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Rapid simultaneous screening of multiple pesticide residues in Food matrices

Joerg Riener
Agilent Technologies, Waldbronn, Germany

Introduction

With increased international trade in food and food ingredients, there is even more emphasis on food safety. Especially in "QuEChERS-times", highly selective methods are obligatory to eliminate matrix interferences. GC with triple quadrupole mass spectrometry (GC-MS/MS) is the gold standard for the target analysis of volatile contaminants. However, if a residue is not on the target list, it will not be detected. Although many targeted approaches have been successfully applied for the analysis of pesticides in food, accurate and reliable improvement for high-throughput applications of untargeted residue remained so far an elusive goal.

Using a GC/MS with high mass accuracy and full scan acquisition opens such possibilities of highly selective determination of a theoretically unlimited number of compounds. GC coupled with high-resolution QTOF MS is a powerful analytical tool for the identification of unknown compounds and provides increased selectivity for the determination of target compounds. A method featured with higher accuracy, resolution, and detection sensitivity as well as fast speed is being explored for monitoring multi-residues of pesticides, especially those that are banned or severely restricted, even present in trace amounts and complicated matrices. This poster demonstrates a rapid, simultaneous, and multi-species screening and identification method capable of monitoring multi-residues of pesticide remaining in food extracts using a 7200 Q-TOF GC/MS with accurate mass.

Experimental

The analyses were performed on an Agilent 7890A GC system combined with an Agilent 7200 Quadrupole Time of Flight system. The GC configuration and conditions were as shown in Table 1 and Figure 1. The MS operating conditions were as shown in Table 2. A mass calibration using PFTBA was done prior to the start of the sequence, but not between runs. The Internal Reference Mass for auto mass recalibration was not applied.

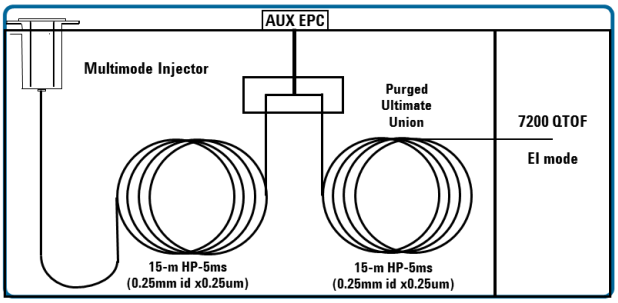


Figure 1. GC QTOF configuration with mid-column backflush.

Experimental

Table 1. GC Conditions

Gas chromatograph	Agilent 7890A
Inlet	Air cooled multimode inlet (MMI), equipped with an ultrainert splitless liner with glass wool
Columns	Two 15.0 m x 0.25 mm ID x 0.25 µm HP-5MS Ultra Inert were connected to the MS via a pressure controlled tee.
Carrier gas	Helium
Carrier gas mode	Constant flow
Column flows	1.25 mL/min (col. 1) and 1.45 mL/min (col. 2)
Autosampler	Agilent 7693A
Retention Time Locking	Chlorpyrifos-methyl locked to 9.143 min
Injection mode	Cold splitless, purge flow 50.0 mL/min at 2.0 min
MMI Temperature program	70 °C (0.02 min), 600 °C/min to 310 °C (1 min), 100 °C/min to 310 °C Backflush: 280 °C
Injection volume	1.0 µL
Oven program	60 °C (1 min), 40 °C/min to 170 °C, 10 °C/min to 310 °C
Backflush conditions	Post run, 5 min, oven 300 °C, 40 psi at pressure controlled tee, inlet 1 psi
Transfer line	280 °C

Table 2. QTOF Conditions

Mass spectrometer	Agilent 7200 Q-TOF
Ionisation	Electron impact ionization (EI)
Source temperature	280 °C
Quadrupole temperature	150 °C
Quadrupole mode	Total ion transmission, cutoff at m/z 45
Collision gas	Nitrogen @ 1.5 mL/min
Scan range	m/z 45 to 1000
Acquisition rate	6 Hz
Acquisition mode	4 GHz High Resolution mode
Solvent delay	4 min

Results and Discussion

As currently no large exact mass EI library exists, a different approach was taken. A total of 500 pesticides and organic pollutants were measured by GC/Q-TOF MS to create an exact mass database, in combination with an Retention Time locked method.

The workflow consisted of a TOF screening for possible organic pollutants by exact mass match for at least two fragments for each compound. (Figure 2) Detected compounds were then set up for quantitation and automatically matched against an accurate mass reference spectra. To evaluate the applicability of the database, three different matrices (Citrus, Pepper, Garlic) were prepared by solid phase extraction, spiked with a mixture of 93 pesticides at different concentrations between 1 and 100 ppb, and analyzed by GC/Q-TOF MS.

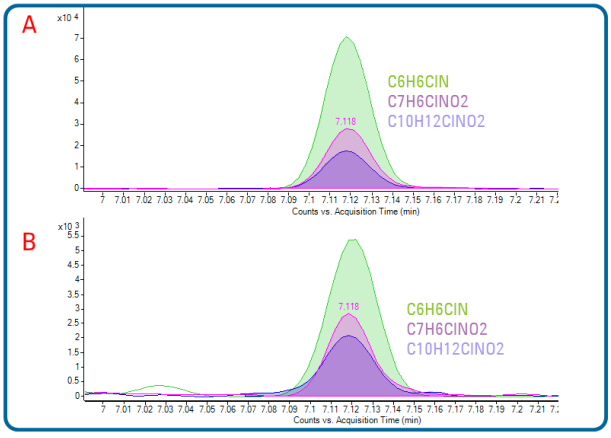


Figure 2. Detection of Chlorproham in pepper matrix samples by using three fragments and an Retention time window of 0.5 minutes at a concentration of 46.5 pg/µl (A) and 0.9 µg/µL (B).

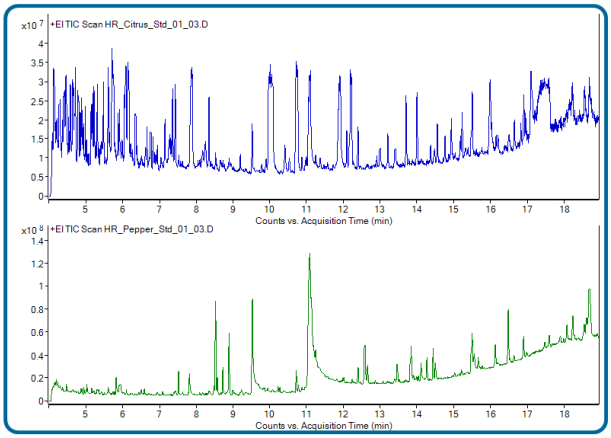
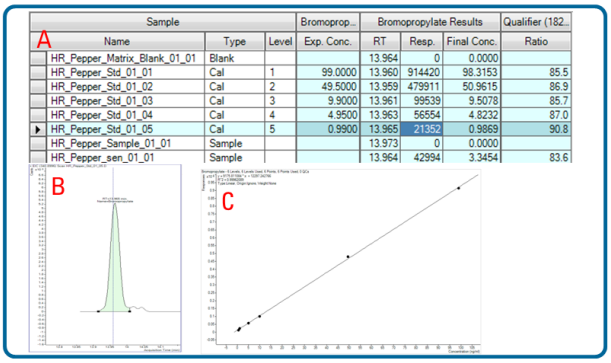


Figure 3. Total Ion Chromatogram of Citrus (top) and Pepper Extract (bottom).

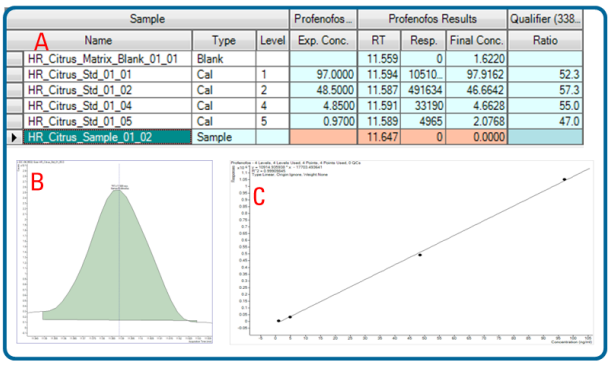
It is well known that not all matrices are alike. Figure 3 compares the TICs of two samples run under the previously listed conditions: Citrus (blue) and Pepper (green).

Spiking 93 pesticides at levels of 1, 5, 10, 50 and 100 ng/mL in the different matrices showed that most pesticides have good linear response, some are listed in table 2. It was found that all of the 93 pesticides with concentrations down to as low as 1 ppb were detected and the accurate masses were identified with errors less than 10 ppm, indicating high sensitivity, accuracy, selectivity and specificity.



Sample			Bromoprop...	Bromopropylate Results			Qualifier (182...
A Name	Type	Level	Exp. Conc.	RT	Resp.	Final Conc.	Ratio
HR_Pepper_Matrix_Blank_01_01	Blank			13.964	0	0.0000	
HR_Pepper_Std_01_01	Cal	1	99.0000	13.960	914420	98.3153	85.5
HR_Pepper_Std_01_02	Cal	2	49.5000	13.959	479911	50.9615	86.9
HR_Pepper_Std_01_03	Cal	3	9.9000	13.961	99539	9.5078	85.7
HR_Pepper_Std_01_04	Cal	4	4.9500	13.963	56554	4.8232	87.0
HR_Pepper_Std_01_05	Cal	5	0.9900	13.965	21352	0.9869	90.8
HR_Pepper_Sample_01_01	Sample			13.973	0	0.0000	
HR_Pepper_sen_01_01	Sample			13.964	42994	3.3454	83.6

Figure 4. Quantitation of Bromopropylate in Pepper. A: the top table shows the summary of the calibration; B: the extracted ion chromatogram of Bromopropylate at the spiking level of 1 ng/ml; C: linear regression calibration curve with regression coefficient of 0.9996 .



Sample			Profenofos...	Profenofos Results			Qualifier (338...
A Name	Type	Level	Exp. Conc.	RT	Resp.	Final Conc.	Ratio
HR_Citrus_Matrix_Blank_01_01	Blank			11.559	0	1.6220	
HR_Citrus_Std_01_01	Cal	1	97.0000	11.594	10510...	97.9162	52.3
HR_Citrus_Std_01_02	Cal	2	48.5000	11.587	491634	46.6642	57.3
HR_Citrus_Std_01_04	Cal	4	4.8500	11.591	33190	4.6628	55.0
HR_Citrus_Std_01_05	Cal	5	0.9700	11.589	4965	2.0768	47.0
HR_Citrus_Sample_01_02	Sample			11.647	0	0.0000	

Figure 5. Quantitation of Profenofos in Citrus. A: the top table shows the summary of the calibration; B: the extracted ion chromatogram of Profenofos at the spiking level of 1 ng/ml; C: linear regression calibration curve with regression coefficient of 0.9990.

Results and Discussion

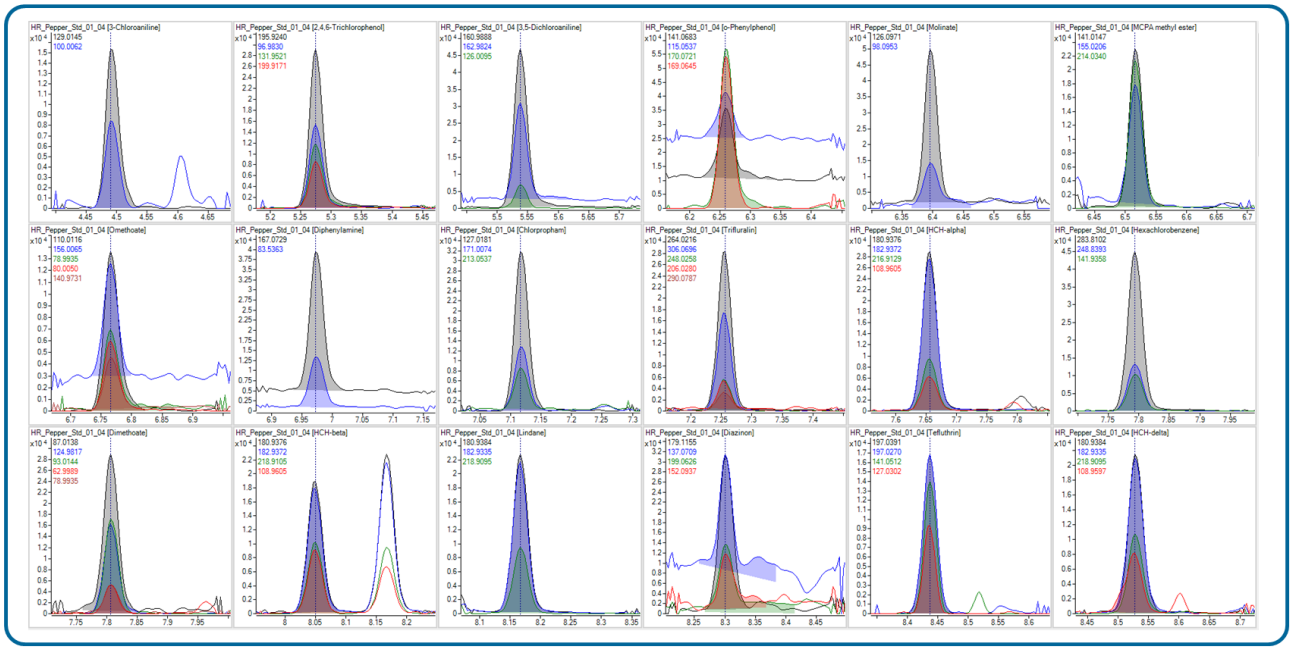


Figure 6. Overlap of Quantifier with Qualifiers for various compounds in pepper Extract at a concentration of 5 ng/ml.

Table 3. Summary for various Compounds at the calibration level of 5 ng/ml in pepper extract

Name	CF Formula	CF R2	RT	S/N
3-Chloroaniline	y = 4233.421703 * x - 465.722244	0.9998	4.4904	41186.3
o-Phenylphenol	y = 6380.635068 * x + 8262.480950	0.9982	6.2588	150.9
MCPA methyl ester	y = 6304.336498 * x + 4707.788905	0.9991	6.5157	89.9
Lindane	y = 6557.562264 * x + 2366.066879	0.9997	8.1674	1063.8
Diazinon	y = 7845.599700 * x + 11355.550885	0.9973	8.3008	57.4
Chlorothalonil	y = 10864.714124 * x + 5887.043240	0.9998	8.6078	71.4
Pirimicarb	y = 17810.795049 * x + 20244.204457	0.9977	8.7479	113.1
Endosulfan ether	y = 1371.687157 * x + 1913.985849	0.9993	8.8781	150.5
Pirimicarb desmethyl	y = 12726.237402 * x + 22151.460574	0.9994	8.8914	59.6
Tolclofos-methyl	y = 3687.327601 * x + 1261.637368	0.9997	9.2518	75.0
Fenitrothion	y = 4783.290173 * x + 1713.932083	0.9999	9.6155	30.2
Anthraquinone	y = 7446.816414 * x + 5224.213624	0.9989	9.9458	23605.2
Triadimefon	y = 2096.831026 * x + 1222.420435	0.9996	10.033	38.4
Chlorthal-dimethyl	y = 12948.923502 * x + 3201.242273	0.9997	10.083	418.0
Endosulfan lactone	y = 2763.456131 * x + 1261.205277	0.9999	10.583	709.6
Oxy-chlordane	y = 2663.874818 * x + 792.009069	0.9998	10.667	21.0
Triadimenol	y = 3405.352025 * x + 3966.781540	0.9996	10.757	8.4
Chlordane-trans	y = 3978.154053 * x - 1657.558187	0.9982	11.06	33605.1
Endosulfan alpha	y = 964.902805 * x + 995.982784	0.9993	11.297	26.8
Chlordane-cis	y = 4547.336133 * x + 301.991975	0.9999	11.331	36175.2
Hexaconazole	y = 6349.743314 * x + 2232.414865	0.9998	11.477	156.1
Profenofos	y = 5570.008894 * x + 3368.207836	0.9998	11.577	32.8
Dieldrin	y = 1674.654203 * x + 1414.523728	0.9995	11.754	36.5
Endrin	y = 2010.066924 * x + 573.304864	0.9996	12.155	18.9
Endosulfan sulfate	y = 860.524805 * x + 460.856612	0.9999	13.062	16965.1
Bromopropylate	y = 9282.652371 * x + 8028.900631	0.9986	13.963	1183.3
Etoxazole	y = 5305.899860 * x + 2300.856853	0.9996	14.123	25.3
Azinphos-methyl	y = 6411.580243 * x + 2602.574758	0.9998	14.654	1656.0
Cyhalothrin lambda	y = 8477.913406 * x + 9037.423784	0.9973	14.921	17.7
Acrinathrin	y = 5078.173819 * x + 3247.589847	0.9974	15.068	28.5
Permethrine	y = 8389.980247 * x + 9837.260949	0.9979	15.658	62.1
Cyfluthrin	y = 1917.148714 * x - 2110.683305	0.9986	16.532	3.3

Conclusions

- An exact mass database and GC/Q-TOF MS were combined for the monitoring of pesticides in food matrices.
- In the database, both retention time and characteristic ion were included for the rapid screening and the identification of the pesticides. GC coupled with tandem high-resolution QTOF MS provided a powerful analytical method for the selective identification of the pesticides
- It was found that all of the 93 pesticides with concentrations down to as low as 1 ppb were detected and the accurate masses were identified with errors less than 10 ppm, indicating high sensitivity, accuracy, selectivity and specificity.
- Backflushing reduces the runtime as well as the amount of matrix reaching the mass spectrometer.