

Fast analysis of multi-class pesticides panel in wine using single run LC-triple quadrupole mass spectrometry

Authors

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Keywords

SANTE/11813/2017, TSQ Quantis, Vanquish Flex, pesticides, QuEChERS, sample prep, Pesticide Explorer II

Goal

Demonstrate a fully tested LC-MS/MS workflow for fast and robust quantification of more than 400 pesticides below maximum residue limits (MRLs) with accuracy and precision that meet the EU SANTE guidelines.

Introduction

Pesticides are chemical or biological agents that repel, destroy, or mitigate plants or animals considered to be pests. Their benefits include improved productivity and protection against the loss of crops. However, if these compounds are misused or used indiscriminately, they can have adverse effects on human health. Therefore, the identification and quantification of pesticide residues in food products is an important part of routine food control.

In this application note we present the Thermo Scientific™ Pesticide Explorer II solution for fast, robust, accurate, and reproducible quantitation of more than 400 pesticides below their maximum residue limits. The solution includes the

Thermo Scientific™ QuEChERS sample preparation kit, Thermo Scientific™ Vanquish™ Flex Binary UHPLC system, Thermo Scientific™ TSQ Quantis™ triple quadrupole mass spectrometer, Thermo Scientific™ TraceFinder™ software, Thermo Scientific™ Accucore™ aQ C18 Polar Endcapped LC column, and method parameters to provide a start-to-finish workflow for pesticide analysis. The method was tested according to the requirements of the EU SANTE guidelines, which provide best practices for analytical quality control and method validation procedures for pesticide residue analysis in foodstuffs.¹

Experimental

Materials

- Thermo Scientific™ HyperSep™ Dispersive SPE Mylar Pouch 4000 mg magnesium sulfate, 1 g sodium chloride, 500 mg sodium citrate dibasic sesquihydrate, 1000 mg sodium citrate tribasic, 50/pack (P/N 60105-344-SP)
- Thermo Scientific™ Nunc™ 50 mL Conical Sterile Polypropylene Centrifuge Tubes (50/pack) (P/N 339652)
- Thermo Scientific™ Target2™ Regenerated Cellulose Syringe Filters, 0.45 µm, 30 mm, 100/pack (P/N F2500-7)
- Thermo Scientific™ National Target All-Plastic Disposable Syringes 3 mL luer-lock syringe, 100/pack (P/N S7510-3)
- Methanol, Thermo Scientific™, 1 L (P/N 458-1)
- Water, Thermo Scientific™ ultra-grade, 1 L (P/N W8-1)
- Ammonium formate, Fisher Chemical™ Optima™ (P/N A11550)
- Formic acid, 99%+, Thermo Scientific™ Pierce™, 10 × 1 mL ampules (P/N 28905)
- Acetonitrile, Thermo Scientific™ ultra-grade, 1 L (P/N A9561)

Sample preparation

Wine extraction

Ten milliliters of wine were added to a 50 mL Nunc polypropylene centrifuge tube (P/N 339652), followed by addition of 10 mL of acetonitrile (P/N 10784551). The tube was capped and shaken vigorously for approximately 1

minute. The tube was uncapped and a salt mixture (P/N 60105-344) was added. It was then shaken for approximately one minute and centrifuged at 4000 rpm for five minutes. Next, 1.5 mL of supernatant was aspirated into a National Target all-plastic disposable 3 mL luer-lock syringe (P/N S7510-3) and filtered through a Target2 45 µm syringe filter (P/N F2500-7) into an HPLC vial before the sample was submitted for LC/MS analysis.

Pesticide stock solution

A stock solution was created from all individual pesticide vials and labeled Solution K = 1 ppm final concentration. A second sub-stock solution was created (labeled Solution Y) by taking 100 µL of solution K and adding 900 µL of acetonitrile.

Internal standard, triphenyl phosphate (TPP), was added according to the wine extraction procedure above for testing of recovery. Tables 1 and 2 describe the preparation of the matrix extracted spikes (MES) and the matrix-matched calibration solutions (MMS), respectively.

Table 1. Matrix extracted spikes (MES) preparation

| Concentration (ppb) | Mix standard | CH ₃ CN (mL) | Matrix (mL) wine |
|---------------------|--------------|-------------------------|------------------|
| 100 | 1000 µL of K | 9.000 | 10.00 |
| 25 | 250 µL of K | 9.750 | 10.00 |
| 10 | 100 µL of K | 9.900 | 10.00 |
| 2.5 | 25 µL of K | 9.975 | 10.00 |
| 1 | 100 µL of Y | 9.900 | 10.00 |
| 0.5 | 50 µL of Y | 9.950 | 10.00 |

Table 2. Matrix-matched calibration solutions (MMS)

| Matrix (µL) wine | CH ₃ CN (µL) | Mix standard | Cal. point |
|------------------|-------------------------|--------------|------------|
| 900 | - | 100 µL K | G |
| 900 | 50 | 50 µL K | F |
| 900 | 75 | 25 µL K | E |
| 900 | 90 | 10 µL K | D |
| 900 | 50 | 50 µL K | C |
| 900 | 75 | 25 µL Y | B |
| 900 | 90 | 10 µL Y | A |

Chromatographic conditions

| | |
|---------------------|--|
| HPLC system: | Vanquish Flex Binary UHPLC system |
| Column: | Accucore aQ C18 column, 100 × 2.1 mm, with a particle size of 2.6 µm |
| Mobile phase A: | Water with 5 mM ammonium formate and 0.1% formic acid |
| Mobile phase B: | Methanol with 5 mM ammonium formate and 0.1% formic acid |
| Injection volume: | 1 µL |
| Flow rate: | 300 µL/min |
| Column temperature: | 25 °C |
| Run time: | 15 min |
| Tray temperature: | 4 °C |
| Gradient: | Table 3 |

Table 3. HPLC gradient

| Time (min) | Flow (mL/min) | % A | % B |
|------------|---------------|-----|-----|
| 0.0 | 0.300 | 98 | 2 |
| 1.0 | 0.300 | 98 | 2 |
| 2.0 | 0.300 | 50 | 50 |
| 9.0 | 0.300 | 2 | 98 |
| 12.0 | 0.300 | 2 | 98 |
| 12.1 | 0.300 | 98 | 2 |
| 15.0 | 0.300 | 98 | 2 |

Mass spectrometry conditions

| | |
|----------------------------------|---|
| MS system: | TSQ Quantis triple quadrupole mass spectrometer |
| Ionization mode: | Heated electrospray (HESI) |
| Scan type: | Timed-SRM |
| Polarity: | Positive and Negative |
| Spray voltage for positive mode: | 3500 V |
| Spray voltage for negative mode: | 2500 V |
| Sheath gas pressure: | 30 arb |
| Aux gas pressure: | 6 arb |
| Sweep gas pressure: | 1 arb |
| Ion transfer tube temp.: | 290 °C |
| Vaporizer temp.: | 350 °C |
| CID gas pressure: | 2.0 |
| Cycle time: | 0.5 s |
| Q1 resolution (FWHM): | 0.7 |
| Q3 resolution (FWHM): | 0.7 |

Data analysis

Fully automated data analysis was carried out using TraceFinder software during acquisition of the next sample to speed up data review.

Results and discussion

Samples of various red and white wines were obtained for method validation. Typically, matrix-matched standards (MMS) are required for calibration, and matrix-extracted spikes (MES) are used to assess recovery. For excellent quantitation, there must be enough scans across all the target quantitation peaks. At least one or two SRMs can be used for confirmation. Figure 1 shows a 10 ppb MES for a method containing over 400 pesticides with positive and negative polarity switching occurring throughout the run. The number of scans across each peak are sufficient for accurate and reproducible quantitation.

Figure 2 shows some typical results of calibration curves from 0.5 to 100 ppb. Over 95% of the pesticides studied had calibration curves with $r^2 \geq 0.990$. Confirmation ions are displayed in the middle of each panel at 1 ppb for each pesticide, with indicator colors (green) easily visible to show passing ion ratio criteria. The ISVEA laboratory then wanted to expand the list of analytes beyond the original scope and decided to create a comprehensive and validated quantitation method using the SRM

compound database. A method of over 400 compounds was developed and optimized to ensure that at least two SRM transitions were detected per compound (one for quantitation and the other for confirmation) while still maintaining polarity switching throughout the run.

Recovery criteria for MES, as outlined by the EU guidelines, state the value must fall between 70% and 120%. A summary of results is shown in Figure 3. The method allowed ISVEA to quickly quantitate samples with confidence at or below the EU MRL for a wide variety of pesticides, giving their clients added confidence in the safety of their products. See Table A1, Appendix.

Method robustness is key to any laboratory. The screening and quantitation method showed excellent reproducibility in terms of consistent peak shapes and long column lifetime over 1000 injections (and still going strong), with consistent peak response over time. Figure 4 shows some select pesticides across the retention time range of the method (1–10 minutes) for approximately 300 injections.

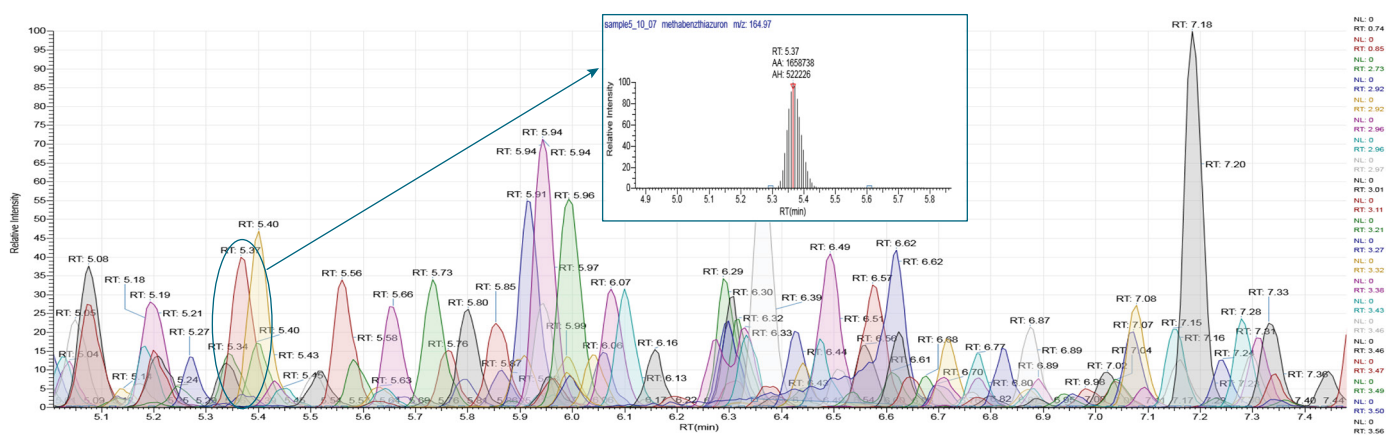
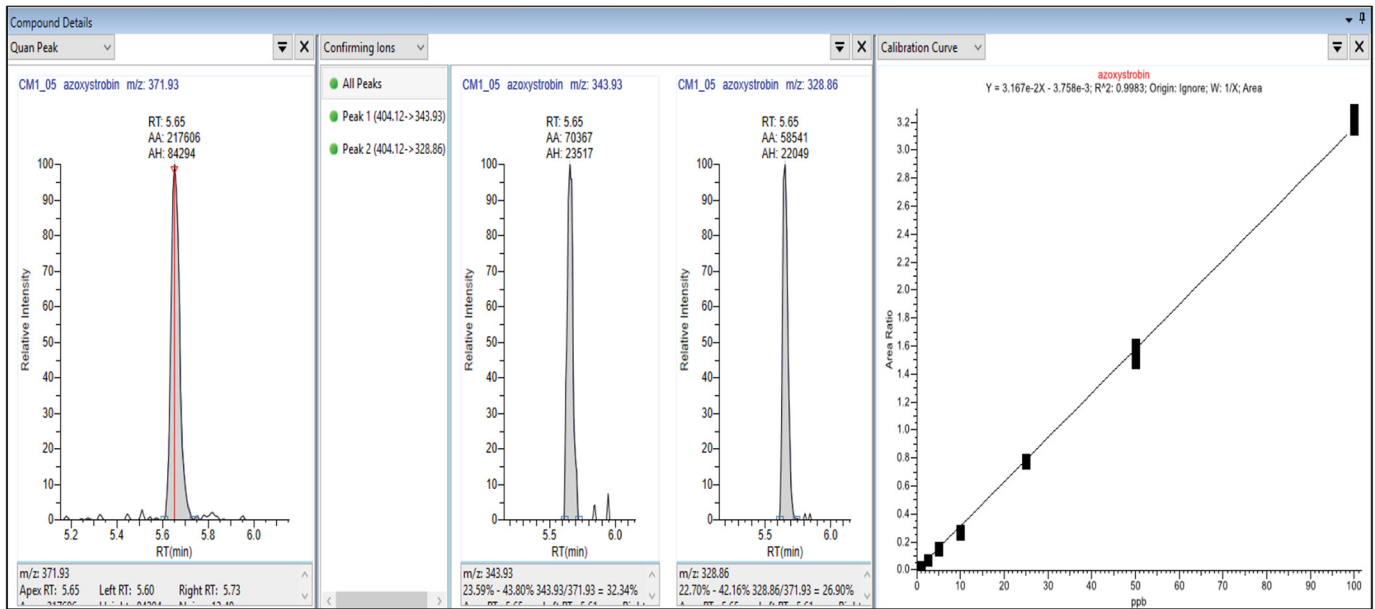


Figure 1. White wine MES standard at 10 ppb. The peak at 5.37 minutes is methabenzthiazuron, showing over 15 scans across the quantitation ion used for the analysis. Large pesticide panels of extracted SRMs are easily displayed in TraceFinder software.

A. Azoxystrobin



B. Flusilazole

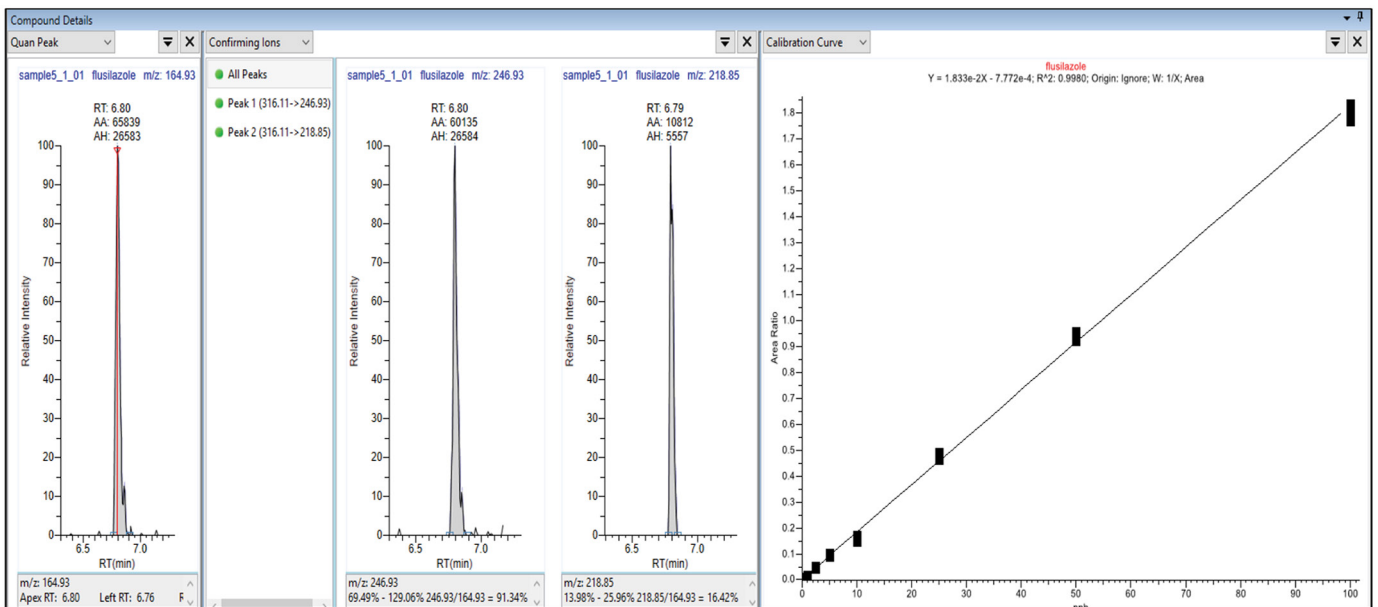


Figure 2. Quantitation and confirming ions at 1 ppb in a MES, along with calibration range from 0.5 to 100 ppb in white wine for azoxystrobin (A) and flusilazole (B). The technique allows for confident screening with confirmation well below the MRL concentration.

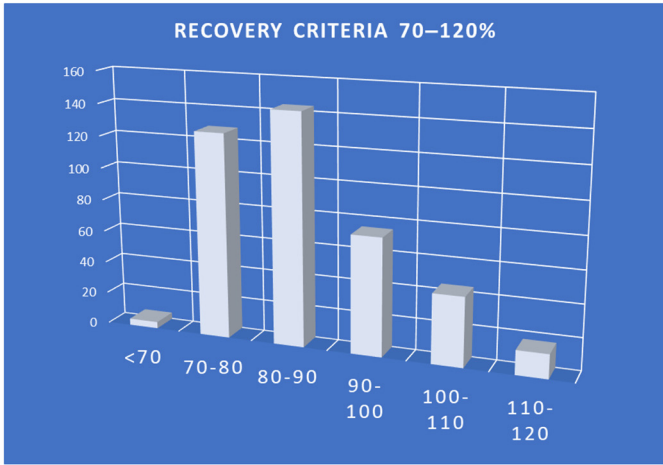


Figure 3. Recovery results for pesticide residues in wine matrix at the LOQ

Conclusion

European Union regulations that set maximum residue limits of pesticides in foods are analytically challenging due to the low LOQs that must be achieved in complex matrices. This application note describes a multi-residue LC-MS/MS method that uses the TSQ Quantis triple quadrupole mass spectrometer-based Pesticide Explorer II solution, for rapid and robust quantitation of more than 400 pesticides in wine at or below their respective MRLs and conforming to the EU SANTE guidelines. The LC-MS/MS system enabled analysis of 1 µL sample injections, without the need for dispersive SPE sample cleanup or sample dilution, with increased robustness and throughput.

Reference

1. SANTE/11813/2017. Guidance document on analytical quality control and method validation procedures for pesticides residues analysis in food and feed. Supersedes SANTE/11945/2015. Implemented by 01/01/2018. https://ec.europa.eu/food/sites/food/files/plant/docs/pesticides_mrl_guidelines_wrkdoc_2017-11813.pdf

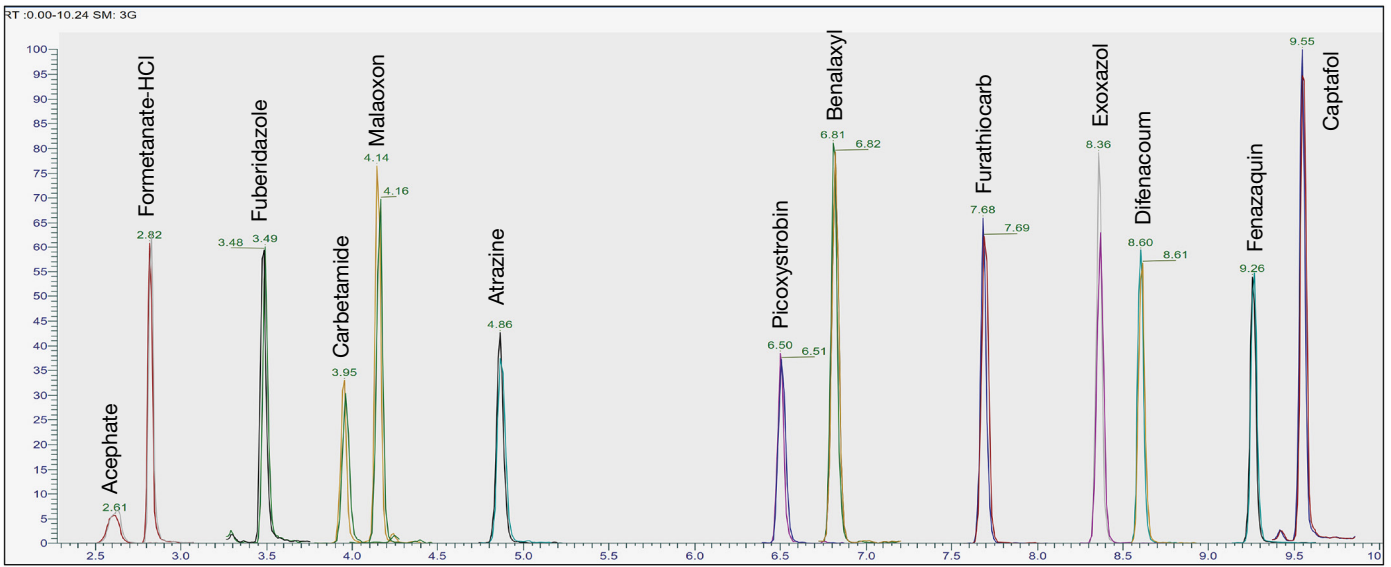


Figure 4. LC-MS/MS extracted ion chromatograms of spiked white wine of select pesticides (overlay of injection #1 and injection # 300) demonstrate good robustness of the analytical system and API source.

Appendix

Table A1 (part 1). Name of the compound, RT, polarity, SRM, LOQ, and %Recovery

| Compound | Retention time (min) | Polarity | Precursor (m/z) | Product (m/z) | Product (m/z) | Product (m/z) | MES LOQ (µg/kg) | Average % recovery at LOQ (µg/kg) (n=6) |
|---|----------------------|----------|-----------------|---------------|---------------|---------------|-----------------|---|
| 2-methyl-4-6-dinitrophenol (DNOC) | 5.01 | Negative | 197.020 | 109.042 | 137.000 | | 25 | 75 |
| 3,4,5-trimethacarb | 5.17 | Positive | 194.117 | 106.899 | 122.000 | | 1 | 86 |
| 3-hydroxycarbofuran | 3.38 | Positive | 238.107 | 135.000 | 163.054 | | 1 | 70 |
| Abamectin | 8.99 | Positive | 890.512 | 305.012 | 306.970 | | 25 | 71 |
| Acetamiprid | 3.52 | Positive | 223.074 | 89.774 | 98.702 | 125.702 | 10 | 98 |
| Acetochlor | 6.44 | Positive | 270.125 | 133.042 | 148.071 | 224.060 | 10 | 72 |
| Albendazole | 5.38 | Positive | 266.095 | 158.970 | 190.845 | 233.929 | 0.5 | 110 |
| Aldicarb | 3.86 | Positive | 208.050 | 69.929 | 88.970 | 115.929 | 10 | 102 |
| Aldicarb-sulfone-NH ₄ ⁺ | 3.00 | Positive | 240.101 | 86.000 | 166.042 | 222.970 | 5 | 70 |
| Allethrin | 7.90 | Positive | 303.195 | 90.929 | 122.982 | 134.929 | 5 | 77 |
| Allidochlor | 3.91 | Positive | 174.068 | 80.929 | 97.946 | 105.774 | 2.5 | 76 |
| Alloxidim-sodio | 6.44 | Positive | 324.181 | 178.083 | 234.083 | 266.155 | 0.5 | 100 |
| Ametoctradin | 7.51 | Positive | 276.218 | 149.000 | 176.000 | 176.970 | 100 | 83 |
| Ametryn | 5.09 | Positive | 228.127 | 67.917 | 95.899 | 185.899 | 1 | 94 |
| Amicarbazone | 4.06 | Positive | 242.161 | 42.857 | 84.929 | 142.857 | 25 | 73 |
| Ancymidol | 4.27 | Positive | 257.128 | 76.857 | 80.827 | 134.845 | 2.5 | 87 |
| Anilofos2 | 6.86 | Positive | 368.030 | 124.845 | 170.887 | 198.762 | 1 | 99 |
| Aramite-NH ₄ ⁺ | 8.04 | Positive | 352.134 | 57.054 | 191.125 | 255.054 | 2.5 | 102 |
| Aspon | 8.47 | Positive | 379.092 | 114.762 | 210.607 | 336.774 | 0.5 | 100 |
| Atraton | 4.14 | Positive | 212.150 | 99.929 | 113.857 | 169.929 | 0.5 | 106 |
| Atrazine | 4.98 | Positive | 216.101 | 95.970 | 103.917 | 173.970 | 1 | 90 |
| Atrazine-desethyl | 3.68 | Positive | 188.069 | 103.845 | 109.917 | 145.917 | 2.5 | 104 |
| Atrazine-desisopropyl | 3.34 | Positive | 174.054 | 95.917 | 103.845 | 131.917 | 10 | 11 |
| Azaconazole | 5.32 | Positive | 300.030 | 122.845 | 158.845 | 230.845 | 2.5 | 95 |
| Azamethiphos | 4.09 | Positive | 324.980 | 111.845 | 138.845 | 182.833 | 0.5 | 83 |
| Azimsulfuron | 5.03 | Positive | 425.109 | 139.000 | 181.917 | 226.970 | 0.5 | 110 |
| Azinphos-ethyl | 6.43 | Positive | 346.044 | 76.917 | 131.917 | 260.887 | 25 | 74 |
| Azoxystrobin | 5.51 | Positive | 404.124 | 328.857 | 343.929 | 371.929 | 10 | 81 |
| Beflubutamid | 6.73 | Positive | 356.126 | 64.857 | 90.845 | 161.929 | 2.5 | 82 |
| Benalaxyl | 6.95 | Positive | 326.175 | 148.000 | 207.929 | 293.929 | 2.5 | 87 |
| Benazolin-ethylester | 5.55 | Positive | 272.014 | 169.774 | 197.833 | 225.744 | 1 | 84 |
| Benodanil | 4.90 | Positive | 323.987 | 75.929 | 202.762 | 230.762 | 1 | 104 |
| Benoxacor | 5.34 | Positive | 260.023 | 119.917 | 133.857 | 148.929 | 2.5 | 84 |
| Bensulfuron-methyl | 5.32 | Positive | 411.096 | 91.000 | 149.000 | 181.970 | 0.5 | 89 |
| Bensulide | 6.66 | Positive | 398.067 | 157.917 | 217.845 | 313.690 | 25 | 83 |
| Benthiavalicarb-isopropyl | 5.91 | Positive | 382.159 | 115.929 | 179.845 | 196.845 | 2.5 | 96 |
| Benzoaminopurine | 3.94 | Positive | 226.108 | 64.917 | 90.845 | 147.988 | 1 | 71 |
| Benzofap | 7.64 | Positive | 431.092 | 104.857 | 118.875 | 132.988 | 0.5 | 87 |
| Benzoximate | 7.24 | Positive | 364.094 | 104.845 | 183.815 | 198.774 | 2.5 | 93 |

Table A1 (part 2). Name of the compound, RT, polarity, SRM, LOQ, and %Recovery

| Compound | Retention time (min) | Polarity | Precursor (m/z) | Product (m/z) | Product (m/z) | Product (m/z) | MES LOQ (µg/kg) | Average % recovery at LOQ (µg/kg) (n=6) |
|--|----------------------|----------|-----------------|---------------|---------------|---------------|-----------------|---|
| Benzyltrimethylhexadecylammonium chloride | 7.33 | Positive | 305.307 | 57.929 | 90.857 | 213.083 | 2.5 | 89 |
| Benzyltrimethylhexadecylammonium chloride | 9.05 | Positive | 361.370 | 57.929 | 90.845 | 269.095 | 1 | 87 |
| Benzyltrimethyltetradecylammonium chloride | 8.27 | Positive | 333.339 | 58.000 | 90.786 | 241.167 | 2.5 | 97 |
| Bifenazate | 6.19 | Positive | 301.154 | 151.929 | 170.000 | 197.857 | 10 | 94 |
| Bifenthrin-NH ₄ ⁺ | 9.51 | Positive | 440.088 | 165.083 | 166.125 | 181.125 | 10 | 82 |
| Bioallethrin | 7.95 | Positive | 303.195 | 92.845 | 122.929 | 134.857 | 0.5 | 82 |
| Bioresmethrin | 8.99 | Positive | 339.195 | 127.946 | 142.929 | 170.929 | 0.5 | 87 |
| Bolster (sulprofos) | 8.34 | Positive | 323.035 | 154.917 | 218.815 | 246.845 | 2.5 | 90 |
| Boscalid | 5.82 | Positive | 343.039 | 270.940 | 271.970 | 306.845 | 10 | 73 |
| Brodifacoum | 9.25 | Positive | 523.090 | 177.917 | 255.970 | 334.804 | 1 | 89 |
| Bromfeninfos | 7.01 | Positive | 402.926 | 98.762 | 154.845 | 169.762 | 1 | 87 |
| Bromobutide | 6.39 | Positive | 312.095 | 90.899 | 118.929 | 193.774 | 10 | 85 |
| Bromoxynil | 4.93 | Negative | 275.800 | 78.762 | 80.762 | 166.762 | 10 | 72 |
| Bupirimate | 6.28 | Positive | 317.164 | 165.929 | 209.940 | 237.012 | 2.5 | 86 |
| Buprofezin | 7.90 | Positive | 306.163 | 105.857 | 115.845 | 200.857 | 0.5 | 99 |
| Butafenacil-NH ₄ ⁺ | 6.17 | Positive | 492.075 | 179.815 | 330.774 | 348.845 | 2.5 | 73 |
| Butamifos | 7.09 | Positive | 333.103 | 95.851 | 151.857 | 179.857 | 0.5 | 99 |
| Butralin | 8.50 | Positive | 296.160 | 131.929 | 221.857 | 239.929 | 2.5 | 77 |
| Butylate | 7.76 | Positive | 218.157 | 56.929 | 99.929 | 156.012 | 100 | 99 |
| Butylbenzyl-phthalate | 7.59 | Positive | 313.143 | 90.970 | 148.917 | 204.857 | 10 | 93 |
| Cadusafos | 7.41 | Positive | 271.094 | 130.762 | 158.845 | 214.845 | 0.5 | 100 |
| Carbaryl | 4.58 | Positive | 202.086 | 114.929 | 126.929 | 144.929 | 2.5 | 90 |
| Carbetamide | 4.02 | Positive | 237.123 | 117.929 | 119.845 | 191.845 | 1 | 84 |
| Carbofuran | 4.24 | Positive | 222.112 | 76.929 | 122.845 | 164.929 | 10 | 120 |
| Carfentrazone-ethyl | 6.73 | Positive | 412.043 | 345.774 | 365.845 | 383.845 | 10 | 81 |
| Carpropamid | 6.92 | Positive | 334.052 | 102.917 | 138.917 | 195.845 | 10 | 89 |
| Chlorantraniliprole | 5.15 | Positive | 481.978 | 111.845 | 283.875 | 450.815 | 2.5 | 79 |
| Chlordimeform | 3.29 | Positive | 197.084 | 45.857 | 88.857 | 116.857 | 10 | 118 |
| Chlorfenvinphos | 6.98 | Positive | 358.976 | 98.774 | 154.899 | 169.815 | 2.5 | 86 |
| Chlorfluazuron | 8.68 | Positive | 539.970 | 140.988 | 157.970 | 382.833 | 2.5 | 88 |
| Chloridazon | 3.54 | Positive | 222.042 | 76.929 | 91.845 | 103.845 | 10 | 79 |
| Chlorimuron-ethyl | 5.84 | Positive | 415.047 | 82.970 | 120.845 | 185.869 | 1 | 81 |
| Chloroxuron | 6.32 | Positive | 291.089 | 45.857 | 71.917 | 217.845 | 10 | 83 |
| Chlorpyrifos | 8.34 | Positive | 349.933 | 96.833 | 197.762 | 321.679 | 2.5 | 106 |
| Cinidon-ethyl | 8.20 | Positive | 394.060 | 106.857 | 347.917 | 365.917 | 10 | 87 |
| Clethodim | 7.64 | Positive | 360.139 | 163.929 | 166.000 | 267.982 | 10 | 74 |
| Climbazol | 5.12 | Positive | 293.105 | 69.000 | 196.917 | 224.952 | 0.5 | 87 |
| Clodinafop | 5.62 | Positive | 312.000 | 90.970 | 221.917 | 265.970 | 2.5 | 90 |
| Clodinafop-propargyl ester | 6.64 | Positive | 350.058 | 90.970 | 237.917 | 265.899 | 1 | 81 |

Table A1 (part 3). Name of the compound, RT, polarity, SRM, LOQ, and %Recovery

| Compound | Retention time (min) | Polarity | Precursor (m/z) | Product (m/z) | Product (m/z) | Product (m/z) | MES LOQ (µg/kg) | Average % recovery at LOQ (µg/kg) (n=6) |
|--|----------------------|----------|-----------------|---------------|---------------|---------------|-----------------|---|
| Clofentezine | 7.61 | Positive | 303.019 | 74.929 | 101.845 | 137.845 | 25 | 83 |
| Cloquintocet-1-methylhexyl ester | 8.16 | Positive | 336.136 | 178.917 | 191.845 | 237.917 | 0.5 | 84 |
| Coumachlor | 6.46 | Positive | 343.073 | 120.917 | 162.970 | 284.970 | 0.5 | 89 |
| Coumaphos | 7.14 | Positive | 363.021 | 226.774 | 306.762 | 334.762 | 2.5 | 103 |
| Coumatetralyl | 6.31 | Positive | 293.117 | 90.952 | 106.917 | 174.97 | 1 | 73 |
| Crimidine | 3.87 | Positive | 172.063 | 94.970 | 108.929 | 136.000 | 2.5 | 83 |
| Crufomate | 6.61 | Positive | 292.086 | 107.845 | 203.774 | 235.845 | 1 | 85 |
| Cumyluron | 6.07 | Positive | 303.125 | 90.970 | 124.899 | 184.917 | 2.5 | 79 |
| Cyanazine | 4.03 | Positive | 241.096 | 103.845 | 131.845 | 213.929 | 1 | 102 |
| Cyazofamid | 6.50 | Positive | 325.052 | 107.774 | 216.845 | 260.929 | 10 | 86 |
| Cycloate | 7.40 | Positive | 216.141 | 83.054 | 133.970 | 154.054 | 5 | 84 |
| Cyclosulfamuron | 6.33 | Positive | 422.112 | 198.857 | 217.845 | 260.917 | 0.5 | 107 |
| Cycloxydim | 7.58 | Positive | 326.178 | 106.982 | 180.000 | 280.054 | 2.5 | 91 |
| Cyflufenamid | 7.16 | Positive | 413.128 | 202.845 | 240.917 | 294.899 | 2.5 | 101 |
| Cyhalofop-butyl-NH ₄ ⁺ | 7.41 | Positive | 375.171 | 120.000 | 256.054 | 358.083 | 25 | 77 |
| Cyhalothrin-NH ₄ ⁺ | 8.56 | Positive | 467.000 | 224.970 | 423.054 | 450.042 | 10 | 81 |
| Cymiazole | 3.46 | Positive | 219.095 | 104.929 | 143.982 | 171.000 | 10 | 72 |
| Cyprazine | 4.91 | Positive | 228.101 | 107.929 | 143.988 | 185.970 | 0.5 | 94 |
| Cyproconazole | 6.00 | Positive | 292.121 | 69.917 | 88.970 | 124.899 | 2.5 | 80 |
| Cyprodinil | 6.96 | Positive | 226.133 | 92.857 | 107.857 | 117.857 | 25 | 87 |
| DEF | 8.90 | Positive | 315.103 | 112.762 | 168.845 | 224.899 | 0.5 | 85 |
| Deltamethrin-NH ₄ ⁺ | 8.81 | Positive | 522.900 | 180.970 | 280.833 | 505.833 | 10 | 77 |
| Demeton-S-methyl | 4.37 | Positive | 231.027 | 54.929 | 60.917 | 88.899 | 5 | 75 |
| Desmedipham | 5.12 | Positive | 318.145 | 107.857 | 135.899 | 181.982 | 10 | 87 |
| Desmetryne | 4.53 | Positive | 214.112 | 81.845 | 90.845 | 171.899 | 0.5 | 105 |
| Dialifos | 7.42 | Positive | 394.009 | 180.845 | 186.815 | 207.845 | 10 | 76 |
| Diallate | 7.58 | Positive | 270.048 | 85.982 | 108.762 | 128.000 | 25 | 75 |
| Diclobutrazol | 6.76 | Positive | 328.097 | 69.917 | 122.845 | 158.845 | 10 | 84 |
| Diclofop-methyl | 7.97 | Positive | 358.050 | 119.929 | 280.845 | 340.845 | 10 | 66 |
| Diclosulam | 4.52 | Positive | 405.993 | 124.899 | 160.899 | 377.887 | 2.5 | 79 |
| Dicyclohexyl-phthalate | 8.49 | Positive | 331.190 | 148.970 | 166.970 | 249.054 | 0.5 | 101 |
| Diethofencarb | 5.46 | Positive | 268.154 | 123.917 | 179.929 | 225.929 | 0.5 | 92 |
| Difenacoum | 8.68 | Positive | 445.179 | 175.042 | 179.054 | 257.054 | 1 | 72 |
| Difenoconazole | 7.52 | Positive | 406.071 | 187.845 | 250.845 | 336.845 | 2.5 | 105 |
| Difenoxuron | 5.15 | Positive | 287.000 | 71.929 | 94.970 | 122.899 | 1 | 99 |
| Diflufenican | 7.60 | Positive | 395.000 | 217.899 | 245.899 | 265.970 | 2.5 | 81 |
| Dimefox | 3.31 | Positive | 155.074 | 43.929 | 109.917 | 135.000 | 0.5 | 90 |
| Dimefuron | 5.30 | Positive | 339.121 | 71.929 | 166.917 | 255.917 | 10 | 78 |
| Dimepiperate | 7.47 | Positive | 264.141 | 90.970 | 119.000 | 146.000 | 1 | 90 |

Table A1 (part 4). Name of the compound, RT, polarity, SRM, LOQ, and %Recovery

| Compound | Retention time (min) | Polarity | Precursor (m/z) | Product (m/z) | Product (m/z) | Product (m/z) | MES LOQ (µg/kg) | Average % recovery at LOQ (µg/kg) (n=6) |
|-----------------------|----------------------|----------|-----------------|---------------|---------------|---------------|-----------------|---|
| Dimethametrin | 6.39 | Positive | 256.159 | 67.845 | 90.845 | 185.845 | 1 | 89 |
| Dimethenamid | 5.68 | Positive | 276.081 | 110.845 | 167.929 | 243.917 | 2.5 | 79 |
| Dimethirimol | 3.81 | Positive | 210.160 | 70.929 | 97.845 | 139.929 | 10 | 80 |
| Dimethoate | 3.49 | Positive | 230.006 | 124.845 | 170.815 | 198.762 | 1 | 90 |
| Dimethomorph | 5.80 | Positive | 388.131 | 138.845 | 164.929 | 300.845 | 10 | 83 |
| Diniconazole | 7.31 | Positive | 326.082 | 69.929 | 158.887 | 251.917 | 25 | 76 |
| Divinoterb | 7.07 | Negative | 239.000 | 176.000 | 176.899 | 207.000 | 10 | 79 |
| Diphenamid | 5.23 | Positive | 240.138 | 117.857 | 133.929 | 166.929 | 1 | 80 |
| Dipropetryn | 6.27 | Positive | 256.159 | 143.899 | 172.000 | 213.982 | 0.5 | 110 |
| Disulfoton-sulfoxide | 4.78 | Positive | 291.030 | 156.833 | 184.762 | 212.774 | 0.5 | 84 |
| Ditalimfos | 6.44 | Positive | 300.045 | 129.845 | 147.917 | 243.845 | 0.5 | 92 |
| Diuron | 5.34 | Positive | 233.024 | 45.857 | 71.917 | 159.815 | 10 | 79 |
| Dodine | 7.42 | Positive | 228.264 | 42.857 | 56.929 | 59.929 | 10 | 85 |
| Drazoxolon | 6.60 | Positive | 238.037 | 98.988 | 129.786 | 176.756 | 10 | 78 |
| Edifenphos | 6.92 | Positive | 311.032 | 108.845 | 110.845 | 282.845 | 1 | 87 |
| Emamectin-benzoate | 8.17 | Positive | 886.538 | 81.929 | 125.929 | 158.000 | 2.5 | 72 |
| Epoxiconazole | 6.44 | Positive | 330.080 | 100.917 | 120.899 | 122.917 | 2.5 | 79 |
| Etaconazole | 6.40 | Positive | 328.061 | 122.917 | 158.917 | 204.887 | 2.5 | 86 |
| Ethiofencarb-sulfone | 3.26 | Positive | 258.079 | 76.929 | 106.845 | 200.845 | 2.5 | 12 |
| Ethion | 8.12 | Positive | 384.994 | 142.762 | 170.815 | 198.774 | 0.5 | 98 |
| Ethofumesate | 5.57 | Positive | 287.094 | 120.929 | 160.929 | 258.899 | 10 | 90 |
| Ethoprop (ethoprofos) | 6.28 | Positive | 243.063 | 96.905 | 130.905 | 172.958 | 0.5 | 108 |
| Etobenzanid | 7.01 | Positive | 340.050 | 120.970 | 149.000 | 178.970 | 1 | 78 |
| Etrimfos | 6.92 | Positive | 293.071 | 124.845 | 232.845 | 264.917 | 10 | 80 |
| Famoxadone | 7.07 | Positive | 392.160 | 194.827 | 237.911 | 330.911 | 25 | 86 |
| Fenamidone | 5.65 | Positive | 312.116 | 91.899 | 235.929 | 264.000 | 2.5 | 79 |
| Fenamiphos | 6.59 | Positive | 304.113 | 201.774 | 216.845 | 233.917 | 2.5 | 77 |
| Fenamiphos-sulfoxide | 4.22 | Positive | 320.107 | 107.929 | 232.845 | 291.899 | 1 | 96 |
| Fenarimol | 6.32 | Positive | 331.039 | 80.899 | 188.845 | 258.845 | 2.5 | 96 |
| Fenazaquin | 9.38 | Positive | 307.180 | 56.929 | 130.929 | 161.054 | 0.5 | 107 |
| Fenbuconazole | 6.56 | Positive | 337.121 | 69.917 | 88.899 | 124.845 | 10 | 78 |
| Fenbutatin-oxide | 9.94 | Positive | 519.175 | 288.917 | 350.917 | 463.000 | 10 | 112 |
| Fenchlorazol-ethyl | 7.04 | Positive | 401.913 | 285.875 | 355.804 | 373.804 | 2.5 | 80 |
| Fenfuram | 4.65 | Positive | 202.086 | 82.929 | 108.845 | 119.845 | 0.5 | 98 |
| Fenhexamid | 6.18 | Positive | 302.070 | 54.929 | 96.929 | 141.845 | 100 | 84 |
| Fenobucarb | 5.50 | Positive | 208.133 | 76.970 | 94.917 | 151.970 | 2.5 | 81 |
| Fenotiocarb | 6.73 | Positive | 254.121 | 72.000 | 149.054 | 160.125 | 2.5 | 81 |
| Fenoxanil | 6.50 | Positive | 329.081 | 86.054 | 188.887 | 301.917 | 2.5 | 87 |
| Fenoxaprop-p-ethyl | 7.71 | Positive | 362.078 | 119.000 | 121.042 | 243.970 | 1 | 102 |
| Fenpropathrin | 8.45 | Positive | 350.175 | 55.000 | 97.071 | 125.054 | 2.5 | 79 |

Table A1 (part 5). Name of the compound, RT, polarity, SRM, LOQ, and %Recovery

| Compound | Retention time (min) | Polarity | Precursor (m/z) | Product (m/z) | Product (m/z) | Product (m/z) | MES LOQ (µg/kg) | Average % recovery at LOQ (µg/kg) (n=6) |
|---|----------------------|----------|-----------------|---------------|---------------|---------------|-----------------|---|
| Fenpropidin | 5.36 | Positive | 274.252 | 85.929 | 116.857 | 146.929 | 1 | 85 |
| Fenpropimorph | 5.42 | Positive | 304.263 | 117.000 | 130.054 | 147.054 | 0.5 | 99 |
| Fenpyrazamine | 5.95 | Positive | 332.142 | 216.054 | 230.083 | 231.054 | 1 | 105 |
| Fenpyroximate | 8.75 | Positive | 422.207 | 213.958 | 214.929 | 366.012 | 0.5 | 94 |
| Fensulfothion | 5.06 | Positive | 309.037 | 172.845 | 252.845 | 280.845 | 2.5 | 87 |
| Fenthion-sulfone | 4.51 | Positive | 311.017 | 108.917 | 124.917 | 278.917 | 0.5 | 100 |
| Fentrazamide | 6.91 | Positive | 350.137 | 83.000 | 154.054 | 196.929 | 10 | 87 |
| Fenuron | 3.50 | Positive | 165.102 | 45.857 | 71.917 | 76.899 | 10 | 81 |
| Fipronil-sulfone | 6.90 | Negative | 450.926 | 243.970 | 282.000 | 414.917 | 1 | 91 |
| Flamprop | 5.40 | Positive | 322.000 | 76.970 | 104.917 | 171.970 | 2.5 | 93 |
| Flamprop-isopropyl | 6.83 | Positive | 364.111 | 76.970 | 104.917 | 303.917 | 0.5 | 92 |
| Flamprop-methyl | 5.94 | Positive | 336.079 | 77.000 | 104.917 | 303.970 | 10 | 77 |
| Fluazifop | 5.59 | Positive | 328.079 | 90.899 | 253.929 | 281.929 | 10 | 88 |
| Fluazinam | 7.96 | Negative | 462.958 | 369.845 | 397.917 | 415.917 | 10 | 92 |
| Fluazuron | 8.17 | Positive | 506.000 | 140.988 | 157.970 | 348.887 | 0.5 | 102 |
| Flubendiamide | 6.72 | Positive | 683.030 | 255.792 | 273.833 | 407.887 | 100 | 106 |
| Flucycloxuron | 8.30 | Positive | 484.123 | 132.000 | 170.042 | 289.042 | 0.5 | 109 |
| Fludioxonil | 5.95 | Negative | 247.032 | 125.929 | 168.857 | 179.857 | 10 | 71 |
| Flufenacet | 6.31 | Positive | 364.073 | 123.929 | 151.970 | 193.929 | 1 | 91 |
| Flufenoxuron | 8.48 | Positive | 489.043 | 112.917 | 140.917 | 157.970 | 1 | 74 |
| Fluometuron | 4.77 | Positive | 233.089 | 45.857 | 71.917 | 159.899 | 1 | 74 |
| Fluopyram | 6.16 | Positive | 397.053 | 144.845 | 172.845 | 207.845 | 2.5 | 75 |
| Fluorochloridon | 6.04 | Positive | 312.016 | 52.929 | 144.845 | 291.917 | 5 | 80 |
| Fluoroglycofen-ethyl-NH ₄ ⁺ | 7.48 | Positive | 465.000 | 222.845 | 343.560 | 447.774 | 1 | 77 |
| Fluoxastrobin | 6.18 | Positive | 459.086 | 187.845 | 305.845 | 426.917 | 2.5 | 73 |
| Fluridone | 5.35 | Positive | 330.110 | 293.899 | 308.929 | 309.827 | 0.5 | 106 |
| Flurtamone | 5.59 | Positive | 334.104 | 177.786 | 227.000 | 246.929 | 0.5 | 101 |
| Flusulfamide | 7.14 | Negative | 412.938 | 170.845 | 266.714 | 282.756 | 10 | 86 |
| Fluthiacet-methyl | 6.77 | Positive | 404.030 | 214.845 | 273.887 | 343.899 | 1 | 99 |
| Flutolanil | 5.89 | Positive | 324.106 | 241.929 | 261.929 | 281.929 | 0.5 | 90 |
| Flutriafol | 4.87 | Positive | 302.109 | 69.917 | 94.917 | 122.845 | 1 | 85 |
| Fluxapyroxad | 5.87 | Positive | 382.097 | 313.970 | 341.929 | 362.000 | 0.5 | 90 |
| Foramsulfuron | 4.45 | Positive | 453.118 | 139.000 | 181.899 | 272.042 | 0.5 | 100 |
| Forchlorfenuron (CPPU) | 5.25 | Positive | 248.058 | 92.917 | 128.845 | 154.845 | 1 | 75 |
| Formetanate-hydrochloride | 2.83 | Positive | 222.123 | 45.929 | 92.845 | 165.000 | 1 | 77 |
| Formothion | 3.92 | Positive | 258.002 | 124.917 | 170.917 | 198.833 | 10 | 74 |
| Fosthiazate | 4.65 | Positive | 284.053 | 103.845 | 199.762 | 227.845 | 1 | 85 |
| Fuberidazole | 3.51 | Positive | 185.070 | 130.000 | 156.012 | 157.000 | 1 | 87 |
| Furalaxyl | 5.43 | Positive | 302.138 | 94.845 | 242.000 | 269.982 | 0.5 | 98 |

Table A1 (part 6). Name of the compound, RT, polarity, SRM, LOQ, and %Recovery

| Compound | Retention time (min) | Polarity | Precursor (m/z) | Product (m/z) | Product (m/z) | Product (m/z) | MES LOQ (µg/kg) | Average % recovery at LOQ (µg/kg) (n=6) |
|---------------------------|----------------------|----------|-----------------|---------------|---------------|---------------|-----------------|---|
| Furathiocarb | 7.81 | Positive | 383.163 | 166.970 | 194.845 | 251.929 | 2.5 | 93 |
| Furmecycloz | 6.80 | Positive | 252.159 | 109.929 | 122.899 | 169.982 | 0.5 | 80 |
| Guthion (azinphos-methyl) | 5.42 | Positive | 318.013 | 124.875 | 131.804 | 159.893 | 10 | 79 |
| Halosulfuron-methyl | 6.23 | Positive | 435.048 | 83.042 | 138.970 | 181.988 | 0.5 | 117 |
| Haloxypop | 6.62 | Positive | 362.040 | 271.958 | 287.845 | 315.649 | 25 | 84 |
| Haloxypop-2-ethoxyethyl | 7.72 | Positive | 434.097 | 90.929 | 287.845 | 315.845 | 0.5 | 116 |
| Haloxypop-methyl | 7.39 | Positive | 376.055 | 90.857 | 287.917 | 315.845 | 0.5 | 111 |
| Heptenophos | 5.16 | Positive | 251.023 | 108.845 | 124.899 | 126.917 | 2.5 | 72 |
| Hexaconazole | 7.00 | Positive | 314.082 | 69.899 | 124.899 | 158.845 | 10 | 76 |
| Hexaflumuron | 7.71 | Positive | 460.988 | 113.000 | 140.988 | 158.042 | 25 | 95 |
| Hexazinone | 4.38 | Positive | 253.165 | 71.018 | 85.071 | 171.054 | 1 | 77 |
| Hexythiazox | 8.28 | Positive | 353.108 | 115.018 | 168.042 | 227.988 | 2.5 | 77 |
| Hydramethylnon | 7.52 | Positive | 495.197 | 150.929 | 170.970 | 322.982 | 0.5 | 118 |
| Imazalil | 4.78 | Positive | 297.055 | 158.958 | 176.006 | 200.863 | 25 | 73 |
| Imazamethabenz-methyl | 4.13 | Positive | 289.154 | 143.899 | 161.000 | 228.982 | 1 | 102 |
| Imazamox | 3.48 | Positive | 306.144 | 192.917 | 261.054 | 264.000 | 0.5 | 80 |
| Imazapic | 3.55 | Positive | 276.000 | 162.970 | 216.000 | 231.000 | 0.5 | 104 |
| Imazethapyr | 3.87 | Positive | 290.149 | 176.970 | 229.929 | 245.012 | 1 | 86 |
| Imibenconazole | 8.11 | Positive | 410.999 | 124.988 | 170.988 | 341.863 | 10 | 71 |
| Indoxacarb | 7.39 | Positive | 528.077 | 202.845 | 248.970 | 292.899 | 10 | 89 |
| Ipconazole | 7.50 | Positive | 334.168 | 69.929 | 124.899 | 190.899 | 1 | 81 |
| Iprobenfos | 6.71 | Positive | 289.102 | 91.042 | 204.935 | 246.988 | 0.5 | 83 |
| Iprovalicarb | 6.07 | Positive | 321.217 | 119.018 | 186.018 | 203.071 | 2 | 77 |
| Isazophos | 6.02 | Positive | 314.048 | 96.833 | 119.845 | 161.970 | 1 | 83 |
| Isocarbamid | 3.69 | Positive | 186.123 | 44.000 | 87.060 | 130.042 | 10 | 79 |
| Isocarbofos | 4.99 | Positive | 307.000 | 120.988 | 230.917 | 272.988 | 2.5 | 91 |
| Isfenphos | 7.16 | Positive | 346.123 | 120.988 | 216.887 | 244.917 | 0.5 | 117 |
| Isfenphos-methyl | 6.65 | Positive | 332.107 | 120.899 | 230.917 | 272.970 | 1 | 85 |
| Isomethiozin | 6.85 | Positive | 269.143 | 115.917 | 172.054 | 199.929 | 0.5 | 84 |
| Isoprocab | 4.88 | Positive | 194.117 | 76.988 | 94.970 | 137.071 | 1 | 85 |
| Isopropalin | 8.79 | Positive | 310.176 | 206.000 | 207.970 | 226.054 | 10 | 80 |
| Isoprothiolane | 5.96 | Positive | 291.071 | 144.887 | 188.887 | 230.970 | 1 | 96 |
| Isoproturon | 5.10 | Positive | 207.149 | 45.946 | 71.988 | 165.071 | 25 | 71 |
| Isouron | 4.36 | Positive | 212.139 | 45.929 | 71.929 | 167.054 | 0.5 | 106 |
| Isxadifen-ethyl | 6.62 | Positive | 296.128 | 203.929 | 231.929 | 263.054 | 1 | 79 |
| Isoxaflutole | 4.95 | Positive | 360.051 | 143.917 | 219.845 | 250.917 | 10 | 76 |
| Isoxathion | 7.16 | Positive | 314.061 | 96.762 | 104.845 | 285.899 | 1 | 87 |
| Kadethrin | 7.53 | Positive | 397.146 | 128.000 | 143.000 | 171.054 | 50 | 71 |
| Kresoxim-methyl | 6.73 | Positive | 314.138 | 116.000 | 222.071 | 267.071 | 10 | 79 |
| Lactofen | 7.83 | Positive | 462.000 | 222.845 | 299.815 | 343.845 | 50 | 85 |
| Linuron | 5.82 | Positive | 249.019 | 132.905 | 159.976 | 181.988 | 2.5 | 71 |

Table A1 (part 7). Name of the compound, RT, polarity, SRM, LOQ, and %Recovery

| Compound | Retention time (min) | Polarity | Precursor (m/z) | Product (m/z) | Product (m/z) | Product (m/z) | MES LOQ (µg/kg) | Average % recovery at LOQ (µg/kg) (n=6) |
|-------------------------------------|----------------------|----------|-----------------|---------------|---------------|---------------|-----------------|---|
| Lufenuron | 8.22 | Positive | 511.000 | 112.988 | 140.988 | 158.042 | 10 | 72 |
| Malaoxon | 4.21 | Positive | 315.066 | 98.935 | 126.988 | 268.988 | 1 | 78 |
| Malathion | 5.81 | Positive | 331.043 | 98.887 | 126.899 | 284.899 | 2.5 | 81 |
| Mandipropamid | 5.79 | Positive | 412.131 | 124.935 | 328.018 | 356.018 | 2.5 | 86 |
| Mecarbam | 6.30 | Positive | 330.059 | 96.887 | 198.815 | 226.917 | 1 | 98 |
| Mefenacet | 6.17 | Positive | 299.084 | 120.000 | 148.000 | 191.845 | 1 | 83 |
| Mefenpyr-diethyl | 6.92 | Positive | 373.071 | 159.917 | 185.845 | 252.917 | 2.5 | 78 |
| Mephosfolan | 4.09 | Positive | 270.038 | 139.833 | 167.899 | 195.845 | 0.5 | 94 |
| Mepronil | 5.95 | Positive | 270.148 | 91.000 | 118.970 | 228.054 | 1 | 70 |
| Mesosulfuron-methyl | 4.80 | Positive | 504.085 | 139.000 | 181.970 | 305.863 | 0.5 | 98 |
| Metaflumizone | 7.97 | Positive | 507.125 | 177.970 | 220.970 | 287.000 | 10 | 87 |
| Metconazole | 7.13 | Positive | 320.152 | 69.970 | 89.000 | 124.970 | 10 | 70 |
| Methabenzthiazuron | 5.28 | Positive | 222.069 | 95.917 | 149.917 | 164.970 | 0.5 | 73 |
| Methiocarb | 5.78 | Positive | 226.089 | 77.000 | 121.000 | 169.054 | 2.5 | 87 |
| Methiocarb-sulfone | 3.49 | Positive | 258.079 | 106.917 | 122.071 | 200.970 | 5 | 82 |
| Methiocarb-sulfoxide | 3.35 | Positive | 242.084 | 122.000 | 169.970 | 184.970 | 1 | 91 |
| Methomyl | 3.12 | Positive | 163.053 | 57.970 | 87.970 | 105.917 | 2.5 | 72 |
| Methyl-paraoxon | 3.95 | Positive | 248.031 | 89.970 | 108.917 | 201.917 | 25 | 73 |
| Metolachlor | 6.42 | Positive | 284.141 | 134.000 | 176.054 | 252.054 | 0.5 | 102 |
| Metolcarb | 4.06 | Positive | 166.086 | 91.000 | 93.970 | 108.929 | 2.5 | 86 |
| Metosulam | 4.32 | Positive | 418.013 | 139.917 | 174.917 | 189.815 | 10 | 74 |
| Metoxuron | 3.90 | Positive | 229.073 | 45.929 | 71.929 | 155.970 | 2.5 | 77 |
| Metrafenone | 7.28 | Positive | 409.064 | 165.982 | 208.929 | 226.845 | 2.5 | 88 |
| Metsulfuron-methyl | 4.18 | Positive | 382.081 | 134.970 | 166.970 | 198.845 | 2.5 | 71 |
| Mexacarbate | 3.44 | Positive | 223.144 | 136.000 | 151.000 | 166.054 | 0.5 | 103 |
| Molinate | 6.16 | Positive | 188.110 | 54.982 | 98.000 | 126.054 | 10 | 73 |
| Monalide | 6.42 | Positive | 240.114 | 42.929 | 56.929 | 85.054 | 10 | 76 |
| Monocrotophos | 3.18 | Positive | 224.068 | 97.827 | 126.899 | 192.845 | 10 | 78 |
| Monolinuron | 4.78 | Positive | 215.058 | 98.917 | 125.917 | 148.000 | 1 | 83 |
| N-1-naphthylphthalamic acid | 4.17 | Positive | 292.096 | 127.000 | 144.000 | 148.917 | 10 | 79 |
| Naled-NH ₄ ⁺ | 5.17 | Positive | 398.000 | 108.917 | 126.899 | 175.75 | 10 | 73 |
| Napropamide | 6.42 | Positive | 272.164 | 129.054 | 171.054 | 198.899 | 1 | 78 |
| Neburon | 6.77 | Positive | 275.071 | 57.000 | 88.054 | 114.000 | 10 | 86 |
| Nicosulfuron | 4.14 | Positive | 411.108 | 105.917 | 181.988 | 212.970 | 10 | 71 |
| Orbencarb | 7.23 | Positive | 258.071 | 88.970 | 100.000 | 124.899 | 0.5 | 109 |
| Oxadiargyl | 7.00 | Positive | 341.045 | 150.988 | 222.917 | 229.958 | 2.5 | 82 |
| Oxadiazon | 8.01 | Positive | 345.076 | 176.887 | 219.887 | 302.917 | 25 | 113 |
| Oxadixyl | 3.87 | Positive | 279.133 | 116.929 | 132.000 | 219.054 | 1 | 88 |
| Oxamyl-NH ₄ ⁺ | 3.02 | Positive | 237.025 | 71.970 | 89.970 | 220.000 | 1 | 80 |
| Oxathiapiprolin | 5.76 | Positive | 540.148 | 350.054 | 500.012 | 522.083 | 2.5 | 84 |

Table A1 (part 8). Name of the compound, RT, polarity, SRM, LOQ, and %Recovery

| Compound | Retention time (min) | Polarity | Precursor (m/z) | Product (m/z) | Product (m/z) | Product (m/z) | MES LOQ (µg/kg) | Average % recovery at LOQ (µg/kg) (n=6) |
|---|----------------------|----------|-----------------|---------------|---------------|---------------|-----------------|---|
| Oxycarboxin | 3.57 | Positive | 268.063 | 119.970 | 146.917 | 174.899 | 10 | 83 |
| Oxydemeton-methyl | 3.09 | Positive | 247.022 | 108.845 | 124.917 | 168.970 | 0.5 | 113 |
| Paclobutrazol | 5.85 | Positive | 294.136 | 69.970 | 89.000 | 124.899 | 10 | 88 |
| Paraoxon | 4.85 | Positive | 276.063 | 93.970 | 173.97 | 219.917 | 0.5 | 111 |
| Pebulate | 7.35 | Positive | 204.141 | 57.054 | 71.970 | 128.054 | 10 | 94 |
| Penconazole | 6.91 | Positive | 284.071 | 69.917 | 122.917 | 158.917 | 10 | 83 |
| Pencycuron | 7.33 | Positive | 329.141 | 88.970 | 124.917 | 218.000 | 2.5 | 84 |
| Pendimethalin | 8.42 | Positive | 282.144 | 118.000 | 193.917 | 211.970 | 10 | 83 |
| Pentachlor | 6.65 | Positive | 240.114 | 71.000 | 106.929 | 141.988 | 0.5 | 98 |
| Pethoxamid | 6.19 | Positive | 296.141 | 91.000 | 131.000 | 250.000 | 0.5 | 114 |
| Phorate-sulfone | 4.84 | Positive | 293.009 | 114.815 | 142.917 | 170.970 | 1 | 82 |
| Phorate-sulfoxide | 4.76 | Positive | 277.015 | 142.833 | 170.887 | 198.815 | 0.5 | 99 |
| Phosmet | 5.51 | Positive | 318.001 | 77.000 | 132.970 | 159.970 | 1 | 74 |
| Phosphamidon | 3.90 | Positive | 300.076 | 76.113 | 132.167 | 174.167 | 10 | 93 |
| Phoxim | 7.17 | Positive | 299.061 | 77.125 | 97.030 | 129.113 | 2.5 | 92 |
| Picolinafen | 8.20 | Positive | 377.090 | 145.113 | 238.125 | 359.071 | 0.5 | 103 |
| Picoxystrobin | 6.62 | Positive | 368.110 | 115.196 | 145.113 | 205.143 | 10 | 73 |
| Piperophos | 7.44 | Positive | 354.132 | 170.887 | 212.815 | 254.970 | 2.5 | 78 |
| Pirimicarb | 3.95 | Positive | 239.150 | 71.970 | 181.982 | 194.982 | 1 | 91 |
| Pirimicarb-desmethyl | 3.31 | Positive | 225.134 | 71.929 | 168.054 | 180.000 | 1 | 95 |
| Pirimicarb-desmethyl-formamido | 4.17 | Positive | 253.129 | 71.970 | 195.929 | 225.054 | 2.5 | 87 |
| Pirimiphos-ethyl | 7.89 | Positive | 334.134 | 170.000 | 182.054 | 197.929 | 0.5 | 95 |
| Pirimiphos-methyl | 7.09 | Positive | 306.103 | 66.917 | 107.929 | 164.054 | 25 | 77 |
| Pretilachlor | 7.50 | Positive | 312.172 | 132.000 | 176.054 | 252.071 | 0.5 | 97 |
| Primisulfuron-methyl | 5.92 | Positive | 469.043 | 198.845 | 253.899 | 436.899 | 2.5 | 75 |
| Prochloraz | 7.15 | Positive | 376.038 | 69.929 | 265.887 | 307.815 | 10 | 82 |
| Profenophos | 7.80 | Positive | 372.942 | 127.917 | 302.720 | 344.833 | 2.5 | 92 |
| Promecarb | 5.82 | Positive | 208.133 | 91.000 | 108.929 | 151.054 | 2.5 | 89 |
| Prometon | 4.63 | Positive | 226.166 | 85.970 | 142.000 | 184.000 | 0.5 | 102 |
| Prometryn | 5.74 | Positive | 242.143 | 67.917 | 157.970 | 199.929 | 2.5 | 75 |
| Pronamide | 5.97 | Positive | 256.029 | 144.887 | 172.887 | 189.887 | 0.5 | 88 |
| Propamocarb | 2.87 | Positive | 189.159 | 73.970 | 101.917 | 144.000 | 0.5 | 104 |
| Propaquizafop | 7.87 | Positive | 444.132 | 99.929 | 298.899 | 371.000 | 0.5 | 77 |
| Propargite-NH ₄ ⁺ | 8.37 | Positive | 368.000 | 106.970 | 175.054 | 231.065 | 0.5 | 97 |
| Propiconazole | 7.00 | Positive | 342.077 | 69.000 | 122.917 | 158.917 | 2.5 | 88 |
| Propoxur | 4.17 | Positive | 210.112 | 92.970 | 110.917 | 168.054 | 2.5 | 86 |
| Pyracarbolid | 4.37 | Positive | 218.117 | 96.917 | 106.917 | 124.970 | 10 | 95 |
| Pyraclufos | 7.21 | Positive | 361.053 | 137.917 | 139.917 | 256.917 | 25 | 70 |
| Pyraclostrobin | 7.16 | Positive | 388.105 | 162.982 | 164.042 | 193.899 | 2.5 | 83 |
| Pyrazophos | 7.26 | Positive | 374.093 | 175.970 | 193.899 | 221.929 | 10 | 86 |

Table A1 (part 9). Name of the compound, RT, polarity, SRM, LOQ, and %Recovery

| Compound | Retention time (min) | Polarity | Precursor (m/z) | Product (m/z) | Product (m/z) | Product (m/z) | MES LOQ (µg/kg) | Average % recovery at LOQ (µg/kg) (n=6) |
|--|----------------------|----------|-----------------|---------------|---------------|---------------|-----------------|---|
| Pyrazosulfuron-ethyl | 6.19 | Positive | 415.103 | 82.970 | 138.970 | 181.970 | 1 | 105 |
| Pyretrins1 | 8.53 | Positive | 329.000 | 133.054 | 143.000 | 161.042 | 5 | 75 |
| Pyretrins2 | 7.50 | Positive | 373.000 | 104.917 | 133.000 | 143.000 | 10 | 77 |
| Pyributicarb | 8.08 | Positive | 331.147 | 133.000 | 180.899 | 189.929 | 1 | 83 |
| Pyridaben | 8.93 | Positive | 365.144 | 117.000 | 147.054 | 308.988 | 0.5 | 91 |
| Pyridalyl | 9.76 | Positive | 489.975 | 108.887 | 182.917 | 203.970 | 0.5 | 76 |
| Pyridaphenthion | 6.10 | Positive | 341.071 | 91.970 | 188.970 | 204.899 | 0.5 | 90 |
| Pyridate | 9.29 | Positive | 379.124 | 103.774 | 206.845 | 350.982 | 1 | 89 |
| Pyrifenox | 6.10 | Positive | 295.039 | 66.000 | 66.970 | 92.970 | 1 | 89 |
| Pyriftalid | 5.52 | Positive | 319.074 | 138.970 | 178.958 | 219.917 | 1 | 74 |
| Pyrimethanil | 5.78 | Positive | 200.118 | 106.917 | 168.000 | 183.042 | 2.5 | 72 |
| Pyrimidifen | 8.05 | Positive | 378.194 | 150.000 | 156.970 | 183.899 | 0.5 | 82 |
| Pyriproxyfen | 8.19 | Positive | 322.143 | 95.988 | 184.988 | 227.071 | 0.5 | 74 |
| Pyroxsulam | 4.17 | Positive | 435.069 | 124.000 | 166.000 | 194.917 | 2.5 | 83 |
| Quinalphos | 6.85 | Positive | 299.061 | 119.000 | 147.000 | 162.970 | 0.5 | 85 |
| Quinoxiphen | 8.53 | Positive | 308.003 | 161.988 | 196.833 | 271.935 | 2.5 | 83 |
| Quizalofop-ethyl | 7.74 | Positive | 373.094 | 90.970 | 271.000 | 298.899 | 0.5 | 86 |
| Quizalofop-P | 6.41 | Positive | 345.063 | 243.97 | 270.958 | 298.899 | 2.5 | 100 |
| Quizalofop-P-ethyl | 7.74 | Positive | 373.094 | 90.929 | 271.000 | 298.899 | 2.5 | 76 |
| Resmethrin | 9.00 | Positive | 339.195 | 128.000 | 143.000 | 171.071 | 1 | 112 |
| Rimsulfuron | 4.51 | Positive | 432.064 | 138.857 | 181.899 | 324.929 | 0.5 | 110 |
| Rotenone | 6.59 | Positive | 395.148 | 191.917 | 194.917 | 212.929 | 10 | 73 |
| Schradan | 3.50 | Positive | 287.139 | 134.929 | 198.917 | 242.000 | 10 | 74 |
| Sebuthylazine | 5.56 | Positive | 230.116 | 95.917 | 103.863 | 173.988 | 0.5 | 76 |
| Secbumeton | 4.63 | Positive | 226.166 | 99.917 | 113.946 | 170.000 | 0.5 | 91 |
| Sethoxydim | 7.87 | Positive | 328.194 | 178.000 | 220.000 | 282.071 | 2.5 | 70 |
| Siduron | 5.60 | Positive | 233.164 | 77.000 | 93.970 | 137.000 | 0.5 | 112 |
| Silafluofen-NH ₄ ⁺ | 9.99 | Positive | 426.000 | 168.042 | 181.042 | 287.054 | 10 | 81 |
| Simeconazole | 6.24 | Positive | 294.143 | 69.970 | 114.899 | 135.000 | 2.5 | 98 |
| Simetryn | 4.47 | Positive | 214.112 | 67.917 | 95.917 | 124.000 | 1 | 85 |
| Spinetoram | 7.56 | Positive | 748.499 | 97.946 | 142.000 | 202.946 | 10 | 74 |
| Spirodiclofen | 8.54 | Positive | 411.112 | 71.000 | 294.899 | 312.917 | 5 | 87 |
| Spiromesifen | 8.30 | Positive | 371.221 | 227.012 | 255.054 | 273.054 | 25 | 85 |
| Spirotetramat | 6.10 | Positive | 374.196 | 215.982 | 302.054 | 330.065 | 2.5 | 79 |
| Spirotetramat-enol | 4.62 | Positive | 302.175 | 145.000 | 216.000 | 270.012 | 25 | 95 |
| Spiroxamine | 5.65 | Positive | 298.274 | 72.000 | 99.929 | 144.054 | 1 | 89 |
| Succinic acid di-n-butyl ester | 6.67 | Positive | 231.159 | 72.917 | 100.917 | 157.054 | 2.5 | 93 |
| Sulfotepp | 6.72 | Positive | 323.030 | 96.833 | 114.815 | 170.970 | 10 | 74 |
| Tau-fluvalinate | 8.95 | Positive | 503.134 | 152.000 | 181.042 | 207.988 | 2.5 | 70 |
| TCMTB | 5.75 | Positive | 238.976 | 108.845 | 135.917 | 179.845 | 1 | 89 |

Table A1 (part 10). Name of the compound, RT, polarity, SRM, LOQ, and %Recovery

| Compound | Retention time (min) | Polarity | Precursor (m/z) | Product (m/z) | Product (m/z) | Product (m/z) | MES LOQ (µg/kg) | Average % recovery at LOQ (µg/kg) (n=6) |
|------------------------------|----------------------|----------|-----------------|---------------|---------------|---------------|-----------------|---|
| Tebufenpyrad | 7.82 | Positive | 334.168 | 116.917 | 144.970 | 147.054 | 2.5 | 88 |
| Tebupirimphos | 7.86 | Positive | 319.123 | 153.054 | 230.970 | 277.000 | 0.5 | 107 |
| Tebutame | 6.34 | Positive | 234.185 | 64.929 | 90.970 | 192.000 | 0.5 | 96 |
| Tebuthiuron | 4.33 | Positive | 229.111 | 115.917 | 157.000 | 172.054 | 10 | 78 |
| Temephos | 8.02 | Positive | 466.996 | 340.845 | 404.917 | 418.917 | 1 | 101 |
| TEPP | 3.86 | Positive | 291.075 | 98.845 | 178.815 | 206.815 | 0.5 | 96 |
| Tepaloxymdim | 6.16 | Positive | 342.146 | 166.054 | 222.012 | 250.012 | 10 | 76 |
| Terbucarb | 7.34 | Positive | 278.211 | 108.929 | 166.054 | 222.083 | 10 | 85 |
| Terbufos-sulfone | 5.39 | Positive | 321.041 | 96.833 | 114.833 | 142.887 | 10 | 87 |
| Terbufos-sulfoxide | 5.43 | Positive | 305.046 | 96.833 | 130.887 | 186.887 | 0.5 | 101 |
| Terbumeton | 4.69 | Positive | 226.166 | 68.917 | 113.929 | 170.054 | 0.5 | 119 |
| Terbutryn(e) | 5.83 | Positive | 242.143 | 67.988 | 90.988 | 185.988 | 1 | 107 |
| Tetrachlorvinphos | 6.58 | Positive | 364.906 | 126.970 | 203.833 | 238.762 | 0.5 | 100 |
| Tetraconazole | 6.30 | Positive | 372.028 | 69.970 | 122.917 | 158.887 | 10 | 79 |
| Tetramethrin | 7.77 | Positive | 332.185 | 135.054 | 164.000 | 314.071 | 2.5 | 81 |
| Thenylchlor | 6.25 | Positive | 324.081 | 52.929 | 58.917 | 96.863 | 10 | 90 |
| Thiabendazole | 3.47 | Positive | 202.043 | 103.917 | 130.970 | 174.970 | 1 | 78 |
| Thiazafurion | 4.42 | Positive | 241.036 | 73.970 | 163.970 | 183.887 | 0.5 | 81 |
| Thiazopyr | 6.71 | Positive | 397.100 | 316.970 | 334.899 | 377.000 | 1 | 94 |
| Thiobencarb | 7.26 | Positive | 258.071 | 89.000 | 98.917 | 124.970 | 2.5 | 77 |
| Thiodicarb | 4.69 | Positive | 355.056 | 87.970 | 107.845 | 163.042 | 10 | 95 |
| Thionazin | 4.99 | Positive | 249.000 | 96.887 | 112.917 | 192.815 | 10 | 74 |
| Thiophanate-methyl | 4.08 | Positive | 343.052 | 92.899 | 150.827 | 310.631 | 2.5 | 77 |
| Triadimefon | 5.93 | Positive | 294.100 | 140.917 | 196.899 | 224.929 | 10 | 73 |
| Triallate | 8.23 | Positive | 304.009 | 82.887 | 86.113 | 142.833 | 25 | 73 |
| Triasulfuron | 4.02 | Positive | 402.063 | 120.845 | 140.845 | 166.929 | 10 | 70 |
| Triazamate | 6.07 | Positive | 315.148 | 71.857 | 197.899 | 225.911 | 0.5 | 96 |
| Triazophos | 6.15 | Positive | 314.072 | 96.833 | 118.929 | 162.000 | 1 | 87 |
| Triazoxide | 5.46 | Positive | 248.033 | 67.917 | 94.988 | 123.917 | 2.5 | 82 |
| Tributyl phosphate | 7.47 | Positive | 267.171 | 98.815 | 155.000 | 210.839 | 2.5 | 91 |
| Triclocarban | 7.59 | Positive | 314.985 | 126.857 | 127.958 | 161.887 | 10 | 90 |
| Trietazine | 6.28 | Positive | 230.116 | 99.000 | 124.000 | 201.929 | 2.5 | 84 |
| Trifloxystrobin | 7.39 | Positive | 409.136 | 144.917 | 185.917 | 205.929 | 1 | 77 |
| Trifloxysulfuron sodium salt | 4.92 | Positive | 438.069 | 139.000 | 182.000 | 257.000 | 1 | 85 |
| Triflumizole | 7.64 | Positive | 346.092 | 42.929 | 73.000 | 277.970 | 2.5 | 71 |
| Triflumuron | 7.13 | Positive | 359.040 | 110.845 | 138.917 | 155.988 | 10 | 86 |
| Triflusulfuron-methyl | 5.73 | Positive | 493.111 | 95.917 | 263.929 | 460.929 | 0.5 | 106 |
| Tris(isobutyl) phosphate | 7.35 | Positive | 267.171 | 98.762 | 154.899 | 210.857 | 2.5 | 100 |
| Triticonazole | 6.19 | Positive | 318.136 | 42.946 | 69.917 | 124.970 | 2.5 | 81 |
| Tritosulfuron | 5.22 | Positive | 446.035 | 144.917 | 194.917 | 220.929 | 2.5 | 81 |

Table A1 (part 11). Name of the compound, RT, polarity, SRM, LOQ, and %Recovery

| Compound | Retention time (min) | Polarity | Precursor (m/z) | Product (m/z) | Product (m/z) | Product (m/z) | MES LOQ (µg/kg) | Average % recovery at LOQ (µg/kg) (n=6) |
|--------------|----------------------|----------|-----------------|---------------|---------------|---------------|-----------------|---|
| Uniconazole | 6.52 | Positive | 292.121 | 69.970 | 124.917 | 217.929 | 2.5 | 76 |
| Valifenalate | 5.97 | Positive | 399.168 | 144.042 | 155.000 | 214.071 | 2.5 | 81 |
| Vamidothion | 3.38 | Positive | 288.048 | 58.000 | 85.982 | 89.970 | 25 | 94 |
| Vegadex | 6.88 | Positive | 224.032 | 59.970 | 87.970 | 115.970 | 25 | 81 |
| Vernolate | 7.26 | Positive | 204.141 | 43.000 | 86.054 | 128.054 | 10 | 78 |
| Warfarin | 5.67 | Positive | 309.112 | 120.845 | 162.857 | 250.929 | 0.5 | 97 |
| XMC | 4.50 | Positive | 180.101 | 106.946 | 107.845 | 122.929 | 2.5 | 81 |
| Zoxamide | 6.94 | Positive | 336.031 | 122.917 | 132.000 | 158.917 | 1 | 101 |

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