SHIMADZU

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

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1. 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 complicate an accurate pesticide quantification. Due to this drawback the use of tandem MS instruments using multiple reaction mechanisms (MRM) became more frequent in the last years, as it increases selectivity and sensitivity. Beside matrix interference the analysis time is a crucial point when handling a high sample load in routine work. The usage of narrow bore capillary columns has been shown to be a powerful tool to drastically reduce the analysis time while maintaining chromatographic resolution in different GCMS applications[2]. Combining the speed of fast GC and the selectivity of tandem MS is a powerful tool to increase laboratory efficiency and reduce working costs. As fast GC reduces the peak width at half height (FWHM) down to about 1 s the detector must be able to follow sharp increases of signals. Therefore, fast MRM switching modes with no interfering cross talks are needed.

The potential of this approach is demonstrated in the actual study by analyzing 360 pesticides in apple QuEChERS extract in less than 10 minutes.

2. Experimental

2.1 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. A 6-point calibration curve (0.5 ppb to 100 ppb) was created by spiking the blank sample matrix using internal standard technique. The spiking solution contained an overall number of 360 different pesticides and TPP as internal standard.

Table 1: Analytical Conditions

GC	
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 20 m, 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
MS	
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

2.2 Sample measurement

A Shimadzu GCMS-TQ8040 equipped with the GL Sciences multi-mode inlet Optic-4 and an AOC5000 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 actual version of GCMSSolution. SmartMRM was utilized for the measurement time optimization. The algorithm guaranteed a processing time window not below 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. Table 1 gives a detailed summary of analytical conditions.

3. Results

Figure 1 shows the full chromatogram of the measured 360 pesticides. It can be seen that all compounds elute in less than 10 minutes. Moreover, a strong tendency for co-elutions is evident. To follow such a high information density, the use of a highly selective detector like a triple quad MS is inevitable.
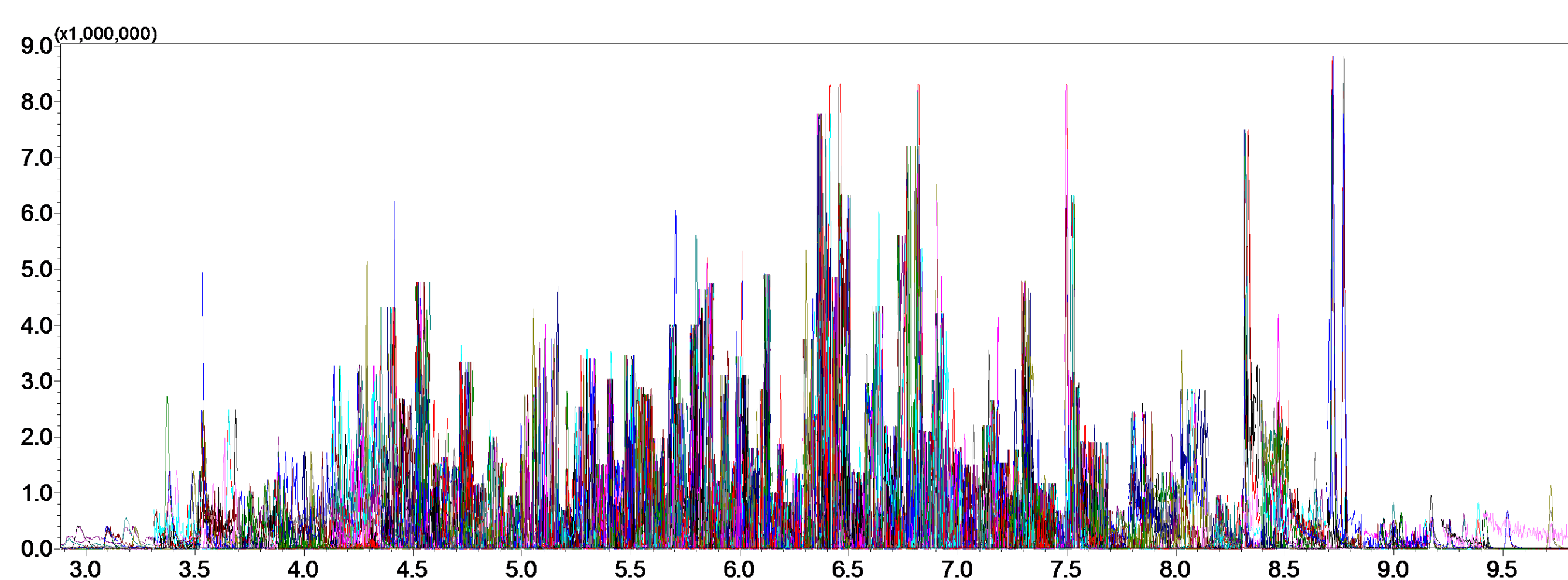
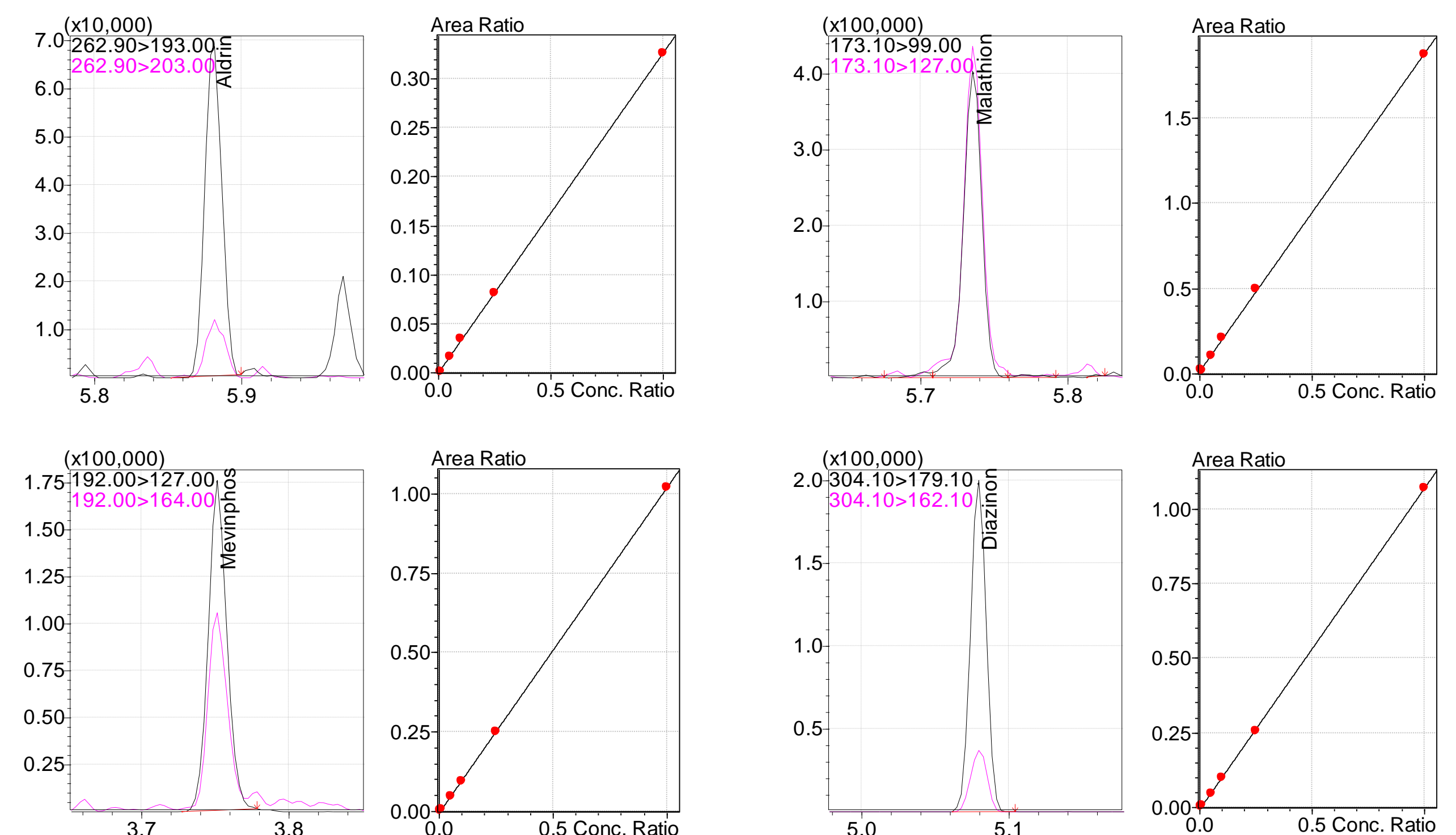Figure 1: Chromatogram 360 Pesticides In Apple Matrix

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

Results shown in figure 1 were obtained using a 5 ms 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 contradictory effects have to be taken into account when choosing ideal measurement 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 sample capacity decreases by lowering the column dimensions, which results in lower absolute sample amounts and minimization of sensitivity[3]. Therefore, the used intermediate column is a good compromise to decrease analysis time while maintaining high sensitivity.

The calibration results determined with the setup can prove the aforementioned assumption. 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 is very good for all compounds.
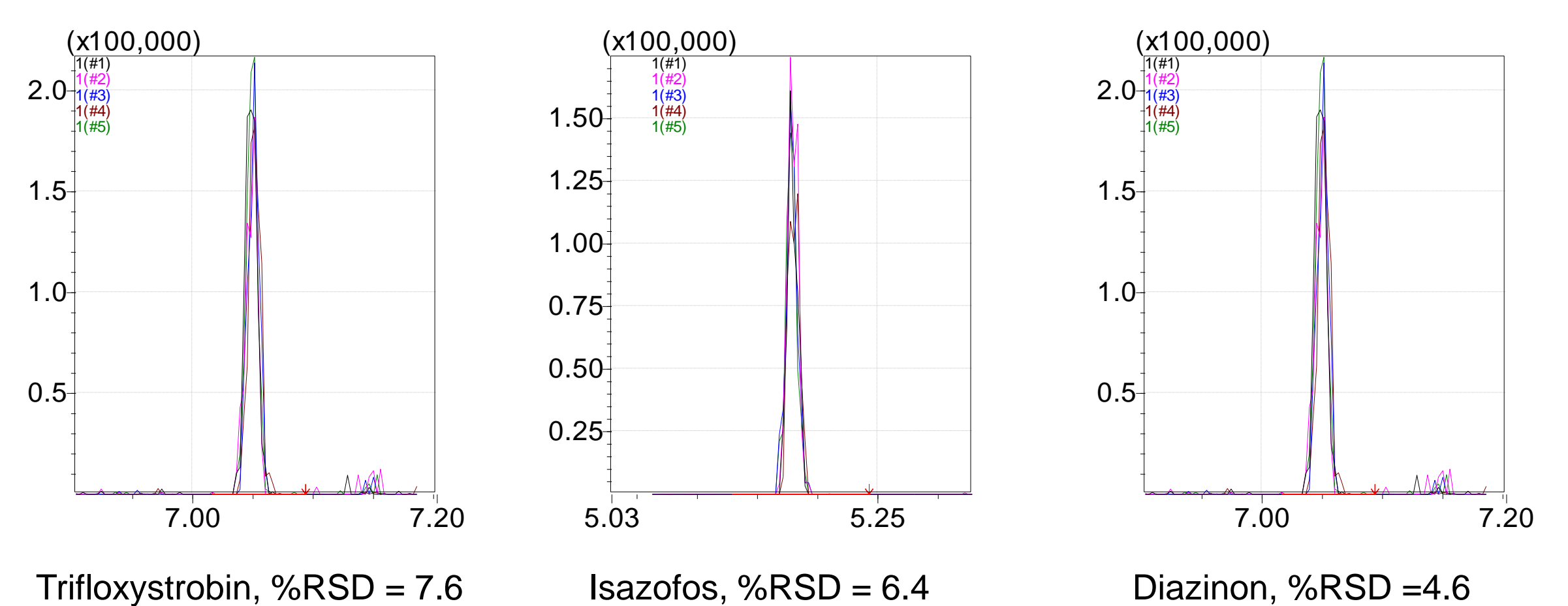
| Trifloxystrobin, %RSD = 7.6 | Isazofos, %RSD = 6.4 | Diazinon, %RSD =4.6 |

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

Peak widths at half maximum (FHMW) are easily decreased below 1 sec using fast GC separation. This decline was also found for the peaks shown in figure 2. Furthermore, it is known that for a 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. As 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, the total number of transitions reached up to 60 per data point. Consequently, the lowest dwell time per MRM was in some cases 3 msec. At this short dwell times, precision and speed of the instrument become very important to obtain good reproducibility for all measured transitions. Figure 3 shows superimpositions and RSD-values of three different peaks measured with a data point dwell time of 3 msec. It is evident that RSDs for this peaks are below 10%. This high degree of precision was found for most of the compounds. It has to be mentioned that for some compounds %RSD-values were merely below 15%. As this %RSD-values are also found at higher dwell times, it can be concluded that the lack of precision is not caused by the mass spectrometer but by active sites in liner or column. Further optimization of the sample introduction by improved liner deactivation will help to decrease %RSD for these few compounds as well.

4. Conclusion

The actual 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.

5. 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.