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APPLICATION NOTE 665

Pesticide residues screening analysis in tea and honey using a Q Exactive Focus High-Resolution Mass Spectrometer

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Keywords

Q Exactive Focus, Vanquish Flex, QuEChERS, pesticide residues, vDIA

Goal

To develop and test a multi-residue instrumental method that can be applied for high-throughput screening and semi-quantitation of pesticide residues in food matrices at or below the current legislative requirements. A high-resolution, accurate-mass mass spectrometer operated in Full Scan – Variable Data-Independent Analysis (FS-vDIA)* mode providing an option for full spectrum filtering, retrospective analysis, and multi-parameter-based compound identification was applied. The method was validated for 328 target pesticides, with an option for the future extension to a larger number of analytes.

Introduction

European Commission directive EC 396/2005 sets maximum residue levels for pesticides in different products of plant and animal origin. The regulation presents significant analytical challenges with respect to the low limits of quantification and high number of target analytes. Nowadays, many GC- and LC-based methods are in routine use employing mostly low-resolution triple quadrupole mass spectrometric detection.

*vDIA method is not available in the United States of America.

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In recent years, Thermo Scientific™ Orbitrap™ mass analyzers (R > 50,000 FWHM) have become available, providing higher confidence in compound identification and confirmation along with good quantitative capabilities compared to triple quadrupole MS/MS. Mass accuracy (typically below 5 ppm) minimizes interferences from co-eluting analytes and matrix co-extractives, and thus reduces the potential for false positive and negative results.

This work describes the method performance parameters using the latest benchtop LC-Orbitrap instrument, the Thermo Scientific™ Q Exactive™ Focus Hybrid Quadrupole-Orbitrap mass spectrometer, applied for screening hundreds of target analytes at or below legislative levels (maximum residue levels – MRLs) in two difficult matrices: honey and tea.

Experimental

Reagents

	Fisher Chemical™ P/N
• Acetonitrile, LC-MS grade	A/0638/17
• Ammonium formate, for HPLC	A/5080/53
• Methanol, Optima™ LC-MS grade	A456-212
• Formic acid, extra pure for HPLC	F/1850/PB08
• Water, LC-MS grade	W/0112/17

Standards

Pesticides

- All standards were purchased from Sigma-Aldrich®. See result tables for the identity of the 328 compounds investigated.

Standards and reagent preparation

Certified reference compound mixes were obtained from Lab® Instruments Srl, Italy. Pesticides of interest not included were prepared from standard reference materials. Individual stock standard solutions (10 mg/mL) were prepared gravimetrically and were used for preparation of intermediate stock solutions.

Pesticide working stock solutions were prepared from intermediate stock standard solutions by appropriate dilution with methanol.

Apparatus

- Fisher precision balance, P/N XP-1500FR
- Sartorius™ ME235S analytical balance, P/N 1056-4833
- Thermo Scientific™ Barnstead™ Easypure™ II water, P/N 1010682
- Ultrasonic bath, Elmasonic® S40H, P/N 1002006
- ULTRA-TURRAX® G25 homogenization tool, P/N 1713300
- IKA® 501 horizontal shaker, P/N 053-6011
- BrandTech® accu-jet® pipettor, P/N 3140246
- Thermo Scientific™ Heraeus™ Multifuge™ X3R centrifuge, P/N 10667815
- Thermo Scientific™ Vanquish™ Flex UHPLC system
  - Vanquish Flex Base System, P/N VF-S01-A
  - Quaternary Pump F, P/N VF_P20-A
  - Split Sampler FT, P/N VF-A10-A
  - Column Compartment H, P/N VH-C10-A
  - 150 µL static mixer, 150 MPa, P/N 6044.5110
  - MS Connection Kit, P/N 6720.0405
- Q Exactive Focus mass spectrometer

Consumables

- LC vials, P/N 24014019
- Pipette, Thermo Scientific™ Finnpipette™ 100-1000 µL, P/N 3214535
- Pipette, Thermo Scientific Finnpipette 10-100 µL, P/N 3166472
- Pipette, Thermo Scientific Finnpipette 500-5000 µL, P/N 3166473
- Pipette holder, P/N 3651211
- Pipette tips 0.5–250 µL, 500/box, P/N 3270399
- Pipette tips 1–5 mL, 75/box, P/N 3270420
- Pipette tips 100–1000 µL, 200/box, P/N 3270410
- Spatula, 18/10 steel, P/N 3458179
- Spatula, nylon, P/N 3047217
- Tube holder, P/N 3204844

- Wash bottle, PTFE, P/N 3149330
- 2 mL vial rack, P/N 12211001
- 0.2 µm PTFA syringe filter, P/N F2513-4
- 1 mL disposable plastic syringe, P/N S7510-1
- Thermo Scientific™ Accucore™ aQ 100 × 2.1, 2.6 µm column, P/N 17326-102130
- QuEChERS extraction tube, 50 mL, 250 pack, P/N 60105-216
- QuEChERS cleanup (PSA, C18) tubes, 50 pack, P/N 60105-344

Glassware

- Volumetric flask, 10 mL, P/N FB50143
- Volumetric flask, 25 mL, P/N FB50147
- 1 mL glass pipette, P/N FB50211
- 1 L bottle, P/N 9653650
- 500 mL bottle, P/N 9653640

Sample preparation

Honey samples

Honey samples were taken directly from the jar obtained from local stores in Germany.

Tea samples

Black tea samples were collected from filtered tea bags obtained from local stores in Germany.

Sample extraction

The honey and tea extractions followed the same procedure. Ten grams of sample were weighed into 50 mL plastic centrifuge tubes and 10 mL water were added. After a short period of vortexing, the mixture was left untouched for 20 minutes and 10 mL acetonitrile (ACN) were added. The mixture was shaken on a horizontal shaker for 10 minutes, followed by the addition of salts from pre-prepared QuEChERs extraction tubes. This was shaken for an additional 5 minutes and centrifuged at 5000 rpm for 5 minutes. Approximately 8 mL of supernatant were transferred into prepared QuEChERS cleanup tubes. The mixture was shaken again for 5 minutes and centrifuged at 5000 rpm for 5 minutes. The recovered supernatant was passed through a 0.2 µm syringe filter and transferred into LC vials for spiking or direct injection into the UHPLC-HRMS system.

Instrumental analysis

Sample measurements were carried out on a Vanquish Flex Quaternary UHPLC system coupled to a Q Exactive Focus mass spectrometer.

LC parameters	
Mobile phases:	A: Water/methanol (98:2 v/v%) + 5 mM ammonium formate + 0.1 v/v% formic acid B: Methanol/water (98:2 v/v%) + 5 mM ammonium formate + 0.1 v/v% formic acid
Analytical column:	Accucore aQ, 100 × 2.1 mm, 2.6 µm
Injection volume:	1 µL
Column temperature:	25 °C
Flow rate:	300 µL/min
Total run time:	15 min
Gradient run program:	Table 1

Table 1. UHPLC gradient run program.

Time [min]	Flow rate [mL/min]	A%	B%	Curve
0.0	300	100	0	5
0.5	300	100	0	5
7.0	300	30	70	5
9.0	300	0	100	5
12.0	300	0	100	5
12.1	300	100	0	5
15.0	300	100	0	5

HRAM-MS parameters	
Scan type:	Full Scan–Variable Data-Independent Analysis (FS-vDIA)
Ionization:	HESI II
Microscans:	1
Capillary temperature:	270 °C
Vaporizer temperature:	290 °C
Sheath gas pressure:	40 arb
Aux gas pressure:	10 arb
Ion sweep pressure:	0 arb
Spray voltage:	3500 V
Polarity:	Positive and negative (separate runs for polarities)
Full Scan range:	120–1000 *m/z*
Full Scan resolution:	70,000
Full Scan AGC target:	1e6
Full Scan maximum injection time:	Auto
Full Scan spectrum data by:	Profile
vDIA resolution:	17,500
vDIA segments:	8 symmetric (90 *m/z* increments) segments in range 50–780 *m/z*
Collision energy:	Stepped 30, 50, and 70 eV
vDIA AGC target:	5e5
vDIA maximum injection time:	Auto
vDIA Spectrum data by:	Centroid

Data analysis

Fully automated data evaluation was carried out using Thermo Scientific™ TraceFinder™ 4.1 software.

Results and discussion

Simplified in-house validation for screening and semi-quantitative methods were carried out on both matrices and target pesticides. European pesticide guidelines[1,2] served as general reference for evaluation; however, establishment of some parameters was simplified as the method was meant to be a proof of concept. The goal was also to demonstrate method performance characteristics against the relevant legislation for pesticide residues maximum residue limits.[2]

Method selectivity was evaluated by comparison of blank and spiked samples (n=5). The evaluation was based on accurate mass of the analyte at the specified retention time window (±0.1 min). Full-scan-based isotopic pattern (IP) match, presence of fragment ions (FI), and high-resolution library match (LS) were additionally applied for identification according to References 1 and 3. Acceptance values were set as less than 5 ppm for mass accuracy, ± 0.1 min for retention time, greater than 75% for IP, at least one fragment ion present for FI, and greater than 50% for LS matching; however, only mass accuracy and retention time for parent ion and presence of FI were taken as identification criteria according to Reference 1. The relevant ion ratio limits were set to less than 30%.

The percentages of both false negative results and positive defects were established for each matrix. False negative results were established (using automated data evaluation) for all compounds by repeated injection (n=10) of the quality control matrix-matched standard at 10 ng/mL (proof of concept). The acceptance criterion of less than 5% false negatives was achieved for all reported compounds detectable at the given concentration level. Related to the total number of detectable compounds, 0.3% false negative detects in solvent and 2% false negative detects in both matrices were found as no accurate parent masses at the corresponding retention time were found. In solvent 9%, in honey 11%, and in tea 12% accurate mass parent peaks at the correct retention times were present; however, no fragment ions for identification were detected. False positive values in all cases were less than 3% (related to the total number of detectable compounds) providing fit for purpose values according to the guideline recommendations for screening methods (Figure 1).

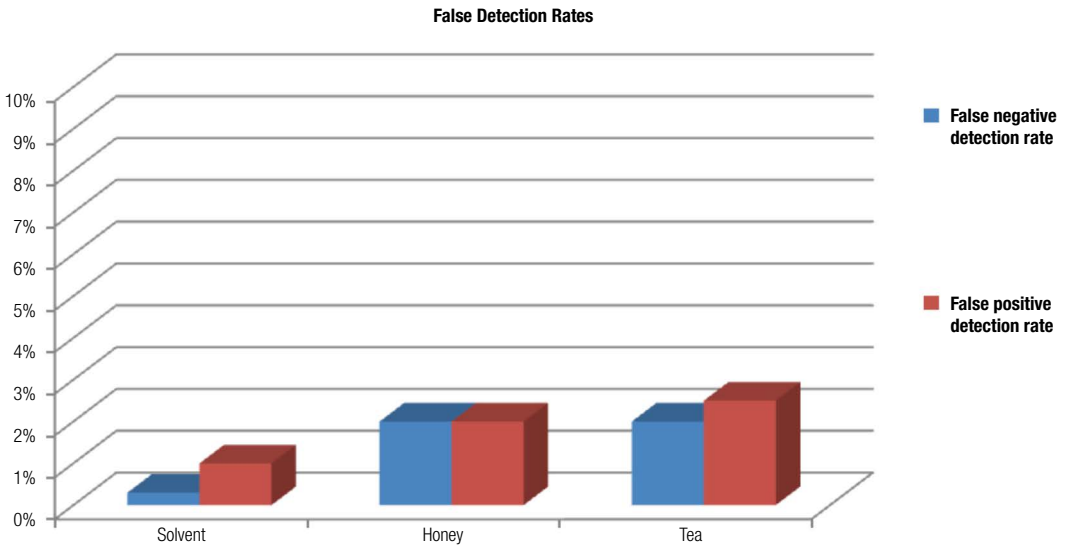

Figure 1. Screening method selectivity: % of false negative and positive detects related to the total number of detectable compounds in both solvent and matrix matched standards at 10 ng/g.

The linearity of the calibration curves was assessed over the range from 0 to 100 ng/mL to demonstrate the potential of the method for quantitative analysis. The calibration curves were created by spiking matrix extract at five levels (matrix matched) and injected in duplicate. Linearity was proven by the Mandel's test method. In all cases, the correlation coefficients of linear functions were better than 0.985. The relevant residual plot values showed less than 20% for most of the compounds. The established values are shown in Table 3.

Since sample extracts were used for spiking, Instrument Detection Limits (IDL) were calculated according to the EPA definition as:

$$IDL = t_{(n-1,\ 0.95)} \times SD$$

Where

t: Student factor for n-1 degree of freedom and 95% confidence interval

SD: standard deviation of standard solutions at ~5–10 S/N level

n=10

The method was expected to meet MRL values at equivalent or lower values than the IDL levels. The lowest of these MRL values was 10 ng/g, and this was achieved in most cases. For compounds IDL > 10 ng/g, the relevant MRL values were compared with the current MRL values. Table 2 gives an overview of the results indicating some compounds that do not meet this criteria. In total, 315 compounds in standard solution, 297 in tea matrix, and 305 compounds in honey matrix could be measured and quantified at or lower than 10 ng/g. Established IDL values are summarized in Figures 2a and 2b and Table 3.

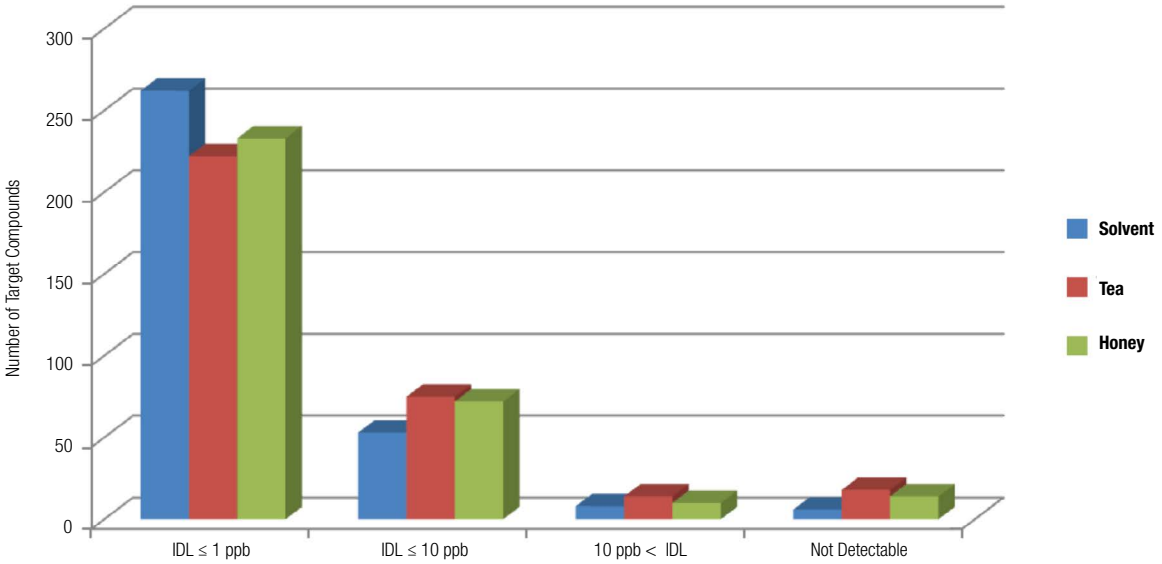

Figure 2a. Overview of IDL values for 328 compounds in solvent, tea, and honey matrices. The majority of the compounds can be quantified at or lower than the legislative requirement (10 ng/g).

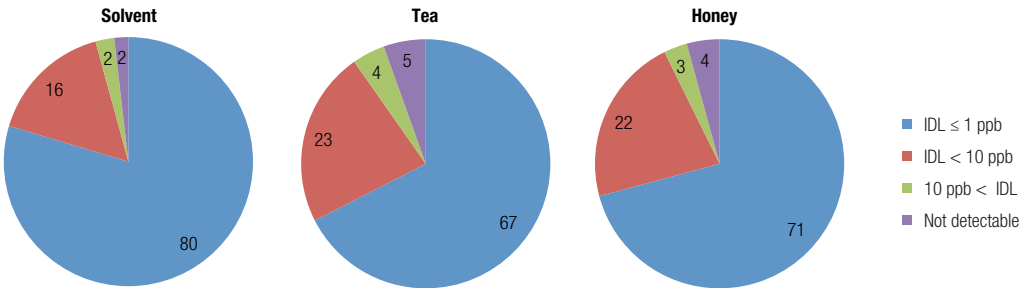

Figure 2b. Relative percentages of different IDL values [ng/g] for the target compounds (328) in solvent, tea, and honey matrices. More than 85% of target compounds can be detected at ≤10 ng/g, and ~70% of target compounds can be detected at ≤1 ng/g.

Table 2. Compounds with IDL > 10 ng/g compared to the maximum residue limits (MRL).[2]

	IDL in Tea [ng/g]	MRL for Tea [ng/g]	IDL in Honey [ng/g]	MRL for Honey [ng/g]
Allethrin	30	10*	30	nd
Aramite	100	nd	100	100
Bentazone	50	100*	0.5	50*
Butafenacil	40	nd	60	nd
Carbaryl	40	50	35	50
Dimefuron	30	nd	25	nd
Dimethachlor	40	20	40	nd
Fenthion-sulfone	50	50**	5	10*
Hexaflumuron	30	nd	3	nd
Isoxathion	50	nd	50	nd
Mesotrione	>100	100	>100	nd
Pyridate	15	50	20	50
Sethoxydim	40	100	50	50
Thiazopyr	50	nd	10	nd

nd – MRL not defined by EC 396/2005, default MRL set to 10 ng/g[2]

* MRL defined for sum of parent and conjugates

** Fenthion and its oxygen analogue, their sulfoxides, and sulfone expressed as parent

For compounds with higher IDL values or poor qualitative identification data (e.g. absence of fragment ion), more selective and sensitive scan events are also available. Parallel Reaction Monitoring (PRM) can provide better sensitivity and qualitative/quantitative results as demonstrated in Figure 3. However, the PRM method is more limited in the total number of target compounds that can be analyzed simultaneously, but it can be applied complementarily to the presented vDIA-based method.

Intermediate method precision values were determined for each matrix at 10 ng/g in 6 replicates and expressed as %RSD over three days with spiked extract samples. Intermediate precision values were within 25% for the vast majority (266) of target compounds. An overview of intermediate precision values for tea matrix and compounds exceeding 25% and undetectable (due to higher detection limits) are summarized in Figure 4.

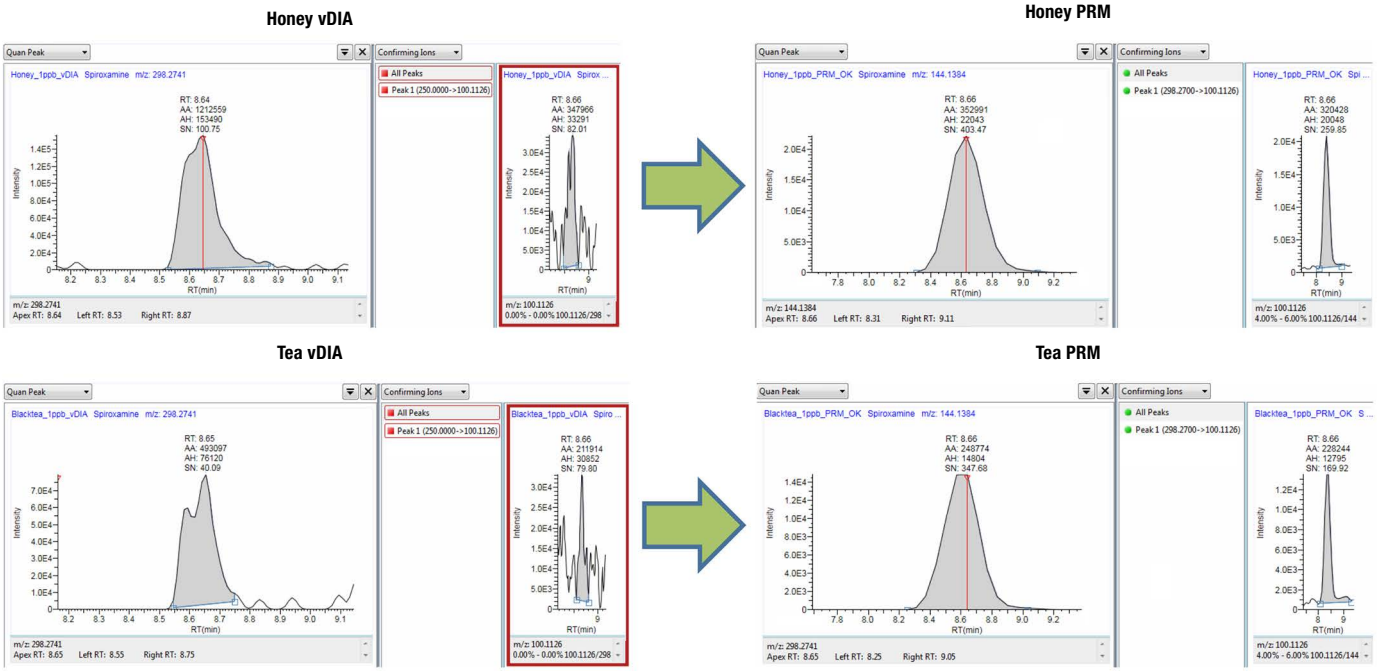

Figure 3. Sensitivity and qualitative information improvement for spiroxamine by application of complementary PRM scan events. Fragment information and parent peak improved substantially in both matrices at 1 ng/g.

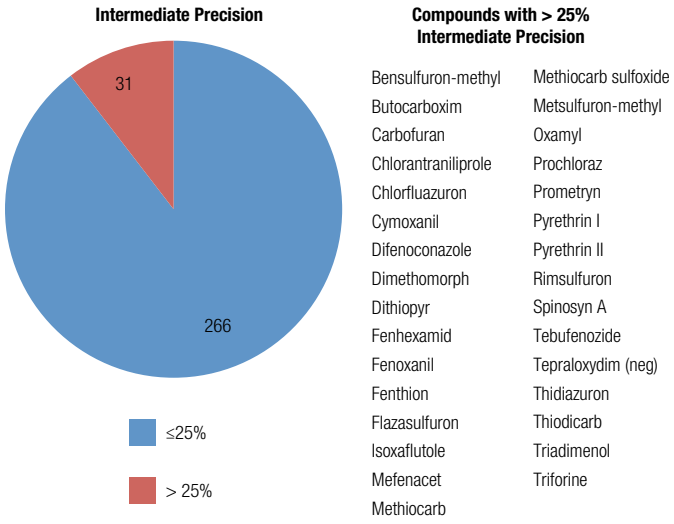

Figure 4. Intermediate precision values for all target compounds detectable at 10 ng/g in tea.

A robustness study of the chromatographic separation was performed by varying the mobile phase composition and temperature. Results were compared to the original method and significant differences were evaluated based on ANOVA analysis. Precise preparation of the mobile phase composition is critical, since even minor changes in organic additive concentration or pH value can cause variation in retention times.

Figure 5 documents the examples of chromatographic data evaluation using TraceFinder software, showing quantitative and identification details (fragment ions overlay, spectral comparison). Figure 6 shows detectability of randomly selected components at the 5 ng/g spiking level.

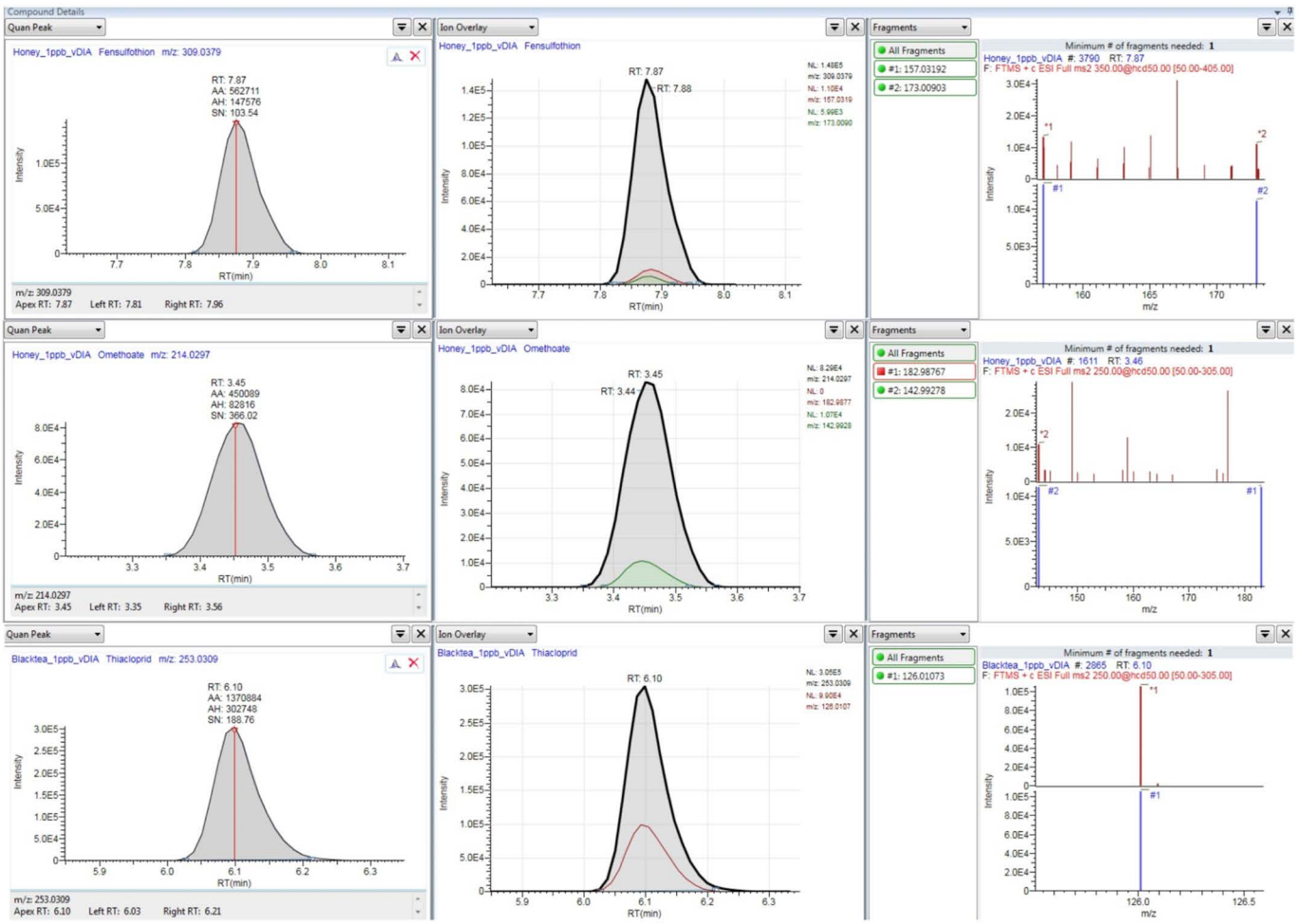

Figure 5. Example chromatograms (random selection) with parent peak and confirmation ion identification in both honey (upper traces) and tea (lower trace) matrices at 1 ng/g. Left pane: quantitative peak, middle pane: confirmation ion overlapped with parent ion, right pane: presence of fragment ion compared to reference spectrum peak. Compounds from above: fensulfothion, omethoate, and thiacloprid.

Figure 6. Randomly chosen parent ion peaks in tea matrix at 5 ng/g concentration level. Compounds from top left to right bottom: Acephate, acetamiprid, chloroxuron, clofentezin, aminocarb, azaconazole, isocarbophos, diethofencarb, trietazin, azinphos-me, ethiofencarb, bromacyl, carbendazim, carbofuran, chlorantraniliprole, mepronil, etoxazole, chloridazon, dimetamethrin, cyflufenamide, flutriafol, triazophos, fenthion-sulfoxide, diflubenzuron, trifloxystrobin, flazasulfuron, tralkoxydim, benfuracarb, propazine, ethofumesate, dithiopyr, desmethyl-primicarb, desmethryn, flumetsulam, bensulfuron-me, prosulfocarb, tebufenozide, carfentrazone-et, esprocarb, hexazinone, neburon, diuron, piperonyl-butoxide, sulfotep, triticonazole, buprofezin, cyazofamide, bitertanol, benzoximate, hexaflumuron, forchlorfenuron, cyromazine, metholcarb, methomyl, metobromuron, metosulam, metoxuron, metribuzin, metazachlor, and piperophos. Compounds marked with red refer to asymmetry factor > 1.5 for carbendazim and missing fragment ion ratio for metholcarb at concentration level close to IDL.

Table 3A. Overview of target compounds and their detection parameters, established IDL values, and linearity data. Residual plot values were not defined where MDL > 10 ng/g due to insufficient number of points to evaluate (nd: no data recorded).

Compound Name	Retention Time [min]	Precursor *m/z*	Confirmation *m/z*	Ion Ratio [%]	Confirmation *m/z*^{2}	Ion Ratio [%]	Peak Polarity	Adduct	IDL [ng/g] in Solvent	IDL [ng/g] in Tea	IDL [ng/g] in Honey	Residual Plot RSD%
24D	10.0	218.9621	160.9566	5	124.9800	10	Neg	M-H	0.5	2	2	12
Acephate	0.7	184.0192	113.0025	2	142.9928	45	Pos	M+H	0.8	0.8	0.8	8.5
Acetamiprid	6.8	223.0745	126.0107	24	56.0505	15	Pos	M+H	0.5	0.6	0.6	9.3
Acibenzolar-S-methyl	10.6	210.9996	167.9700	20	91.0543	75	Pos	M+H	0.5	0.6	0.6	6.2
Aclonifen	9.1	265.0374	248.0347	nd	194.0475	nd	Pos	M+H	nd	nd	nd	nd
Alachlor	10.6	270.1255	162.1278	30	238.0995	450	Pos	M+H	1	5	5	33
Alanycarb	9.0	400.1359	138.0371	46	238.0890	6	Pos	M+H	0.4	1	1	25
Aldicarb	7.3	208.1114	89.0425	5	116.0533	15	Pos	$M+NH_4$	6	7	7	6.1
Aldicarb sulfone	0.9	240.1013	86.0601	11	148.0427	35	Pos	$M+NH_4$	0.5	0.6	0.6	18
Aldicarb sulfoxide	0.8	207.0798	89.0426	5	132.9458	30	Pos	M+H	0.5	0.6	0.6	13
Allethrin	9.9	303.1950	123.1168	8	135.0805	60	Pos	M+H	20	30	30	nd
Ametryn	9.5	228.1277	186.0809	4	96.0562	2	Pos	M+H	0.3	0.8	0.8	11.5
Aminocarb	0.8	209.1285	152.1073	27	137.0838	18	Pos	M+H	0.4	0.8	0.8	13.8
Ancymidol	6.8	257.1287	185.0964	10	81.0448	50	Pos	M+H	0.8	3	3	24
Anilofos	9.0	368.0305	170.9699	11	142.9928	6	Pos	M+H	0.4	0.9	0.9	20
Aramite	6.4	335.1078					Pos	M+H	100	100	100	nd
Atrazine	9.3	216.1011	174.0541	2	132.0300	1	Pos	M+H	6	6	6	nd
Azaconazole	9.8	300.0302	230.9975	0.5	158.9764	55	Pos	M+H	0.4	0.7	0.7	7.9
Azamethiphos	6.2	324.9809	182.9958	6	127.9899	13	Pos	M+H	1	1	1	20
Azinphos-ethyl	10.7	346.0443	114.9613	18	142.9387	15	Pos	M+H	0.5	0.7	0.6	17.1
Azinphos-methyl	9.9	318.0130	142.9927	30	132.0445	25	Pos	M+H	0.6	0.9	0.8	24.3
Azoxystrobin	10.0	404.1241	344.1031	8	372.0981	2.5	Pos	M+H	0.1	0.2	0.2	10.1
Barban	10.4	258.0083	240.0968	2.5	178.0422	15	Pos	M+H	0.1	2	2	18.5
Bendiocarb	8.4	224.0917	109.0289	30	167.0703	10	Pos	M+H	5	5	5	nd
Benfuracarb	11.5	411.1948	252.0689	2	195.0474	6	Pos	M+H	0.2	0.2	0.2	10.2
Benodanil	7.4	323.9880	323.9878	20	230.9301	21	Pos	M+H	0.1	0.5	0.5	19
Benoxacor	7.8	260.0240	260.0239	100	149.0836	10	Pos	M+H	0.4	0.6	0.6	19
Bensulfuron-methyl	9.9	411.0969	182.0563	33	156.0770	20	Pos	M+H	0.6	0.6	0.6	37
Bentazone	8.0	239.0496	197.0026	3	132.0329	12	Neg	M-H	0.4	50	0.5	8.7
Benzoximate	9.4	364.0946	199.0158	13	183.9924	3	Pos	M+H	0.9	3	3	22
Benzoylprop-ethyl	10.1	366.0658	105.0336	nd	95.0492	nd	Pos	M+H	nd	nd	nd	nd
Bifenazate	13.0	301.1547	198.0918	32	170.0968	14	Pos	M+H	0.4	0.9	0.9	20
Bitertanol	9.4	338.1863	70.0413	1	99.0804	10	Pos	M+H	0.1	0.7	0.7	19
Boscalid	10.3	343.0399	307.0632	9	139.9898	6	Pos	M+H	0.3	0.8	0.6	16.6
Brodifacoum	10.4	523.0903	256.1246	32	178.0778	66	Pos	M+H	0.5	0.8	0.8	17
Bromacil	8.2	261.0233	187.9341	12	204.9609	13	Pos	M+H	0.2	0.5	0.5	10.7
Bromoxynil	7.6	273.8509	78.9180	38			Neg	M-H	0.6	1	1	10.5
Bromuconazole	10.6	375.9614	158.9764	40	70.0409	10	Pos	M+H	0.7	1.5	1.5	26
Bupirimate	8.8	317.1642	166.0975	55	272.1063	0.2	Pos	M+H	2	5	5	19
Buprofezin	9.7	306.1635	116.0532	0.5	201.1057	0.5	Pos	M+H	4	4	4	17
Butachlor	3.2	312.1725	238.0993	75	162.1278	20	Pos	M+H	5	8	8	20

Table 3B. Overview of target compounds and their detection parameters, established IDL values, and linearity data. Residual plot values were not defined where MDL > 10 ng/g due to insufficient number of points to evaluate (nd: no data recorded).

Compound Name	Retention Time [min]	Precursor *m/z*	Confirmation *m/z*	Ion Ratio [%]	Confirmation *m/z*[2]	Ion Ratio [%]	Peak Polarity	Adduct	IDL [ng/g] in Solvent	IDL [ng/g] in Tea	IDL [ng/g] in Honey	Residual Plot RSD%
Butafenacil	10.5	475.0878	179.9848	1	331.0093	18	Pos	M+H	40	40	60	nd
Butocarboxim	4.5	191.0849	213.0668	2	156.0453	10	Pos	M+H	0.3	0.3	0.3	55
Butoxycarboxim	6.8	223.0747	106.0322	3	62.9901	8	Pos	M+H	0.9	0.9	0.9	9.2
Carbaryl	8.9	202.0863	145.0648	25	117.0705	40	Pos	M+H	30	40	35	nd
Carbendazim	3.0	192.0768	160.0506	20	192.0768	95	Pos	M+H	0.8	0.7	0.6	15.2
Carbetamide	6.2	237.1234	120.0445	5	118.0863	1	Pos	M+H	3	4	4	20
Carbofuran	8.3	222.1125	165.0911	0.7	123.0443	22	Pos	M+H	1	1	1	32
Carbofuran-3-hydroxy	6.0	255.1339	163.0754	24	135.0804	25	Pos	$M+NH_4$	3	5	5	65
Carbosulfan	12.4	381.2206	118.0685	12	160.1155	20	Pos	M+H	0.5	0.8	0.8	8.4
Carboxin	8.8	236.0740	143.0162	10	124.0216	0.5	Pos	M+H	2	5	5	17.7
Carfentrazone-ethyl	10.8	412.0437	384.0124	15	366.0019	90	Pos	M+H	2	3	3	21
Carpropamide	9.1	334.0527	196.0291	0.6	132.0575	1	Pos	M+H	0.2	0.8	0.8	19
Chlorantraniliprole	9.7	481.9781	452.9336	11	285.9198	30	Pos	M+H	2	0.9	0.9	31.3
Chlorbromuron	10.4	292.9686	203.9211	4	182.0242	2	Pos	M+H	0.1	0.3	0.3	7.5
Chlorfenvinphos	9.2	358.9768	127.0156	1	98.9847	2	Pos	M+H	0.1	0.5	0.5	14.2
Chlorfluazuron	12.0	539.9702	382.9362	120	158.0412	140	Pos	M+H	4	5	5	34
Chloridazon	6.2	222.0429	104.0499	10			Pos	M+H	0.1	0.2	0.2	5.3
Chlorotoluron	9.3	213.0789	72.0452	35	168.0209	12	Pos	M+H	0.4	0.4	0.4	8
Chloroxuron	10.6	291.0895	72.0453	45			Pos	M+H	0.1	0.1	0.1	5.1
Chlorpyrifos	10.0	349.9336	114.9617	110	197.9275	15	Pos	M+H	0.1	0.7	0.7	20
Cinosulfuron	9.2	414.1078	157.072	4	183.0514	12	Pos	M+H	0.3	0.7	0.7	20
Clethodim	11.5	360.1395	206.1178	1	166.0865	8	Pos	M+H	0.2	1.3	1	18.3
Clofentezine	11.5	303.0199	138.0106	20	130.0400	2	Pos	M+H	0.2	3	2	20.1
Clomazone	9.9	240.0786	125.0155	50	128.0708	5	Pos	M+H	0.1	0.1	0.1	7.2
Clopyralid	0.9	191.9614	127.9910	5			Pos	M+H	7	9	8	nd
Clothianidin	5.6	250.0160	169.0542	3	131.9670	10	Pos	M+H	0.2	0.5	0.5	14.8
Coumaphos	11.2	363.0219	226.9929	23	334.9906	3	Pos	M+H	0.5	0.5	0.5	11.2
Crotoxyphos	5.6	315.0992	211.0367	6	193.0261	500	Pos	M+H	5	5	5	19
Cumyluron	8.5	303.1259	185.0480	2	125.0155	3	Pos	M+H	0.2	0.7	0.7	15
Cyanazine	6.3	241.0963	214.0855	2	174.0546	12	Pos	M+H	0.6	0.7	1	19
Cyazofamid	10.8	325.0521	108.0119	22	217.0403	0.6	Pos	M+H	0.1	0.1	0.1	8.8
Cycloate	11.4	216.1418	154.1227	10	134.0634	20	Pos	M+H	0.1	0.5	0.5	7.1
Cycluron	7.7	199.1809	111.1170	0.5	89.0711	3	Pos	M+H	2	4	4	14
Cyflufenamid	11.2	413.1283	295.0860	5	241.0390	4	Pos	M+H	0.1	0.3	0.3	7.6
Cymoxanil	6.4	221.0645	126.0106	40	147.0400	8	Pos	M+Na	3	2	2	31
Cypermethrin	10.3	433.1080	191.0022	20	192.9995	2	Pos	$M+NH_4$	5	5	5	20
Cyproconazole	8.5	292.1211	70.0409	30	125.0155	30	Pos	M+H	0.2	0.7	0.7	15
Cyprodinil	9.1	226.1339	108.0812	4	93.0580	12	Pos	M+H	0.2	0.7	0.7	16
Cyromazine	0.7	167.1042	125.0824	5	85.0510	25	Pos	M+H	0.8	0.9	0.9	22.4
Deltamethrin	9.3	521.0070	280.8992	nd	278.9014	nd	Pos	$M+NH_4$	nd	nd	nd	nd
Demeton-S-methyl sulfone	1.6	263.0171	169.0083	1.5	121.0321	0.2	Pos	M+H	0.8	0.4	0.4	23.4
Desmedipham	9.8	318.1448	136.0394	33	154.0500	7	Pos	$M+NH_4$	0.8	0.8	0.8	18

Table 3C. Overview of target compounds and their detection parameters, established IDL values, and linearity data. Residual plot values were not defined where MDL > 10 ng/g due to insufficient number of points to evaluate (nd: no data recorded).

Compound Name	Retention Time [min]	Precursor *m/z*	Confirmation *m/z*	Ion Ratio [%]	Confirmation *m/z*^{2}	Ion Ratio [%]	Peak Polarity	Adduct	IDL [ng/g] in Solvent	IDL [ng/g] in Tea	IDL [ng/g] in Honey	Residual Plot RSD%
Desmethyl-pirimicarb	5.4	225.1346	72.0452	25	168.1132	0.4	Pos	M+H	0.8	1	1	12.8
Desmetryn	8.6	214.1121	172.0651	2	106.0656	1	Pos	M+H	0.2	0.8	0.8	7.3
Dichlofenthion	9.4	314.9773	286.9460	3	258.9147	5	Pos	M+H	0.9	5	5	20
Dichlorvos	6.6	220.9532	109.0288	65	127.0154	33	Pos	M+H	0.1	0.5	0.5	18
Diclobutrazol	10.9	328.0978	199.0077	6	158.9763	8	Pos	M+H	0.6	0.9	1	8.1
Dicrotophos	5.3	238.0839	112.0761	2	127.0157	9	Pos	M+H	0.8	0.9	0.9	17.8
Diethofencarb	9.9	268.1543	180.1019	0.5	152.0707	5	Pos	M+H	0.8	2	2	20.9
Difenacoum	10.1	445.1798	257.1325	14	179.0855	2	Pos	M+H	0.2	0.4	0.5	16
Difenoconazole	11.4	406.0720	251.0024	28	252.9993	20	Pos	M+H	0.1	1	0.7	33
Diflubenzuron	10.9	333.0213	230.9877	5	116.0498	70	Pos	M+Na	0.2	0.4	0.4	11.9
Dimefuron	7.8	339.1220	256.0484	0.2	167.0008	21	Pos	M+H	0.8	30	25	nd
Dimethachlor	7.8	256.1099	224.0837	6	148.1121	1	Pos	M+H	10	40	40	nd
Dimethametryn	10.8	256.1590	186.0809	8	96.0556	1	Pos	M+H	0.8	0.8	0.8	14
Dimethenamide	10.1	276.0820	244.0558	2.5	168.0842	10	Pos	M+H	0.1	0.3	0.3	5.3
Dimethoate	5.7	230.0069	170.9698	4	198.9648	17	Pos	M+H	0.3	0.3	0.3	10.3
Dimethomorph	10.4	388.1310	301.0627	10	165.0547	190	Pos	M+H	1	1	1	32
Dimetilan	5.5	241.1298	196.0710	3	72.0440	10	Pos	M+H	0.9	4	4	20
Dimoxystrobin	11.0	327.1703	116.0499	28	205.0973	8	Pos	M+H	0.1	0.1	0.6	10.9
Diniconazole	7.9	326.0821	70.0409	85	158.9763	0.4	Pos	M+H	0.1	0.4	0.3	15
Dinotefuran	3.6	203.1139	129.0897	0.1	114.1026	0.6	Pos	M+H	0.9	0.8	0.7	14
Dioxacarb	8.4	224.0917	167.0704	0.1	123.0441	100	Pos	M+H	1	0.9	0.9	20
Disulfoton	10.4	275.0358	89.0602	4			Pos	M+H	3	3	3	7
Dithiopyr	8.5	402.0619	271.9988	8	248.0340	40	Pos	M+H	0.6	0.8	0.9	29
Diuron	9.7	233.0243	72.0453	25			Pos	M+H	0.1	0.2	0.2	5.6
DNOC	7.6	197.0204	137.0244	1	109.0295	3	Neg	M-H	0.8	0.9	0.9	10.6
Dodemorph	12.7	282.2792	116.1070	nd	98.0965	nd	Pos	M+H	nd	nd	nd	nd
Epoxiconazole	10.8	330.0804	121.0450	4	123.0243	7	Pos	M+H	0.1	0.2	0.2	9.2
Esprocarb	10.0	266.1575	196.0793	4	142.1228	2	Pos	M+H	0.5	0.5	0.5	15
Etaconazole	10.8	328.0619	204.9822	2	158.9766	18	Pos	M+H	0.1	0.8	0.8	8.4
Ethiofencarb	10.3	226.0896	169.0682	37	121.0651	25	Pos	M+H	4	0.9	0.9	12.1
Ethiofencarb_ sulfoxide	5.2	242.0845	107.0491	35	79.0542	1	Pos	M+H	3	1	1	20
Ethiofencarb-sulfone	4.3	258.0795	185.0632	1	107.0492	2	Pos	M+H	3	1	1	20
Ethiprole	8.1	396.9899	350.9483	23	319.9840	41	Pos	M+H	0.7	0.7	0.7	10
Ethirimol	7.2	210.1601	140.1073	4			Pos	M+H	0.5	nd	0.5	15.4
Ethofumesate	10.0	304.1213	121.0651	2	241.0529	36	Pos	$M+NH_4$	0.2	0.4	0.3	10.6
Ethoxyquin	8.0	218.1542	190.1228	0.2	148.0759	3	Pos	M+H	0.7	0.9	0.8	12
Etofenprox	10.0	394.2377	177.1273	0.1	107.0495	0.3	Pos	$M+NH_4$	0.1	0.2	0.2	10.7
Etoxazole	12.1	360.1770	158.0415	0.8	304.1144	0.2	Pos	M+H	0.1	0.8	0.8	6.7
Etrimfos	9.1	293.0719	265.0407	10	142.9928	5	Pos	M+H	3	4	4	19
Famoxadone	11.1	392.1605	93.0579	24	327.0266	2	Pos	$M+NH_4$	0.6	nd	nd	12.9
Fenamidone	10.1	312.1165	236.1183	2.5	165.0482	0.3	Pos	M+H	0.6	0.5	0.5	7.7

Table 3D. Overview of target compounds and their detection parameters, established IDL values, and linearity data. Residual plot values were not defined where MDL > 10 ng/g due to insufficient number of points to evaluate (nd: no data recorded).

Compound Name	Retention Time [min]	Precursor *m/z*	Confirmation *m/z*	Ion Ratio [%]	Confirmation *m/z*^{2}	Ion Ratio [%]	Peak Polarity	Adduct	IDL [ng/g] in Solvent	IDL [ng/g] in Tea	IDL [ng/g] in Honey	Residual Plot RSD%
Fenamiphos	8.9	304.1131	217.0085	15	234.0350	1	Pos	M+H	0.8	0.9	0.9	12
Fenarimol	8.6	331.0399	268.0518	3	81.0455	30	Pos	M+H	0.8	0.9	0.9	15
Fenazaquin	10.6	307.1805	161.1325	0.1	57.0709	20	Pos	M+H	1	1	1	10
Fenbuconazole	8.8	337.1215	70.0409	52	125.0155	55	Pos	M+H	4	4	4	19
Fenhexamid	10.5	302.0709	97.1017	15			Pos	M+H	0.9	3	4	31
Fenobucarb	10.2	208.1332	152.0708	4	95.0492	1	Pos	M+H	1	5	5	27
Fenoxanil	8.8	329.0818	188.9868	14	141.1148	9	Pos	M+H	5	5	5	29
Fenoxycarb	10.0	302.1387	88.0400	28	116.0710	0.3	Pos	M+H	0.1	0.9	0.9	7.1
Fenpiclonil	10.0	236.9981	219.0320	3	202.0292	17	Pos	M+H	0.3	nd	0.9	8.1
Fenpyroximate	12.1	422.2074	366.1449	0.6	138.0662	7.5	Pos	M+H	0.4	1	1	9.8
Fensulfothion	7.9	309.0379	157.0319	8	173.0090	6	Pos	M+H	0.2	0.7	0.7	17
Fenthion	7.6	279.0273	216.9720	4.5	169.0140	1	Pos	M+H	2	4	3	38
Fenthion-sulfone	9.1	311.0171	124.9823	1	142.9927	12	Pos	M+H	0.2	50	5	7.7
Fenthion-sulfoxide	8.9	295.0222	279.9987	2	127.0156	13	Pos	M+H	0.1	0.2	0.2	5.6
Fenuron	5.7	165.1022	72.0440	18	165.1022	2	Pos	M+H	0.8	nd	nd	4.1
Fipronil	10.8	453.9725	367.9512	3	289.9767	0.5	Pos	M+NH_4	0.9	nd	nd	32
Flazasulfuron	9.9	408.0584	301.0909	0.5	227.0098		Pos	M+H	0.7	0.7	0.7	29
Flonicamid	1.6	230.0536	182.0562	50	174.0162	22	Pos	M+H	1	0.9	0.9	15
Florasulam	7.4	360.0373	129.0386	90			Pos	M+H	0.3	nd	nd	36
Fluazifop	10.9	328.0791	282.0738	18	91.0549	5	Pos	M+H	4	5	5	23
Fluazinam	10.0	464.9587	415.9438	2	397.9776	1	Neg	M-H	0.1	0.7	0.7	9.3
Flubendiamide	9.1	681.0160	271.9220	17	254.0407	120	Neg	M-H	0.9	2	2	11.4
Flufenacet	8.7	364.0737	152.0507	18	194.0977	4	Pos	M+H	0.1	0.8	1	12
Flufenoxuron	11.9	511.0255	158.0414	3	141.0146	4	Pos	M+Na	1	4	4	9.7
Flumetsulam	5.1	326.0517	129.0385	85	262.0898	51	Pos	M+H	0.2	0.7	0.7	14
Flumioxazin	9.8	355.1089	327.1137	5	299.0830	25	Pos	M+H	2	nd	nd	10.2
Fluometuron	9.1	233.0898	168.0257	1	72.0445	0.3	Pos	M+H	0.1	0.5	0.5	7.4
Fluopicolide	10.3	382.9730	364.9625	80	172.9558	48	Pos	M+H	0.2	0.7	0.7	8.8
Fluopyram	10.5	397.0537	173.0210	39	208.0137	18	Pos	M+H	0.7	3	2	7.7
Fluoxastrobin	10.5	459.0866	427.0606	5	188.0380	15	Pos	M+H	0.3	0.6	0.6	6.8
Fluquinconazole	10.6	376.0163	349.0056	1	306.9838	3	Pos	M+H	2	nd	0.8	5
Flurochloridone	8.5	312.0164	310.0209	12	240.0632	8	Pos	M+H	0.3	0.7	0.7	12
Fluroxypyr	7.9	254.9734	180.9730	45	208.9679	8	Pos	M+H	2	5	5	23
Flusilazole	10.9	316.1076	165.0700	25	247.0750	3	Pos	M+H	0.2	0.5	0.5	20
Flutriafol	9.3	302.1099	70.0409	45	123.0244	13	Pos	M+H	0.8	6	5	8.9
Fonofos	9.1	247.0375	137.0058	12	108.9877	5	Pos	M+H	0.7	0.8	0.8	12
Forchlorfenuron	9.7	248.0585	155.0007	0.7	129.0214	0.5	Pos	M+H	0.4	0.4	0.4	13.1
Formetanate	0.9	222.1237	165.1022	3	120.0440	5	Pos	M+H	2	0.7	0.7	45
Formothion	6.1	258.0018	170.9698	2	142.9928	0.2	Pos	M+H	1	1	1	27
Fosthiazate	9.1	284.0538	104.0170	55	227.9914	1	Pos	M+H	0.1	0.2	0.2	7.7
Fuberidazole	6.0	185.0709	92.0494	2			Pos	M+H	0.3	0.4	0.4	11

Table 3E. Overview of target compounds and their detection parameters, established IDL values, and linearity data. Residual plot values were not defined where MDL > 10 ng/g due to insufficient number of points to evaluate (nd: no data recorded).

Compound Name	Retention Time [min]	Precursor *m/z*	Confirmation *m/z*	Ion Ratio [%]	Confirmation *m/z*[2]	Ion Ratio [%]	Peak Polarity	Adduct	IDL [ng/g] in Solvent	IDL [ng/g] in Tea	IDL [ng/g] in Honey	Residual Plot RSD%
Furathiocarb	11.6	383.1635	195.0475	6	252.0689	1	Pos	M+H	0.1	0.5	0.6	11.9
Halofenozide	8.1	331.1208	138.9945	3	105.0340	1	Pos	M+H	0.8	3	3	18
Haloxyfop	10.8	362.0401	316.0347	590	91.0548	10	Pos	M+H	0.8	1.2	1.2	13.3
Haloxyfop-methyl	11.3	376.0558	316.0348	5	91.0549	50	Pos	M+H	0.8	1.5	1.5	8.2
Heptenophos	10.0	251.0235	127.0157	36	125.0155	8	Pos	M+H	0.3	2	0.8	10
Hexaconazole	11.2	314.0821	70.0408	160	158.9765	65	Pos	M+H	0.1	0.4	0.4	23
Hexaflumuron	11.6	460.9889	158.0413	430	130.1591	23	Pos	M+H	3	30	3	57
Hexazinone	8.6	253.1659	171.0876	8	71.0611	28	Pos	M+H	0.1	0.8	0.6	7.3
Hexythiazox	12.0	353.1085	168.0574	20	116.0620	3	Pos	M+H	0.6	nd	1	16.5
Imazalil	11.1	297.0556	158.9763	6	200.9870	2	Pos	M+H	0.5	0.5	0.5	8
Imazaquin	8.6	312.1343	86.0971	10	267.1122	1	Pos	M+H	0.1	0.5	0.5	8.1
Imazethapyr	7.8	290.1499	245.1283	0.4	177.0658	4	Pos	M+H	0.1	0.4	0.4	7.9
Imidacloprid	5.8	256.0596	175.0979	10	209.0589	8	Pos	M+H	1	1	1	35
Indoxacarb	11.4	528.0780	218.0421	10	203.0189	25	Pos	M+H	0.8	0.9	0.9	20
Iprovalicarb	10.5	321.2173	119.0859	55	116.0711	6	Pos	M+H	0.1	0.9	0.9	10.8
Isocarbophos	9.5	230.9878	216.9722	1.5	121.0285	0.5	Pos	M+H	0.1	0.3	0.3	7.1
Isofenphos	9.3	346.1236	216.9720	50	245.0032	1	Pos	M+H	0.4	0.6	0.6	14
Isoprocarb	9.3	194.1176	95.0497	40	137.0962	4	Pos	M+H	1	1	1	17.4
Isoprothiolane	8.3	291.0719	188.9674	20	231.0145	2	Pos	M+H	0.3	0.6	0.6	19
Isoproturon	9.5	207.1492	72.0452	22	165.1022	1	Pos	M+H	0.1	0.5	0.5	5.3
Isoxaben	10.2	333.1813	165.0546	65	122.0362	2	Pos	M+H	0.1	0.4	0.4	8.1
Isoxadifen-ethyl	10.9	296.1281	232.0757	2	263.1067	1	Pos	M+H	0.1	0.7	0.4	10.8
Isoxaflutole	9.5	360.0512	250.9985	30			Pos	M+H	3	3	3	70
Isoxathion	11.3	314.0610	178.0322	0.3	114.9614	20	Pos	M+H	0.1	50	50	6.3
Kresoxim-methyl	9.0	314.1387	222.0914	0.5	223.0983	2	Pos	M+H	0.5	0.8	0.8	15
Lenacil	7.4	235.1441	153.0660	21	136.0395	7	Pos	M+H	0.5	3	0.7	17
Malaoxon	8.6	315.0662	99.0082	46	127.0392	2	Pos	M+H	0.1	0.3	0.3	7.9
Malathion	9.0	331.0433	99.0082	40	127.0391	2	Pos	M+H	0.5	1	0.8	23
Mandipropamide	10.2	412.1310	328.1099	4	125.0155	41	Pos	M+H	0.1	0.7	0.7	5.9
MCPA	7.8	199.0168	141.0112	10			Neg	M-H	0.1	0.2	0.2	12.3
Mefenacet	8.5	299.0849	120.0809	22	148.0758	4.5	Pos	M+H	0.1	0.7	0.7	122
Mepanipyrim	10.8	224.1182	106.0654	7			Pos	M+H	0.1	0.2	0.2	7.8
Mepronil	10.3	270.1489	119.0494	40	228.1019		Pos	M+H	0.1	0.6	0.6	5.3
Mesotrione	9.3	340.0487	227.9962	35	104.0131	20	Pos	M+H	100	150	150	nd
Metalaxyl	11.3	280.1543	220.1334	0.1	160.1121	7	Pos	M+H	0.1	0.5	0.5	18
Metamitron	9.9	203.0927	175.0979	0.2	104.0498	1	Pos	M+H	4	5	5	12
Metazachlor	9.4	278.1055	134.0965	70	210.0681	5	Pos	M+H	0.1	0.3	0.3	10.4
Metconazole	11.2	320.1524	70.0408	80	125.0151	5	Pos	M+H	0.1	0.6	0.6	15.3
Methabenzthiazuron	9.8	222.0700	165.0485	16	124.0219	6	Pos	M+H	0.1	2	2	10
Methamidophos	0.7	142.0086	124.9824	3	112.0162	5	Pos	M+H	0.1	0.8	0.8	6.9

Table 3F. Overview of target compounds and their detection parameters, established IDL values, and linearity data. Residual plot values were not defined where MDL > 10 ng/g due to insufficient number of points to evaluate (nd: no data recorded).

Compound Name	Retention Time [min]	Precursor *m/z*	Confirmation *m/z*	Ion Ratio [%]	Confirmation *m/z*[2]	Ion Ratio [%]	Peak Polarity	Adduct	IDL [ng/g] in Solvent	IDL [ng/g] in Tea	IDL [ng/g] in Honey	Residual Plot RSD%
Methidathion	2.5	302.9691	85.0403	12	145.0067	10	Pos	M+H	0.1	0.7	0.7	16
Methiocarb	10.2	226.0896	169.0682	40	121.0651	61	Pos	M+H	5	1	1	60
Methiocarb sulfoxide	6.3	242.0845	185.0631	30	122.0729	12	Pos	M+H	1	1	1	28
Methiocarb-sulfone	4.3	275.1060	122.0729	nd	201.0581	nd	Pos	$M+NH_4$	nd	nd	nd	nd
Metholcarb	7.8	166.0863	109.0652	12			Pos	M+H	0.5	2	2	24
Methomyl	0.8	163.0536	106.0325	0.1	88.0222	5	Pos	M+H	0.1	0.3	0.3	6.5
Methoprotryne	9.5	272.1537	240.1276	1	230.1069	0.3	Pos	M+H	0.4	0.7	0.7	8
Methoxyfenozide	10.4	369.2173	149.0599	43	133.0650	24	Pos	M+H	0.3	0.4	0.4	17.3
Metobromuron	9.4	259.0077	148.0632	4	169.9600	8	Pos	M+H	0.1	0.7	0.7	10.1
Metolachlor	8.8	284.1412	252.1151	3.5	176.1436	12	Pos	M+H	3	5	5	20
Metosulam	8.8	418.0138	174.9951	54	189.9821	1	Pos	M+H	0.8	0.8	0.8	27
Metoxuron	7.7	229.0738	72.0452	10	156.0208	0.9	Pos	M+H	0.1	0.6	0.6	6.3
Metrafenone	9.3	409.0645	209.0810	30	226.9703	3	Pos	M+H	0.4	0.7	0.7	8
Metribuzin	8.0	215.0961	187.1013	18	84.0813	2	Pos	M+H	0.1	0.2	0.2	8.4
Metsulfuron-methyl	8.7	382.0816	167.0563	21	199.0060	1.5	Pos	M+H	0.6	0.6	0.6	28
Mevinphos	5.7	225.0523	127.0157	30	193.0262	3	Pos	M+H	3	6	6	20
Mexacarbate	5.2	223.1440	166.1226	25	151.0992	5	Pos	M+H	1	1	1	19
Monocrotophos	3.0	224.0682	127.0157	42	98.0606	3	Pos	M+H	5	5	5	18
Monolinuron	9.0	215.0582	126.0107	8	148.0632	2	Pos	M+H	0.3	0.4	0.4	6.3
Napropamide	8.8	272.1645	129.1151	0.9	171.0806	2.5	Pos	M+H	0.5	0.8	0.8	19
Naptalam	6.7	292.0968	274.0863	2	256.0757	0.7	Pos	M+H	2	5	5	10
Neburon	10.9	275.0712	88.1127	3	114.0917	0.2	Pos	M+H	0.1	0.8	0.8	5.6
Nicosulfuron	8.8	411.1081	182.0560	25	106.0292	20	Pos	M+H	0.2	nd	nd	14.9
Nitenpyram	1.0	271.0956	196.0637	0.2	99.0917	1	Pos	M+H	1	1	1	15.1
Nuarimol	8.1	315.0694	252.0819	3	243.0372	0.5	Pos	M+H	0.6	4	2	21
Ofurace	6.7	282.0892	160.1120	25	224.0837	1	Pos	M+H	0.4	0.9	0.8	12
Omethoate	3.4	214.0297	182.9877	0.6	142.9928	12	Pos	M+H	0.3	0.6	0.3	10.4
Oxadixyl	6.2	279.1339	219.1130	0.1	133.0889	7	Pos	M+H	0.8	0.8	0.8	9
Oxamyl	1.0	237.1016	72.0452	70	90.0556	2.5	Pos	$M+NH_4$	0.8	0.7	0.7	56
Oxyfluorfen	9.4	362.0401	237.0396	nd	140.0493	nd	Pos	M+Na	nd	nd	nd	nd
Paclobutrazol	10.3	294.1368	70.0408	50	87.0812	3.5	Pos	M+H	0.5	nd	nd	9.3
Penconazole	11.1	284.0716	70.0408	58	158.9763	21	Pos	M+H	0.2	0.7	0.7	39
Pencycuron	11.3	329.1415	125.0155	80	127.0125	25	Pos	M+H	0.5	0.5	0.5	6
Permethrin	10.6	408.1128	183.0804	64	95.0497	35	Pos	$M+NH_4$	1	3	3	19
Phenmedipham	9.8	318.1448	168.0654	8	136.0392	32	Pos	$M+NH_4$	50	0.8	0.8	20
Phenthoate	8.9	321.0379	135.0442	1	107.0497	0.3	Pos	M+H	0.5	0.8	0.8	10
Phoxim	11.2	299.0614	114.9617	18	163.0326	2	Pos	M+H	0.9	0.9	0.9	13
Picoxystrobin	10.8	368.1104	145.0649	42	117.0700	0.6	Pos	M+H	0.2	0.5	0.5	11.7
Piperonyl butoxide	10.7	356.2432	177.0910	13	119.0859	60	Pos	$M+NH_4$	0.7	0.7	0.7	6.8
Piperophos	8.8	354.1321	170.9336	12	212.9806	0.5	Pos	M+H	0.4	0.7	0.7	9
Pirimicarb	6.4	239.1503	72.0452	25	182.1289	1	Pos	M+H	1	1	1	16

Table 3G. Overview of target compounds and their detection parameters, established IDL values, and linearity data. Residual plot values were not defined where MDL > 10 ng/g due to insufficient number of points to evaluate (nd: no data recorded).

Compound Name	Retention Time [min]	Precursor *m/z*	Confirmation *m/z*	Ion Ratio [%]	Confirmation *m/z*^{2}	Ion Ratio [%]	Peak Polarity	Adduct	IDL [ng/g] in Solvent	IDL [ng/g] in Tea	IDL [ng/g] in Honey	Residual Plot RSD%
Pirimiphos-ethyl	9.8	334.1349	198.1060	16	182.1289	6	Pos	M+H	0.3	0.7	0.7	18
Pirimiphos-methyl	14.7	306.1036	164.1184	5	108.0559	12	Pos	M+H	0.3	0.7	0.7	14
Pretilachlor	3.2	312.1727	252.1152	5	176.1436	1	Pos	M+H	0.9	2	3	21
Primisulfuron-methyl	8.3	469.0436	254.0181	12	199.0059	9	Pos	M+H	0.7	2	0.9	8
Prochloraz	11.3	376.0381	70.0296	25	308.0006	0.2	Pos	M+H	0.8	0.8	0.8	33
Profenofos	9.7	372.9424	304.8617	12	302.8640	11	Pos	M+H	0.5	0.8	0.8	26
Promecarb	10.2	208.1332	151.1119	2	119.0605	1	Pos	M+H	0.8	1	1	27
Prometon	9.1	226.1662	184.1193	1	142.0724	10	Pos	M+H	0.8	0.9	0.8	7
Prometryn	8.4	242.1434	200.0964	1	158.0494	12	Pos	M+H	2	5	5	28
Propamocarb	0.9	189.1598	102.0554	6	144.1020	1	Pos	M+H	0.7	0.8	0.8	5.6
Propanil	8.0	218.0135	161.9872	3	127.0184	30	Pos	M+H	0.5	0.7	0.7	9
Propargite	11.9	368.1890	175.1115	5	231.1742	15	Pos	M+NH_4	0.1	0.3	0.3	8.5
Propazine	10.1	230.1167	188.0698	1	146.0227	12	Pos	M+H	0.1	0.5	0.5	7.4
Propetamphos	8.4	282.0923	194.9877	21	156.0243	3	Pos	M+H	0.5	0.8	0.8	14
Propiconazole	9.2	342.0771	69.0707	3	158.9764	58	Pos	M+H	0.4	0.9	0.8	12
Propoxur	8.2	210.1125	111.0445	26	168.0656	3	Pos	M+H	3	3	3	22
Propyzamide	8.3	256.0290	189.9822	5	172.9557	6	Pos	M+H	0.7	3	1.5	7.4
Prosulfocarb	11.4	252.1417	91.0549	15	128.1072	0.1	Pos	M+H	0.1	0.2	0.2	5.2
Pymetrozine	0.9	218.1037	105.0448	45	79.0416	4	Pos	M+H	1	4	4	16
Pyraclostrobin	11.2	388.1059	163.0628	17	164.0706	2	Pos	M+H	0.5	0.5	0.5	11.5
Pyrazophos	8.3	374.0934	222.0875	9	238.0645	0.4	Pos	M+H	0.4	0.9	0.7	26
Pyrethrin I	12.0	329.2111	161.0962	12			Pos	M+H	2	4	1	40
Pyrethrin II	11.4	390.2275	161.0960	14			Pos	M+NH_4	2	4	1	38
Pyridaben	10.4	365.1449	147.1169	62	309.0824	3	Pos	M+H	0.7	0.8	0.8	18
Pyridate	12.5	379.1242	207.0319	15	104.0497	1	Pos	M+H	2	15	20	23
Pyrimethanil	8.1	200.1182	107.0607	3	82.0657	5	Pos	M+H	0.5	0.7	0.7	9
Pyroquilon	6.8	174.0913	117.0574	20	132.0809	5	Pos	M+H	2	1	0.8	12
Pyroxsulam	6.7	435.0693	276.0397	0.4			Pos	M+H	5	8	7	22
Quinoxyfen	10.2	308.0040	272.0271	4			Pos	M+H	0.4	0.8	0.8	14
Quizalofop	10.8	345.0637	299.0583	3	301.0554	1	Pos	M+H	0.8	0.7	0.7	36
Quizalofop-p-ethyl	11.6	373.0950	299.0583	3	91.0548	40	Pos	M+H	0.7	1	1	2.2
Resmethrin	10.2	339.1955	171.0805	1	143.0856	51	Pos	M+H	3	7	6	23
Rimsulfuron	9.1	432.0642	182.0561	51			Pos	M+H	3	0.9	0.9	60
Rotenone	10.8	395.1489	213.0911	5	192.0781	3.5	Pos	M+H	0.6	0.9	0.9	16.9
Schradan	5.7	287.1396	242.0818	2	135.0681	30	Pos	M+H	0.5	0.7	0.7	9
Sethoxydim	11.6	328.1941	178.0862	40	180.1019	35	Pos	M+H	0.5	40	50	14.8
Simeconazole	8.7	294.1432	135.0605	3	91.0574	1	Pos	M+H	0.4	0.8	0.8	20
Simetryn	8.6	214.1121	124.0872	8	144.0594	2	Pos	M+H	0.7	2	2	7.3
Spinosyn A	11.3	732.4681	142.1228	100	98.0970	20	Pos	M+H	0.6	0.7	0.7	41
Spiromesifen	10.1	371.2217	273.1485	5	255.1380	2	Pos	M+H	0.3	0.7	0.8	14
Spiroxamine	8.6	298.2741	144.1384	15	100.1126	22	Pos	M+H	0.3	0.9	0.6	15.3

Table 3H. Overview of target compounds and their detection parameters, established IDL values, and linearity data. Residual plot values were not defined where MDL > 10 ng/g due to insufficient number of points to evaluate (nd: no data recorded).

Compound Name	Retention Time [min]	Precursor *m/z*	Confirmation *m/z*	Ion Ratio [%]	Confirmation *m/z*^{2}	Ion Ratio [%]	Peak Polarity	Adduct	IDL [ng/g] in Solvent	IDL [ng/g] in Tea	IDL [ng/g] in Honey	Residual Plot RSD%
Sulfotep	9.2	323.0300	114.9616	73	96.9515	2	Pos	M+H	0.3	0.7	0.7	17
Sulprofos	10.1	323.0358	236.9803	2	218.9698	10	Pos	M+H	0.3	0.7	0.7	15
Tebuconazole	6.6	308.1524	70.0408	85	125.0156	2	Pos	M+H	0.2	0.7	0.7	7
Tebufenozide	10.9	353.2224	133.0649	90	105.0702	65	Pos	M+H	0.9	0.7	0.7	51
Tebufenpyrad	9.8	334.1681	147.1169	40	145.0529	10	Pos	M+H	0.2	0.7	0.7	21
Tebuthiuron	6.8	229.1118	172.0903	8	116.0277	11	Pos	M+H	3	6	6	26
Teflubenzuron	9.9	402.9635	272.0271	12			Pos	M+Na	30	nd	nd	nd
Tepraloxydim	10.6	340.1321	248.1290	8	220.0970	7	Neg	M-H	0.5	0.9	0.9	31
Terbacil	7.0	215.0593	158.9966	1.5	115.9966	1	Neg	M-H	0.5	0.9	0.9	21
Terbufos	6.2	289.0514	57.0709	90	103.0581	5	Pos	M+H	0.8	0.8	0.8	12
Terbumeton	9.1	226.1661	170.1036	5	114.0662	2	Pos	M+H	0.8	1	1	7.1
Terbuthylazine	10.0	230.1167	174.0542	5			Pos	M+H	0.4	0.8	0.8	11
Terbutryn	8.6	242.1434	186.0807	10			Pos	M+H	3	5	5	20
Tetrachlorvinphos	8.9	364.9065	238.8985	8	203.9297	50	Pos	M+H	0.2	0.7	0.7	12
Tetraconazole	8.7	372.0288	70.0409	1	158.9764	0.2	Pos	M+H	0.2	0.7	0.7	10
Tetramethrin	9.6	332.1856	164.0707	2.5	135.1169	1	Pos	M+H	0.5	0.9	0.8	15
Thiabendazole	6.0	202.0433	175.0979	0.1	142.9926	0.5	Pos	M+H	0.2	0.7	0.7	7
Thiacloprid	6.1	253.0309	126.0107	35			Pos	M+H	0.7	0.6	0.6	5.6
Thiamethoxam	2.4	292.0266	211.0649	1.5	131.9671	10	Pos	M+H	3	0.8	0.8	13.7
Thiazopyr	9.0	397.1004	377.0942	10	335.0471	6	Pos	M+H	30	50	10	nd
Thidiazuron	6.5	221.0491	127.9913	1	102.0120	18	Pos	M+H	3	5	5	29
Thiobencarb	11.3	258.0714	125.0153	54	100.0757	5	Pos	M+H	0.5	0.8	0.8	5.23
Thiodicarb	9.3	355.0563	88.0222	44	107.9941	4.5	Pos	M+H	0.6	3	3	27
Thiofanox	7.0	219.1162	76.0393	25	58.0287	10	Pos	M+H	4	8	8	23
Thionazin	7.5	249.0457	113.0168	65	192.9831	2	Pos	M+H	1	1	1	17
Tolfenpyrad	9.9	384.1479	197.0965	10	171.0323	1.5	Pos	M+H	0.5	0.8	0.8	9
Tralkoxydim	11.8	330.2064	138.0551	5	284.1647	1.5	Pos	M+H	0.6	0.9	0.9	16.3
Triadimefon	8.4	294.1004	197.0728	40	69.0707	10	Pos	M+H	0.8	0.6	0.6	9
Triadimenol	10.5	296.1160	70.0408	55	99.0807	15	Pos	M+H	0.8	4	4	31
Triazophos	10.6	314.0723	162.0662	22	114.9618	27	Pos	M+H	0.1	0.2	0.2	5.2
Trichlorfon	4.9	256.9299	78.9951	20			Pos	M+H	0.9	0.9	0.9	6
Tricyclazole	8.2	190.0433	163.0324	8			Pos	M+H	0.7	0.9	0.9	18
Tridemorph	11.2	298.3106	130.1228	12	116.1071	2	Pos	M+H	0.9	4	4	20.6
Trietazine	10.0	230.1168	202.0855	8	132.0324	3	Pos	M+H	0.5	0.7	0.7	8
Trifloxystrobin	11.5	409.1370	186.0526	20	116.0499	7	Pos	M+H	0.9	0.7	0.7	14
Triflumizole	5.9	346.0929	278.0550	0.2	69.0449	0.1	Pos	M+H	0.3	0.4	0.5	10
Triflumuron	11.2	381.0224	240.1242				Pos	M+Na	0.9	4	4	21.5
Triforine	9.8	454.9140	389.9082	4	387.9096	7	Pos	M+Na	0.8	3	3	40
Triticonazole	10.7	318.1368	70.0409	55			Pos	M+H	0.6	0.9	0.9	13.5
Vamidothion	10.8	288.0488	146.0634	1	118.3240	2	Pos	M+H	0.5	1	0.8	10.3
Zoxamide	6.2	336.0319	186.9712	42	158.9767	2	Pos	M+H	0.5	0.6	0.5	12

Conclusion

The presented method allows for convenient, fast, and effective determination of a high number of pesticides covering polar to non-polar compound chemistry in difficult matrix types. HRAM provides a selective detection mechanism, and the method is very simple to adapt and apply. The method performance indicates it is suitable for routine use for regulatory purposes and can be readily extended to a larger and wider range of pesticide residues.

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