

ANALYSIS OF CURRENT USE PESTICIDES IN ENVIRONMENTAL AND WASTEWATER SAMPLES BY HIGH RESOLUTION GC WITH HIGH RESOLUTION MASS SPECTROMETRIC DETECTION

Hamilton MC, Woudneh M, Grace R
 AXYS Analytical Services Ltd. Sidney, BC, Canada

Abstract

A new method has been developed for analysis of 76 pesticides in aqueous and solid environmental and wastewater samples in a single analytical procedure. The method uses gas chromatography with high resolution mass spectrometry to quantify organonitrogen, organophosphorus, triazine, pyrethroid and organochlorine pesticides at concentrations lower than prescribed by established reference methods. The high resolution of the mass spectrometer minimizes the potential for false positives even in complex sample matrices. Method performance data is presented as are the results for the analysis of ground and surface water and wastewater treatment influent, effluent and biosolid samples.

Introduction

A variety of pesticides and herbicides are routinely included in environmental monitoring programs. Recent demands for pesticide monitoring have included many newly developed pesticides as well as the traditional or legacy compounds. A new analytical method has been developed to monitor this complete range of pesticides in a single analysis with higher specificity and sensitivity than established reference methods. A key driving force for this method has been the need for low detection limits for application to transport and pathway surveys, mass balance studies on large waterways, atmospheric tracking and deposition and other scientific studies. A second goal was that the method should have a high degree of specificity to avoid production of false positives even in complex sample matrices.

In this study we have used high resolution gas chromatography with high resolution mass spectrometry to monitor a total of 76 pesticides in solid and aqueous samples. These consist of 34 organochlorines (OC), 19 organophosphorus (OP), 7 triazine (TZ), 14 organonitrogen (ON) and 2 pyrethroid (PY) pesticides. This target list was developed in consultation with environmental scientists conducting pesticides in both Canada and the USA. Because the target compounds have a wide range of chemical and physical properties, the method is not able to employ elaborate extract cleanup procedures but relies on HRGC/HRMS to provide the high degree of selectivity and mass resolution needed to minimize interferences and sample matrix effects. The sensitivity of the high resolution mass spectrometer operated in the Voltage SIR mode permits analysis at environmentally relevant detection limits for surface and groundwater. In addition, application of this method to wastewater treatment plant streams, samples which contain a high background of complex organic matrix, shows the versatility of this procedure as a multi-residue analysis method.

Materials and Methods

Silica (pesticide grade, Silica AR 100-200 mesh) was obtained from Mallinckrodt (Phillipsburg, NJ, USA). The NH₂ solid phase extraction cartridges were obtained from Varian Canada, Mississauga, Ontario). Stable isotope labeled standards ¹³C₁₂-aldrin, ¹³C₁₀- cis-nonachlor, ¹³C₁₀- heptachlor, ¹³C₁₀- oxychlorodane, ¹³C₁₀- trans-chlordane, ¹³C₁₀- trans-nonachlor, ¹³C₆] β-HCH, ¹³C₁₂- 2,4'-DDE, ¹³C₁₂]-4,4'-DDE, ¹³C₁₂- 2,4'-DDT, ¹³C₁₂- 4,4'-DDT, ¹³C₆- γ-HCH, ¹³C₆- δ-HCH, ¹³C₉- α-endosulphan, ¹³C₉- β-endosulphan, ¹³C₁₂- dieldrin, ¹³C₁₂- endrin, ¹³C₁₀- heptachlor epoxide, ¹³C₁₂-methoxychlor, ¹³C₆- hexachlorobenzene, ¹³C₁₀- mirex, ¹³C₆- alachlor, ¹³C₆- metolachlor, ¹³C₆- fonofos, ¹³C₃- atrazine and ¹³C₆- permethrin mix of stereoisomers were all obtained from Cambridge Isotope Laboratories, Inc. (Andover, MA, USA). ²H₆- azinphos-methyl, ²H₁₀- diazinon and ²H₆- linuron were obtained from Dr Ehrenstorfer GmbH (Augsburg, Germany). The injection standards [¹³C₁₂- PCB 52 and [¹³C₁₂-PCB 138 were obtained from Wellington Laboratories Inc. (Guelph, Ontario, Canada). All non-labeled target analytes were obtained from AccuStandards (New Haven, CT, USA).

Aqueous samples were spiked with an aliquot of stable isotope labeled internal standards and liquid-liquid extracted three times with dichloromethane. Solid samples were spiked with an aliquot of labeled internal

standards and soxhlet extracted with dichloromethane. The dichloromethane extracts were dried and the solvent exchanged to 1:2:1 ethylacetate:acetonitrile:toluene in preparation for extract cleanup.

Extracts were first cleaned up on an aminopropyl solid phase extraction cartridge (500 mg aminopropyl bonded silica NH₂ cartridge, Varian Canada, Mississauga, Ont.) which had been pre-conditioned with 1:2:1 ethylacetate:acetonitrile:toluene, the elution solvent. The eluate was then applied to a silica column (0.75 g, 10% deactivated) using rinses of hexane and 10% methanol in dichloromethane. The silica column was eluted with 10 % methanol in dichloromethane, and an aliquot of labeled injection standards was added to the eluate. The volume of the extract was adjusted to 300 µL in preparation for GC/MS analysis.

Analyses were conducted using Micromass Autospec Ultima HRMS systems each equipped with an HP 6890 GC, a CTC auto-sampler and an Alpha data system running Opus 6.3 software. A DB-5 capillary GC column (30 m, 0.25 mm i.d., and 0.1 µm film thickness) was directly coupled to the MS source. Prior to running samples the mass spectrometer was tuned to have a static mass resolution of at least 8,000 and operated using electron impact (EI) ionization the data acquired in multifunction selected ion recording VSIR mode with PFK reference for lock mass. Two characteristic ions were monitored for target compounds and labeled standards using mono-isotopic accurate ion masses calculated to 0.1 mDa. To maintain instrument focus, masses and scan functions were selected to minimize voltage step. Analysis of the full suite of target pesticides was conducted using two instrumental runs. The run used to acquire data for the OC, OP, TZ and PY pesticides included the following oven temperature program for analyte separation: initial temperature 50°C hold for 0.5 min, ramp at a rate of 20°C/min to 150°C, ramp at a rate of 3°C/min to 230°C, hold for 12 min, ramp at a rate of 10°C/min to 320°C and hold for 2.8 min. Injection temperature and interface temperatures were set at 220°C and 280°C, respectively. The second instrumental run was used to acquire the ON pesticides and used an oven temperature program with initial temperature of 75°C hold for 1 min, ramp at a rate of 25 °C/min to 150°C, ramp at a rate of 15°C/min to 300 °C and hold for 9 min. Injection temperature and interface temperatures were set at 250°C and 280°C, respectively.

Results and Discussion

Method validation was demonstrated by analysis of blanks, spiked blanks, matrix spikes and analysis duplicates. A method detection limit (MDL) was determined for each target compound and is listed in Table 1. The MDL was determined by analysis of 7 replicates of low level spiked matrix samples according to published protocols¹.

The accuracy of the analytical method was demonstrated by performing analysis of “known” samples. The results for analysis of laboratory control samples, matrix to which known amounts of the target analytes have been spiked, is one way to achieve this. The results of such control samples analyzed in our laboratory over a period of several months are summarized in Table 1. These data indicate that the method described here is able to detect a large range of pesticides in both solid and aqueous with a high degree of precision and accuracy.

Application of this method to environmental samples, surface water and groundwater samples resulted in the detection of a selection of pesticides in many of the samples. These data are summarized in Table 1. These water samples were collected from agricultural areas in Western Canada during periods of high pesticide use. The data in Table 1 indicate that the surface water samples contained pesticides at concentrations detected by this method. The ON pesticides linuron and metolachlor, the TZ pesticides atrazine, desethylatrazine and simazine, and the OP diazinon were found at the highest concentration in the surface waters. There are fewer pesticides detected in the ground water samples and those present are at lower concentration than in the surface water. The triazine pesticides were present in many of the ground waters as well as a few organochlorine pesticides.

These methods have also been applied to the analysis of wastewater treatment plant (WWTP) samples, which have a complex background matrix and can be challenging for HRMS analysis. The results for analysis of WWTP influent, effluent and biosolid samples are also summarized in Table 1. These samples are from 4 different WWTP, from mainly urban centers in North America. The influent samples contained a range of pesticides including ONs, TZ and several OCs. Many of the same compounds were found in the WWTP

effluent but usually at lower concentrations except for the TZs simazine, atrazine and desethylatrazine which are present at the same concentrations in influent and effluent. Some influent samples contained diazinon which was not found in either the effluent or biosolid. Methoprene and tebuconazol were found in the influent and effluent and methoprene was found in the biosolids. Permethrins were found in all 3 types of WWTP matrices while the cypermethrins were found only in influent and biosolids.

The data summarized in Table 1 indicate that this method shows good performance for the four classes of pesticides studied, namely the OC, ON, TZ and PY compounds. It is a true multi-residue analysis in that this wide range of compounds can be monitored in a single analysis. An extensive suite of stable isotope labeled compounds used as surrogate and internal standards allows reliable quantification of target compounds even in the presence of a complex background matrix. The HRGC/HRMS provides a high degree of specificity for the target compounds, minimizing the chance of false positives while good detection limits are achieved for surface and groundwater monitoring. New target compounds can easily be added as they become of interest. Application of this new method has demonstrated the presence of many of these compounds in the environment.

References

1. Federal Register (USA) 40 CFR Part 136. Appendix B, October 26, 1984.

Table 1. Results of Method Performance Studies, Analysis of Ground and Surface Water Samples from agricultural areas and WWTP streams for ON, TZ, OP and OC pesticides.

| Compound | Average Spike Recovery | | Detection Limit | | No. Times Detected / Maximum Concentration Detected | | | | |
|----------------------------------|------------------------|----------------|-----------------|---------------|---|-------------------------------|------------------------------|------------------------------|-------------------------|
| | Aqueous n = 38 | Solid n = 9 | Aqueous ng/L | Solid ng/g | Surface water ng /L n=22 | Ground water ng /L n=12 | WWTP Influent ng/L n=4 | WWTP Effluent ng/L n=6 | Biosolid ng/g n=5 |
| <i>Organonitrogen pesticides</i> | | | | | | | | | |
| ALACHLOR | 99% | 96% | 0.24 | 0.6 | 1 / 2.5 | 1 / 0.9 | | 1 / 0.6 | 1 / 4.0 |
| BUTRALIN | 81% | 100% | 1.52 | 3.2 | | | | | |
| BUTYLATE | 53% | 37% | 0.42 | 0.98 | | | | | |
| DIMETHENAMID | 90% | 117% | 0.61 | 3.7 | | | 2 / 7.8 | | |
| ETHALFLURALIN | 68% | 53% | 5.82 | 13.1 | | | | | |
| FLUFENACET | 90% | 114% | 1.48 | 6.3 | | | | | |
| FLUTRIAFOL | 76% | 67% | 9.41 | 66.7 | | | | | |
| LINURON | 99% | 100% | 1.31 | 3.0 | 8 / 1,050 | | | | |
| METHOPRENE | 88% | 103% | 2.7 | 19.2 | 1 / 7.8 | | 1 / 3,100 | 1 / 27 | 2 / 8,650 |
| METOLACHLOR | 96% | 101% | 0.18 | 2.3 | 14 / 66.7 | | 4 / 11.9 | 6 / 9.2 | |
| PENDIMETHALIN | 90% | 87% | 5.41 | 10.3 | | | | | |
| TEBUCONAZOL | 103% | 59% | 4.68 | 31.5 | | | 2 / 111 | 2 / 66.2 | |
| TRIALATE | 75% | 68% | 0.47 | 1.4 | | | | | |
| TRIFLURALIN | 68% | 57% | 0.53 | 1.3 | 2 / 1.5 | | | | |
| <i>Triazine Pesticides</i> | | | | | | | | | |
| AMETRYN. | 98% | 71% | 0.39 | 5.6 | 3 / 0.3 | | | | |
| ATRAZINE | 92% | 99% | 0.12 | 0.7 | 18 / 52.9 | 11 / 11.2 | 3 / 87.6 | 4 / 87.6 | 1 / 14.8 |
| CYANAZINE. | 102% | 64% | 0.84 | 10.7 | | | | | |
| DESETHYLATRAZINE | 78% | 81% | 0.08 | 4.9 | 17 / 6.4 | 12 / 4.9 | 4 / 27.3 | 6 / 28.9 | |
| HEXAZINONE. | 101% | 32% | 1.37 | 1.5 | 5 / 17.1 | | | | |
| METRIBUZIN. | 91% | 74% | 0.14 | 1.8 | 10 / 1.5 | | | | |
| SIMAZINE | 96% | 99% | 0.18 | 2.4 | 19 / 890 | 9 / 90.0 | 3 / 19.2 | 5 / 5.1 | 1 / 23.5 |
| <i>Pyrethroid Pesticides</i> | | | | | | | | | |
| CYPERMETHRIN | 98% | 98% | 0.92 | 2.9 | | | 3 / 64.7 | | 3 / 154 |
| PERMETHRIN | 106% | 97% | 0.11 | 0.2 | 4 / 2.4 | | 1 / 27.5 | 3 / 6.5 | 4 / 1,060 |

Table 1. Continued.

| Compound | Spike Recovery | | Detection Limit | | No. Times Detected / Maximum Concentration Detected | | | | |
|------------------------------------|----------------|-------|-----------------|-------|---|--------------|----------|----------|-----------|
| | Aqueous | Solid | Aqueous | Solid | Surface water | Ground water | Influent | Effluent | Biosolid |
| <i>Organophosphorus Pesticides</i> | | | | | | | | | |
| AZINPHOS-METHYL | 94% | 78% | 0.33 | 2.0 | | | | | |
| CHLORPYRIPHOS. | 86% | 69% | 0.44 | 4.4 | 15 / 8.5 | | 4 / 27.1 | | 3 / 127.4 |
| CHLORPYRIPHOSMETH | 81% | 76% | 0.52 | 4.8 | | | | | |
| CHLORPYRIPHOSOXON | 101% | 10% | 0.48 | 0.7 | | | | | |
| DIAZINON | 99% | 90% | 0.15 | 1.2 | 19 / 12,500 | 2 / 1.1 | 3 / 37.5 | | |
| DIAZINON-OXON | 139% | 18% | 0.76 | 0.6 | 11 / 233 | | | 6 / 7.1 | |
| DIMETHOATE. | 100% | 63% | 2.25 | 44.5 | 4 / 15.0 | | | | |
| DISULFOTON SULFONE | 124% | 193% | 1.12 | N/A | 2 / 3.5 | | | | |
| DISULFOTON. | 20% | 28% | 0.77 | - | | | | | |
| FENITROTHION. | 93% | 71% | 0.47 | 5.0 | | | | | |
| FONOFOS | 99% | 96% | 0.08 | 0.9 | | | | | |
| MALATHION. | 86% | 70% | 5.37 | 50.3 | 1 / 20.9 | | | | |
| METHAMIDOPHOS. | 4% | 59% | 0.47 | 3.6 | | | | | |
| PARATHION-ETHYL. | 91% | 71% | 0.44 | 3.9 | 4 / 3.1 | | | | |
| PARATHION-METHYL. | 91% | 76% | 1.34 | 11.8 | | | | | |
| PHORATE. | 37% | 56% | 0.61 | 1.3 | | | | | |
| PHOSMET. | 101% | 68% | 1.91 | 6.8 | | | | | |
| PIRIMIPHOS-METHYL. | 90% | 75% | 0.40 | 6.6 | | | | | |
| TERBUFOS. | 53% | 66% | 0.17 | 0.4 | | | | | |
| <i>Organochlorine Pesticides</i> | | | | | | | | | |
| 2,4'-DDD | 83% | 90% | 0.16 | 0.9 | | | 2 / 4.2 | | 2 / 6.5 |
| 2,4'-DDE | 88% | 100% | 0.03 | 0.3 | | | | | |
| 2,4'-DDT | 95% | 100% | 0.02 | 0.2 | | | | | |
| 4,4'-DDD | 96% | 91% | 0.17 | 1.5 | | | | | |
| 4,4'-DDE | 96% | 100% | 0.02 | 0.1 | 1 / 0.03 | | | | 3 / 11.4 |
| 4,4'-DDT | 99% | 97% | 0.01 | 0.3 | 1 / 0.1 | | | | |
| ALDRIN | 96% | 98% | 0.10 | 1.1 | 4 / 0.2 | | | | |
| ALPHA-ENDOSULPHAN | 98% | 94% | 0.08 | 0.4 | 19 / 2.2 | 4 / 3.2 | 1 / 4.1 | 1 / 2.1 | 1 / 3.1 |
| ALPHA-HCH | 86% | 99% | 0.07 | 0.6 | 15 / 0.19 | | 1 / 0.26 | | 1 / 0.35 |
| BETA-ENDOSULPHAN | 99% | 91% | 0.12 | 0.9 | 18 / 5.6 | 4 / 5.4 | 3 / 2.4 | | 1 / 2.8 |
| BETA-HCH | 98% | 92% | 0.08 | 0.5 | 2 / 0.1 | | | | |
| CAPTAN. | 108% | 55% | 0.84 | 2.5 | 1 / 6.3 | | | | |
| C-CHLORDANE | 98% | 99% | 0.08 | 0.8 | | | 4 / 12.2 | | 3 / 38.1 |
| CHLOROTHALONIL. | 82% | 19% | 0.15 | 0.9 | 19 / 4.0 | | 1 / 1.0 | 1 / 1.0 | |
| C-NONACHLOR | 99% | 93% | 0.05 | 0.3 | | | 1 / 0.31 | | 3 / 5.1 |
| DACTHAL. | 87% | 92% | 0.08 | 0.9 | 19 / 0.2 | | | | |
| DELTA-HCH | 98% | 92% | 0.07 | 0.4 | | | | | |
| DIELDRIN | 99% | 93% | 0.02 | 0.3 | 21 / 2.6 | 10 / 2.3 | 4 / 3.1 | | 5 / 7.9 |
| ENDOSULPHANSULPH | 111% | 91% | 0.15 | 1.3 | 22 / 8.7 | 3 / 1.7 | | 1 / 2.9 | |
| ENDRIN | 98% | 86% | 0.02 | 0.5 | 3 / 0.3 | 2 / 0.04 | 1 / 0.12 | | |
| ENDRIN-KETONE | 87% | 127% | 0.37 | 1.9 | | | | 4 / 5.5 | |
| ETHION. | 107% | 83% | 0.17 | 1.2 | | | 1 / 3.7 | | |
| GAMMA-HCH | 99% | 99% | 0.05 | 0.3 | 13 / 0.67 | 2 / 0.2 | 4 / 7.1 | 5 / 3.8 | 3 / 2.4 |
| HCB | 100% | 100% | 0.01 | 0.2 | 9 / 0.16 | 1 / 0.12 | 4 / 0.46 | 2 / 0.13 | 4 / 5.8 |
| HEPTACHLOR | 99% | 102% | 0.18 | 0.8 | | | | | |
| HEPTACHLOR EPOXID | 98% | 101% | 0.04 | 0.3 | 8 / 0.8 | 2 / 0.04 | 2 / 1.5 | 2 / 0.49 | |
| METHOXYCHLOR | 101% | 98% | 0.04 | 0.2 | | 1 / 0.24 | | | |
| MIREX | 99% | 105% | 0.19 | 0.5 | 2 / 0.2 | | | | |
| OCTACHLOROSTYREN | 109% | 107% | 0.06 | 0.6 | | | | | |
| OXYCHLORDANE | 99% | 94% | 0.10 | 0.6 | | | | | |
| QUINTOZENE | 127% | 106% | 0.37 | 2.5 | 6 / 0.11 | | | | |
| T-CHLORDANE | 97% | 96% | 0.05 | 0.7 | | | 4 / 16.3 | | 3 / 53.9 |
| TECNAZENE | 108% | 77% | 0.12 | 1.3 | | | | | |
| T-NONACHLOR | 98% | 105% | 0.07 | 0.4 | | | 3 / 7.8 | | 3 / 25.4 |