ms 20 m, 0.18 mm, 0.18 µm fast GC column. It is noteworthy that there are columns available, which have lower dimensions and offer even faster chromatographic results. Using fast GC columns, two main properties need to be taken into account when choosing ideal separation conditions. On the one hand the lower inner diameter and higher possible heating rates enable sharpened peaks and consequently higher S/N ratios. On the other hand the peak capacity decreases by lowering the column dimensions, which results in lower absolute sample amounts and reduced sensitivity[3]. Therefore, in this work an intermediate column was used which provided decreased analysis time whilst maintaining high sensitivity.

Calibration curve results were therefore determined with the aforementioned intermediate column. Matrix calibration curves (0.5 ppb – 100 ppb) were measured for all 360 pesticides. The linear correlation factor was higher than 0.9980 for every compound. Nearly all components were detectable at the lowest concentration of 0.5 ppb. Figure 2 shows peak profiles and calibration curves for some typical pesticides. As already indicated by the correlation factor, linearity was very good for all compounds.

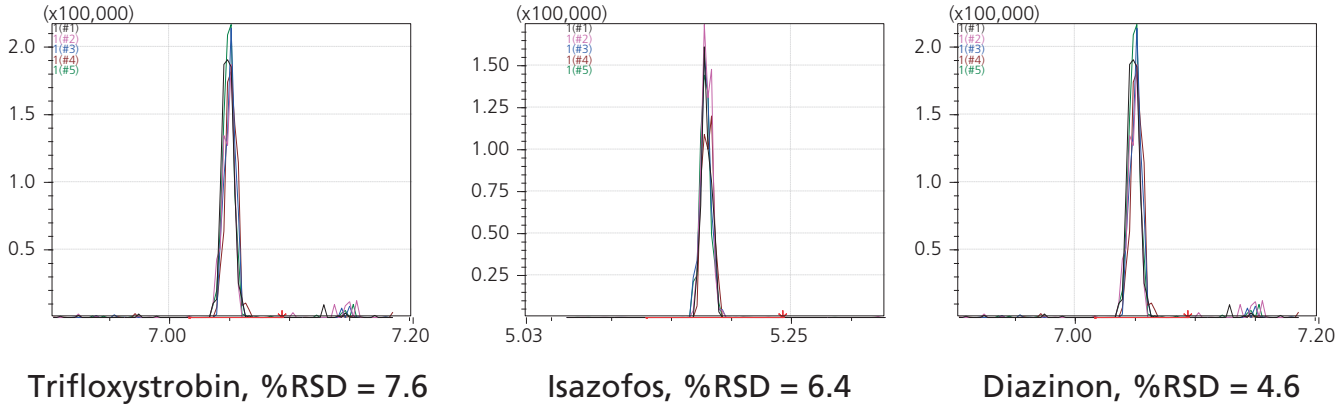

Figure 3: Superimposition of 5 unsmoothed peaks and RSD% of 3 compounds measured at 3 ms dwell time

Peak widths at half maximum (FHMW) were typically less than 1 sec using fast GC separation compared to standard GC. Furthermore, it was known that for good reproducibility, at least 10 data points per peak are needed[4]. To enable this number of data points a loop time of 0.18 s was chosen. In some parts of the chromatogram up to 30 compounds eluted in the same processing window and for each compound two transitions (1 Quantifier and 1 Quantifier) were needed. Consequently, dwell time per MRM was in some cases reduced to as short as 3 msec. Figure 3 shows superimposed chromatograms and %RSD of three different peaks measured with a dwell time of 3 msec. It was therefore evident that %RSDs for these peaks are within acceptable limits even with such short dwell times. This degree of high precision was found for most of the compounds, and for all compounds %RSD values were below 15%. It is thought that compounds exhibiting worse precision was caused by active sites in liner or column. Therefore further optimization of the sample introduction by improved liner deactivation will help to improve %RSD for these few compounds.

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Conclusions

This study shows the successful combination of fast GC and tandem mass spectrometry. It was possible to determine 360 pesticides spiked in a QuEChERS apple extract with excellent calibration curve linearity and good reproducibility in less than 10 minutes. The shown application can help to increase routine laboratory efficiency.

Literature

[1] QuEChERS, European Standard, EN 15662,
[2] Baier, H.-U. In *Practical Gas Chromatography: A Comprehensive Reference;* Dettmer-Wilde, K.; Engewald, W., Eds.; **2014**; Chapter 12; *to be published*,
[3] Mondello, L. et al., *Journal of Chromatography A*, **2004**, *1035*, 237-247,
[4] Mastovska, K., Lehotay, S. J.; *Journal of Chromatography A*, **2003**, *1000*, 153–180.

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