[APPLICATION NOTE]

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Determination of 208 Pesticide Residues and their Metabolites in Foods Using Oasis PRiME HLB and Xevo TQ-GC

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APPLICATION BENEFITS

Efficient workflows enable reliable determination of multiple residues across a variety of challenging food commodities. Waters offers a range of sample preparation techniques that provide improved accuracy for quantifying contaminants.

- Simple pass-through cleanup is readily incorporated into the QuEChERS workflow to maintain accuracy and precision in the quantitative performance, while improving overall method robustness.
- Easy method transfer, development, and updates.
- Fit-for-purpose to achieve Chinese National Standard Method regulatory requirements for GC-MS/MS pesticides.

WATERS SOLUTIONS

Xevo™ TQ-GC System

DisQuE™ QuEChERS Dispersive Solid Phase Extraction

Oasis™ PRiME HLB Plus Short Cartridge

TruView™ LCMS Certified Vials

MassLynx™ MS Software

Quanpedia™ Database

KEYWORDS

GC-MS, mass spectrometry software, QuEChERS, sample extraction, sample cleanup, pesticides, GB 23200.113-2018

INTRODUCTION

Gas chromatography-mass spectrometry (GC-MS) has been a common analytical method for pesticide measurement due to its high efficiency of separation, along with its qualitative and quantitative performance. As a milestone of pesticides analysis, Lehotay[1] and Nguyen, et al.[2] established a sample preparation method based on QuEChERS technology in 2015 for the simultaneous detection of multiple pesticide residues in vegetables and other foods using LC-MS/MS and GC-MS/MS. In recent years GC-MS/MS analysis has become the preferred method for pesticides analysis due to its advantages in selectivity, sensitivity, high throughput, and accurate quantitative performance.[3]

Recently, the first Chinese National Standard Method (GB 23200.113-2018)[4] for multiple pesticide residues using GC-MS/MS was released. For the first time in GB methodology, two efficient technologies have been adopted: QuEChERS for sample extraction, and GC-MS/MS for detection.

In this application note, foodstuffs of plant origin were further cleaned using Waters™ Oasis PRiME HLB following QuEChERS extraction and run on the Xevo TQ-GC to quantify 208 pesticides and their metabolites in fruits and vegetables. Rigorous method verification was carried out following the SANTE/11813/2017 guidance document,[5] which provided strong evidence that the method is fit for purpose and will achieve the method validation criteria set by the GB 23200.113-2018.

EXPERIMENTAL

Sample preparation

Cucumber, grape, and rice samples were purchased from local retail outlets and prepared using a modified version of QuEChERS sample preparation as reported in CEN method 15662.[6] The sample preparation used is summarized in Figure 1.

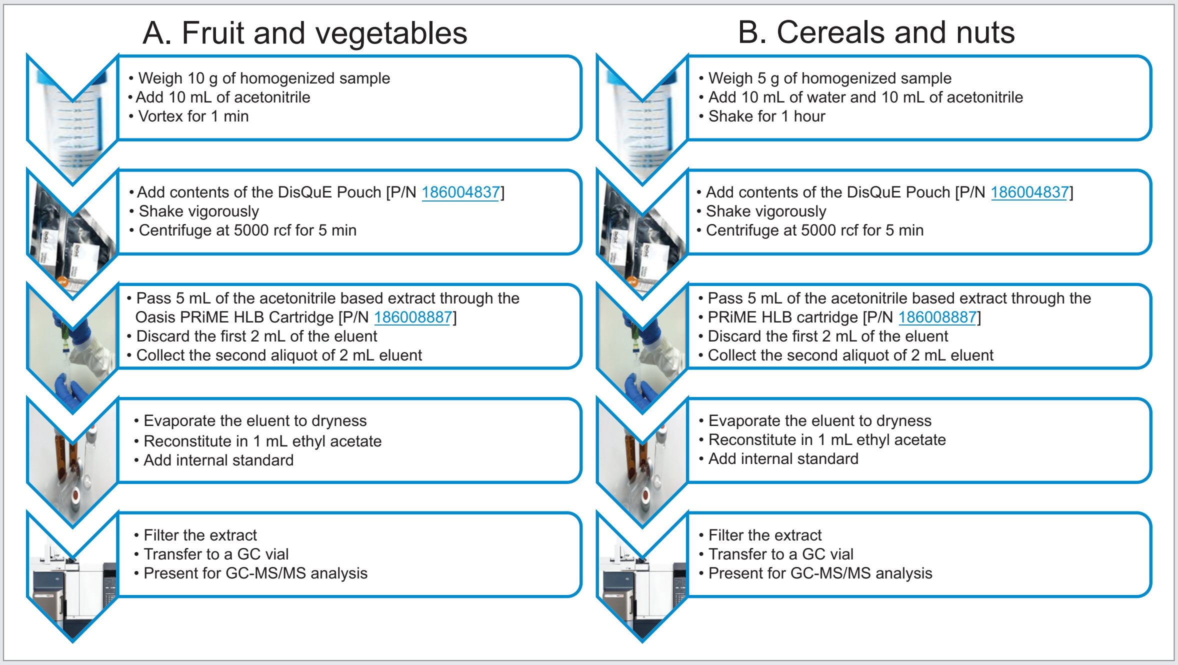

Figure 1. Sample preparation for A. fruits and vegetables, and B. cereal and nuts.

GC conditions

Column:	Rtx-1701 (30 m × 0.25 mm × 0.25 µm)
Carrier gas:	Helium
Gas flow rate:	1.0 mL/min
Injection type:	Pulsed splitless
Injection liner:	Gooseneck splitless 4 mm × 6.5 × 78.5 (Restek)
Inlet temp:	280 °C
Pulse time:	1.0 min
Pulse pressure:	170 kPa
Purge flow:	30 mL/min
Septum purge flow:	3 mL/min
Wash solvent:	Hexane
Oven program:	80 °C (hold 1.1 min) to 120 °C at 40 °C/min, then to 240 °C at 5 °C/min, then 295 °C at 12 °C/min and hold 8 min
Run time:	38.68 min
Injection volum:	1 µL

MS conditions

MS system:	Xevo TQ-GC
Software:	MassLynx v4.2
Ionization mode:	EI, 70 eV
Source temp.:	250 °C
GC interface:	300 °C
MRM conditions:	All transitions were imported from the Waters™ Quanpedia Database. IntelliStart™ Custom Resolution settings were used.

RESULTS AND DISCUSSION

OPTIMIZATION OF SAMPLE PREPARATION

Typically for GC, pigments are undesirable because they can potentially contaminate the injection liner and the GC column. Graphitized carbon black (GCB) is commonly used to remove pigments. However caution is advised with the level of GCB used since it is both a reverse phase and an anion exchange sorbent and can potentially trap certain pesticides, especially for pesticides with planar structure. Therefore it is important to optimize the amount of GCB used to capture the maximum amount of pigment while maintaining good recovery of pesticides, which can be a time-consuming exercise. In this work GCB was not used, but instead a novel sorbent, Oasis PRiME HLB was employed. Oasis PRiME HLB has recently been used to quickly and efficiently remove co-extractives including fats and phospholipids, as well as pigments from food matrices, using a simple and fast pass-through protocol.[7] In this study, Oasis PRiME HLB provided excellent pigment removal, thus reducing the contamination of the GC inlet liner and extending the lifetime of the GC consumables.

QUANPEDIA FOR METHOD CREATION

GC-MS/MS methods for GB 23300.113-2018 were easily generated using Quanpedia Database. This provided the creation of the GC, MS/MS, and processing methods in three simple clicks, as shown in Figure 2. Quanpedia can greatly reduce time and lab resources employed for setting up new multi-residue methods.[8]

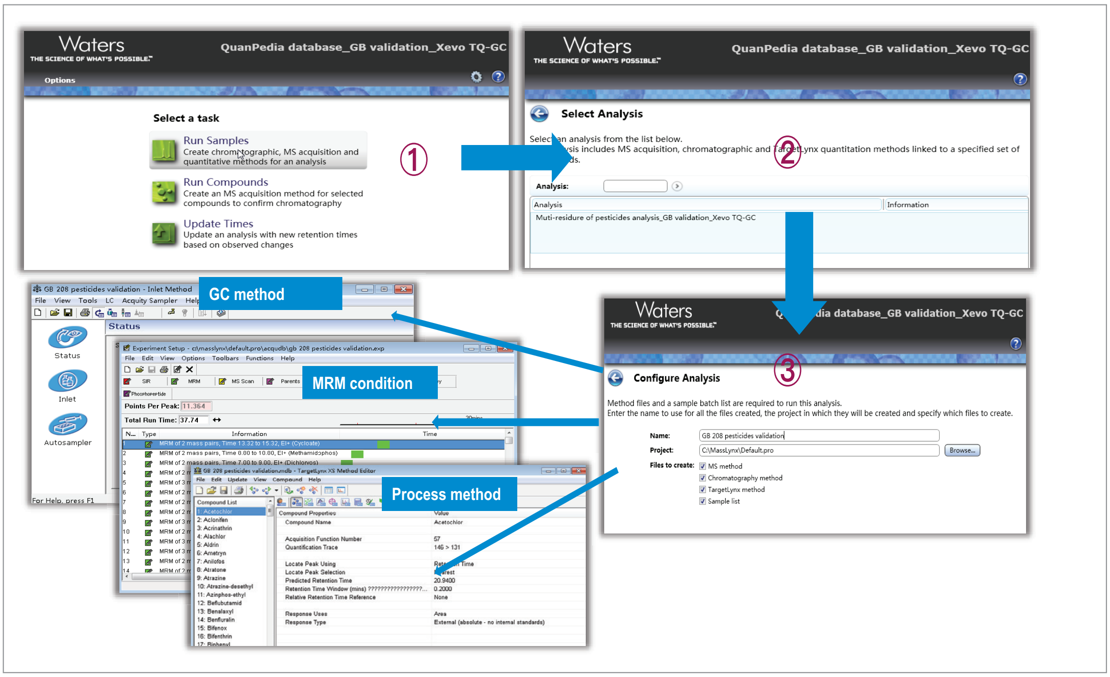

Figure 2. The complete GB method is available in the Quanpedia Database which can be set up with only three clicks. Click 1: Run Samples. Click 2: Select Method. Click 3: Configure Analysis parameters required (GC, MS, and processing methods).

METHOD PERFORMANCE

In-house method verification was carried out to determine the overall method performance in accordance with the requirements of GB method 23300.113-2018, referencing the SANTE/11813/2017 guidance document and associated analytical and validation criteria.5 The method performance was assessed for trueness, reproducibility, quantification, and identification of 208 pesticides and associated metabolites in cucumber, grape, and rice. For each commodity (n=3), matrix matched calibration curves were generated and replicate spikes (n=6) were extracted at three concentrations (LOQ, 2x LOQ, and 5x LOQ. The results, as summarized in Table 1, were within the permitted tolerances of the required guidelines demonstrating that this method is fit for purpose.

Table 1. Summary of the in-house verification results for pesticides and associated residues in rice, cucumber, and grape at relevant concentrations (LOQ, 2x LOQ, and 5x LOQ).

Parameter	SANTE criteria	Rice	Grape	Cucumber	Criteria satisfied
Retention time	±0.1 minute	20.49–20.50	18.69–18.70	18.67–18.70	✓
Ion ratio	±30%	1.92–2.28	1.55–2.43	1.92–2.28	✓
Residuals	±20%	≤20%	≤20%	≤20%	✓
Recovery (trueness)	70 to 120%	103.6%	93.4%	96.9%	✓
Repeatability (RSDr)	≤20%	2.6%	3.5%	2.8%	✓
LOQ	≤MRL	0.02 mg/kg	0.01 mg/kg	0.01 mg/kg	✓

TRUENESS AND REPRODUCIBILITY

Trueness and repeatability were assessed from the analysis of the three commodities: cucumber, grape, and rice. Each commodity was spiked at three concentration levels: LOQ, 2x LOQ, and 5x LOQ with five replicates (n=5) of each concentration prepared. In this study, the method performance is reported for each commodity spiked at the LOQ only, namely cucumber at 0.01 mg/kg, grape at 0.01 mg/kg, and rice at 0.02 mg/kg. These spiked concentrations were selected based on the LOQs defined in GB method 23200.113-2018. Figure 3 shows the chromatograms from some of the pesticides spiked at 0.01 mg/kg in rice, demonstrating that the sensitivity for these compounds is much lower than the required LOQ specified in the GB method.

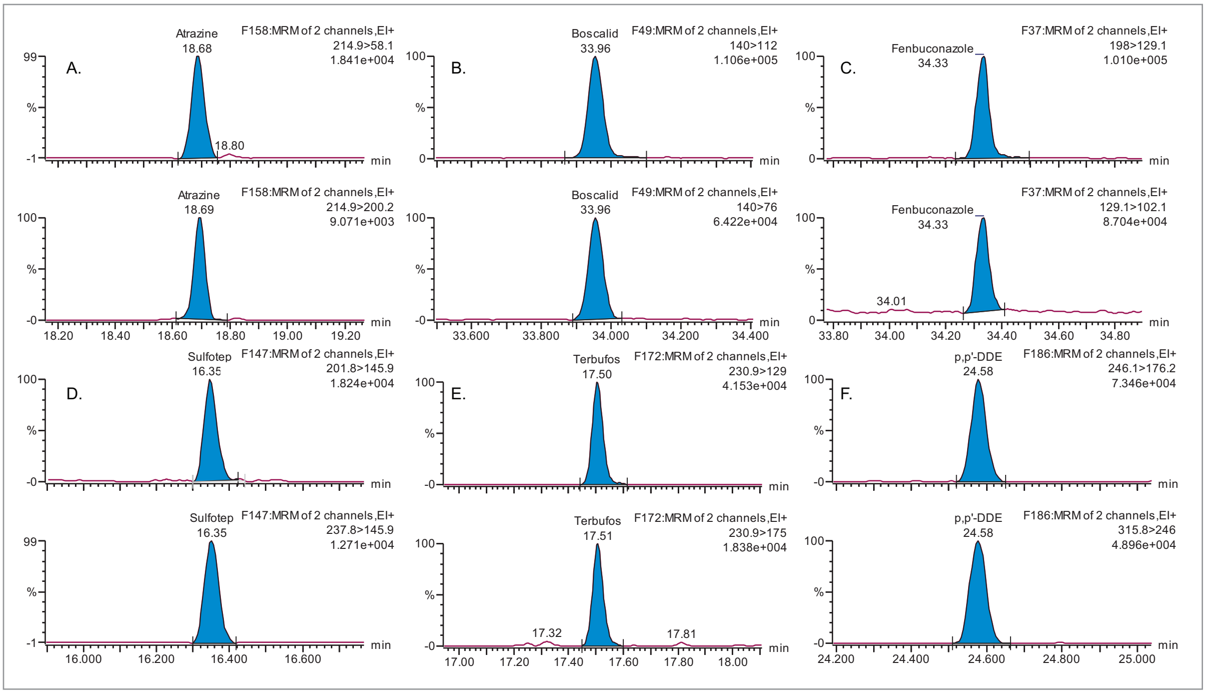

Figure 3. Two MRM transitions of A. atrazine, B. boscalid, C. fenbuconazole, D. sulfotep, E. terbufos, and F. p,p'-DDE spiked at 0.01 mg/kg (typical MRL) in rice.

Figure 4 shows the measured percentage recovery (trueness; between 70 and 120%) and repeatability (%RSD; <20%) for a representative selection of 15 pesticides in all of the commodities tested. Further details on recovery and repeatability for all 208 pesticides at the required LOQ across each commodity are summarized in Table 2, in the Appendix, which meet the acceptance criteria of the GB method.

QUANTIFICATION

Matrix-matched calibration curves allowed for accurate quantification of pesticides spiked in the commodity at the required LOQs. Calibrations were prepared over the concentration range of 0.005 mg/kg to 0.2 mg/kg for each target compound using internal standards. A weighted linear regression (1/x) was applied. Individual back-calculated concentrations were calculated automatically by TargetLynx™ Application Manager, and all were within the tolerance set in the SANTE guidelines (±20%). Figure 5 shows matrix-matched calibration plots for five representative pesticides.

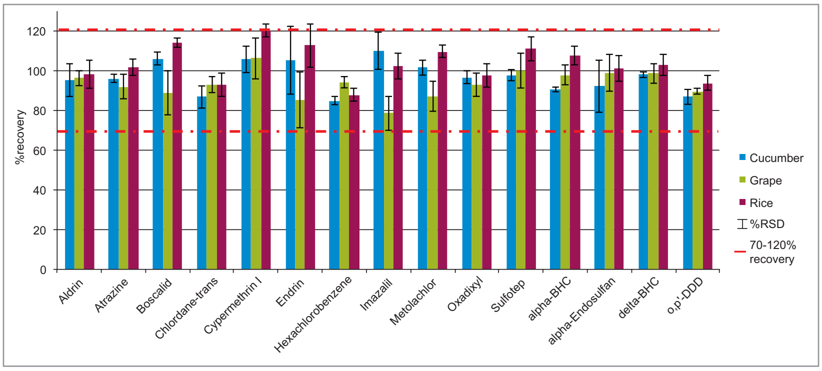

Figure 4. The measured recoveries (trueness) and repeatability (%RSD) of pesticides spiked at the required LOQ.

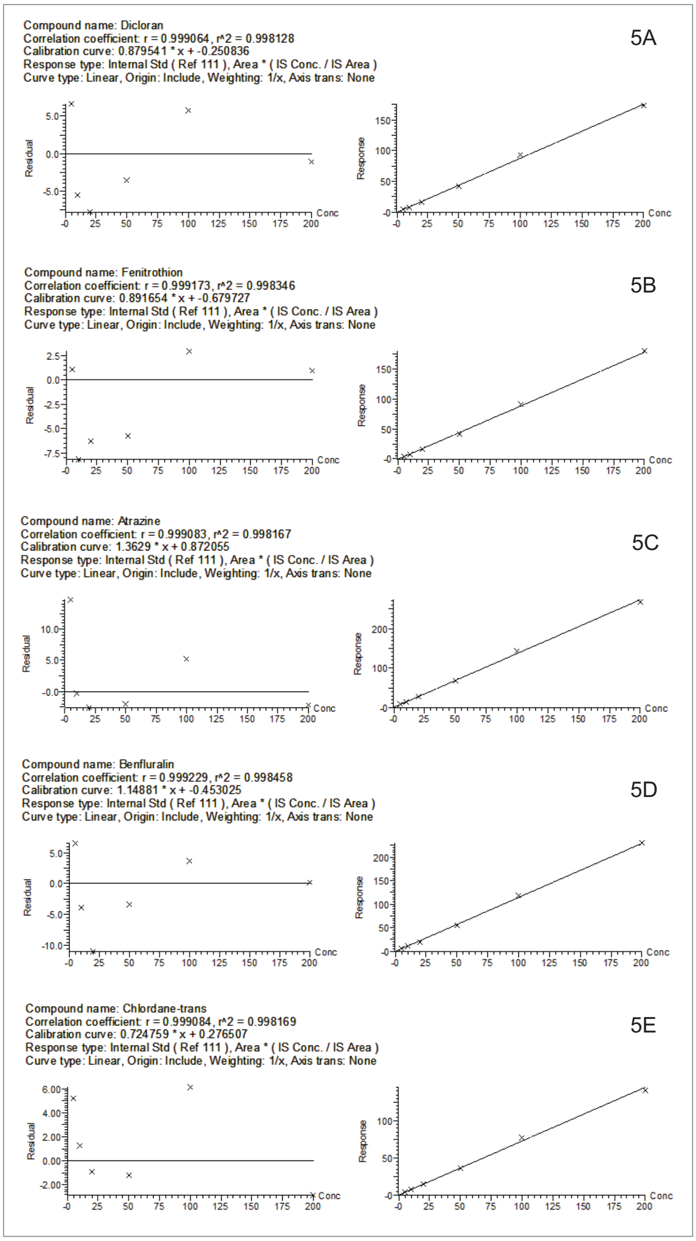

Figure 5. Examples of matrix-matched calibration graphs and residual plots for typical pesticides in the study generated automatically in a TargetLynx report (dicloran, fenitrothion, atrazine, benfluralin, and chlordane-trans).

IDENTIFICATION CRITERIA

The GC-MS GB Methods reference the SANTE requirements with respect to retention time and ion ratio tolerances. The guidelines state that the retention time of the analyte in the extract should be ±0.1 min to that of the calibration standard, and that ion ratios from sample extracts should be within ±30% of the reference (averaged calibration standards in the same sequence).

Using atrazine as an example, Figure 6 and Figure 7 show the plot of ion ratios and delta retention time, demonstrating that the analytical criteria within the guidelines were met.

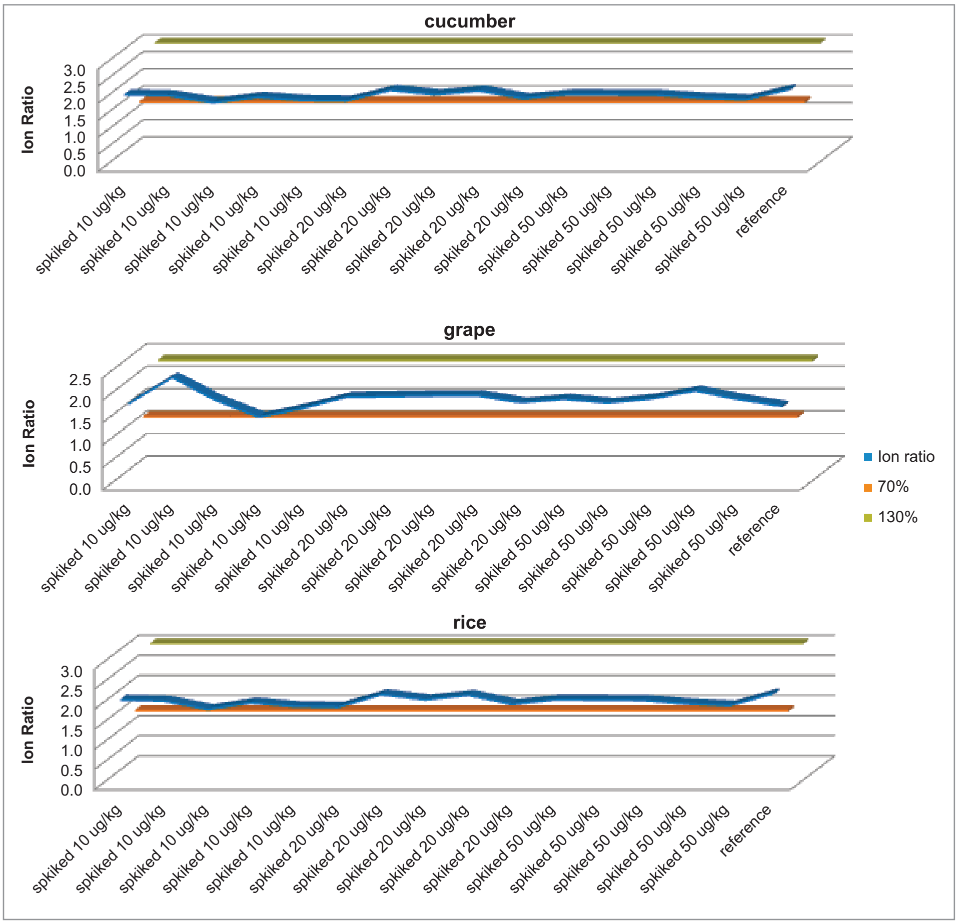

Figure 6. Plots of ion ratios for atrazine fortified in cucumber, grape, and rice showing that the ion ratios are within ±30%, per the SANTE guidelines.

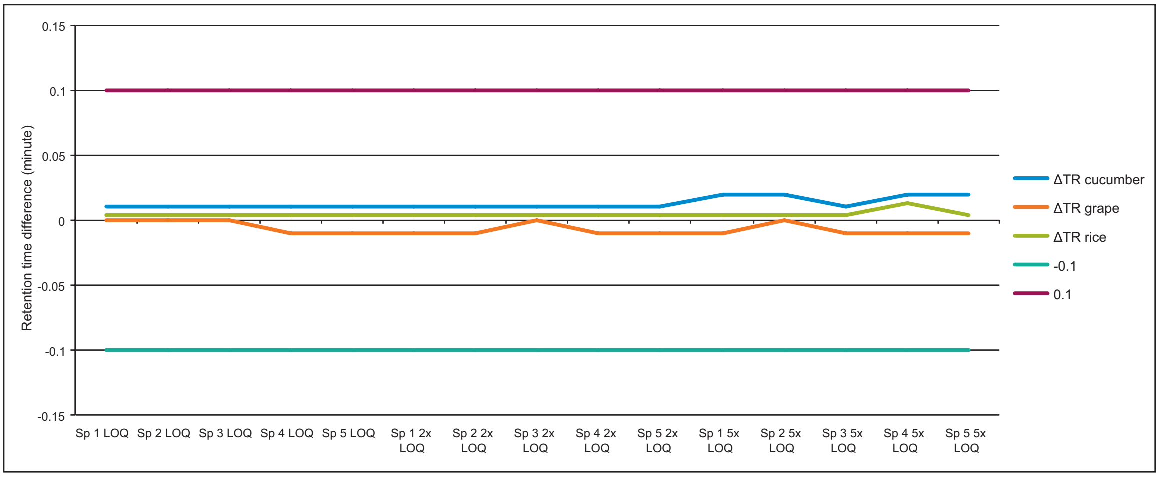

Figure 7. Plots showing retention time differences for atrazine fortified in cucumber, grape, and rice showing consistent retention times within ±0.1 min, meeting the SANTE guidelines.

CONCLUSIONS

- The Xevo TQ-GC System is supplied with a Quanpedia method containing the appropriate GC conditions, MRM transitions, associated parameters, and processing methods that will facilitate implementation of GB method 23200.113-2018 in any food safety laboratory.
- The addition of Oasis PRiME HLB Plus clean up to QuEChERS extraction, instead of dSPE, produced cleaner samples, allowing for a more robust analytical method.
- More than 95% of the pesticides showed measured recoveries within the range of 70% to 120% range and repeatability (RSD) was <20% (n=5) for all compounds in all commodities.
- The Xevo TQ-GC was able to easily meet the LOQs required by GB method 23200.113-2018, and in many cases surpassed them.

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Appendix

Table 2. The trueness (percentage recovery) and precision (%RSD) of pesticides spiked at LOQ levels.

	Cucumber 0.01 mg/kg		Grape 0.01 mg/kg		Rice 0.02 mg/kg	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Acetochlor	90.9	11.5	85.7	9.0	110.6	5.4
Aclonifen	87.1	18.5	82.4	10.7	97.5	2.7
Acrinathrin	106.8	4.8	96.9	7.3	109.7	3.8
Alachlor	102.1	5.8	84.5	7.1	116.1	5.7
Aldrin	95.3	8.3	96.3	3.8	98.3	7.1
Ametryn	103.7	5.3	72.9	9.1	91.0	3.0
Anilofos	96.1	6.0	94.7	3.8	110.7	5.2
Atratone	99.8	5.0	77.2	4.6	110.6	10.0
Atrazine	96.0	2.1	91.9	6.1	101.8	4.2
Atrazine-desethyl	92.5	9.3	87.4	11.6	102.8	6.3
Azinphos-ethyl	100.1	4.9	99.0	4.7	114.2	3.0
Beflubutamid	96.7	5.6	81.3	6.3	108.3	2.6
Benalaxyl	100.0	5.4	82.0	3.0	112.8	6.9
Benfluralin	91.6	3.2	89.8	8.4	113.1	3.3
Bifenox	103.3	13.0	98.2	6.7	101.9	8.1
Bifenthrin	89.2	3.3	84.2	11.8	106.7	2.9
Biphenyl	64.9	2.2	99.7	7.5	84.2	10.9
Boscalid	106.0	3.3	88.9	11.1	114.0	2.2
Bromacil	99.9	6.4	78.3	14.4	97.3	11.9
Bromfenvinfos	99.4	4.6	84.1	5.1	104.0	5.3
Bromophos	96.7	8.8	81.4	6.5	106.1	5.8
Bromophos-ethyl	92.9	5.5	80.8	2.9	98.9	4.4
Bromopropylate	96.7	4.9	91.6	8.6	100.4	1.6
Bupirimate	88.3	6.3	80.1	10.8	96.8	5.1
Butachlor	113.7	6.0	82.2	10.8	116.4	2.3
Butamifos	94.3	7.6	84.3	8.2	108.3	2.8
Carbofuran	110.3	7.0	99.8	6.9	114.5	7.1
Carbophenothion	85.1	6.0	77.9	12.0	94.6	5.0
Chlordane-trans	86.9	5.7	93.1	4.1	93.0	5.9
Chlorfenson	94.5	3.2	91.1	4.6	105.1	3.5
Chlorfenvinphos	98.0	5.9	79.5	7.1	105.2	5.1
Chloroneb	75.5	1.0	103.6	7.7	103.4	3.6
Chlorpropham	89.4	3.5	100.1	6.2	88.7	1.6
Chlorpyrifos	105.0	5.5	88.8	8.6	110.9	4.3
Chlorpyrifos-methyl	100.3	3.6	91.0	7.6	111.5	3.4
Chlorthiophos-1	99.3	6.4	83.7	12.4	99.7	4.7
Chlorthiophos-2	96.6	3.0	93.7	6.1	88.5	4.7
Clomazone	94.9	2.2	88.2	5.0	105.0	3.9
Coumaphos	99.2	4.1	94.9	5.5	111.8	3.6

	Cucumber 0.01 mg/kg		Grape 0.01 mg/kg		Rice 0.02 mg/kg	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Cycloate	90.2	4.4	99.2	9.8	105.6	3.7
Cyflufenamid	91.9	11.2	81.2	18.3	101.0	18.3
Cyfluthrin-1	106.0	2.7	110.3	10.1	120.0	5.6
Cyfluthrin-2	101.1	1.5	101.8	4.8	118.7	2.3
Cyfluthrin-3	92.9	2.5	94.8	7.0	117.8	4.4
Cyfluthrin-4	100.2	11.2	104.6	1.8	120.1	4.1
Cypermethrin -1	105.8	6.7	106.2	10.3	120.2	3.3
Cypermethrin -2	96.4	2.5	97.4	7.3	116.0	3.2
Cypermethrin -3	92.2	5.5	100.5	4.5	118.2	4.2
Cypermethrin -4	97.4	9.8	97.0	5.1	127.7	6.7
Cyproconazole-1	97.9	4.3	86.0	1.3	105.7	3.8
Cyproconazole-2	103.3	4.8	76.0	9.8	106.2	3.4
Cyprodinil	93.8	3.4	72.1	13.6	97.6	4.2
DEF	100.6	10.5	81.4	2.9	111.9	8.5
Deltamethrin	92.2	13.2	92.6	6.1	112.5	4.3
Desmetryn	94.9	3.2	70.6	6.9	107.3	4.5
Diazinon	94.4	3.2	89.2	5.7	114.8	6.2
Dichlofenthion	98.9	2.5	89.6	5.9	114.0	7.6
Dichlorobenzonitrile	79.9	1.6	100.8	9.2	89.9	13.6
Dichlorvos	102.9	6.4	105.4	4.3	94.6	11.0
Diclofop-methyl	96.3	4.6	85.8	6.2	105.5	3.9
Dicloran	97.8	7.5	86.3	4.4	108.3	4.5
Dicofol	95.5	2.0	84.6	6.4	104.3	3.6
Dicrotofos	103.2	2.4	75.3	9.7	112.5	6.5
Dieldrin	96.1	16.1	92.7	5.4	102.5	6.9
Difenoconazole-1	101.4	5.5	91.1	6.2	123.1	7.7
Difenoconazole-2	93.6	5.1	91.8	10.3	116.3	3.0
Diniconazole	96.6	6.8	85.3	6.6	107.7	4.8
Dioxathion	99.1	4.5	88.8	5.7	122.6	4.9
Diphenylamine	85.2	1.6	85.1	8.7	65.9	5.4
Dipropetryn	95.8	5.5	70.9	4.4	110.2	2.0
Ditalimfos	92.5	3.8	80.4	8.3	96.5	6.6
EPN	106.4	4.2	93.7	6.6	107.8	2.5
Edifenphos	99.9	1.6	82.2	7.0	108.0	4.7
Endrin	105.3	17.1	85.5	14.2	112.7	11.1
Epoxiconazole-1	101.8	5.9	88.0	6.6	111.1	1.3
Epoxiconazole-2	98.3	4.4	84.7	7.9	112.5	3.5
Ethalfluralin	99.3	5.8	96.0	7.8	115.0	8.1
Ethion	95.7	4.1	90.9	7.8	114.5	2.7
Ethofumesate	77.8	2.5	95.7	8.6	109.4	9.6
Ethoprophos	97.3	3.4	93.2	9.6	117.1	5.3
Etoxazole	90.0	9.5	91.2	8.4	109.7	7.6
Etridiazole	60.8	2.7	96.8	8.1	99.5	10.8
Etrimfos	94.3	6.4	94.4	11.6	113.9	4.0

	Cucumber 0.01 mg/kg		Grape 0.01 mg/kg		Rice 0.02 mg/kg	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Famphur	101.7	1.3	96.0	5.1	100.1	3.8
Fenamidone	92.2	1.7	88.6	2.3	105.6	2.9
Fenarimol	93.9	5.1	92.6	3.4	104.8	3.8
Fenbuconazole	100.2	2.5	97.7	4.6	110.1	2.5
Fenitrothion	102.3	6.5	92.8	5.9	103.5	8.9
Fenobucarb	111.2	2.5	99.1	6.8	126.9	7.2
Fenpropathrin	93.4	4.8	85.3	11.7	111.6	5.1
Fensulfothion	102.2	1.3	96.0	10.8	128.3	11.3
Fenthion	96.5	5.6	82.0	3.8	98.7	3.6
Fenthion sulfone	102.0	2.8	84.8	8.6	106.9	4.3
Fenthion sulfoxide	96.4	5.8	80.6	5.2	99.0	4.6
Fenvalerate-1	97.7	5.9	103.9	2.9	114.3	4.1
Fenvalerate-2	101.2	3.9	106.9	4.1	113.0	3.8
Fipronil	97.8	12.8	81.1	18.2	105.9	4.1
Fluazifop-butyl	95.6	5.0	79.8	7.9	103.9	3.4
Flucythrinate-1	100.9	3.7	101.4	3.8	113.6	2.8
Flucythrinate-2	102.9	4.7	112.5	1.3	112.9	2.9
Fludioxonil	97.8	3.6	124.8	10.3	100.0	3.2
Fluorodifen	92.5	6.9	88.5	3.0	104.9	4.0
Flutolanil	95.7	2.8	82.2	7.2	112.9	2.2
Fluvalinate-1	88.1	7.1	86.1	5.0	118.4	7.1
Fluvalinate-2	94.6	7.1	89.4	11.3	117.7	2.3
Fonofos	92.0	3.8	92.2	8.5	94.0	5.3
Formothion	95.6	4.7	87.6	15.6	64.4	3.9
Fosthiazate-1	97.6	7.7	92.3	10.8	118.5	12.4
Fosthiazate-2	102.4	9.7	87.3	3.2	120.2	2.8
Hexachlorobenzene	84.8	2.0	94.2	2.8	87.9	3.4
Hexaconazole	96.6	12.1	78.7	18.2	109.5	8.7
Hexazinone	94.4	2.2	92.3	2.3	100.9	2.5
Imazalil	110.1	9.4	78.6	8.6	102.2	6.4
Iprobenfos	106.0	2.4	98.4	9.6	121.4	5.2
Iprodione	103.2	7.9	101.0	6.4	103.2	6.5
Isazofos	99.6	1.9	93.7	11.9	116.8	4.1
Isocarbophos	101.7	3.4	82.1	4.3	106.5	4.1
Isofenphos	100.9	5.7	82.2	2.0	103.7	1.9
Isofenphos oxon	106.8	3.9	81.7	2.7	119.8	3.6
Isofenphos-methyl	103.1	5.4	90.5	5.3	108.9	3.7
Isoprocarb	116.0	2.3	94.1	6.1	112.0	4.9
Isoprothiolane	104.1	6.4	80.0	10.3	111.4	2.5
Kresoxim-methyl	92.9	2.0	90.0	8.4	111.0	3.8
Leptophos	74.4	6.5	101.1	5.9	99.7	3.0
Malaoxon	101.7	9.8	83.2	11.2	112.4	4.9
Malathion	99.9	2.8	89.7	9.0	111.0	3.6
Mefenacet	102.4	3.3	97.4	1.3	109.3	2.9

	Cucumber 0.01 mg/kg		Grape 0.01 mg/kg		Rice 0.02 mg/kg	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Mepanipyrim	97.2	4.6	81.6	1.9	92.4	5.2
Mephosfolan	97.5	3.8	75.1	4.3	110.6	4.9
Metalaxyl	107.3	5.7	80.1	11.9	101.1	7.9
Methacrifos	89.6	1.7	97.9	8.1	109.1	5.8
Methamidophos	92.8	3.2	67.2	5.0	76.9	12.7
Methidathion	97.1	1.3	78.6	7.1	106.4	3.9
Methoprene	83.6	15.7	77.8	10.4	111.8	7.2
Methoxychlor	102.7	6.0	86.2	8.0	100.6	5.4
Metolachlor	101.6	3.8	87.3	7.7	109.7	3.0
Metribuzin	86.4	8.3	75.4	7.6	94.4	4.6
Mevinphos	102.5	2.7	88.8	4.2	66.4	2.9
Molinate	73.4	2.0	95.1	5.0	94.7	5.0
Monocrotophos	106.9	4.2	77.4	10.9	118.5	8.6
Monolinuron	86.5	10.2	101.4	3.8	97.5	3.9
Myclobutanil	95.0	2.8	82.3	5.6	108.2	4.3
Napropamide	101.6	4.2	76.5	10.3	129.0	13.8
Nitrofen	98.7	4.4	91.5	5.4	100.4	2.5
Omethoate	104.5	4.9	72.7	9.3	108.3	16.5
Oxadiazon	95.9	5.5	88.1	7.5	109.4	3.0
Oxadixyl	96.6	3.3	93.1	6.0	97.6	5.9
Oxyfluorfen	99.1	13.2	87.9	7.5	95.5	8.4
Paclobutrazol	102.1	4.7	82.9	9.0	98.1	1.7
Paraoxon	103.0	7.1	87.2	7.8	50.0	14.2
Paraoxon-methyl	101.0	8.1	71.0	11.5	118.0	17.9
Parathion	92.2	1.9	81.1	8.3	108.3	4.8
Parathion-methyl	94.1	3.8	83.3	3.5	99.5	3.2
Penconazole	109.6	6.5	79.1	6.0	98.9	3.0
Pendimethalin	90.4	5.7	75.6	7.2	98.5	6.5
Pentachloroaniline	90.2	6.1	84.5	5.9	96.9	5.3
Pentachloronitrobenzene	102.8	6.6	94.6	2.3	106.0	5.5
Permethrin-1	86.5	13.1	84.8	10.7	121.1	9.1
Permethrin-2	83.7	7.4	107.9	3.4	103.2	9.0
Phorate	84.9	2.8	90.9	7.2	100.6	7.1
Phosalone	101.6	6.9	101.8	3.9	112.9	3.2
Phosfolan	97.2	4.8	81.4	4.2	105.6	4.2
Phosmet	100.2	1.8	106.3	5.4	105.0	3.2
Phosphamidon-1	100.0	9.1	90.0	14.0	99.2	11.0
Phosphamidon-2	104.8	6.3	93.3	8.2	113.7	2.3
Piperonyl butoxide	99.8	6.6	82.0	8.4	113.0	3.8
Piperophos	101.9	5.5	95.4	3.6	106.9	3.2
Pirimicarb	102.0	6.2	74.3	11.8	112.9	13.4
Pirimiphos-ethyl	97.4	3.4	74.8	6.9	107.9	6.3
Pirimiphos-methyl	106.1	5.2	77.4	3.8	101.8	3.9
Pretilachlor	103.2	1.7	80.7	14.5	112.8	1.2

	Cucumber 0.01 mg/kg		Grape 0.01 mg/kg		Rice 0.02 mg/kg	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Profenofos	94.8	8.1	87.2	6.0	115.5	2.8
Profluralin	86.5	12.3	87.3	5.5	102.8	12.0
Prometryn	94.7	5.8	78.0	9.8	104.0	4.2
Pronamide	97.4	2.5	84.2	10.7	115.8	4.9
Propanil	93.8	3.3	82.3	2.8	106.3	3.9
Propazine	99.3	3.3	98.0	10.3	110.1	5.1
Propetamphos	103.1	4.8	86.8	5.5	116.5	6.2
Propiconazole-1	101.8	3.3	82.5	6.1	114.1	3.0
Propiconazole-2	95.2	2.1	89.8	10.9	109.0	2.4
Propoxur	97.3	3.9	91.8	7.5	112.4	4.5
Prothiofos	90.7	6.7	76.4	2.7	104.6	5.8
Pyrazophos	108.0	7.1	100.1	5.6	112.4	2.8
Pyridaben	95.3	1.8	93.4	3.6	110.0	2.5
Pyridaphenthion	100.3	3.7	87.4	4.9	106.7	5.8
Pyrimethanil	117.7	5.3	82.6	5.3	109.5	2.4
Pyriproxyfen	94.5	3.0	88.6	11.9	105.8	4.5
Quinalphos	97.1	4.7	78.3	4.9	110.9	3.3
Quinoxyfen	84.9	5.7	71.1	9.2	92.1	3.9
Ronnel	90.0	1.5	82.5	6.2	107.3	6.6
Simazine	100.1	7.8	94.2	6.1	112.6	7.7
Sulfotep	97.8	2.8	100.1	8.8	111.0	6.0
Tebuconazole	97.9	11.1	91.4	9.4	110.1	4.0
Tebufenpyrad	94.0	6.2	91.6	5.2	98.0	4.6
Tebupirimfos	93.4	6.9	97.6	8.1	110.4	8.1
Tecnazene	80.6	1.2	100.0	3.0	95.0	4.4
Terbufos	91.2	3.4	95.3	4.1	109.6	6.5
Terbufos sulfone	99.2	4.4	84.4	6.7	110.9	1.8
Terbuthylazine	103.2	5.0	87.5	4.0	109.3	6.0
Terbutryn	97.2	6.7	76.7	4.2	96.6	8.2
Tetrachlorvinphose	103.2	2.4	81.3	6.1	106.4	3.5
Tetraconazole	99.8	6.8	80.7	8.2	109.8	1.8
Tetradifon	89.9	13.7	104.7	5.5	102.3	7.0
Tetramethrin-1	97.1	6.4	92.5	11.5	103.8	10.9
Tetramethrin-2	94.6	4.4	86.3	10.2	113.3	1.2
Thionazin	96.5	2.9	95.0	6.6	112.1	4.9
Tolclofos-methyl	99.2	2.9	88.3	6.6	111.6	2.1
Triadimefon	103.1	8.6	82.5	5.5	108.0	2.8
Triadimenol	98.5	8.6	80.0	3.5	110.9	2.2
Triallate	90.9	4.4	89.8	4.4	99.2	4.1
Triazophos	104.3	11.4	93.1	6.9	113.9	3.5
Trichloronat	93.6	6.0	80.8	8.0	102.8	5.7
Trifloxystrobin	96.7	2.2	78.4	11.6	109.3	4.6
Vinclozolin	96.9	5.7	91.1	6.3	112.0	5.6
alpha-BHC	90.6	1.3	97.9	5.2	107.7	4.7

	Cucumber 0.01 mg/kg		Grape 0.01 mg/kg		Rice 0.02 mg/kg	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
alpha-Endosulfan	92.1	13.0	99.0	9.3	101.0	6.4
beta-BHC	100.5	5.2	99.3	5.9	102.9	5.3
beta-Endosulfan	92.5	13.7	95.4	12.1	95.4	9.1
delta-BHC	98.1	1.5	98.6	4.9	102.8	5.4
gamma-BHC	89.9	4.3	102.2	5.0	102.8	4.3
lambda-Cyhalothrin-1	103.0	5.6	81.6	8.8	123.8	3.3
lambda-Cyhalothrin-2	98.9	2.8	100.5	2.9	113.1	4.0
o,p'-DDD	86.8	3.7	89.6	1.4	93.8	3.6
o,p'-DDE	79.1	1.0	91.4	1.6	89.1	2.3
o,p'-DDT	77.3	2.4	81.7	4.2	86.9	1.6
p,p'-DDD	90.0	1.7	83.2	3.2	91.0	2.5
p,p'-DDE	67.7	4.3	88.2	4.0	95.6	2.4
p,p'-DDT	77.9	5.7	78.5	6.7	85.2	2.5