**Supplemental Table 1: EPA Compound Specific Analysis Parameters**

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Analyte | Sample Diluent | Extraction Solvent | Instrument | Mode | Precursor Ion, *m/z* | Quant Ion, *m/z* | DP, V | EP, V | CE, V | EXP, V | LOQ, ng/mL | Internal Standard |
| Qual Ion, *m/z* |
| Bensulide | 0.5 M NH4OH | Ethyl acetate | TSQ | + | 398.0 | 314.0 |  |  | 12 |  | 5.0 | Isoxaben |
| 158.0 | 25 |
| Bensulide (IS) |  |  | TSQ | - | 396.0 | 213.0 |  |  | 30 |  |  |  |
| S-Bioallethrin | Water | 1:1 Dichloro-methane:Hexane | Qtrap | + | 303.0 | 135.0 | 70 | 10 | 13 | 8.0 | 1.0 | Isoxaben |
| 151.0 | 12 | 9.0 |
| Bisphenol A | 0.1% Formic acid | Dichloro-methane | Qtrap | - | 227.0 | 211.6 | -70 | -10 | -26 | -3.0 | 1.0 | Bisphenol A-13C12 |
| 132.8 | -38 | -9.0 |
| Bisphenol A-13C12 |  |  | QTrap | - | 241.1 | 141.8 | -65 | -10 | -38 | -11 |  |  |
| Boscalid | 0.5 M NH4OH | Dichloro-methane | TSQ | + | 343.2 | 307.0 |  |  | 19 |  | 0.025 | Isoxaben |
| 271.0 | 34 |
| Carbaryl | 0.5 M NH4OH | Ethyl acetate | TSQ | + | 202.1 | 145.0 |  |  | 12 |  | 1.0 | Isoxaben |
| 127.0 | 30 |
| Cyclanilide | 0.5 M NH4OH | Ethyl acetate | TSQ | - | 271.7 | 159.9 |  |  | -23 |  | 1.0 | 2,4-D |
| 227.9 | -12 |
| 2,4-D (IS) |  |  | TSQ | - | 218.8 | 160.9 |  |  | -17 |  |  |  |
| Dimethenamid | 0.5 M NH4OH | Ethyl acetate | Qtrap | + | 276.0 | 168.0 | 70 | 10 | 33 | 10 | 0.10 | Isoxaben |
| 243.9 | 17 | 16 |
| Etoxazole | 0.5 M NH4OH | Ethyl acetate | TSQ | + | 360.2 | 177.1 |  |  | 22 |  | 0.10 | Isoxaben |
| 304.2 | 22 |
| Fenarimol | 0.5 M NH4OH | Ethyl acetate | TSQ | + | 331.1 | 267.9 |  |  | 13 |  | 0.025 | Isoxaben |
| 138.8 | 31 |
| Formetanate hydrochloride | 0.5 M NH4OH | Ethyl acetate | Qtrap | + | 222.1 | 165.0 | 66 | 10 | 23 | 10 | 1.0 | Propamocarb hydrochloride |
| 120.0 | 37 | 8.0 |
| Imazalil | 0.5 M NH4OH | Ethyl acetate | TSQ | + | 297.2 | 159.0 |  |  | 24 |  | 0.10 | Isoxaben |
| 201.0 | 18 |
| Imidacloprid | 0.5 M NH4OH | Ethyl acetate | Qtrap | + | 256.0 | 209.1 | 61 | 10 | 21 | 10 | 1.0 | Formetanate hydrochloride |
| 175.1 | 25 | 6.0 |
| Isoxaben (IS) |  |  | Qtrap | + | 333.1 | 165.0 | 70 | 10 | 21 | 10 |  |  |
| Isoxaben (IS) |  |  | TSQ | + | 333.1 | 165.0 |  |  | 30 |  |  |  |
| Novaluron | 0.5 M NH4OH | Dichloro-methane | TSQ | - | 491.2 | 471.0 |  |  | -15 |  | 0.50 | Bensulide |
| 305.0 | -19 |
| *cis/trans-*Permethrin | 0.5 M NH4OH | Dichloro-methane | TSQ | + | 408.0 | 183.0 |  |  | 22 |  | 1.0 | Phenoxy-13C6-*cis*-permethrin |
| 355.0 | 10 |
| Phenoxy-13C6-*cis*-permethrin (IS) |  |  | TSQ | + | 414.0 | 189.0 |  |  | 22 |  |  |  |
| PFOA | 0.1% Formic acid | Ethyl acetate | TSQ | - | 412.8 | 168.9 |  |  | 20 |  | 0.10 | 13C2-PFOA |
| 368.9 | 12 |
| 13C2-PFOA (IS) |  |  | TSQ | - | 414.9 | 369.9 |  |  | -10 |  |  |  |
| Propamocarb hydrochloride | 0.5 M NH4OH | Ethyl acetate | Qtrap | + | 189.2 | 102.0 | 61 | 10 | 25 | 6.0 | 1.0 | Formetanate hydrochloride |
| 144.0 | 19 | 8.0 |
| Propyzamide | Water | Dichloro-methane | Qtrap | + | 256.0 | 173.0 | 70 | 10 | 14 | 10 | 1.0 | Isoxaben |
| 189.7 | 17 | 12 |
| Resmethrin | 0.5 M NH4OH | Dichloro-methane | TSQ | + | 356.0 | 143.0 |  |  | 26 |  | 1.0 | Phenoxy-13C6-*cis*-permethrin |
| 171.0 | 15 |
| Simazine | 0.5 M NH4OH | Ethyl acetate | TSQ | + | 202.1 | 104.0 |  |  | 27 |  | 0.010 | Isoxaben |
| 127.0 | 30 |
| Triclosan | - | Acetonitrile with 0.1% Formic acid | Qtrap | - | 286.9 | 35.0 | -60 | -10 | -35 | -3.0 | 1.0 | 13C12-Triclosan |
| 288.9 |
| 13C12-Triclosan |  |  | Qtrap | - | 299.0 | 35.0 | -60 | -10 | -35 | -3.0 |  |  |

Quant Ion: Ion used for quantitation

Qual Ion: Ion used for confirmation

DP: Declustering Potential

EP: Exit Potential

CE: Collision Energy

EXP: Exit Potential

IS: Internal standard

Supplemental Table 2: EPA Mass Spectrometer Source Parameters

|  |  |  |  |
| --- | --- | --- | --- |
| **Thermo Electron TSQ Quantum Ultra AM** | | **AB Sciex 4000 QTrap** | |
| Parameter | Setting | Parameter | Setting |
| Spray Voltage | 3500 V | Spray Voltage | 5500 V/-4500 V |
| Sheath Gas | 55 AU | Curtain Gas | 30 psi |
| Aux Gas | 15 AU | Ion Source Gas 1 | 40 psi |
| Capillary Temp. | 280 °C | Ion Source Gas 2 | 45 psi |
| Heater Temp. | 295 °C | Collision Gas | Medium |
| Collision Gas | 1.5 Torr |

AU: Arbitrary Units

Supplemental Table 3: RTI Test Articles

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Test Article | CAS # | Supplier | Lot Number | Manufacturer’s Purity | MW (g/mol |
| 2,4-D | 94-75-7 | Sigma Aldrich | SZBA102XV | 99.8 | 221.04 |
| Alachlor | 15972-60-8 | Sigma Aldrich | SZB9139XV | 99.2 | 269.77 |
| Flufenacet | 142459-58-3 | Sigma Aldrich | SZBA029XV  **SZBD038XV** | 99.8  99.5 | 363.33 |
| Chloridazon | 1698-60-8 | Sigma Aldrich | SZBD100XV | 99.7 | 221.64 |
| Bensulide | 741-58-2 | Sigma Aldrich | SZBD044XV | 99.3 | 397.51 |
| Propyzamide | 23950-58-5 | Sigma Aldrich | SZB9023XV | 99.6 | 256.13 |
| Pyrithiobac sodium | 123343-16-8 | Crescent Chemical Co | 10211  **40722** | 99.5  99.0 | 348.70 |
| Diazinon-o-analog | 962-58-3 | Crescent Chemical Co | 2645800 | 97 | 288.30 |

Supplemental Table 4: RTI Internal Standards and Vehicle Components

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Compound | CAS # | Supplier | Lot # | Purity |
| Isoxaben (internal std) | 82558-50-7 | Sigma Aldrich | SZX8092XV | 97.6 |
| 2-methyl-4-chlorophenylacetic acid (MCPA, internal standard | 94-74-6 | Sigma Aldrich | SZB129XV |  |
| EtOH | 64-17-5 | Decon Laboratories | None | 200 proof USP grade |
| Cremophor | 61791-12-6 | Sigma | BCBB1383 |  |
| PBS | NA | Amresco | 1974C491 |  |

Supplemental Table 5: LC/MS Methods Instrumentation and Analysis Parameters for Flufenacet, Bensulide and Propyzamide

Instrumentation

| **Mass Spectrometer** | API 4000 Triple Quadrupole with Turbo Ion Spray source (Beryllium) |
| --- | --- |
| **HPLC** | Agilent 1100 Binary Pumps, Autosampler, Diode Array Detector and Column Compartment |

Chromatography Conditions

| **Column** | Restek Ultra C18 (50 x 2 mm, 5 μm) with C18 guard cartridge |
| --- | --- |
| **Injection Volume** | 10 microliters |
| **Mobile Phase** | A: 0.1% Formic Acid in Water; B: Methanol |
| **Flow Rate** | 0.3 mL/min |
| **Gradient** | Initially 20% B, changing linearly to 100% B over 4.5 min, beginning 0.5 min post injection. Hold at 100% B for 1 min, then return to initial conditions over 0.5 min |
| **Internal Standard** | Isoxaben – MRM (333.198 → 167.7), DP=61, CE=23, CXP=12 |

MS Parameters

| **Parameter** | **Flufenacet** | **Bensulide** | **Propyzamide** |
| --- | --- | --- | --- |
| Polarity | Positive | Positive | Positive |
| Ion Source | TurboSpray | TurboSpray | TurboSpray |
| Time | 75 msec | 75 msec | 75 msec |
| Curtain Gas | 14 | 14 | 14 |
| Gas 1 | 60 | 60 | 60 |
| Gas 2 | 60 | 60 | 60 |
| IonSpray Voltage | 2000 | 2000 | 2000 |
| Source Temperature | 550 | 550 | 550 |
| Collision Gas (CAD) | 10 | 10 | 10 |
| Declustering Potential | 51 | 61 | 51 |
| Entrance Potential | 10 | 10 | 10 |
| Collision Cell Exit Potential | 10 | 10 | 12 |
| Collision Energy | 17 | 29 | 19 |
| MRM | 363.9 → 193.9 | 398.0 → 157.9 | 256.0 → 189.5 |

Supplemental Table 6: LC/MS Methods Instrumentation and Analysis Parameters for 2,4-D

Instrumentation

| **Mass Spectrometer** | API 4000 Triple Quadrupole with Turbo Ion Spray source (Beryllium) |
| --- | --- |
| **HPLC** | Agilent 1100 Binary Pumps, Autosampler, Diode Array Detector and Column Compartment |

Chromatography Conditions

| **Column** | Restek Ultra C18 (50 x 2 mm, 5 μm) with C18 guard cartridge |
| --- | --- |
| **Injection Volume** | 10 microliters |
| **Mobile Phase** | A: 0.1% Acetic Acid + 10 mM Ammonium Acetate in Water; B: Methanol |
| **Flow Rate** | 0.3 mL/min |
| **Gradient** | Initially 5% B, changing linearly to 100% B over 4.5 min, beginning 0.5 min post injection. Hold at 100% B for 1 min, then return to initial conditions over 0.5 min |
| **Internal Standard** | MCPA – MRM (198.84 → 140.5), DP=-45, CE=-20, CXP=-11 |

MS Parameters

| **Parameter** | **2,4-D** |
| --- | --- |
| Polarity | Negative |
| Ion Source | TurboSpray |
| Time | 75 msec |
| Curtain Gas | 14 |
| Gas 1 | 60 |
| Gas 2 | 60 |
| IonSpray Voltage | 2000 |
| Source Temperature | 550 |
| Collision Gas (CAD) | 10 |
| Declustering Potential | -45 |
| Entrance Potential | -10 |
| Collision Cell Exit Potential | -11 |
| Collision Energy | -18 |
| MRM | 218.758 → 160.6 |

Supplemental Table 7: LC/MS Methods Instrumentation and Analysis Parameters for Chloridazon, Diazoxon and the Diazoxon Metabolite IMP

Instrumentation

| **Mass Spectrometer** | API 5000 Triple Quadrupole with Turbo Ion Spray source (Cobalt) |
| --- | --- |
| **HPLC** | Waters Acquity UPLC System |

Chromatography Conditions

| **Column** | Phenomenex Synergi Hydro-RP (50 x 2 mm, 4 μm) with C18 guard cartridge |
| --- | --- |
| **Injection Volume** | 10 microliters |
| **Mobile Phase** | A: 0.1% Formic Acid in Water; B: Methanol |
| **Flow Rate** | 0.5 mL/min |
| **Gradient** | Initially 20% B, changing linearly to 100% B over 4.5 min, beginning 0.5 min post injection. Hold at 100% B for 1 min, then return to initial conditions over 0.5 min |
| **Internal Standard** | Isoxaben – MRM (333.198 → 167.7), DP=61, CE=23, CXP=12 |

MS Parameters

| **Parameter** | **Chloridazon** | **Diazoxon** | **IMP** |
| --- | --- | --- | --- |
| Polarity | Positive | Positive | Positive |
| Ion Source | TurboSpray | TurboSpray | TurboSpray |
| Time | 50 msec | 50 msec | 50 msec |
| Curtain Gas | 14 | 14 | 14 |
| Gas 1 | 60 | 60 | 60 |
| Gas 2 | 60 | 60 | 60 |
| IonSpray Voltage | 2000 | 2000 | 2000 |
| Source Temperature | 650 | 550 | 550 |
| Collision Gas (CAD) | 10 | 10 | 10 |
| Declustering Potential | 71 | 61 | 61 |
| Entrance Potential | 10 | 10 | 10 |
| Collision Cell Exit Potential | 2 | 10 | 10 |
| Collision Energy | 33 | 27 | 27 |
| MRM | 222.13 → 104.2 | 289.082 → 153.1 | 152.937 → 84.0 |

Supplemental Table 8: LC/MS Methods Instrumentation and Analysis Parameters for Pyrithiobac Sodium and Alachlor

Instrumentation

| **Mass Spectrometer** | API 5000 Triple Quadrupole with Turbo Ion Spray source (Cobalt) |
| --- | --- |
| **HPLC** | Waters Acquity UPLC System |

Chromatography Conditions

| **Column** | Waters Acquity UPLC HSS C18 (2.1 x 5 mm, 1.8 μM) with C18 guard cartridge |
| --- | --- |
| **Injection Volume** | 10 microliters |
| **Mobile Phase** | A: 0.1% Formic Acid in Water; B: Methanol |
| **Flow Rate** | 0.3 mL/min |
| **Gradient** | Initially 20% B, changing linearly to 100% B over 4.5 min, beginning 0.5 min post injection. Hold at 100% B for 1 min, then return to initial conditions over 0.5 min |
| **Internal Standard** | Isoxaben – MRM (333.198 → 167.7), DP=61, CE=23, CXP=12 |

MS Parameters

| **Parameter** | **Pryrithiobac Na** | **Alachlor** |
| --- | --- | --- |
| Polarity | Positive | Positive |
| Ion Source | TurboSpray | TurboSpray |
| Time | 50 msec | 50 msec |
| Curtain Gas | 14 | 14 |
| Gas 1 | 60 | 60 |
| Gas 2 | 60 | 60 |
| IonSpray Voltage | 2000 | 2000 |
| Source Temperature | 650 | 550 |
| Collision Gas (CAD) | 10 | 10 |
| Declustering Potential | 51 | 36 |
| Entrance Potential | 10 | 10 |
| Collision Cell Exit Potential | 6 | 16 |
| Collision Energy | 23 | 15 |
| MRM | 327.228 → 309.000 |  |