Analysis of multiple pesticide residues in scallion by gas chromatography quadrupole time of flight–mass spectrometry (GC /Q-TOF)

Wenwen Wang[1], Shan Zhou[1], Zhe Cao[1], Chongtian Yu[2]. 1. Agilent Technologies, No. 3 Wangjing North Road, Chaoyang Distr., Beijing, 100102, China
2. Agilent Technologies, No. 16,east building,140 tianlin road, xuhui Distr., Shanghai, 200233, China

Agilent Technologies

Introduction

Scallion is not only a Chinese traditional food condiment, but also one of the important agricultural goods for export. Traditional analysis methods, such as gas chromatography or gas chromatography-single-quadrupole mass spectrometry, were susceptible to the strong interference of scallion matrix, resulting in inaccurate test results. The analytical power of GC/MS with high mass accuracy is useful in two broad-defined ways: to identify unknown compounds, and to provide increased selectivity for the determination of target compounds, especially in complicated sample matrices, like scallion. This poster demonstrates the use of exact mass measurement using a 7200 Q-TOF GC/MS to identify and quantify pesticides in scallion.

Experimental

Sample Preparation

GC Conditions

GC system: Agilent 7890A;
Column: Agilent HP-35 capillary column(30 m×0.25 mm×0.25 μm);
Column temperature: 80 °C hold 1 min , at 25 °C /min to 170 °C, at 6 °C /min to 300 °C, hold 10 min;
Carrier gas: Helium;
Flow rate: 1.1mL/min;
Injection port temperature: 270 °C;
Injection volume: 1μL;
Injection mode: Splitless, purge on after 1.5 min

QTOF Conditions

Mass system : 7200 Q-TOF;
Ion source: EI;
Ion source polarity: Positive ion;
Ionization voltage: 70 eV;
Ion source temperature: 250°C;
Interface temperature: 280°C;
Solvent delay: 5 min
Pesticides were analysed in scan mode and in MS/MS mode
Scan mass range:45-450amu

Results and Discussion

Choose SPE Cartridge

Bond Elut NH_2 is a weaker anion exchanger than sorbents such as SAX (a quaternary amine sorbent that is always charged) and is therefore a better choice for retention of very strong anions, such as sulfonic acids, which may retain irreversibly on a SAX sorbent. Bond Elut Carbon cartridges are packed with ultra-pure graphitized carbon particles that have been optimized for the absorption of pigments in food, fruits and vegetables.Scallion is a very complex matrix,which is difficult to clean up. Agilent Bond Elut Carb/ NH_2 has excellent recoveries and precisions for the analysis of pesticides. So the high-quality Agilent Bond Elut Carb/ NH_2 is chosen as clean-up cartridge.

Results and Discussion

Target compound quantitation and confirmation

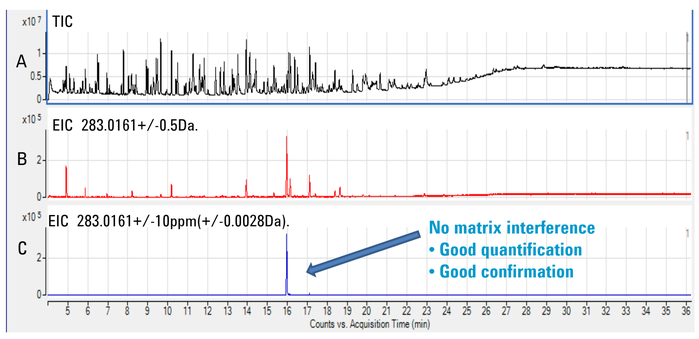

Figure 1.A:Separation of 100 Pesticides in Scallion Matrix at the Concentration of 100 ng/ml;
B: the extracted ion chromatogram (283.0161+/-0.50Da)obtained by MS scanning;
C: the extracted ion chromatograms(283.0161+/-10ppm)obtained by MS scanning.

Figure 1A showed the TIC of 100 Pesticides in Scallion Matrix at the Concentration of 100 ng/ml. Figure 1B showed the EIC for m/z 283.0161 using an extraction window of +/- 0.5 Da, which represents the performance of a low resolution single quadrupole MS. An extraction window of +/- 10 ppm is shown in Figure 1C and demonstrates the advantage of high resolution, accurate mass for reducing the interferences from the chemical matrix.

Mass accuracy

Table 1. Summary some Resolution and Accuracy of compounds

Name	Formula	Extract Mass	Measured Mass	Resolution	Accuracy (ppm)
Metolachlor	C11H16N	162.1277	162.1272	11327	3.24
Diphenylamine	C12H11N	169.0886	169.0879	11036	4.14
Norflurazon	C12H9ClF3N3O	303.0381	303.0369	12448	3.88
Procymidone	C13H11Cl2NO2	283.0161	283.0154	12686	2.6
p,p-DDD	C13H9Cl2	235.0076	235.0076	12207	-0.08
o,p-DDT	C13H9Cl2	235.0076	235.0068	12274	3.33
o,p-DDD	C13H9Cl2	235.0076	235.0068	12274	3.33
Cyprodinil	C14H14N3	224.1182	224.1177	12138	2.34
Mirex	C5Cl6	269.8126	269.8119	12364	2.47
Tecnazene	C5HCl4	200.8824	200.882	11686	3.42
PCNB	$C6^{35}Cl4^{37}ClNO2$	294.8337	294.833	12288	2.27
HCB	$C6^{35}Cl5^{37}Cl$	283.8096	283.8096	13151	0.06
Gamma-BHC	C6H4Cl3	180.9373	180.9369	11576	2.26
Delta-BHC	C6H4Cl3	180.9373	180.9368	11489	2.82
Tetradifon	C6H4ClOS	158.9666	158.9662	10728	2.45
Pentachlorobenzene	C6HCl5	247.8515	247.8509	12734	2.58
Simazine	C7H12ClN5	201.0776	201.0769	11692	3.35
Propyzamide	C7H3OCl2	172.9555	172.9554	10809	0.85
Buprofezin	C7H7N	105.0573	105.057	9159	2.86
Pirimicarb	C8H12N3O	166.0975	166.0971	11369	2.34

The table1 showed the resolution and accuracy of some compounds. 7200 GC-Q/TOF exhibits high resolution and accuracy , especially the long-time stability of the entire machine(No internal standard calibration quality axis, and the tuning is done two days ago).Mass measurements obtained with errors below 5 ppm of most compounds can be used to eliminate many of the possible molecular formula.

Calibration Curves

Calibration -Propanil A

Sample			Propanil M...	Propanil Results				
	Type	Level	Exp. Conc.	RT	Resp.	Calc. Conc.	Final Conc.	Accuracy
10ppb-1.D	Cal	1	10.0000	13.302	138383	11.6879	11.6879	116.9
10ppb-2.D	Cal	1	10.0000	13.304	136088	11.5346	11.5346	115.3
20ppb-2.D	Cal	2	20.0000	13.309	245832	18.8652	18.8652	94.3
20ppb-1.D	Cal	2	20.0000	13.304	259625	19.7864	19.7864	98.9
50ppb-2.D	Cal	3	50.0000	13.304	714546	50.1737	50.1737	100.3
50ppb-1.D	Cal	3	50.0000	13.302	726235	50.9544	50.9544	101.9
100ppb-1.D	Cal	4	100.0000	13.307	1396189	95.7050	95.7050	95.7
100ppb-2.D	Cal	4	100.0000	13.305	1444127	98.9071	98.9071	98.9
200ppb-2.D	Cal	5	200.0000	13.309	3006233	203.2506	203.2506	101.6
200ppb-1.D	Cal	5	200.0000	13.307	2944620	199.1350	199.1350	99.6

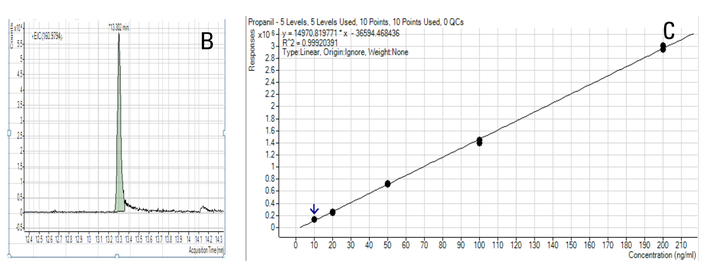

Figure 2. Matrix-Matched Linear Regression Calibration Curve For Quantitation of Propanil in Scalion. A: the top table lists the summary of the calibration; B: the extracted ion chromatogram of Propanil with S/N of 63.39 at the spiking level of 10 ng/ml; C: the matrix matched linear regression calibration curve for Propanil with regression coefficient of 0.9992 .

Results and Discussion

Spiking 100 pesticides at levels of 10, 20, 50, 100 and 200 ng/mL in scallion matrix showed that most pesticides have good linear response, some are listed in table 2. By calculating the signal-to-noise ratio (S/N) at the lowest calibration level (10 ng/mL), it has found that the values of S/N are all greater than 3.It indicates that the method allows to quantitative analyze these pesticides at 10 ng/mL spiking level, corresponding 1 ng/g of these pesticides in scallion matrix.

Table 2. Summary part of Matrix-Matched Calibration Curves for Compounds at the lowest calibration level of 10 ng/ml.

Name	Transition	CF R^2	Calibration Equations	RT	S/N
Tecnazene	200.8824	0.9909	y = 4095.027642 * x - 30577.870392	9.01	156.55
Chloropropham	152.9976	0.9954	y = 7092.601730 * x + 48191.083853	9.27	17.8
Propyzamide	172.9555	0.9934	y = 8304.809563 * x - 46134.488386	10.84	22.9
Atrazine	200.0697	0.9984	y = 9101.833985 * x - 47722.228992	11.10	27.59
Simazine	201.0776	0.9924	y = 7578.038792 * x - 78149.289905	11.25	21.04
Triallate	268.0324	0.9985	y = 7986.199920 * x - 52590.735124	11.29	32.86
gamma-BHC	180.9373	0.9962	y = 8726.987120 * x + 49308.857981	12.40	170.07
delta-BHC	180.9373	0.9977	y = 9157.270018 * x + 36314.754743	13.23	46.18
Propanil	160.9794	0.9991	y = 14957.345808 * x - 34585.622954	13.30	63.39
Metolachlor	162.1277	0.9944	y = 17624.239299 * x + 75524.644092	13.94	43.16
Procymidone	283.0161	0.9975	y = 8896.827415 * x - 58260.346419	15.96	21.76
Chlordane,trans	405.7972	0.9937	y = 197.427713 * x - 1726.549027	16.38	5.38
Flutolanil	173.0209	0.9910	y = 19614.367785 * x - 165403.175911	17.00	29.73
p,p-DDE	315.9375	0.9988	y = 10313.454014 * x - 5414.070924	17.12	101.25
o,p-DDT	235.0076	0.9928	y = 9629.021215 * x - 86959.517973	18.60	63.66
o,p-DDD	235.0076	0.9929	y = 9629.950061 * x - 87083.933279	18.60	61.63
Tetradifon	158.9666	0.9921	y = 13361.221743 * x - 126790.472215	22.96	22.37
Fenarimol	138.9945	0.9845	y = 5303.206687 * x - 59282.421023	24.07	7.46
Pyridaben	147.1168	0.9974	y = 10216.672091 * x - 70929.067213	24.67	21.72
Ethofenprox	163.1117	0.9904	y = 15134.825141 * x - 88245.742936	26.34	25.13

According to the requirement of EU regulations for pesticide detection, two ions with accurate mass are required to confirm each compound. The figure 3 showed part of the overlapping EIC with two accurate mass ions in 10ng/ml scallion extract.

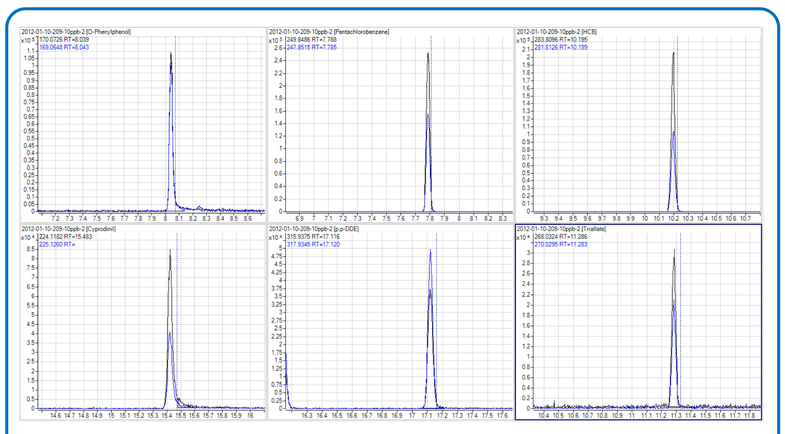

Figure 3.Part of the overlapping EIC with two accuracy mass ions in 10ng/ml scallion extract

MS/MS accurate mass EIC

Atrazine –10 ng/ml in scallion extract (EIC m/z = 215.0932)

Figure 4.A:the extracted ion chromatogram (215.0932+/-0.50Da)obtained by TOF mode;
B: the extracted ion chromatograms(215.0932+/-20ppm)obtained by TOF mode.
C: the extracted ion chromatograms of product ion(215>200.0689+/-20 ppm)obtained by MS/MS mode.

Figure 4 showed that use of high resolution TOF may also has some interference background. Further, MS/MS experiments allowed to generate 'clean' spectra in the presence of matrix interference.

Conclusion

- By the high-resolution capability and the accurate acquisition of ions, 7200 QTOF GC/MS exhibits high sensitivity and high reliability in the detection of trace pesticides in scallion.
- The ultra-high full scan sensitivity of TOF mode is suitable for the screening of a number of compounds in the short time.
- In the further confirmation of analysis results, MS/MS provides a more reliable mode: the quadrupole screening excludes most of the interference, and then to obtain reliable results using the technical advantages of TOF.