

Increased Mass Resolution to Reduce Matrix Interference with the LC-MS/MS Analysis of Pesticides in Food Residues

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Overview

Purpose: To demonstrate the use of increased mass resolution by using Highly-Selective Reaction Monitoring (H-SRM) to reducing the matrix effects of the analysis of food residues

Methods: A triple quadrupole mass spectrometer with an Electro spray Ionization source (ESI), two LC quaternary pumps, an auto sampler, and a LC column.

Results: By using the H-SRM scan function utilizing increased mass resolution a lower detection limit was achieved in matrix samples.

Introduction

With the recent trend of increased concern about food safety, the number of regulated pesticide residues in food has increased rapidly. Consequently, an accurate high throughput multi-pesticide screening method which can quantitate high number of pesticide residues during a single analysis is required. LC-MS/MS is fast becoming the technique of choice for the identification and quantitation of pesticide residues. This is due, in part, to the ease of sample preparation and chromatographic conditions that LC-MS/MS allows, when compared to other techniques such as GC or HPLC with UV absorbance, nitrogen phosphorus detection, or electron capture detection. However, it can be extremely challenging to quantitate multi-pesticide residues in food because of interference from complex sample matrices. Although matrix-related interferences can be decreased by various sample clean up procedures, the analytical instrument used for the quantitation also has to be highly selective and sensitive. The unique Highly-Selective Reaction Monitoring (H-SRM) detection method available with the Thermo Scientific TSQ Quantum Discovery has proven to be very useful for this purpose. The analytical results of 35 pesticide residues in food with the H-SRM detection method are reported in this poster.

FIGURE 3. Comparison of SRM to H-SRM on phoxim 0.05 and 0.5 ppb in Matrix

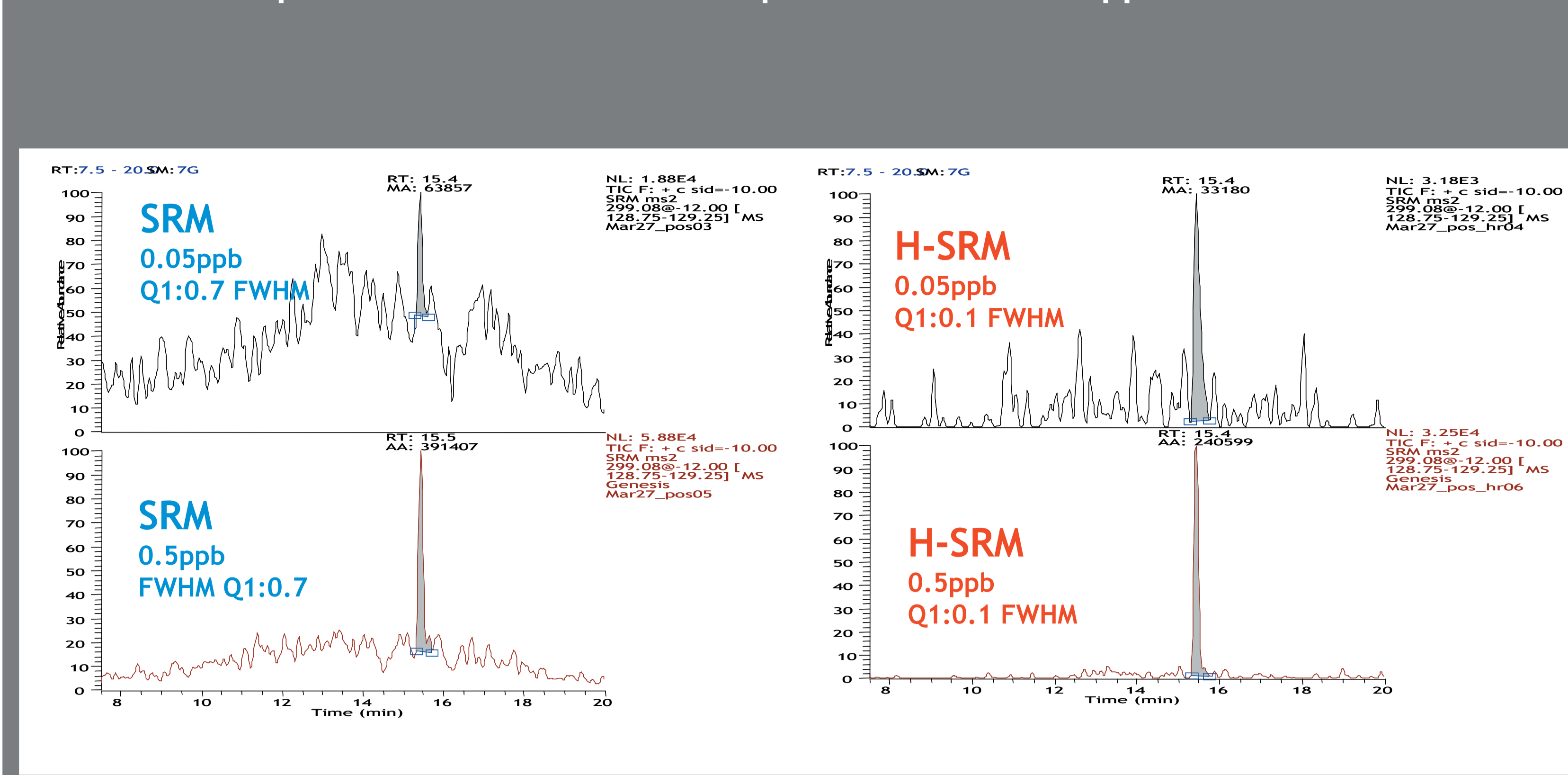
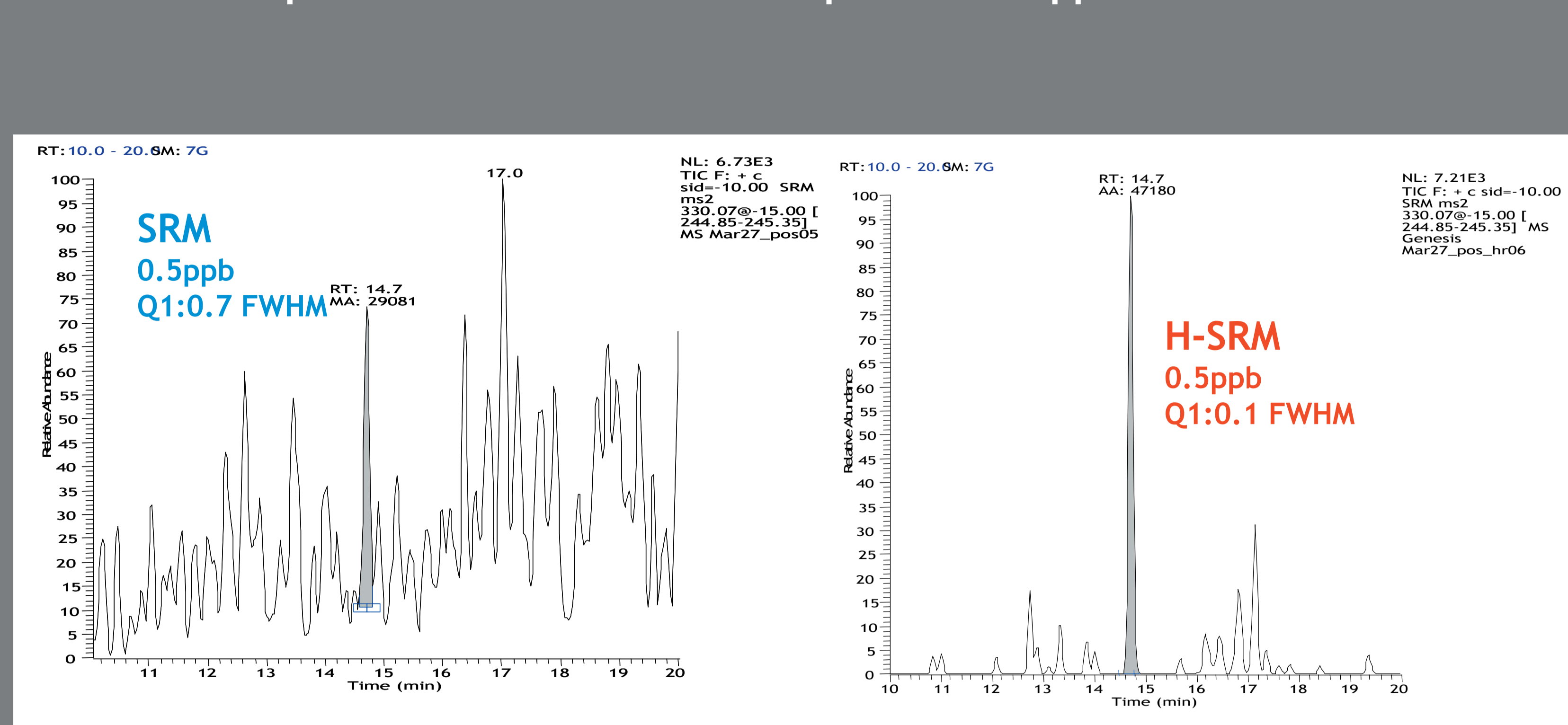


FIGURE 4. Comparison of SRM to H-SRM on Iprodione 0.5ppb in Matrix



Results

In the figures 3 and 4 a comparison between SRM and H-SRM is shown (at different concentration levels) to demonstrate the difference in ability to detect.

In the comparison of Phoxim in SRM substantial noise is present in the chromatogram with the H-SRM the noise is almost not present and the slightly lower signal is better because of the significant reduction of noise and thus with phoxim a lower concentration can easily be detected and integrated.

FIGURE 5. Results of the standard curve for Phoxim from 0.05 to 100ppb

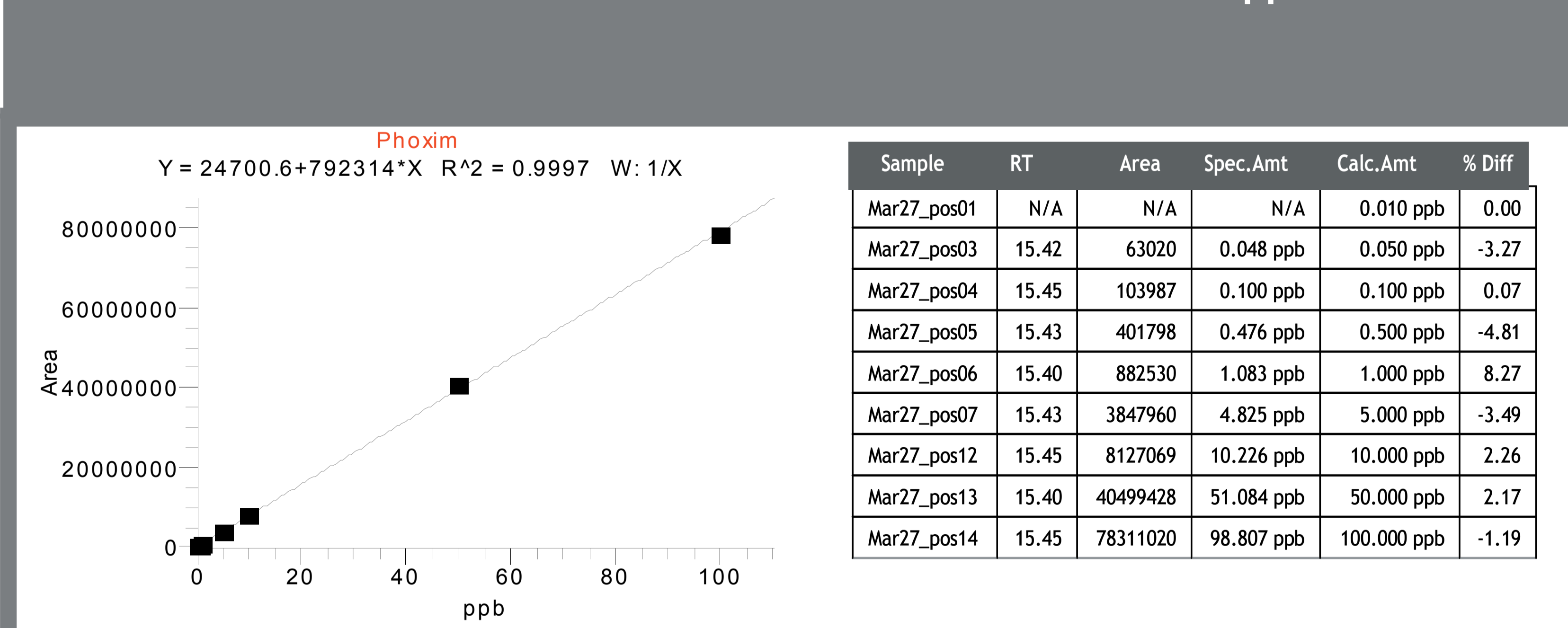


FIGURE 6. Calibration range and linearity

Compound Name	S/N		Calibration		Compound Name	S/N		Calibration	
	Value	Conc. (ppb)	R ²	Range (ppb)		Value	Conc. (ppb)	R ²	Range (ppb)
Oxamyl	N/A	0.01	1.0000	0.01-100	Methiocarb	3	0.01	0.9997	0.01-100
Imidacloprid	3	0.05	0.9994	0.05-100	Daimuron	5	0.01	0.9992	0.01-100
Acetamiprid	11	0.05	0.9987	0.05-100	Cumyluron	4	0.01	0.9993	0.01-100
Aldicarb	N/A	0.05	0.9993	0.05-100	Tebufenozide	8	0.05	0.9995	0.05-100
Propoxur	3	0.01	0.9997	0.01-100	Iprodion	2	0.5	0.9979	0.5-100
Carbofuran	8	0.05	0.9996	0.05-100	Diflubenzuron	3	0.01	0.9997	0.01-100
Bendiocarb	6	0.01	0.9992	0.01-100	Etobenzamid	3	0.05	0.9997	0.05-100
Carbaryl	2	0.01	0.9999	0.01-100	Cyprodinil	3	0.1	0.9998	0.1-100
Ethiofencarb	3	0.01	0.9996	0.01-100	Phoxim	2	0.05	0.9997	0.05-100
Pirimicarb	6	0.01	0.9995	0.01-100	Bitertanol	3	0.05	0.9996	0.05-100
Methabenzthiazuron	2	0.01	0.9989	0.01-100	Piperonyl butoxide	6	0.01	0.9996	0.01-100
MIPC	4	0.01	0.9987	0.01-100	Hexythiazox	6	0.01	0.9999	0.01-100
Diuron	3	0.05	0.9987	0.05-100	Flufenoxuron	4	0.01	0.9997	0.01-100
Azoxystrobin	11	0.01	0.9989	0.01-100	Fenpyroximate	10	0.01	0.9999	0.01-100
BPMC	6	0.05	0.9999	0.05-100	Chlorfluazuron	N/A	0.01	0.9987	0.01-100
Siduron	5	0.05	0.9989	0.05-100	Teflubenzuron	N/A	0.01	0.9986	0.01-100
Linuron	3	0.05	0.9989	0.05-100	Hexaflumuron	2	0.01	0.9973	0.01-100
					Lufenuron	N/A	0.01	0.9998	0.01-100

Conclusions

Despite that LC-MS/MS with SRM scan function is selective, still matrix effect can be observed with challenging matrices used in food and residue analysis. The H-SRM method described can substantially reduce the interferences and leading to improved LOQ's by reducing the peak with at Full Width Height Medium (FWHM) is from 0.7 Da (equivalent to unit resolution) to 0.1 Da enabling selectivity particularly at the low mass range typical for many residue compounds.

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FIGURE 1. List of compounds and MS parameters

Compound Name	Polarity	Precursor Ion (m/z)	Product Ion (m/z)	Collision Energy (V)	Compound Name	Polarity	Precursor Ion (m/z)	Product Ion (m/z)	Collision Energy (V)
Oxamyl		237.17	72.0	15	Methiocarb		226.14	169.1	10
Imidacloprid		256.12	209.1	16	Daimuron		269.21	151.1	14
Acetamiprid		223.12	126.0	23	Cumyluron		303.14	185.0	14
Aldicarb		208.17	116.0	8	Tebufenozide		353.24	133.0	19
Propoxur		210.16	111.0	14	Iprodion		330.07	245.1	15
Carbofuran		222.16	165.1	14	Diflubenzuron		311.04	158.0	14
Bendiocarb		224.14	167.0	10	Etobenzamid		340.08	121.0	36
Carbaryl		202.15	145.0	10	Cyprodinil	Positive	226.18	93.0	38
Ethiofencarb	Positive	226.13	107.0	14	Phoxim		299.08	129.0	12
Pirimicarb		239.22	182.1	16	Bitertanol		338.21	269.2	10
Methabenzthiazuron		222.12	165.0	17	Hexythiazox		353.13	228.0	16
MIPC		194.17	95.0	20	Piperonyl butoxide		356.26	177.1	13
Diuron		233.06	72.1	19	Flufenoxuron		489.09	158.0	20
Azoxystrobin		404.17	372.1	15	Fenpyroximate		422.26	366.1	15
BPMC		208.19	152.0	10	Chlorfluazuron		540.03	389.0	20
Siduron		233.20	137.0	17	Teflubenzuron		379.00	339.0	12
Linuron		249.09	182.0	18	Hexaflumuron	Negative	459.02	439.0	12
					Lufenuron		509.00	326.0	18

Methods

Samples:

The samples (onion) for this method were extracted and cleaned up according to protocol: Analytical Methods for Residual Compositional Substances of Agricultural Chemicals, Feed Additives, and Veterinary Drugs in Food using several techniques depending on the matrix.

Liquid Chromatography:

HPLC : Surveyor w/MS Pump (Thermo Scientific)

Column : HyPURITY™ 150 x 2.1mm,5u (Hypersil)

Mobile Phase (A) : Water (B) : Methanol (C) : 10mM NH4OAc ac.

Gradient	No.	Time (min)	A(%)	B(%)	C(%)
	1	0.00	79	20	1
	2	15.00	0	99	1
	3	18.00	0	99	1
	4	18.10	79	20	1
	5	23.00	79	20	1

Flow : 200 µl/min

Mass Spectrometry Conditions:

Ionization (ESI): Positive

Needle Voltage: 5000 V

Ion Transfer Tube Temp: 380C

Sheath Gas: 40 Arb. Units

Auxiliary Gas: 40 Arb. Units

Collision Gas (Ar): 1.0 mtorr

Scan Type SRM or H-SRM

Peak Resolution SRM(H-SRM) 0.7 Da (0.1 Da)

Negative

4250 V

350 C

50 Arb.Units

5 Arb.Units

1.0 mtorr

SRM or H-SRM

0.7 Da (0.1 Da)

FIGURE 2. Chromatogram of all compounds

