Chromatography Technical Note No AS150

Fully automated solution for the extraction of Non-Polar Pesticides by GC

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Introduction

Non polar pesticides are a group of chemicals which are present in the environment at low concentrations. Pesticides are used on farmland and through leaching can enter the river water and therefore the water treatment processes.

Due to their non-polar nature they have very low solubility in water, but may be found at low concentrations in environmental waters. These pesticides have relatively low predicted no effect concentration (PNEC, the highest predicted concentration in solution whereby the chemical has no toxic effect to the environment) as to the high K_{ow} (the octanol – water partitioning coefficient) values which means the chemicals will favour partitioning from water to the lipids of plants and animals through natural processes. This causes bio-concentration which can cause levels with animals to be at a level which maybe toxic. As well as the environment it is important to have a low concentration of pesticides in drinking water as the same concentration effects. The level of these pesticides must be controlled and strict measurement and control of concentrations in our water systems is required.

This application note follows on from Application note AS144 whereby an off-line solution for non-polar pesticides was developed at ALS Wakefield in May 2015 using a standalone Dual-Head MPS. This solution was taken a stage further by David Evans at ALS. David has now developed a fully automated solution using a dual head MPS with an Agilent 7000C (QQQ) at ALS Coventry. This method now uses automated liquid-liquid extraction with vigorous agitation using the *m*Vorx. Figure 1 shows the fully automated solution at ALS Coventry.

Figure 1 Gerstel Dual Head with Agilent 7000C at ALS Coventry

A suite of fifty five non-polar pesticides were prepared between 10 ng/L and 150 ng/L in treated water. This suite included 1, 2, 4 Trichlorobenzene, Dichlobenil, HCH-alpha, op-DDE, pp-TDE, permethrin-cis, cypermethrin, and Deltamethrin. Analytes present in the aqueous standards were extracted in hexane and injected into an Agilent multimode inlet (MMI).

Instrumentation

Dual Head Gerstel MPS 2
Gerstel *m*Vorx
Maestro software integrated
Agilent 7890 GC with a 7000C Triple quadrupole mass spectrometer

Method

A set of aqueous standards were prepared by spiking the pesticide mixture into the treated water at six different concentrations : 10, 20, 50, 80 and 150 ng/L with internal standard. 8 mL of each were pipetted into 10 mL vials and placed in the sample tray for analysis. From then on the sample preparation was performed by the Dual-Head MPS fitted with a 2.5 mL and a 100 µL syringe. A small aliquot of ethyl acetate was added into each vial to aid recovery of the more polar analytes. After addition of 1 mL hexane, each standard was agitated using the *m*Vorx. To break up the emulsions a small volume of a polar solvent was added. 20 µL was then taken from the top hexane layer and injected directly into the MMI inlet. Each non-polar pesticide was monitored using individual MS/MS Multireaction Mechanism (MRM) transitions.

Results

Figure 2 shows extracted MRM chromatograms for selected pesticides at 10 ng/L.
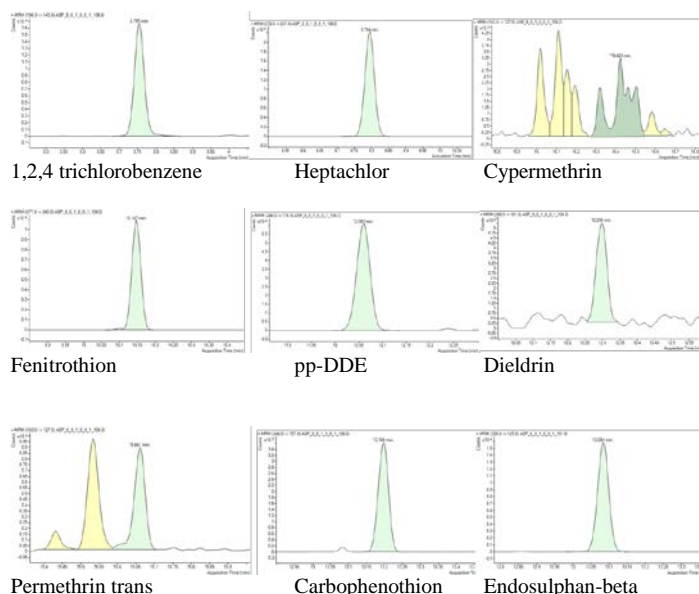

Figure 2 Example chromatograms at the lowest calibrant (10ng/L)

Good linearity was observed for the majority of analytes. Table 1 shows correlation coefficients for a number of pesticides in the test mixture.

Pesticide	Transition	Correlation coefficient (r2)	Fit
124-Trichlorobenzene	180.0 -> 145.0	0.9985	Linear
HCH-beta	181.0 -> 145.0	0.9982	Linear
Dichlobenil	171.0 -> 100.0	0.9998	Linear
Chlordane-#1-trans	372.8 -> 265.9	0.9952	Linear
Tecnazene	261.0 -> 203.0	0.9988	Quadratic
Cyfluthrin	163.0 -> 127.0	0.9987	Quadratic
Trifluralin	306.0 -> 264.0	0.9998	Linear
Cypermethrin	163.0 -> 127.0	0.9998	Linear
Fenitrothion	277.0 -> 260.0	0.9991	Linear
pp-DDT	235.0 -> 165.0	0.9999	Quadratic
Carbophenothion	342.0 -> 157.0	0.9980	Linear
Chlordane-#2-alpha or cis	372.8 -> 265.9	0.9984	Linear
Chlorthal-dimethyl	330.0 -> 298.9	0.9992	Linear
Dieldrin	260.9 -> 191.0	0.9959	Quadratic
Isodrin	193.0 -> 157.0	0.9931	Linear
Permethrin-cis	163.0 -> 127.0	0.9999	Linear

Table 1: Selected correlation coefficients from 6 point calibration

Figure 3 shows two example linearity plots (HCH-alpha and Dieldrin) from the automated liquid-liquid extraction.
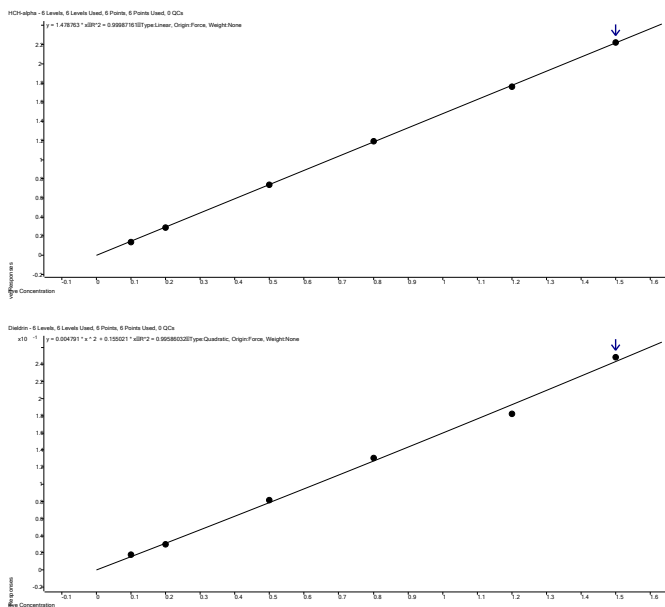
Although precision experiments have not yet been performed on the 55 non polar pesticide suite, % relative standard deviation (% rsd) were calculated on internal standards present from the six different calibration solutions. Table 2 shows % rsd

to indicate the good reproducibility can be achieved using this method.

Standard	D3 1,2,4 Trichlorobenzene Area	13C6-HCH-gamma Area	d14-Trifluralin Area	d10-Parathion-ethyl Area
1	299878	366733	579973	131833
2	313286	379972	580459	123728
3	313128	369943	552668	119763
4	312448	364992	549098	121595
5	309863	360063	559213	126399
6	314287	362141	529283	114059
Standard deviation	5404.3	7102.1	19595.0	6040.4
Mean	310481.7	367307.3	558449.0	122896.2
%RSD	1.7	1.9	3.5	4.9

Discussion

This method offers a fully automated solution for non-polar pesticides in water. Please contact Anatune if you need any further information on this technique. Further work could be performed to reduced volumes of hexane to increase the concentration factor and improve detection limits. Analysis on the Agilent 7010 QQQ could further improve detection limits for the non-polar pesticides.