Development of an Atmospheric Pressure Chemical Ionization Interface for GC-MS

Christian Lipok, Florian Uteschil and Oliver J. Schmitz *

University of Duisburg-Essen, Applied Analytical Chemistry, Universitaetsstr. 5, 45141 Essen, Germany; christian.lipok@uni-due.de (C.L.); florian.uteschil@uni-due.de (F.U.)

* Correspondence: oliver.schmitz@uni-due.de; Tel.: +49-201-183-3950; Fax: +49-201-183-3951

Academic Editor: Tomasz Tuzimski

1. GC-APCI-QqQ-coupling

The model of the prototype GC-APCI-MS is shown in Figure S1A and S1B.

A. Schematically drawing of the GC-APCI ion source with:

1. Make-up gas connection
2. Corona needle
3. GC column
4. Transfer line

B. Realized coupling of the GC-APCI ion source with the 6495B QqQ form Agilent

Thermo couple

Figure S1. Developed prototype GC-APCI ion source. In S1A the optimum column position at 2 mm and the position of the GC column and corona needle in relation to each other. S1B shows the coupled system and the addition of the thermo couple.

2. Pesticide Residues

2.1. Humidity

The dependence of the detector response as a function of the make-up gas humidity is plotted in Figure S2A-F and shows that for almost all pesticides the detector response (Intensity in a.u.) are increased with the humidity. For all experiments 3 (n=3) replicates were measured.
Figure S2A–D. Comparison of the detector response (a.u.) for pesticides with and without water addition to the make-up gas.
2.2. dMRM-Method

The dMRM-method are summarized in Table S 1, Table S2 and Table S3. The retention time, transient, collision energy, recovery rates and LOD of the compounds are shown. The corona needle was set to 1 µA and the transfer capillary to 250 V. The ion source was operated at 200 °C without humidified make-up gas (Nitrogen). Substances with (–) showing LODs higher than 500 g L⁻¹. For all substances 2 µL were injected in splitless mode at 250 °C.
**Table S1.** dMRM-Method Information for OPP.

| Name                  | Retention time (min) | Precursor m/z | Product Ion m/z | Energy (V) | Recovery (%) | Lod (µg/L) |
|-----------------------|----------------------|---------------|-----------------|------------|--------------|------------|
| Azinphos ethyl        | 41.63                | 346.1         | 132             | 10         | 55.3         | 25.0       |
| Azinphos methyl       | 31.4                 | 318           | 131.9           | 10         | 40.1         | 125        |
| Bromfenvinphos-methyl | 32.46                | 377           | 126.9           | 5          | 52.2         | 12.5       |
| Bromfenvinphos        | 34.01                | 405           | 127             | 20         | 37.1         | 12.5       |
| Bromophos ethyl       | 33.17                | 395           | 338.7           | 20         | 56.0         | 12.5       |
| Bromophos methyl      | 31.49                | 367           | 124.8           | 20         | 73.5         | 12.5       |
| Carbophenothenion     | 36.88                | 343.1         | 157.8           | 20         | 34.8         | 125        |
| Chlorfenvinphos       | 32.54                | 359.1         | 155             | 10         | 54.3         | 25.0       |
| Chlorpyrifos          | 30.92                | 350           | 197.8           | 20         | 49.9         | 5.00       |
| Chlorpyrifos methyl   | 28.96                | 324           | 124.9           | 20         | 81.8         | 1.25       |
| Choloriophos          | 36.3                 | 361           | 326             | 10         | 169.5        | -          |
| Coumaphos             | 43.1                 | 363.1         | 108.9           | 20         | 87.5         | -          |
| Diazinon              | 27.3                 | 305.2         | 153.1           | 20         | 56.7         | 1.25       |
| Edifenphos            | 36.9                 | 311.1         | 109             | 30         | -            | 25.0       |
| EPN                   | 39.16                | 324.1         | 296             | 10         | 35.0         | 1.25       |
| Fenchlorphos          | 29.52                | 321           | 124.9           | 30         | 80.2         | 50.0       |
| Fenitrothion          | 30.13                | 278.1         | 124.9           | 20         | 71.0         | 0.50       |
| Fenthion              | 30.86                | 279.1         | 108.9           | 20         | 63.3         | 25.0       |
| Fonofoes              | 25.85                | 247.1         | 109.1           | 20         | -            | 1.25       |
| Iodofenphos           | 33.97                | 413           | 124.7           | 30         | 64.9         | 50.0       |
| Leptophos             | 33.94                | 413           | 170.9           | 20         | 65.6         | -          |
| Malathion             | 30.64                | 331.1         | 127             | 10         | 23.4         | 0.50       |
| Methyl parathion      | 29.29                | 264.1         | 109.1           | 20         | 50.2         | 1.25       |
| Phosalone             | 40.42                | 368.1         | 181.9           | 10         | 39.8         | 5.00       |
| Phosmet               | 39.00                | 318           | 159.9           | 5          | 64.8         | 12.5       |
| Pirimiphos ethyl      | 31.91                | 334.2         | 198             | 20         | 75.1         | 1.25       |
| Pirimiphos methyl     | 30.26                | 306.2         | 164             | 20         | 41.6         | 2.50       |
| Profenofos            | 34.26                | 375.0         | 304.8           | 20         | 58.3         | 1.25       |
| Prothiofos            | 34.1                 | 345.0         | 240.8           | 20         | 42.4         | 12.5       |
|                        |       |       |     |     |     |     |
|------------------------|-------|-------|-----|-----|-----|-----|
| Pyraclofos             | 42.02 | 361.1 | 256.9 | 20 | 31.5 | 50.0 |
| Pyrazofos              | 41.77 | 374.2 | 222.2 | 20 | 43.1 | 5.00 |
| Pyridaphenthion        | 39.03 | 341.1 | 189  | 20 | 37.7 | 25.0 |
| Quinalphos             | 32.61 | 299.2 | 147  | 20 | 49.3 | -    |
| Sulfotepp              | 24.81 | 323.2 | 145.9 | 30 | 39.8 | 100  |
| Sulprofos              | 36.55 | 323.1 | 96.6  | 30 | -    | 125  |
| Tetrachlorvinfos       | 33.53 | 367   | 126.9 | 20 | 60.3 | -    |
| Tolclofos-methyl       | 29.10 | 301   | 124.9 | 20 | 71.6 | 0.5  |
| Triazophos             | 26.80 | 314.2 | 162  | 20 | -    | 25   |
**Table S2. dMRM-Method Information for ONP.**

| Name                        | Retention time | Precursor | Product Ion | Energy | Recovery | Lod  |
|-----------------------------|----------------|-----------|-------------|--------|----------|------|
| 2. 3. 5. 6-Tetrachloroaniline | 23.45          | 231.4     | 195.7       | 20     | 200.0    | 25.0 |
| 2. 6-Dichlorobenzonitrile   | 16.83          | 172       | 136         | 30     | 312.5    | 2.50 |
| 3. 4-Dichloroaniline        | 19.16          | 162       | 127         | 20     | 7.8      | 50.0 |
| Atrazine                    | 26.26          | 216.1     | 174         | 20     | 106.1    | 2.50 |
| Biphenyl                    | 17.7           | 155.1     | 77.1        | 30     | 117.8    | 50.0 |
| Bupirimate                  | 35.05          | 317.2     | 209.1       | 20     | 71.9     | 2.50 |
| Dichlofluanid               | 30.27          | 223.9     | 122.9       | 20     | 119.1    | 5.00 |
| Dimethachlor                | 28.61          | 256.1     | 224.1       | 20     | 120.0    | 0.50 |
| Diphenamid                  | 31.61          | 240.2     | 134         | 30     | 145.5    | 2.50 |
| Diphenylamine               | 23.66          | 170.1     | 92.1        | 20     | 105.8    | 5.00 |
| Ethalfurinal                | 24.34          | 334.2     | 317.2       | 5      | 64.5     | 12.5 |
| Etridiazole                 | 19.38          | 248.9     | 220.8       | 5      | 135.7    | 0.50 |
| Fenarimol                   | 41.3           | 331.1     | 139         | 5      | 110.0    | 50.0 |
| Fipronil                    | 32.82          | 437.1     | 367.8       | 20     | 96.9     | 2.50 |
| Fluchloralil                | 27.53          | 356.2     | 314         | 10     | 75.0     | 0.50 |
| Flutriafol                  | 33.72          | 302.1     | 70          | 20     | 91.7     | 12.5 |
| Hexazinone                  | 37.76          | 253.2     | 171         | 10     | 75.0     | 2.50 |
| Lenacil                     | 37.23          | 235.1     | 153         | 20     | 71.2     | 12.5 |
| MGK-264                     | 31.48          | 276.1     | 210.1       | 10     | 58.7     | 2.50 |
| Myclobutanil                | 34.79          | 289.2     | 70.1        | 20     | 124.3    | 2.50 |
| Oxadiazon                   | 34.71          | 345.1     | 219.9       | 20     | 77.4     | 0.50 |
| Paclobutrazol               | 33.25          | 294.2     | 276.1       | 10     | -        | 25.0 |
| Pebulate                    | 19.55          | 204.1     | 128.1       | 10     | 90.0     | 2.50 |
| Penconazole                 | 32.25          | 284.1     | 70          | 30     | 32.0     | 100  |
| Pendimethalin               | 32.13          | 282.1     | 211.9       | 5      | 15.3     | 0.5  |
| Prodiamine                  | 30.4           | 351.2     | 246.9       | 20     | 7.0      | 2.50 |
| Profluralin                 | 27             | 348.2     | 232         | 10     | 4.2      | 0.5  |
| Propargite                  | 38.08          | 350.2     | 201         | 10     | 70.7     | 5.0  |
| Pyrimethanil                | 27.27          | 200.1     | 82.2        | 20     | 177.6    | 12.5 |
| Pyriproxyfen                | 40.81          | 322.2     | 95.9        | 30     | 68.4     | 100  |
| Compound            | 37.81 | 308.1 | 70   | 20   | 94.3 | 12.5 |
|---------------------|-------|-------|------|------|------|------|
| Tebuconazole        |       |       |      |      |      |      |
| Terbacil            | 27.71 | 161   | 144  | 20   | 81.3 | 12.5 |
| Terbuthylazine      | 26.75 | 230.1 | 174  | 20   | 85.0 | 2.5  |
| Tetrahydrophthalimide | 20.15 | 152.2 | 81.1 | 10   | 78.0 | 5.0  |
| Triadimefon         | 31.09 | 294.2 | 224.9| 10   | 64.6 | 2.50 |
| Tricyclazole        | 35.13 | 190.1 | 163  | 20   | 88.9 | -    |
| Triflumizole        | 33.12 | 346.1 | 278  | 5    | 66.2 | 12.5 |
| Vinclozolin         | 29.06 | 286   | 241.9| 10   | 108.4| 0.50 |
Table S3. dMRM-Method Information for HME.

| Name                  | Retention time | Precursor m/z | Product Ion m/z | Energy V | Recovery % | Lod µg/L |
|-----------------------|----------------|---------------|-----------------|----------|------------|----------|
| 2-Phenylphenol        | 6.98           | 171           | 142             | 30       | 164.7      | -        |
| Chlorpropham          | 7.7            | 172           | 154             | 10       | 86.5       | 0.50     |
| Metalaxyl             | 9.8            | 280           | 220             | 10       | -          | 0.50     |
| DCPA methyl ester     | 9.52           | 333           | 301.9           | 20       | 64.8       | 125.0    |
| Chlozolinate          | 9.82           | 332.1         | 186.9           | 10       | 84.7       | 25.0     |
| Chlorobenzilate       | 10.5           | 307.2         | 250.9           | 20       | 64.7       | 2.50     |
| Acequinocyl           | 12.85          | 343.3         | 188.9           | 20       | 176.5      | 12.5     |

Table S4. dMRM-Method Information for SPP.

| Name      | Retention time | Precursor m/z | Product Ion m/z | Energy V | Recovery % | Lod µg/L |
|-----------|----------------|---------------|-----------------|----------|------------|----------|
| Allethrin | 10.4           | 303.2         | 135.0           | 10       | 64         | 20       |
| Bifenthrin| 13.8           | 181.0         | 165.0           | 30       | 62         | 2        |
| Cypermethrin| 16.5         | 416.1         | 191.0           | 10       | 69         | 10       |
| Deltamethrin| 17.9          | 504.0         | 278.8           | 10       | 69         | 100      |
| Tetramethrin| 13.8          | 332.2         | 164.0           | 30       | 129        | 20       |
| Transfluthrin| 8.8           | 371.0         | 163.0           | 20       | 69.9       | 20       |
| Phenoxythrin| 14.2          | 351.2         | 183.0           | 20       | 64         | 100      |

Overlaid EICs of the analyzed pesticides standards (1 mg L\(^{-1}\) in toluene) from Restek are shown in Figure S3 OPP, Figure S4 ONP, Figure S5 SPP and Figure S6 HME.
Figure S3. Overlaid EICs for OPP standards from Restek 32563; 32570 and 32571 at 1 mg L$^{-1}$. GC-Method: 50 (1 min) to 330 °C (2 min); 5 °C/min; transfer line: 290 °C; injector: 250 °C; injection: 1 µL; constant flow: 1 mL/min He.

Figure S4. Overlaid EICs for ON standard from Restek 32565; 32566, 32567 at 1 mg L$^{-1}$. GC-Method: 50 (1 min) to 330 °C (2 min); 5 °C/min; transfer line: 290 °C; injector: 250 °C; injection: 1 µL; constant flow: 1 mL/min He.
**Figure S5.** Overlaid EICs for SPP standard from Restek 32568 at 1 mg L$^{-1}$. GC-Method: 100 (1 min) to 150 °C; 25 °C/min; 150 to 300 °C (3 min); 10 °C/min; transfer line: 290 °C; injector: 250 °C; Injection: 1 µL; constant flow: 1 mL/min He.

**Figure S6.** Overlaid EICs for HME standard from Restek 32569 at 1 mg L$^{-1}$. GC-Method: 100 (1 min) to 150 °C; 25 °C/min; 150 to 300 °C (3 min); 10 °C/min; transfer line: 290 °C; injector: 250 °C; Injection: 1 µL; constant flow: 1 mL/min He.