Multi-Residue Pesticide Analysis in Herbal Products Using Accelerated Solvent Extraction with a Triple Quadrupole GC-MS/MS System

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Application Note 52291

Key Words
Pesticides, Tea, Herbal products, ASE, SRM, MRM, Multi-residue analysis, TSQ 8000 GC-MS/MS

Introduction

The residue analysis of pesticides has developed in recent years into a comprehensive methodology for the detection of many hundreds of potential contaminating compounds. A multi-residue method for herbal products and teas is faced with additional challenges from the worldwide origin of the products and the complex matrix of the dried materials. In the due quality control of raw materials, the unknown or undeclared local plant protection treatments must be taken into account with a wide variety of potential pesticide contaminations.

Dried leaves, fruits or seeds and other herbal products of medical use deliver highly complex extracts from the sample preparation due to the rich content of active ingredients, essential oils and the typical high boiling natural polymer compounds from broken cells, leaves or fruit skins. A thorough clean up of the extracted sample can lead to losses of critical analytes of interest. A complete characterization of pesticide, and other residue, contamination is done by both LC and GC-MS/MS to cover the complete range of functional groups.

This application report describes the methodology used for the multi-residue pesticide analysis of herbal products using accelerated solvent extraction (ASE) and gel permeation chromatography (GPC) sample preparation with detection and quantitation by the Thermo Scientific TSQ 8000 GC-MS/MS system.

A routine screening method for more than 200 pesticide compounds was applied to a wide variety of different sample types, ranging from regular black tea or sage leaves, to seeds like fennel and herbs of medical and fragrance use like thyme and chamomile. The data processing and reporting was achieved by using the Thermo Scientific TraceFinder quantitation software suite.

The sensitivity requirement for this analysis was determined by the regulatory background. The analysis of pesticide residues in tea and herbal products follows the regulations of the European Directorate General for Health and Consumer Affairs (SANCO) for “Method Validation and Quality Control Procedures for Pesticide Residue Analysis in Food and Feed” [1]. The sensitivity requirements for these products as referenced in the Codex Alimentarius [2] result in maximum residue levels of 0.01 mg/kg for most of the pesticide compounds.

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Sample Preparation

Herbal and tea samples were extracted with an accelerated solvent extraction method using the Thermo Scientific Dionex ASE 350 Accelerated Solvent Extractor. The ASE method used is described in an official pesticide standard method [3]. The collected extracts were concentrated using a rotary evaporator (Rotavap) and further cleaned up via gel permeation chromatography (GPC). The GPC step used a polystyrene gel (Bio-Beads® S-X3) with an ethylacetate/cyclohexane mobile phase. After additional concentration by the Rotavap, the extracts were ready for GC injection using ethylacetate as the main solvent.

Method Setup

The analytical method comprised sample handling and injection using the Thermo Scientific TriPlus RSH liquid autosampler, TRACE GC 1310 gas chromatograph equipped with an instant connect, temperature programmable PTV injection system, and the TSQ™ 8000 triple quadrupole GC-MS/MS detection system. The MRM detection method was taken from a routinely employed Thermo Scientific TSQ Quantum XLS GC-MS/MS method without any further optimization on the TSQ 8000 GC-MS/MS system [4]. The TSQ 8000 system automatically optimized acquisition windows and optimized instrument duty cycle using timed-SRM (t-SRM) for maximum sensitivity. This enabled the avoidance of lengthy manual set-ups usually required when adopting new instrumentation (Figure 1).

ASE™ 350 Accelerated Solvent Extraction

Sample weight	10 g
Extraction solvent	Ethylacetate/cyclo-Hexane 1:1, same as GPC solvent
Temperature	120 °C
Pressure	100 bar
Extraction time	5 min, 1 cycle
Flushing with solvent	60% of cell volume
Flushing with nitrogen	100 s

TriPlus™ RSH Autosampler

Syringe	10 µL
Injection volume	1 µL
Injection type	Fast liquid band injection, 100 ms injection time
Washing cycles	3 x 10 µL, solvent ethylacetate

TRACE™ 1310 Gas Chromatograph

Injector PTV	Splitless mode
Base temperature	50 °C
Transfer	10 °C/s to 250 °C, until end of run
Flow	Constant flow, 1.2 mL/min, helium
Analytical column	40 m, ID 0.18 mm, 0.18 µm film, 5%-phenyl phase (5MS type)
Pre-column	5 m, ID 0.18 mm, empty deactivated, no backflush
Column oven	Temperature programmed
Start	70 °C, for 1.50 min
Ramp 1	15 °C/min to 190 °C
Ramp 2	7 °C/min to 290 °C, 12 min
Transfer line	250 °C

TSQ 8000 Mass Spectrometer

Ion source temperature	220 °C
MRM Detection	Timed SRM mode (see Appendix)

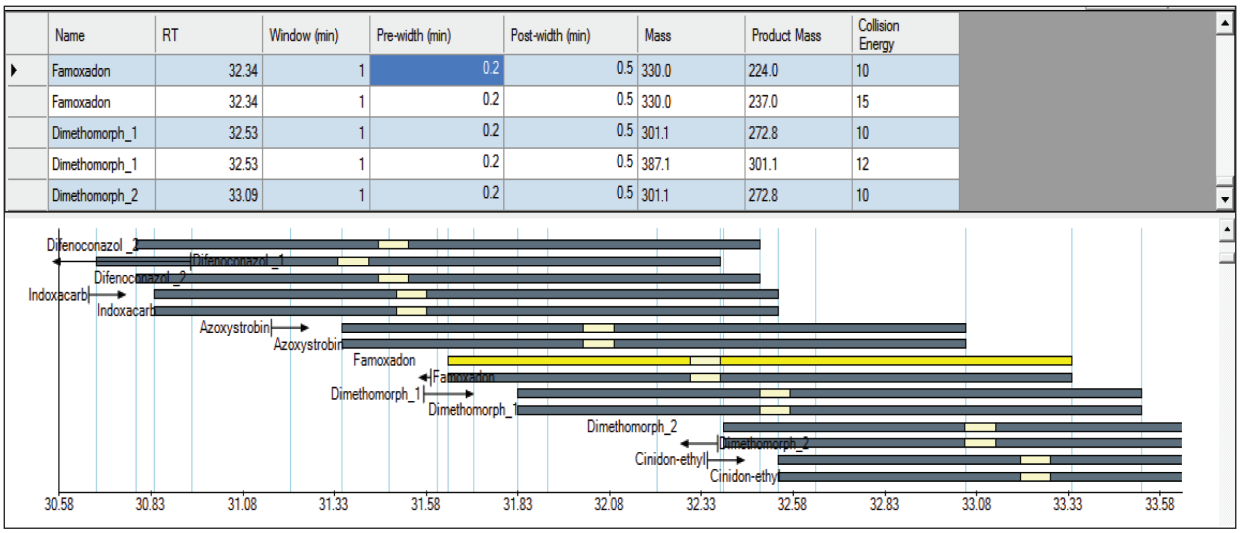

Figure 1. Screenshot of a section of the analytical run showing the "acquisition map" automatically created by the TSQ 8000 system using t-SRM. This mode ensures the instrument only monitors for compounds when they elute to optimize sensitivity.

Calibration and Linearity

The quantitative calibration and linearity check for the method was performed by using six calibration points in the range of 0.004 µg/mL to 1.0 µg/mL. This range represents an analyte concentration of 0.01 to 2.5 mg/kg in the samples (10 – 2500 ppb).

For setting up the calibration solutions, a stock solution containing target pesticide compounds in herbal products was used. The calibration solution was prepared in a standard matrix with a matrix load equivalent to the typical herbal extracts used. The standard matrix blank consisted of lemon peel extracted using the standard procedure. The pesticide blank level was tested before applying as a blank standard matrix. Standard solutions were prepared containing lemon peel extract dissolved 1:1 with ethyl acetate. The correlation coefficients, R^2, achieved during method calibration exceeded 0.99 for all compounds (Figure 2).

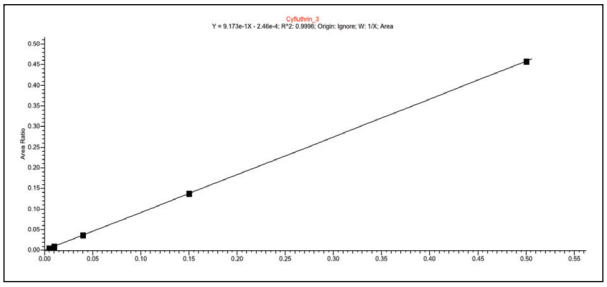

Figure 2. Calibration curve for Cyfluthrin, $R^2 = 0.9996$

Results and Discussion

Sensitivity (LOD)

Using the standard pool of pesticides, the method detection limits in the standard lemon peel were estimated. Using the 4 ppb (pg/µL) matrix standard level, S/N values were used to estimate the limits of detection (LOD). The S/N values in matrix are given in Table 1 for a selection of critical compounds taken at retention times that are affected most from the eluting matrix. Although the compounds are eluting in heavily impacted matrix regions of the chromatogram, the high selectivity of the TSQ 8000 GC-MS/MS for the target pesticides at low level against an intense matrix load is demonstrated in Figure 3 and Figure 4.

Table 1. Detection limit S/N for selected pesticide compounds in matrix

Pesticide	RT [min]	S/N @ 4 ppb
Terbacil	13:83	24
Alachlor	14:78	12
Tolylfluanid	16:75	44
Pyridaben	24:17	83

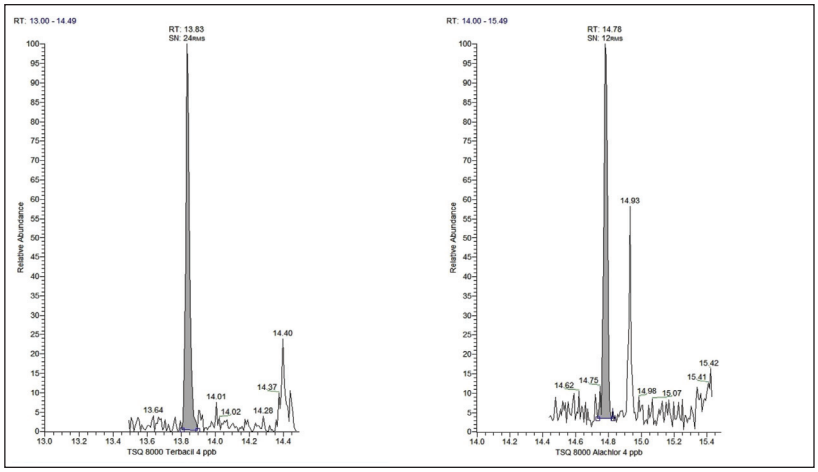

Figure 3. SRM peaks at 4 ppb from Terbacil (left, 161.1 › 88.0, CE 15 V) and Alachlor (right, 188.1 › 130.1, CE 25 V). SRM transitions were taken from the Pesticide Method Reference, 2nd ed. 2011. [4]

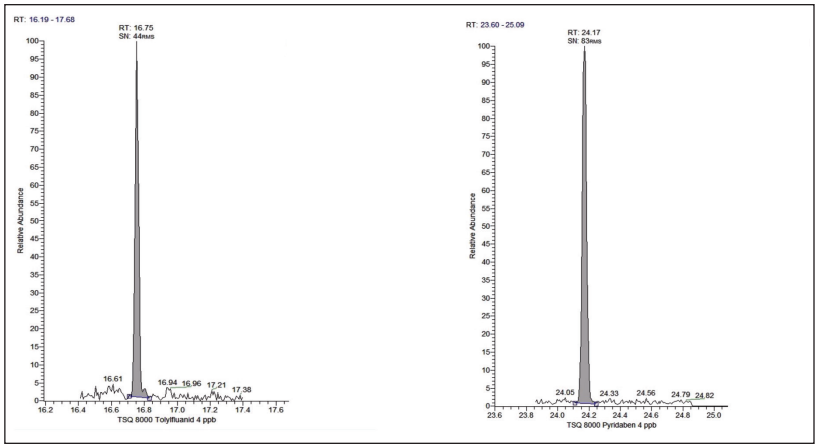

Figure 4. SRM peaks at 4 ppb from Tolylfluanid (left, 238.1 › 137.1, CE 15 V) and Pyridaben (right, 309.1 › 147.1, CE 15 V). SRM transitions were taken from the Pesticide Method Reference, 2nd ed. 2011. [4]

Robustness and Maintenance

Routine preventative maintenance on the GC was performed using routine standard operating procedures. The calibration chromatograms seen in Figures 3 and 4 have been acquired after a persistent matrix load to the system through routine analysis of more than 500 matrix samples.

This level of robustness meant that even with persistent and very high matrix load, it was not necessary to clean the removable ion source short term.

The innovative instant connect modularity of the injectors and detectors of the TRACE 1310 GC, used here as the front-end to the mass spectrometer, allows the user quick accessibility to any injector part for rapid cleaning. Furthermore the unique ability to replace the entire injector module within minutes represents an excellent way of postponing routine maintenance to when the laboratory schedule allows while keeping the GC-MS/MS system operational.

Analytical Precision

Within a routine series of 50 commercial samples, the quality control samples were measured with replicate injections. The results for a range of compounds is given in Table 2. The relative effects on known problematic pesticide compounds can be seen, while coefficients of variation (CV%) for unaffected compounds all stay well below 10% even within this long series of matrix injections.

Table 2. Coefficients of variation for lemon peel matrix spiked QC samples for a set of 60 pesticides under investigation (avg. 7.4%, 24 injections)

Diflubenzofuron	10.0%	Penconazol	7.5%	Diniconazol	2.9%
Biphenyl-d10	7.5%	Allethrin	8.4%	Aclonifen	9.0%
Biphenly	9.5%	Pyrifenox	5.5%	Trifloxystrobin	6.0%
o-Phenylphenol	8.2%	Procymidon	5.7%	Propiconazol	3.1%
Fenobucarb	6.0%	Triadimenol	11.5%	Propargit	6.0%
Diphenylamin	5.7%	Picoxystrobin	7.0%	Tebuconazol	4.3%
Terbutylazin	4.4%	Flutriafol	6.3%	Nitralin	9.2%
Propyzamid	3.1%	Hexaconazol	9.2%	Piperonyl butoxid	8.3%
Terbazil	5.8%	Isoprothiolan	9.7%	Brompropylat	5.8%
Fipronil-desulfinyl	6.9%	Uniconazol	7.0%	Fenoxycarb	9.1%
Alachlor	6.7%	Kresoxim-methyl	9.9%	Etoxazol	8.8%
Prometryn	8.3%	Myclobutanil	9.2%	Fenazaquin	3.3%
Ethofumesat	7.4%	Flusilazol	4.4%	Metconazol	5.3%
Bromacil	8.3%	Cinerin 1	8.1%	Pyriproxyfen	8.5%
Chlorpyrifos	6.9%	Buprofezin	7.4%	Fenamirol	8.5%
Tetraconazol	6.2%	Diclobutrazol	2.6%	Fluquinconazol	4.9%
Triadimefon	11.7%	Cyproconazol	2.6%	Pyridaben	5.2%
Dicapton	10.7%	Chlorbenzilat	3.3%	Etofenprox	10.2%
Butralin	6.6%	Etoconazol	4.4%	Silafluofen	10.2%
Fipronil	5.5%	Iprodion	11.1%	Indoxacarb	8.5%

Results from Real Life Samples

The above method was used for the analysis of a wide variety of herbs, teas and dried fruit known as one of the most challenging analytical task for controlling the pesticide maximum residue levels due to the heavy matrix impact. Table 3 gives a representative overview of positive results from different samples with the indication of the pesticide compound and concentration found. All compounds were detected by using at least two SRM traces and were subsequently confirmed by checking the calibrated ion ratios. The concentration ranges covered were from close to the MRL level of 10 mg/kg to high levels of up to 50 times above the regulated maximum. Figure 5 provides an example of confirmed residue detection in a thyme sample.

Table 3. Positive results above MRL level found in samples of various matrices

Sample Matrix	Pesticide Residues Found	Concentration (mg/kg)
Dried Herbs	o-Phenylphenol	0.017
Dried Herbs	Tebuconazol	0.023
Dried Fruit	Diflubenzuron	0.049
Dried Fruit	Myclobutanil	0.023
Dried Fruit	Propargit	0.479
Dried Fruit	Tebuconazol	0.081
Dried Fruit	Difenconazol	0.013
Dried Herbs	Picoxystrobin	0.228
Dried Herbs	Picoxystrobin	0.233
Dried Herbs	o-Phenylphenol	0.011
Herbal Tea	o-Phenylphenol	0.014
Herbal Tea	o-Phenylphenol	0.011
Herbal Tea	Terbutylazin	0.016

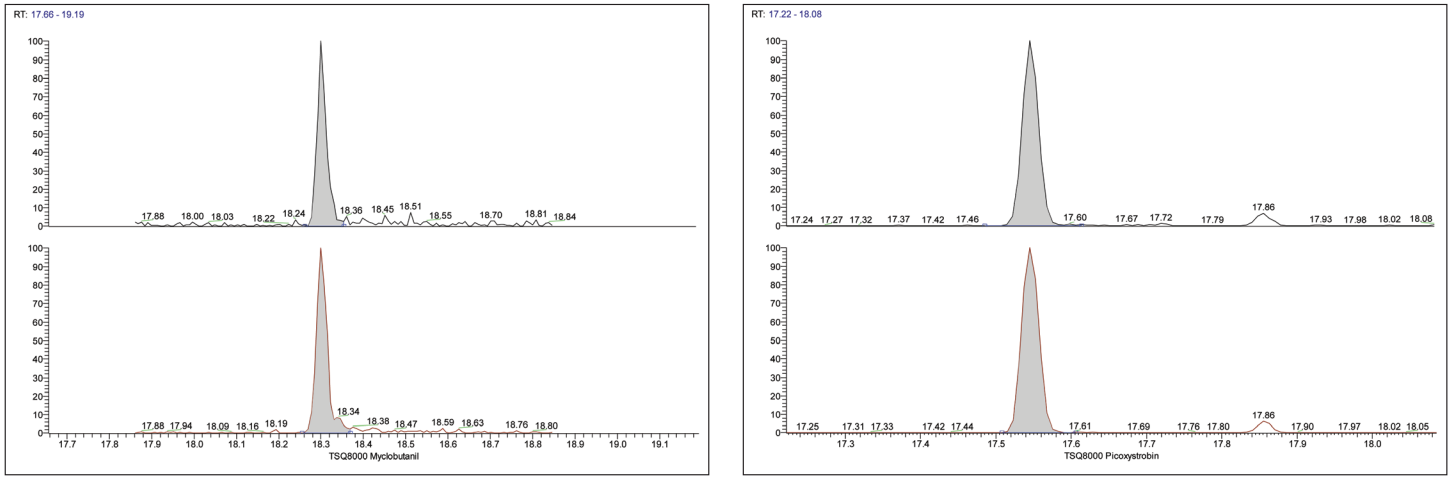

Figure 5. Positive results for Myclobutanil in green apple (0.023 mg/kg, left) and Picoxystrobin in thyme (0.228 mg/kg, right), both detected on two SRM traces

Data Analysis and Reporting

The data processing was performed using TraceFinder™ quantitation software. TraceFinder software contains a compound data store containing a large number of pesticide compound entries from which required compounds for the method had been selected. For each pesticide, the necessary parameters for MRM acquisition and compound identification, such as SRM transition, retention time, and ion ratios, as well as quantitation details like quantitation mass and recovery requirement, are stored.

The analytical sequence setup, data acquisition and result processing was done from one software platform integrating the complete analytical process. In Figure 6, the analytical sequence is shown in the upper part of the screen, with the compounds included in the method to the right. The actual chromatograms for the selected pesticide compounds are displayed in the bottom part for review by the operator.

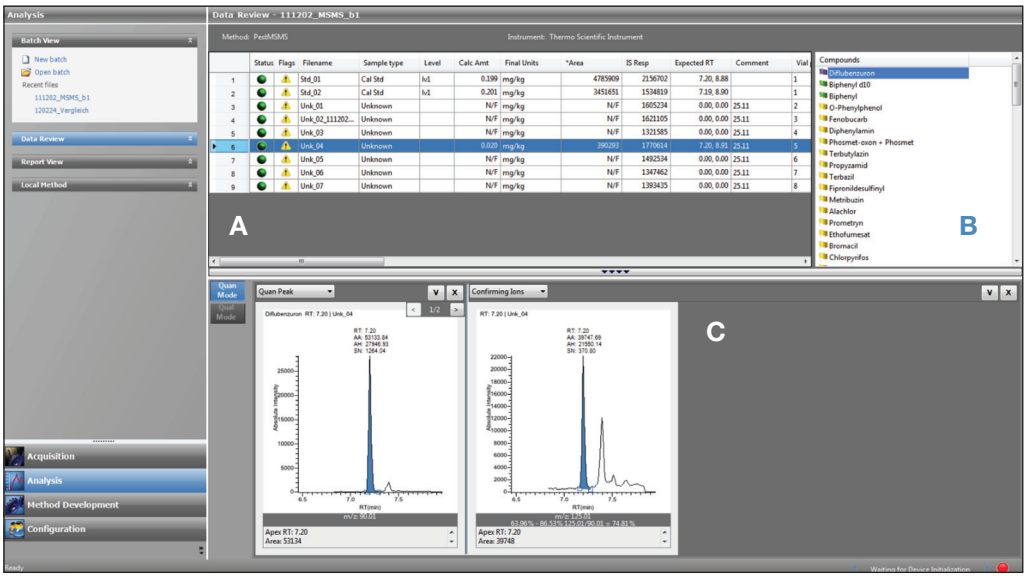

Figure 6. TraceFinder software analysis view:

A. Acquisition sequence table for calibration, QC and sample runs

B. Compound list with status flags

C. Compound chromatogram windows with integrated quantitation and confirmation peaks

Expanded Productivity

The total cycle time of the analytical runs was 30 minutes, which allowed the throughput of two samples per hour and resulted in a load of up to 48 samples, including QC checks during the day for the control of more than 200 pesticide compounds in each run.

This expanded productivity was a combined result of the TSQ 8000 triple quadrupole GC-MS/MS system with its enhanced analyte selectivity in matrix samples, the high method and system robustness, and the advanced data processing using TraceFinder software. Pesticide peaks were typically baseline-separated with a high signal-to-noise ratio allowing for an accurate automated area integration with significantly reduced manual control required. A number of quality control parameters within TraceFinder software immediately provided visible flagging for compounds that may need manual attention. Automatic ion ratio checks provided a fast and solid confirmation in the case of positive findings. The high processing speed of TraceFinder software provided for multi-residue analysis and quick and comprehensive reporting for each sample.

Conclusion

The TSQ 8000 GC-MS/MS delivered high sensitivity and matrix selectivity for routine pesticide analysis even in difficult matrix samples. The data acquisition using the unique timed-SRM allowed for the detection of a virtually unlimited number of pesticide compounds in one run without sacrificing the high sensitivity for individual compounds. Quantitative calibrations were performed in a standard matrix and showed excellent linearity and precision over the relevant concentration range to control the regulated MRL levels.

The high matrix selectivity of the TSQ 8000 system allowed for reduced sample preparation, providing high recoveries for a wide range of chemically diverse pesticide compounds. The very high matrix selectivity delivered low chemical matrix background with well-defined pesticide peaks that were safe and easy to integrate, thus eliminating the need for time-consuming manual baseline corrections.

Positive pesticide compound signals were confirmed by TraceFinder software checking the calibrated ion ration of the two monitored SRM transitions.

The TSQ 8000 GC-MS/MS system is well prepared for routine analysis and provides high robustness of the chromatographic system and ion source, thus reducing the need for frequent maintenance and avoiding system downtime for high sample throughput and productivity. The system is easy to use, durable, and robust even with the most challenging sample types and is fully automated in sampling capabilities to found and not-found report generation.

References

1. SANCO Document N° SANCO/12495/2011, Method Validation and Quality Control Procedures for Pesticide Residue Analysis in Food and Feed, Implemented by 01/01/2012.
2. Codex Alimentarius (www.codexalimentarius.net/mrls/pesticides/jsp/pest-q-e.jsp)
3. Pesticide determination according to § 64 LFGB L 00.00-34 (German legislation) Modul E9 (ASE); GPC
4. Pesticide Method Reference, 2nd Edition, 2011 Thermo Fisher Scientific, p/n 120390.

Appendix: List of pesticides with MRM transitions used (from [4])

Pesticide Name	RT (min)	Precursor Mass (*m/z*)	Product Mass (*m/z*)	Collision Energy (V)
Difluorobenzamid Degradation (Isocyanat)	6.93	152.93	90.01	20
Difluorobenzamid Degradation (Isocyanat)	6.93	152.93	125.01	20
Carbofuran 1	8.80	149.06	121.05	10
Carbofuran 1	8.80	164.08	149.07	10
Difluorobenzamid Degradation	8.62	141.00	63.11	25
Difluorobenzamid Degradation	8.62	141.00	113.09	15
Biphenyl-d10_ISTD	9.24	160.00	160.16	10
Biphenyl	9.28	154.08	153.08	15
Biphenyl	9.28	153.08	152.08	15
Carbofuran-3-hydroxy 1	10.43	137.05	81.01	18
Carbofuran-3-hydroxy 1	10.43	180.05	137.01	15
Tetrahydrophthalimid	10.84	151.04	79.01	25
Tetrahydrophthalimid	10.84	151.04	122.09	10
O-Phenylphenol	11.00	170.07	141.06	20
O-Phenylphenol	11.00	170.07	115.05	20
Molinate	11.10	187.10	126.07	10
Molinate	11.10	126.07	98.05	5
Chlorfenprop methyl	11.59	196.00	165.00	10
Chlorfenprop methyl	11.59	165.00	137.00	10
Fenobucarb	11.20	121.07	77.05	15
Fenobucarb	11.20	150.09	121.07	10
Propachlor	11.76	176.06	120.04	10
Propachlor	11.76	120.04	92.03	10
Propachlor	11.76	169.06	120.04	10
Propachlor	11.76	196.07	120.04	10
Cycloate	11.98	154.10	83.05	10
Cycloate	11.98	215.13	154.10	5
Diphenylamin	11.49	169.01	168.09	20
Diphenylamin	11.49	169.01	167.09	20
Chloropropham	12.26	213.06	127.03	15
Chloropropham	12.26	213.06	171.04	10
Phosmet-oxon	12.09	160.00	132.96	15
Phosmet-oxon	12.09	104.00	75.88	10
Phosmet-oxon	12.09	160.00	76.96	20
Prometon	13.10	225.16	183.13	10
Prometon	13.10	225.16	210.15	10
Carbofuran 2	13.13	149.06	121.05	10
Carbofuran 2	13.13	164.08	149.07	10
Profluralin	13.22	318.10	199.06	15
Profluralin	13.22	330.23	252.45	25
Swep	13.46	187.05	123.95	18
Swep	13.46	219.11	174.02	15
Trietazine	13.48	229.14	200.14	15
Trietazine	13.48	214.14	186.10	15
Dimethipin	13.53	117.98	57.97	10
Dimethipin	13.53	210.10	76.02	10
Terbutylazin	12.97	214.10	132.06	10
Terbutylazin	12.97	214.10	104.05	10
Propyzamid	13.04	173.01	145.01	15
Propyzamid	13.04	173.01	109.01	18
Propyzamid	13.04	175.02	147.01	15
Propyzamid	13.04	254.02	226.02	15
Isocarbamide	13.67	142.03	70.01	15
Isocarbamide	13.67	142.03	113.01	10
Dinoseb	13.92	211.13	116.99	15
Dinoseb	13.92	211.13	163.11	10
Terbazil	13.42	161.05	88.03	15
Terbazil	13.42	160.05	76.02	15
Bromocylen	14.37	358.79	242.85	15
Bromocylen	14.37	356.93	241.24	15
Dimethenamid	14.60	230.06	154.04	10
Dimethenamid	14.60	232.06	154.04	10
Dimethachlor	14.61	197.08	148.06	10
Dimethachlor	14.61	199.08	148.06	10
Acetochlor	14.65	174.11	146.15	15
Acetochlor	14.65	223.19	147.17	10
Desmetryn	14.68	213.11	171.08	10
Desmetryn	14.68	213.11	198.10	10
Flurprimidol	14.77	269.12	106.98	20
Flurprimidol	14.77	270.18	107.04	20
Alachlor	14.26	188.10	160.07	10
Alachlor	14.26	188.10	130.12	25
Alachlor	14.26	237.14	160.15	10
Metribuzin	14.14	198.08	82.03	20
Metribuzin	14.14	198.08	89.04	16
Propanil	15.00	217.01	161.00	10
Propanil	15.00	219.01	163.00	10
Fipronildesulfinyl	14.15	333.00	231.20	20
Fipronildesulfinyl	14.15	333.00	281.30	20
Carbofuran-3-hydroxy 2	15.02	137.05	81.01	18
Carbofuran-3-hydroxy 2	15.02	180.05	137.01	15
Prometryn	14.49	241.14	184.10	15
Prometryn	14.49	226.13	184.10	12
Tridiphan	15.18	186.94	158.94	15
Tridiphan	15.18	219.09	184.09	20
Ethofumesat	14.80	206.82	160.86	10
Ethofumesat	14.80	285.75	206.82	12
Pentanochlor	15.73	141.05	106.05	15
Pentanochlor	15.73	239.05	141.05	15
Chlorpyrifos	15.78	257.97	165.98	20
Chlorpyrifos	15.78	314.05	258.18	15
Bromacil	15.03	205.01	188.01	15
Bromacil	15.03	207.01	190.01	15

Pesticide Name	RT (min)	Precursor Mass (*m/z*)	Product Mass (*m/z*)	Collision Energy (V)
Anthrachinon	15.44	207.97	151.99	20
Anthrachinon	15.44	180.04	152.05	15
Anthrachinon	15.44	207.97	180.10	10
Nithrothal isopropyl	16.09	236.08	194.07	10
Nithrothal isopropyl	16.09	236.08	148.05	20
Triadimefon	15.41	208.07	181.06	10
Triadimefon	15.41	210.07	183.06	10
Tiocarbazil	16.15	156.08	100.05	8
Tiocarbazil	16.15	279.10	156.07	6
Tetraconazol	15.39	336.02	218.01	20
Tetraconazol	15.39	338.02	220.01	20
Butralin	15.54	266.14	220.11	15
Butralin	15.54	266.14	190.10	15
Dicapthon	15.44	262.00	262.00	9
Dicapthon	15.44	262.00	216.00	13
Crufomat	16.30	256.20	226.15	25
Crufomat	16.30	276.20	182.09	10
Allethrin	16.17	123.07	80.98	10
Allethrin	16.17	136.04	92.98	10
Dinobuton	16.89	163.06	116.04	15
Dinobuton	16.89	211.07	117.04	18
Penconazol	16.89	248.06	157.04	25
Penconazol	16.89	248.06	192.04	15
Pyrifenox 1	16.17	262.03	192.02	20
Pyrifenox 1	16.17	262.03	200.02	20
Pyrifenox 2	16.81	262.03	192.02	20
Pyrifenox 2	16.81	262.03	200.02	20
Tolylfluanid	16.92	238.09	137.05	15
Tolylfluanid	16.92	240.09	137.05	15
Fipronil	17.01	368.95	214.97	30
Fipronil	17.01	366.95	254.96	25
Triflumizol	17.20	206.05	179.04	15
Triflumizol	17.20	179.04	144.04	15
Procymidon	17.22	283.05	95.93	10
Procymidon	17.22	285.05	95.97	10
Procymidon	17.22	285.05	257.30	10
Triadimenol 1	16.45	168.11	69.99	15
Triadimenol 1	16.45	128.05	100.04	10
Triadimenol 2	16.64	168.11	69.99	15
Triadimenol 2	16.64	128.05	100.04	10
Butachlor	17.54	237.13	160.09	10
Butachlor	17.54	176.09	146.08	10
Chlorbenside	17.57	124.97	88.98	20
Chlorbenside	17.57	124.97	63.02	30
Fenothiocarb	17.68	160.07	72.01	15
Fenothiocarb	17.68	160.07	106.00	10
Picoxystrobin	17.69	335.09	303.09	10
Picoxystrobin	17.69	303.09	157.04	20
Paclobutrazole	17.75	236.10	125.06	15

Pesticide Name	RT (min)	Precursor Mass (*m/z*)	Product Mass (*m/z*)	Collision Energy (V)
Paclobutrazole	17.75	238.11	127.06	15
Chinomethionat	17.78	206.06	147.98	15
Chinomethionat	17.78	234.08	206.06	10
Napropamid	18.07	271.16	128.07	5
Napropamid	18.07	128.07	72.04	10
Flutriafol	18.11	219.07	123.04	15
Flutriafol	18.11	123.04	75.03	15
Flurodifen	18.14	190.02	126.01	10
Flurodifen	18.14	190.02	146.01	5
Bisphenol A	18.17	213.14	119.06	15
Bisphenol A	18.17	213.14	164.99	20
Bisphenol A	18.17	228.15	213.07	10
Chlorfenson_ISTD	18.20	302.00	110.90	20
Hexaconazol	18.22	214.08	159.07	20
Hexaconazol	18.22	214.08	151.98	25
Imazalil	18.24	172.96	144.96	15
Imazalil	18.24	172.96	108.95	25
Isoprothiolan	18.24	203.99	117.95	7
Isoprothiolan	18.24	203.99	84.90	25
Isoprothiolan	18.24	290.06	118.03	15
Flamprop-methyl	18.39	230.05	170.04	10
Flamprop-methyl	18.39	276.06	105.02	10
Kresoximmethyl	18.48	206.10	131.09	15
Kresoximmethyl	18.48	206.10	116.01	10
Buprofezin	18.51	175.08	116.96	20
Buprofezin	18.51	175.08	131.99	15
Buprofezin	18.51	249.16	105.93	20
Buprofezin	18.51	249.16	193.20	10
Uniconazol	18.57	234.12	136.99	15
Uniconazol	18.57	234.12	101.95	25
Uniconazol	18.57	234.12	165.08	10
Cinerin 1	18.60	123.08	95.06	10
Cinerin 1	18.60	123.08	81.05	10
Cinerin 1	18.60	150.10	108.09	10
Flusilazol	18.60	233.16	165.13	25
Flusilazol	18.60	233.16	152.06	20
Myclobutanil	18.65	179.00	125.00	15
Myclobutanil	18.65	179.00	89.95	25
Methoprotryne	18.66	256.14	212.11	15
Methoprotryne	18.66	256.14	200.11	15
Diclobutrazol	18.75	270.07	159.04	15
Diclobutrazol	18.75	272.08	161.04	15
Azaconazole	18.78	217.02	173.01	15
Azaconazole	18.78	219.02	175.01	15
Perthane	18.95	223.15	179.10	18
Perthane	18.95	223.15	167.06	18
Cyproconazol	19.14	222.09	125.05	20
Cyproconazol	19.14	224.09	127.05	20
Flamprop-isopropyl	19.14	276.08	105.03	15

Pesticide Name	RT (min)	Precursor Mass (*m/z*)	Product Mass (*m/z*)	Collision Energy (V)
Flamprop-isopropyl	19.14	278.17	104.99	20
Chloropropylat	19.16	251.02	139.01	20
Chloropropylat	19.16	251.02	111.01	20
Ancymidol	19.18	228.15	121.02	15
Ancymidol	19.18	215.15	107.02	15
Chlorbenzilat	19.22	251.02	139.01	20
Chlorbenzilat	19.22	251.02	111.01	20
Cyprofuram	19.36	211.12	132.02	10
Cyprofuram	19.36	211.12	166.05	10
Etaconazol 1	19.38	245.04	173.03	15
Etaconazol 1	19.38	245.04	191.03	10
Etaconazol 2	19.38	245.04	173.03	15
Etaconazol 2	19.38	245.04	191.03	10
Diniconazol	19.47	268.06	232.05	15
Diniconazol	19.47	270.06	234.05	15
Jasmolin 1	19.58	123.08	81.05	10
Jasmolin 1	19.58	123.08	95.06	10
Jasmolin 1	19.58	164.16	109.15	10
Aclonifen	19.70	212.02	182.02	10
Aclonifen	19.70	264.03	194.02	15
Tetrasul	19.85	251.92	216.93	20
Tetrasul	19.85	253.92	218.93	20
Carfentrazone ethyl	19.95	340.03	312.03	10
Carfentrazone ethyl	19.95	312.15	150.99	20
Benodanil	19.99	322.98	230.99	15
Benodanil	19.99	322.98	195.99	5
Trifloxystrobin	20.02	222.13	162.14	10
Trifloxystrobin	20.02	115.99	88.95	15
Trifloxystrobin	20.02	222.13	130.02	15
Chlordecone	20.06	271.91	237.16	15
Chlordecone	20.06	273.91	239.15	20
Famophos (Famphur)	20.16	218.07	108.94	15
Famophos (Famphur)	20.16	218.07	126.95	20
Iprodion Degradation	18.63	186.87	123.99	20
Iprodion Degradation	18.63	186.87	159.02	15
Iprodion Degradation	18.63	243.94	187.02	10
Iprodion	20.57	314.06	245.25	15
Iprodion	20.57	186.99	123.87	20
Iprodion	20.57	316.00	247.35	15
Iprodion	20.57	316.00	273.11	10
Propiconazol 1	19.38	259.02	173.02	20
Propiconazol 1	19.38	172.94	144.91	15
Propiconazol 2	19.54	259.02	173.02	20
Propiconazol 2	19.54	172.94	144.91	15
Pyraflufen-ethyl	20.30	412.02	349.02	15
Pyraflufen-ethyl	20.30	349.02	307.02	15
Clodinafop-propargyl	20.36	349.05	266.04	15
Clodinafop-propargyl	20.36	349.05	238.04	15
Lenacil	20.70	153.05	136.06	15

Pesticide Name	RT (min)	Precursor Mass (*m/z*)	Product Mass (*m/z*)	Collision Energy (V)
Lenacil	20.70	153.05	135.15	15
Diclofop methyl	20.77	253.02	162.01	15
Diclofop methyl	20.77	340.04	253.02	15
Propargit	20.79	173.08	135.04	15
Propargit	20.79	173.08	106.93	20
Propargit	20.79	350.21	173.10	15
Diflufenican	20.83	394.07	266.05	10
Diflufenican	20.83	266.05	246.05	10
Piperonylbutoxid	20.87	176.11	131.08	15
Piperonylbutoxid	20.87	176.11	103.06	10
Piperonylbutoxid	20.87	176.11	145.09	15
Tebuconazol	20.97	250.12	125.06	20
Tebuconazol	20.97	252.12	127.06	20
Nitralin	21.09	316.02	274.15	10
Nitralin	21.09	273.99	216.07	10
Benzoylpropethyl	21.22	292.05	105.02	15
Benzoylpropethyl	21.22	172.03	145.02	14
Captafol	21.22	311.06	78.94	20
Captafol	21.22	311.06	276.21	10
Epoxyconazol	21.29	192.04	138.03	10
Epoxyconazol	21.29	192.04	111.02	10
Bromuconazol 1	21.73	294.96	174.98	15
Bromuconazol 1	21.73	292.96	172.98	15
Brompropylat	21.76	340.93	183.05	20
Brompropylat	21.76	340.93	185.04	20
Etoxazol	21.83	300.14	270.38	20
Etoxazol	21.83	330.17	300.44	25
Fenoxycarb	21.85	186.08	109.05	15
Fenoxycarb	21.85	255.11	186.08	10
Phosmet	20.79	160.00	133.00	15
Phosmet	20.78	160.00	104.00	20
Phosmet	20.78	316.99	160.00	5
Fenpiclonil	21.94	235.99	200.99	15
Fenpiclonil	21.94	237.99	200.99	15
Fenazaquin	22.22	160.09	145.08	10
Fenazaquin	22.22	145.05	116.99	15
Fenazaquin	22.22	160.09	117.08	20
Phenothrin 1	22.27	183.10	153.08	18
Phenothrin 1	22.27	183.10	165.09	10
Phenothrin 2	22.42	183.10	153.08	18
Phenothrin 2	22.42	183.10	165.09	10
Bromuconazol 2	22.35	294.97	174.97	15
Bromuconazol 2	22.35	292.97	172.97	15
Metconazol	22.41	125.00	88.93	20
Metconazol	22.41	250.20	124.88	25
Triticonazole	22.80	235.10	217.09	10
Triticonazole	22.80	235.10	182.07	10
Pyriproxyfen	22.82	226.15	186.22	15
Pyriproxyfen	22.82	136.00	95.95	15

Pesticide Name	RT (min)	Precursor Mass (*m/z*)	Product Mass (*m/z*)	Collision Energy (V)
Azinphosmethyl	22.95	160.00	132.00	10
Azinphosmethyl	22.95	160.00	104.64	10
Pyriproxyfen	23.06	136.00	77.92	20
Fenamirol	23.55	251.02	139.01	15
Fenamirol	23.55	330.03	139.01	10
Pyridaben	24.50	364.14	309.12	5
Pyridaben	24.50	309.12	147.06	15
Fluquinconazol	24.59	340.01	298.01	22
Fluquinconazol	24.59	342.01	300.01	22
Etofenprox	26.05	163.09	107.06	16
Etofenprox	26.05	163.09	135.07	10
Etofenprox	26.05	376.14	135.02	30
Etofenprox	26.05	376.14	163.09	10
Silafluofen	26.25	179.00	151.00	7
Silafluofen	26.25	286.13	258.12	15
Difenconazol 1	26.91	323.05	265.04	15
Difenconazol 1	26.91	325.05	267.04	20
Difenconazol 2	27.05	323.05	265.04	15
Difenconazol 2	27.05	325.05	267.04	20
Indoxacarb	28.55	264.02	176.14	10
Indoxacarb	28.55	264.02	148.03	20
Indoxacarb	28.55	321.05	289.34	10

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AN52291_E 05/12S