

Highly Sensitive Pesticide Residue Analysis in Food with GC-MS/MS Instrumentation Using Hydrogen as Carrier Gas

Rebecca Kelting, Stéphane Moreau
Shimadzu Europa GmbH, Duisburg, Germany

1. Pesticide Analysis and Helium Shortage

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 amount of monitored pesticides as well as the number of samples became significantly higher in the last decade.

On the other hand, helium shortage has become a growing topic. Even though currently the discussion has declined, helium price has significantly increased over the last years. Consequently, the search for alternative carrier gases for routine work gained importance. The most promising option is hydrogen, both due to its price and the additional benefit of time saving, resulting from the higher linear velocities possible without loss of separation power. The potential of hydrogen as carrier gas for pesticide residue analysis is investigated in the actual study by analyzing 120 pesticides.

2. Analytical Conditions

For method optimization and transfer from helium to hydrogen a standard mix containing 120 pesticides in toluene was used. In accordance with a 5MS phase being the most common phase in pesticide analysis, a Rxi-5 MS, 30m, 0.25 mm, 0.25 µm column (Restek) was used in this study. To cope with the large matrix signals, resulting from the well-established QuEChERS sample preparation technique and complicating an accurate pesticide quantification, the compounds have been measured in MS/MS (MRM) mode. The respective MRM transitions and collision energies have been taken from Shimadzu's Smart Pesticides Database, smartMRM was utilized to conveniently optimize the measurement time settings. The detailed analytical conditions are summarized in table 1.

Due to the high importance of matrix effects, especially in case of compounds sensitive to degradation, the calibration curve was based on matrix standards increasing the result's reliability for real world sample analysis. Apple extract was used as test sample matrix. The sample matrix was extracted and subjected to cleanup using the QuEChERS procedure. A 5-point calibration curve (5 ppb to 500 ppb) was created by spiking the blank sample matrix with 120 pesticides.

GC	
Instrument:	GCMS-TQ8040 with AOC-6000 (Shimadzu, Japan)
Injector:	Optic-4 PTV Injector
Injector Temperature:	70°C, 15°C/s to 280°C, 1.2min, 15°C/s to 320°C, 10min
Split:	Splitless Injection (1 min)
Injection Volume:	1 µL
Column:	Rxi-5 MS 30m, 0.25 mm, 0.25 µm
GC Oven:	50°C, 0.6 min, 41.7°C/min to 125°C, 16.7°C/min to 320°C, 1min
MS	
Transfer Line:	300°C
Ion Source:	200°C
Ionization Mode:	EI, 70 eV
CID Gas:	Argon (200 kPa)
Acquisition Mode:	MRM

Table 1: Analytical conditions

3. Results

Figure 1 shows full chromatograms of the 120 pesticides standard measured with helium (top) and hydrogen (bottom). By switching from helium to hydrogen the run time can be decreased with the last compound eluting at 13.5 min compared to 22.3 min in case of helium, resulting in a time saving of 40%. Resolution however remains sufficient due to the full optimization of conditions for hydrogen use, as can be seen from Figure 2.

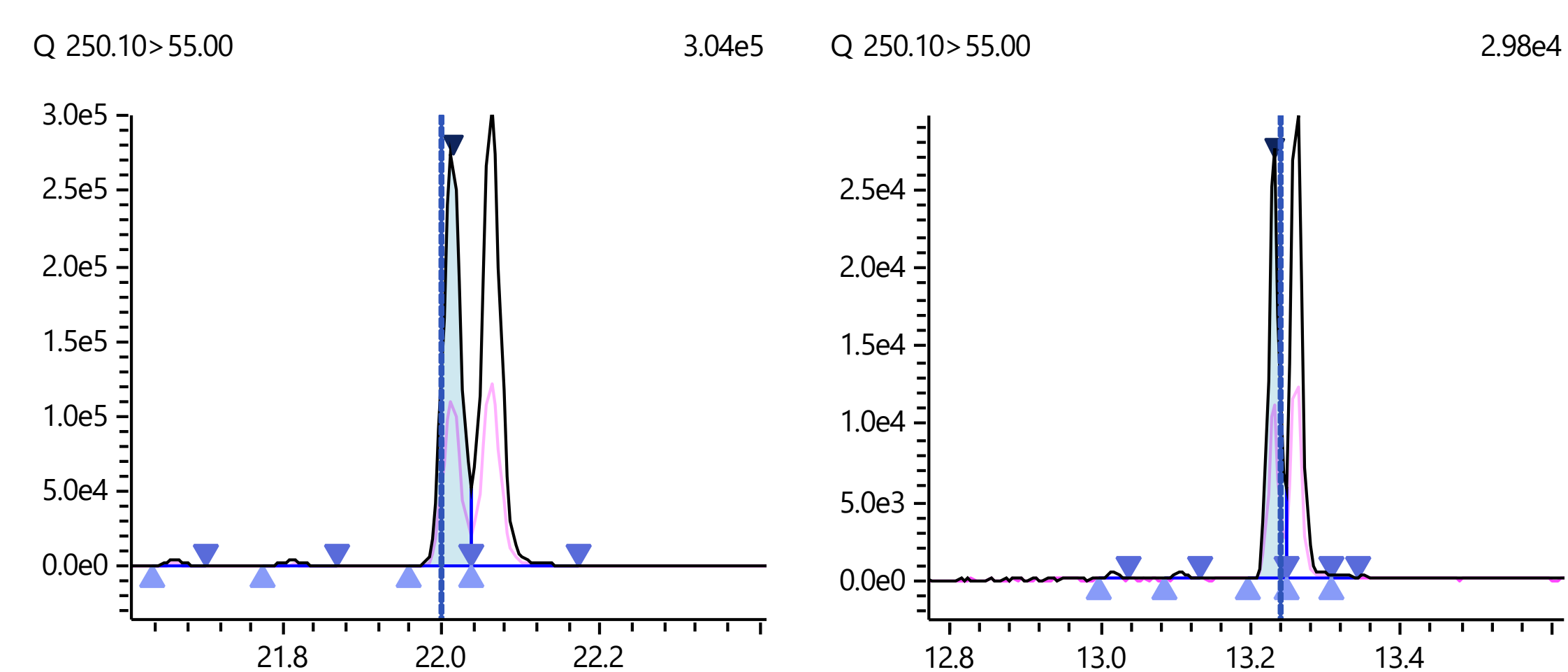
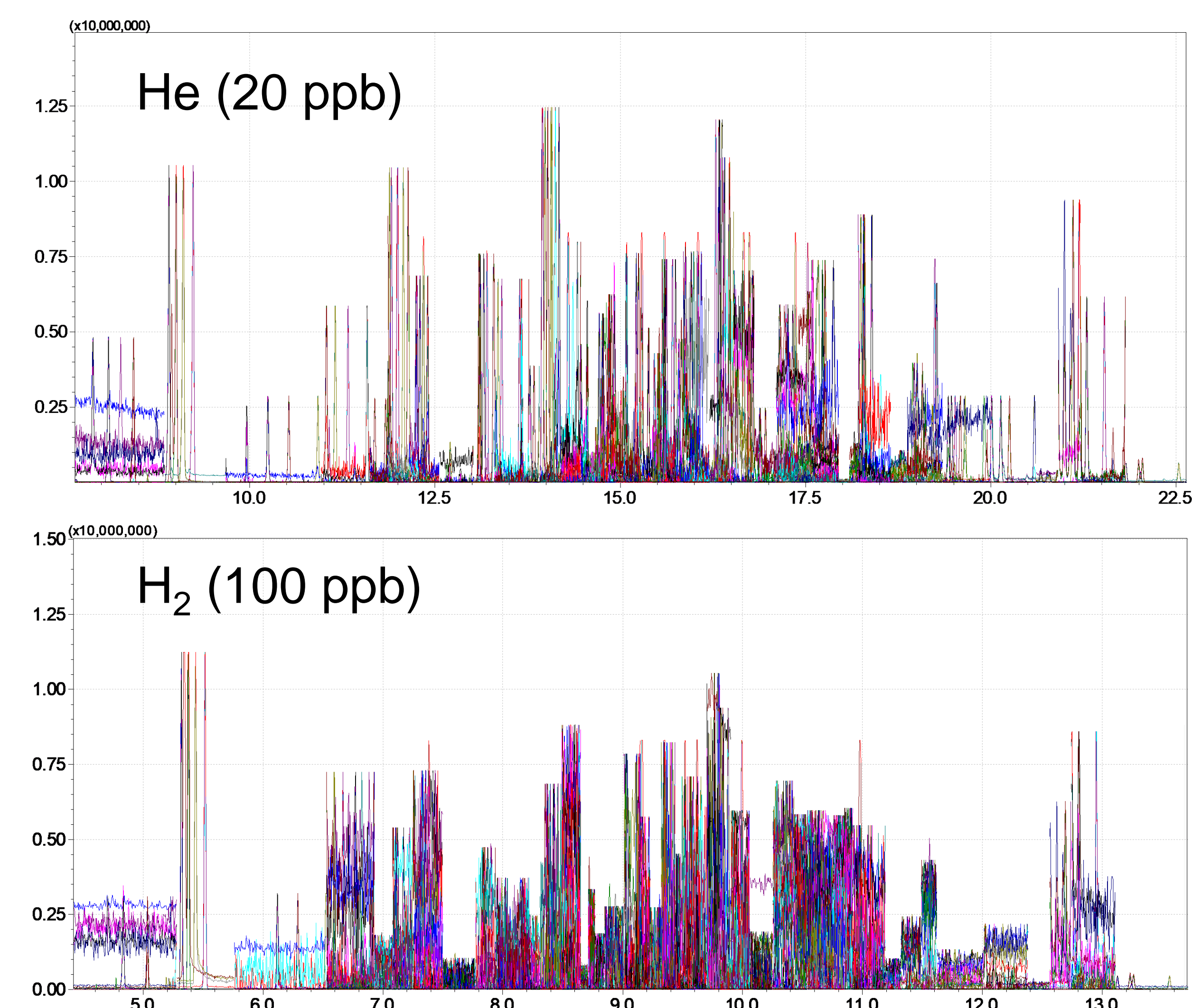


Figure 2: Fluvinate-1 and -2 signals for helium (left) and hydrogen (right)

Even though resolution is maintained, peak intensity typically is decreased when switching from helium to hydrogen. To investigate that regulatory limits are still met, matrix calibration curves (5 ppb – 500 ppb) were measured for all 120 pesticides. The linear correlation factor was higher than 0.9980 for every compound proving good linearity. All components were detectable down to a concentration of 5 ppb. Figure 3 shows peak profiles and calibration curves for some typical pesticides.

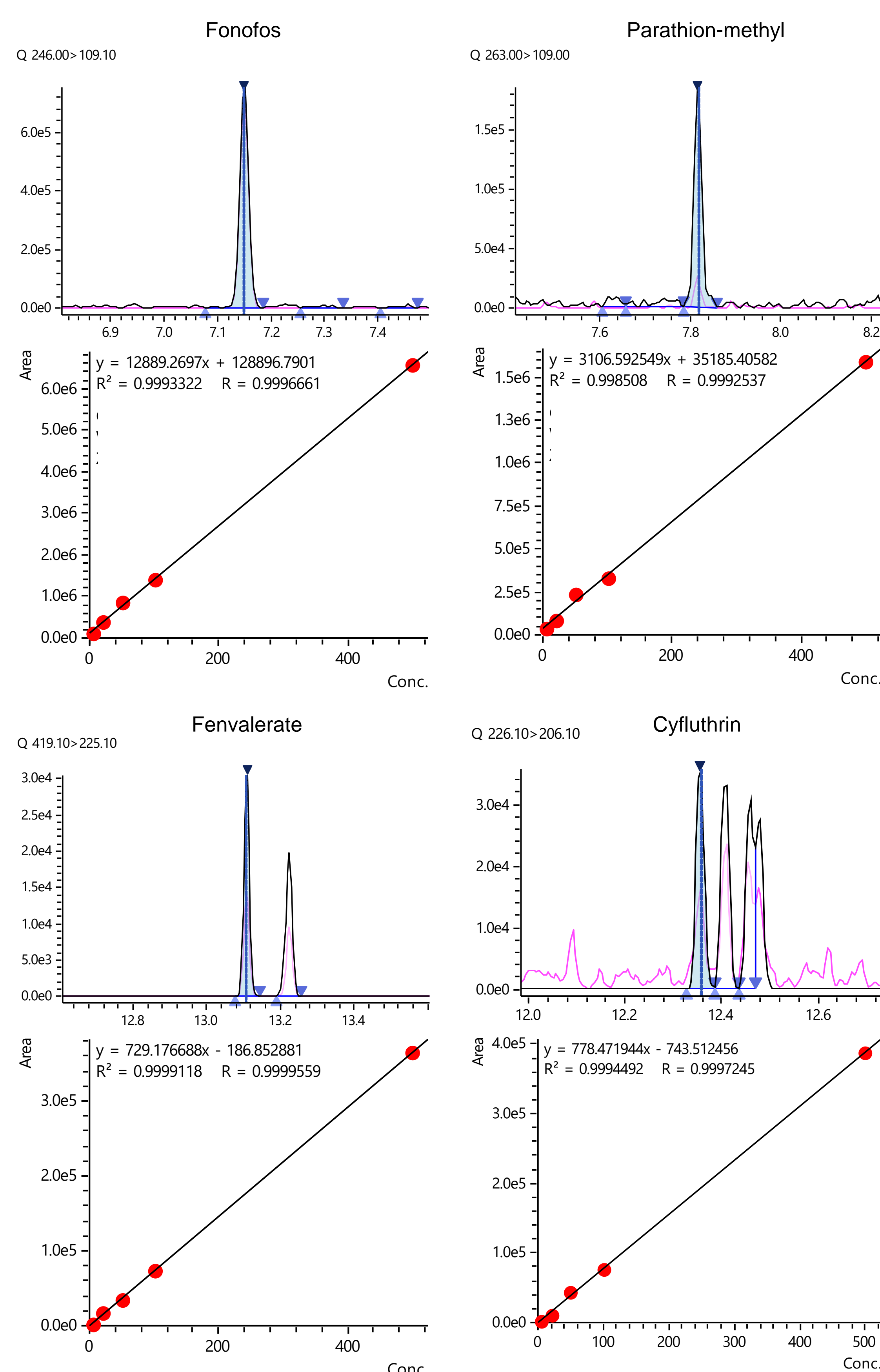


Figure 3: Peak profiles at 50 ppb and calibration curves (5 ppb - 500 ppb)

In addition, a reproducibility test at a concentration of 10 ppb was performed. For many pesticides a %RSD (n=10 injections) below 20% was found, examples are given in Table 2.

Compounds	%RSD at 10 ppb (n=10)	Compounds	%RSD at 10 ppb (n=10)
Mevinphos	17.0	Terbacil	19.4
Etridiazole	13.2	Malathion	10.3
Methacrifos	12.1	Fenthion	11.2
Chloroneb	8.0	4,4-Dichlorobenzophenone	9.0
Pentachlorobenzene	10.0	Bromophos-ethyl	19.7
Sulfotep	8.23	Iodofenphos	14.9
alpha-HCH	17.3	Chlorobenzilate	9.4
Hexachlorobenzene	13.4	Carfentrazone-ethyl	17.0
Atrazine	18.7	Phosalone	13.3
Fonofos	12.6	Flucythrinate	15.3

Table 2: Reproducibility obtained at 10 ppb

4. Conclusion

In the study presented here the use of hydrogen as carrier gas for pesticide residue analysis was investigated on the basis of apple matrix spiked with 120 different pesticides. All compounds were detectable down to 5 ppb, calibration curves and correlation factors proved good linearity. At 10 ppb the %RSD values for many compounds were below 20%.