SHIMADZU

Application News

Chromatography - GCMS

Comprehensive screening of residual 360 pesticides in food using fast GC-MS/MS technology

No. SCA_280_080

Introduction

Contamination of food products with pesticides is a growing concern because of recognized adverse effects on health, increasing world-wide usage of pesticides and higher imports of raw foodstuffs from foreign sources. Consequently, the number of samples as well as pesticides monitored has become 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 popularized the use of highly selective tandem MS. Along with matrix interference, the analysis time is a crucial point when handling a high sample load. The usage of narrow bore capillary columns has been shown to be a powerful tool for drastically reducing 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. Fast MRM (Multiple Reaction Monitoring) switching modes with no interfering cross talks are therefore needed. The potential of this approach is demonstrated by analyzing 360 pesticides in apple QuEChERS extract in less than 10 minutes.

Experimental

QuEChERS apple extract was used as test sample matrix. A 6-point calibration curve (0.5 ppb to 100 ppb) was created by spiking the blank sample matrix with 360 pesticides using TPP as internal standard. A Shimadzu GCMS-TQ8040 triple quadrupole system equipped with the GL Sciences' Optic-4 multi-mode inlet was used for sample measurement. MRMs and collision energies (CE) were taken from Shimadzu´s SmartDB for pesticides. SmartMRM was utilized for the measurement time optimization. All compounds were measured with one quantifier and one qualifier. See detailed summary of analytical conditions below.

GC-MS:	GCMS-TQ8040
Injector:	Optic-4, IP deactivated liner with lass insert
Column:	BPX 5 MS, 20 m x 0.18 mm i.D., 0.18 µm film thickness (SGE)
Software:	GCMSSolution 4.2 with SmartMRM and MRM Optimization Tool

Injector:		MS	
Injection Mode:	Splitless (1.3 min)	Ion Source Temp.:	200 °C
Injection Volume:	1 µl	Interface Temp.:	300 °C
PTV-Program:	70 °C, 15 °C/s to 280 °C, 1.2 min, 15 °C/s to 320 °C, 6 min	Emission current:	100 µA
		Ionization Method:	EI, 70 eV
GC:		Acquisition Mode:	MRM
Column Oven Temp.:	80 °C, 1 min, 35 °C/min to 210 °C, 25 °C/min to 320 °C, 2 min	Mass Resolution:	Q1 0.8 Da, Q3 3.0 Da (FWHM)
		Loop time:	0.18 sec
Linear Velocity:	40 cm/s	Processing time:	±0.1 min

Results

Figure 1 shows the full chromatogram of the 360 pesticides measured. It can be seen that all compounds eluted in less than 10 minutes. Moreover, a strong tendency towards co-elutions was evident. To follow such a high information density, the use of a highly selective detector such as a triple quad MS is inevitable.

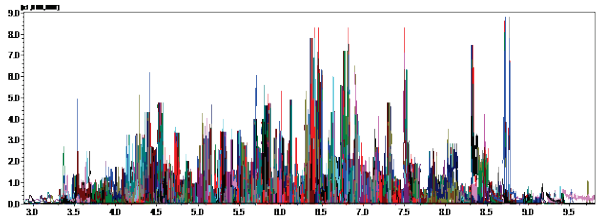


Figure 1: Chromatogram 360 Pesticides In Apple Matrix

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.

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.

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

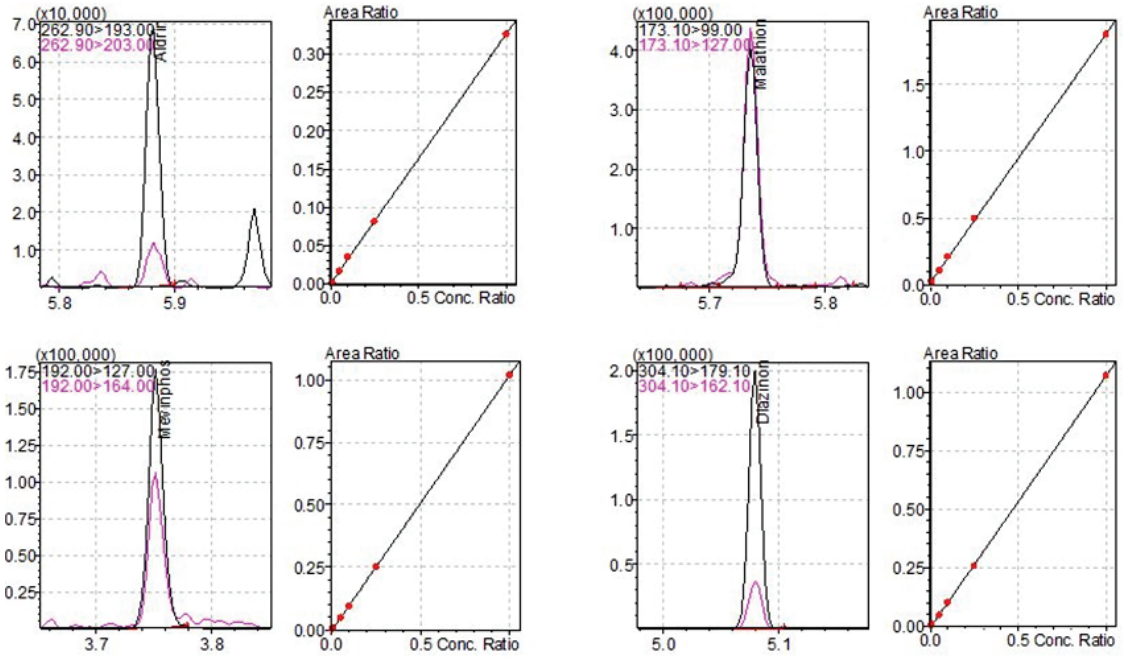
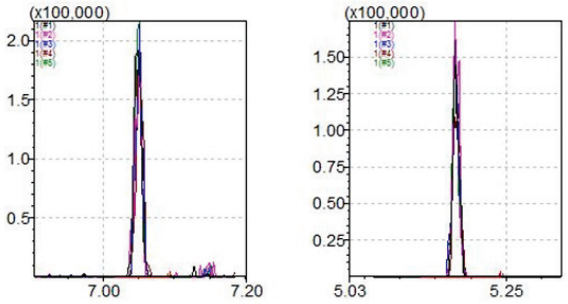


Figure 2: Calibration Curve (0.5 ppb –100 ppb) and Peak Profile at 5 ppb

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 these short dwell times, precision and speed of the instrument become very important in order to obtain good reproducibility for all transitions measured. Figure 3 shows superimpositions and RSD-values of three different peaks measured with a data point dwell time of less than 3 ms. It is evident that RSDs for these peaks are below 10%. This high degree of precision was found for most of the compounds.



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.

Literature

[1] QuEChERS, European Standard, EN 15662,

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