

Analysing 360 Pesticides in less than 10 Minutes Using Fast GC-MS/MS

Uwe Oppermann¹, Waldemar Weber¹ ¹Shimadzu Europa GmbH, 47269 Duisburg, Germany



Overview

Contamination of food products with pesticides has been of concern for many years due to the risk of acute or delayed adverse health and environmental effects. The global use of pesticides is increasing and imports of raw foodstuffs from unknown sources is rising too. Consequently, the number of samples in analytical instrumentation as well as pesticide monitoring has escalated significantly in the last decade. To handle this high sample load, a Quick, Easy and Cheap cleanup procedure called QuEChERS [1] was established [1] and fast GCMS analysis was developed for handling a high sample load

1. Introduction

The usage of narrow bore capillary columns has proven to be a powerful tool for drastically reducing analysis time while maintaining chromatographic resolution in different GCMS applications [2]. Combining the speed of fast gas chromatography (GC) and the selectivity of tandem mass spectrometry (MS) increases laboratory efficiency and reduces working costs. Fast MRM (Multiple Reaction Monitoring) switching modes with no interfering crosstalk's are therefore needed. The potential of this approach is demonstrated by analysing 360 pesticides in QuEChERS apple extract in less than 10 minutes by using a Shimadzu GCMS-TQ8050 NX ultra-high sensitivity Triple Quadrupole system.

2. Method

For a good reproducibility at least 10 data points per peak are needed [3] and 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 Qualifier 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.

2-1. System Configuration

System: GCMS/MS TQ-8050 NX
Column: BPX5 MS, 20 m x 0.18 mm i. D., 0.18 µm film
Injector: OPTIC-4
PTV-program: 70°C → (15°C/s) → 280°C (1.2 min) → (15°C/s) → 320°C (6 min)
Injection mode: Spitless
Injection volume: 1 µL
Sampling time: 1.3 min
Column oven temperature: 80°C (1 min) → (35°C/min) → 210°C → (25°C/min) → 320°C (2 min)
Flow control mode: linear velocity (40 cm/s)
Carries gas: Helium
Software: GCMSsolution™ Ver. 4.45 SP1; Smart MRM and MRM Optimization Tool



Figure 1: Ultra-high sensitivity triple quadrupole GCMS-TQ8050 NX

2-2. Analytical conditions MS

Ion source temperature : 200°C
Interface temperature: 300°C
Emission current: 100 µA
Ionization current: EI, 70 eV
Mass resolution: Q1 0.8 Da; Q3 3 Da
Loop time: 0.18 s
Processing time: ±0.1 min

2-3. Experimental conditions

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-TQ8050 NX 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.

3. Results

Figure 2 shows the full chromatogram of the 360 pesticides measured. All compounds eluted in less than 10 minutes. Moreover, a strong tendency towards coelutions was evident. 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 [4]. Therefore, the used intermediate column is a good compromise to decrease analysis time while maintaining high sensitivity.

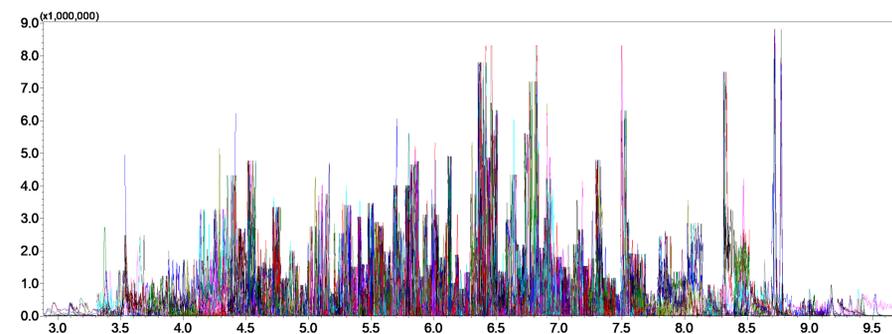


Figure 2. Chromatogram 360 Pesticides in spiked apple matrix

3-1. Calibration curves

Matrix calibration curves (0.5 ppb – 100 ppb) were measured for 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 3 shows peak profiles and calibration curves for some typical pesticides. Peak widths at half maximum (FHMW) are easily decreased below 1 sec.

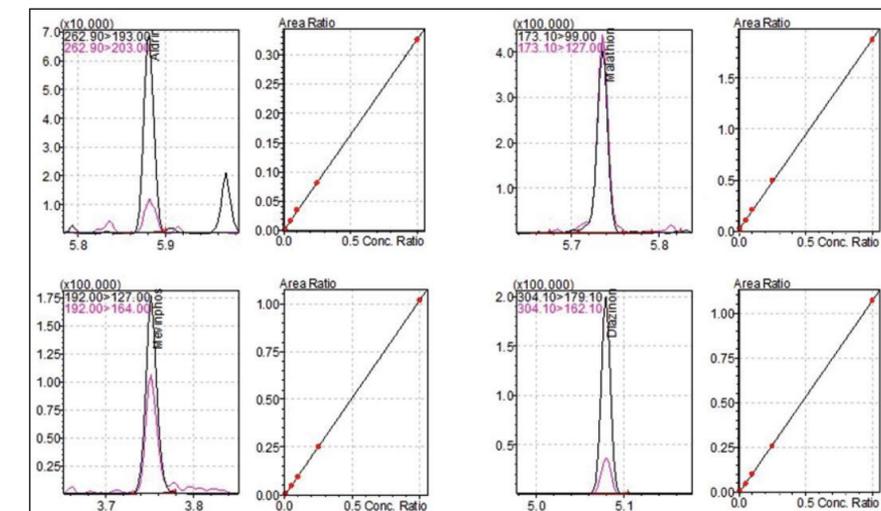


Figure 3: Calibration curve (0.5 ppb – 100 ppb) and peak profile at 5 ppb

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] Mastovska, K., Lehotay, S. J.; Journal of Chromatography A, 2003, 1000, 153–180.
- [4] Mondello, L. et al., Journal of Chromatography A, 2004, 1035, 237-247.