Anatune Ltd
Unit 4, Wellbrook Court, Girton Road, Cambridge, CB3 0NA, UK
Tel: +44 (0) 1223279210 Fax: +44 (0) 1223279253
Email: info@anatune.co.uk Internet: www.anatune.co.uk

Initial GC/Q-TOF Work for Trace Analysis of Organochlorine Pesticides Using NCI

Dan Carrier, Jeff Stubbs, Anatune Ltd., Girton, Cambridgeshire (UK), John Quick, ALS Coventry (UK).

First Published: 2016

Introduction

Organochlorine pesticides (OCPs) need to be controlled down to extremely low levels in water. From the Water Framework Directive (WFD), the aim is to have limits of detection for certain OCPs at 10 fg/l for surface and coastal water.

In recent work on the 7200 Q-TOF [1], low limits for OCPs can be achieved using Negative Chemical Ionisation (NCI) with accurate mass. It was further thought that sensitivity could be enhanced by switching reagent gas from methane to ammonia as this can provide less fragmentation.

To further enhance detection limits for the OCPs, a large volume injection method was used with the Cold Inlet System (CIS 4) inlet.

Figure 1 – GERSTEL Dual Head with Agilent GC/Q-TOF with large volume injection on CIS.

Instrumentation

Dual Head GERSTEL MPS *xt*
Anatune CIS
Maestro software integrated
Agilent 7890B GC with a 7200 Q-TOF mass spectrometer in NCI mode

Method

A suite of OCPs containing heptachlor, heptachlor epoxide, cyfluthrin, cis/trans permethrin and cypermethrin was prepared at two different concentrations 1 µg/l and 10 ng/l in hexane respectively.

Results

Figure 2 shows the Mass Spectra in NCI for the key ions in beta endosulfan. Due to the high MS resolution achieved, it is possible to extract specific masses with a narrow mass range to increase the signal to noise of each chromatographic peak detected.

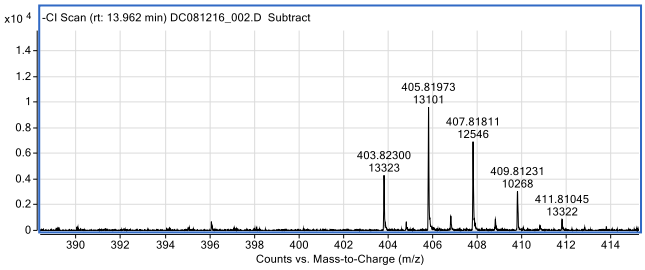

Figure 2 – Mass spectra for beta endosulfan (showing key ions for NCI). The MS resolution is the value below the mass at approximately 12000.

Figure 3a shows a 10 ng/l solution of alpha and beta endosulfan in hexane extracting ion 405.81973. It is also possible to extract and combine other related ions to alpha and beta endosulfan to further increase detection limits (figure 3b).

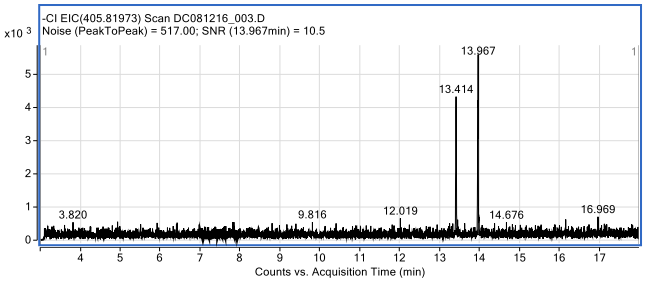

Figure 3a – Extracted ion chromatogram of 10 ng/l alpha and beta endosulfan.

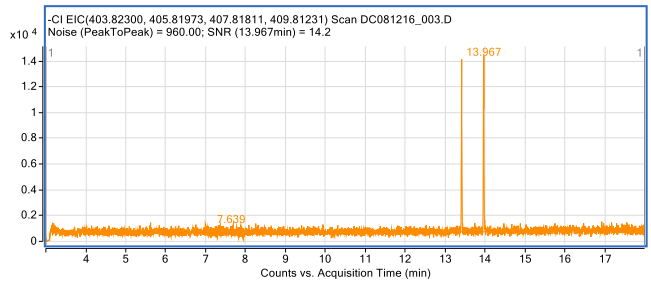

Figure 3b – Combined extracted chromatogram (extracted ions 403.8230, 405.81973, 407.81811 and 409.81231 m/z) of 10 ng/l alpha and beta endosulfan.

By smoothing the data, a further increase in signal to noise for the endosulphans can be achieved.

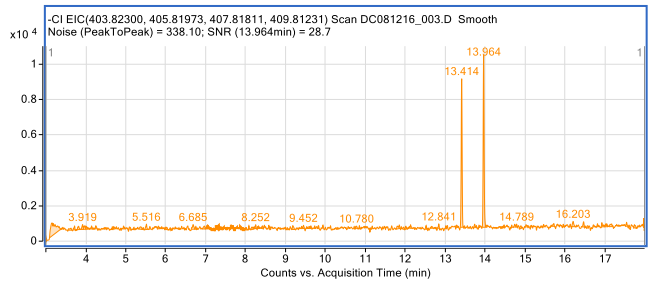

Figure 4 – Combined extracted chromatogram (extracted ions 403.8230, 405.81973, 407.81811 and 409.81231 m/z) of 10 ng/l alpha and beta endosulfan (smoothed).

Further advances in detection limits can be made by increasing the injection volume using the CIS. Figure 3 shows a 20 µl injection of the 10 ng/l solution of alpha and beta endosulfan.

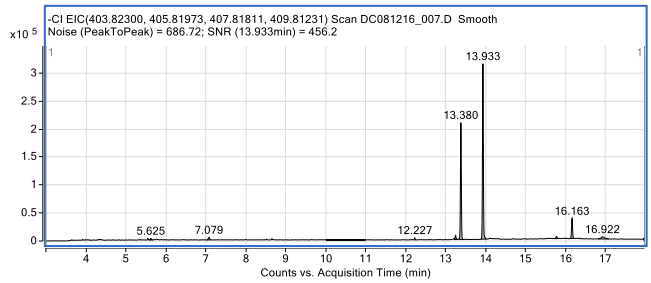

Figure 5 – 20 µl injection combined extracted chromatogram (extracted ions 403.8230, 405.81973, 407.81811 and 409.81231 m/z) of 10 ng/l alpha and beta endosulfan (smoothed).

As you would expect, an increase by a factor of 20 was observed from moving from a 1µl injection to 20 µl injection.

Less sensitive Organochlorine pesticides were then investigated and extracted ion chromatograms of these are shown below. Figure 5 shows a comparison of heptachlor (extracted ion chromatogram) 1 µl and 20 µl injection respectively. Signal to noise ratios are also displayed on the chromatograms.

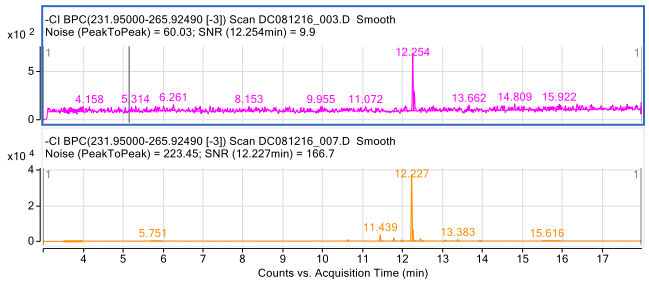

Figure 6 – Extracted ion chromatograms of heptachlor at 10 ng/l (1 µl and 20 µl injection respectively).

Figure 7 shows a comparison of heptachlor epoxide (extracted ion chromatogram) 1 µl and 20 µl injection respectively. Signal to noise ratios are also displayed on the chromatograms.

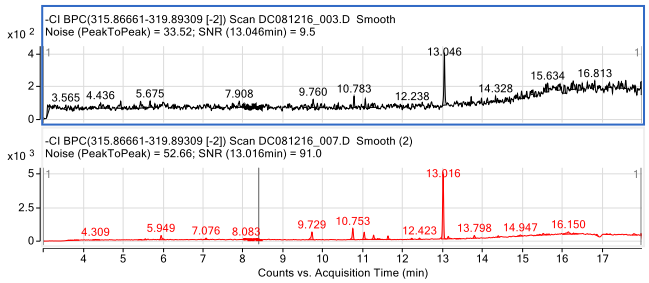

Figure 7 - Extracted ion chromatograms of heptachlor epoxide at 10 ng/l (1 µl and 20 µl injection respectively).

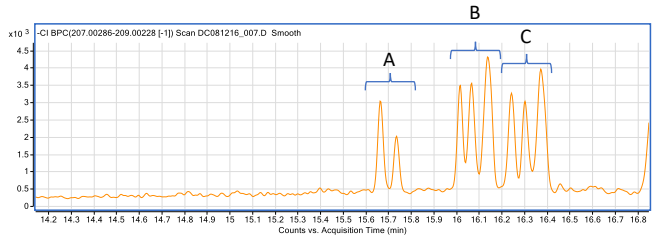

Figure 8 - Extracted ion chromatograms of the pyrethoids at 10 ng/l (20 µl injection respectively). A – cis/trans permethrin B cyfluthrin C cypermethrin.

From this GC/Q-TOF method, we were able to find some positive results in a real sample extract. Figure 9, 10 and 11 show positive results for heptachlor, heptachlor epoxide and the pyrethroids. Note this was only performed on a 1 µl injection.

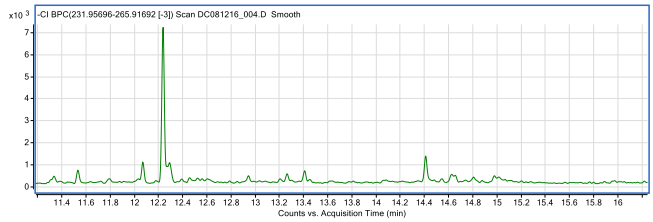

Figure 9 – Real sample extract showing positive result for heptachlor at 12.2 minutes.

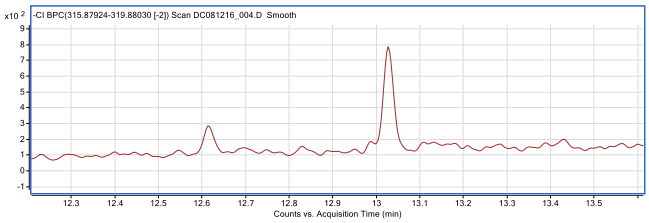

Figure 10 – Real sample extract showing positive result for heptachlor epoxide at 13.04 minutes.

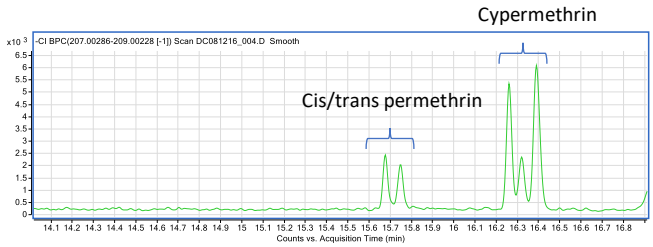

Figure 11 – Real sample extract showing positive result for the pyrethoids between 15 to 16 minutes.

It was noted that some of the isomers are not observed in the real sample.

Discussion

We are currently working with John Quick at ALS to try to get down to the required limit of 3 fg/l. Future work will include looking into a SPE method followed by Stir Bar Sorptive Extraction (SBSE).

I would like to thank John Quick for his help and advice for development of this solution for trace level OCPs in water using the GC/Q-TOF

[1] New Levels of Mass Spectral Selectivity for Pesticide Residue Analysis: GC/Q-TOF in the MS/MS Mode with Chemical Ionization.
Philip L. Wylie Agilent Technologies, Wilmington, DE, USA (phil_wylie@agilent.com).