MULTI RESIDUE ANALYSIS OF PRIORITY POLLUTANTS IN DRINKING AND SURFACE WATER USING SOLID PHASE EXTRACTION AND GC TANDEM QUADRUPOLE MS/MS

Waters

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INTRODUCTION

EU council directive 76/464/EC[1] lists 132 compounds that have restricted levels in drinking and surface waters. Of these compounds, 109 are amenable to gas chromatographic analysis. Currently published methods[2] involve the use of two injections, one using selected ion recording as a screen, followed by a full scan injection for confirmation. The use of tandem quadrupole GC-MS/MS allows the analyst to combine the screening and confirmatory injections into one run, whilst also allowing a reduction of the chromatographic separation required for confirmation of some of the target compounds.
The EU list has many similarities with the target compound lists of USEPA water quality methods such as 625[3] and 8270[4] it should be noted that the list analysed in this method is by no means an exhaustive one.
The compound groups represent a wide range of polarities and compound types, and include benzidines, chloronitrotoluenes, organochloro pesticides, organophosphorus pesticides, chloroanilines, chlorophenols, chloronitrobenzenes, chlorotoluidines, phenylurea pesticides, PCBs, Semi volatile halogenated compounds, PAHs, triazines and volatile amines.
Many of these compound groups will typically have their own dedicated analysis method that requires specific extraction/ clean-up and final analysis. Combining these groups into a single method would allow the laboratory to significantly increase sample throughput.
The high selectivity and specificity of multiple reaction monitoring (MRM) acquisitions also helps to shorten the time required for data processing by reducing the possibility of false positives and the time spent confirming the presence of target compounds. The method presented is intended as an example of what is possible by implementing techniques such as GC-Tandem Quadrupole MS/MS and solid phase extraction.

METHODS AND MATERIALS

All analyses were performed using an Agilent 6890 GC oven fitted with a CTC Combi PAL autosampler. The GC was directly interfaced to a Waters Quattro Micro GC tandem quadrupole mass spectrometer that was operated in the EI+ ion mode. The instrument ion source was operated at 70eV electron energy, with a source temperature of 180 °C. Two GC columns were evaluated, J&W DB17-ms 30m 0.25mm ID, 0.25 µm df and Varian factor four vf5-ms 30m 0.25mm ID, 0.25 µm df. Injections were made using both pulsed splitless and cool on column (COC) injections, with a 2m 0.53mm ID retention gap fitted for COC injections.

MRM analysis was performed using a single transition per compound, where confirmation is based upon one MRM transition plus the retention time, and also using two MRM transitions per compound, where the strictest EU confirmatory criteria are satisfied. The difference in sensitivity between the two approaches was compared.
Calibration curves were acquired over the concentration range 0.05 to 5µg/L.
Extraction and clean-up were performed using Waters Oasis HLB 3cc, 60mg SPE cartridges. 200ml of each filtered water sample was spiked with an internal standard mixture containing d5-nitrophenol, 2-fluorobiphenyl and p-terphenyl-d14 at a level of 500ng for each component. The water was adjusted to pH4 using 1N HCl solution. The SPE cartridges were conditioned with 6 mL DCM, 6 mL acetonitrile and 6 mL of water at a flow rate of 3 mL/min. The water samples were then loaded at a flow rate of *ca* 6 mL/min. After sample loading was completed, the cartridges were washed with 1 mL water. The cartridges were then dried under a flow of nitrogen (ca 1ml/min) for 20mins, followed by final elution with either **A** 2.5ml DCM/ACN (4:1), 5ml DCM; or **B** 5ml DCM. After elution, the extract was adjusted to a volume of ca 0.5ml under a stream of dry nitrogen at ambient temperature, followed by the addition of 500ng of d10-anthracene as a recovery standard.
Drinking and canal water samples were spiked with the analytes at concentrations of 0.5 µg/L and 5µ g/L prior to extraction for recovery tests.

The GC temperature ramps employed were: -

30m DB17-ms
40°C/1min, 3°C/min to 160°C, 7°C/min to 240°C,15°C/min to 305°C, hold 15mins. 1ml/min He flow

30m vf5-ms
40°C/0.8min, 6°C/min to 160°C, 8°C/min to 310°C, hold 2mins. 0.9ml/min He flow

All injections in pulsed splitless mode were made with an injection temperature of 250 °C, using a double gooseneck 4mm ID liner and 1µL injection volume. The injections were made with a 1 min 110kPa pulse, a purge time of 1min and a purge flow of 70ml/min. Cool on column injections were made in track oven mode.

RESULTS AND DISCUSSION

The two GC columns were evaluated for both sensitivity and chromatographic separation. The optimum conditions for separation were obtained using the DB17-ms column with COC injection. However these conditions resulted in a 70 minute run time, with a 22 function MRM experiment required. Figure 1 shows the reconstructed TIC chromatogram from a 1ng/µL (5µg/L) injection in MRM mode.

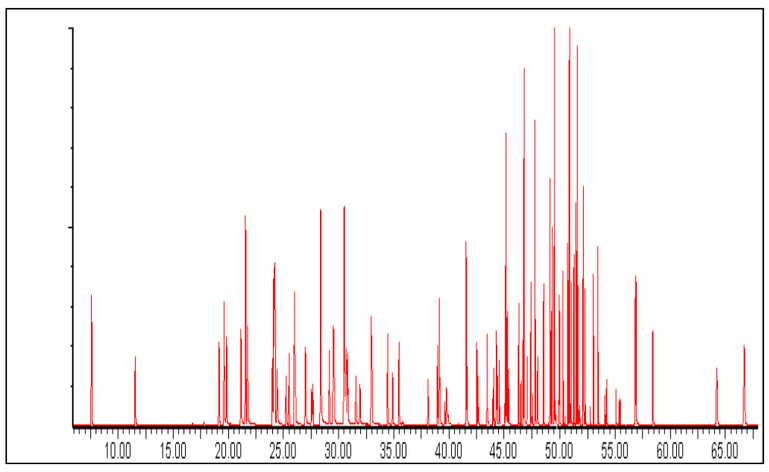

Figure 1, reconstructed TIC for all compounds analysed using DB17-ms column with COC injection

Analysis using the vf5-ms column, combined with pulsed splitless injection afforded the best overall compromise of separation, sensitivity and robustness, making it the most suitable option studied for a robust, high throughput screening/confirmatory method. The vf5-ms resulted in a total run time of <43 minutes, requiring 19 MRM time windows to be employed for confirmatory analysis. Due to the distribution of eluting peaks, it also afforded the opportunity for overlapping time windows in some areas of the elution range, giving more flexibility if retention times were to change for any reason (typically as the GC column is shortened during it's lifetime). Figure 2 shows the reconstructed TIC from a 1ng/µL (5µg/L) injection acquired in MRM mode.

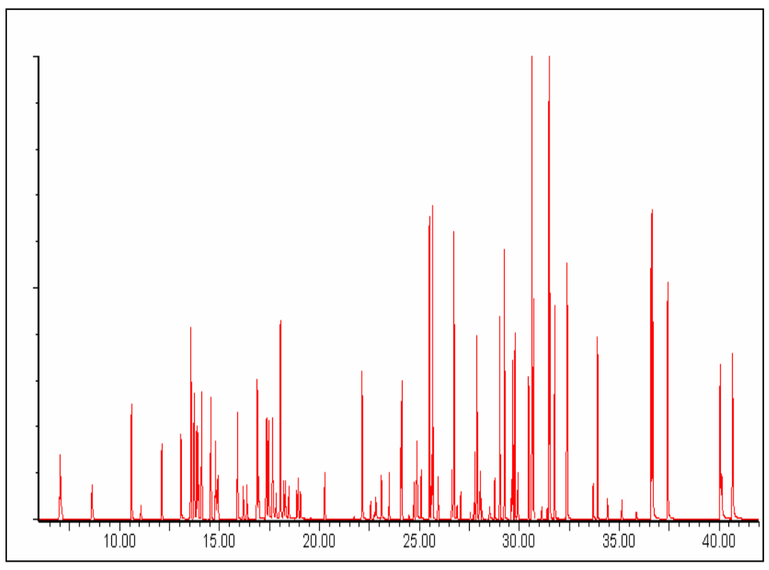

Figure 2, reconstructed TIC for all compounds analysed using the vf5-ms column with pulsed splitless injection

The 0.5µg/L spiked water samples were analysed and quantified to determine the specific recoveries for >100 compounds using the single SPE sorbent, with a single extraction procedure.
Elution method B was found to give the best overall performance with 72% of compounds recovered within the range 70-120%. The compounds recovered <50% included compounds such as disulfoton, which undergoes rapid degradation[5] in aqueous solution. Figure 3 summarises the recoveries for all of the compounds, using elution method B.

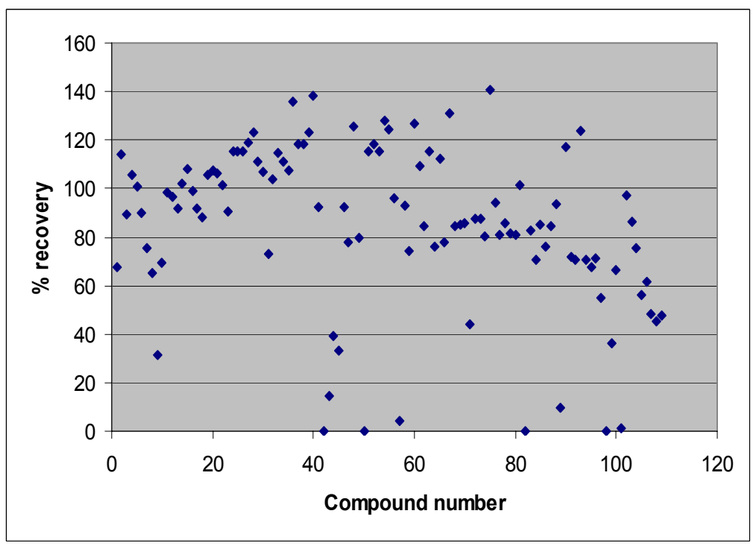

Figure 3, Distribution of average recoveries (n=5) for elution method B (5ml DCM)

The method LODs were assessed, both for the confirmatory (two MRM transitions per compound) and screen (single MRM transition per compound. All LODs are based upon a signal to noise ratio of 3:1, using the confirmatory transition (where applicable). The instrumental LODs are based upon the lowest concentration standard injection where possible. The method LODs are based upon the average LOD obtained from 5 replicate 0.5µg/L spiked water samples, extracted using elution method B.
Figure 4 gives a graphical representation of the LODs for all compounds determined, showing the distribution of LOD across the complete range of compounds analysed.

The LODs reported are excellent for such a wide range of compounds with a single generic extraction, with many method confirmatory LODs in the low ppt (ng/L) range.
The chromatograms for 0.05µg/l Dichlovos, acquired using both the screen (figure 5), and the confirmatory (figure 6) acquisitions are shown below.
Figure 7 shows the reconstructed TIC from MRM acquisition of a 0.1µg/L spiked canal water sample.

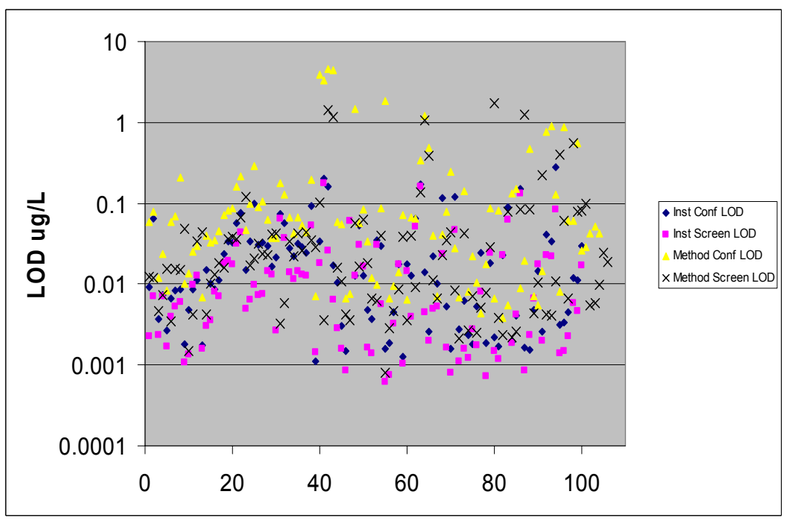

Figure 4, Distribution of instrumental and method LODs for all compounds

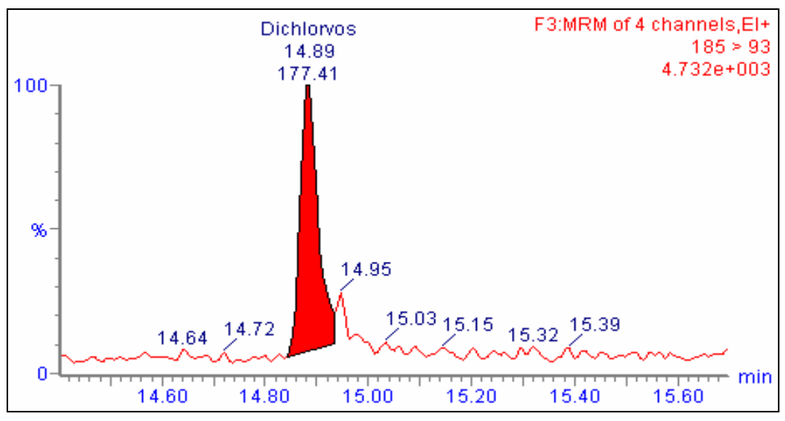

Figure 5, Screening chromatogram for Dichlorvos, at a 0.05µg/L concentration

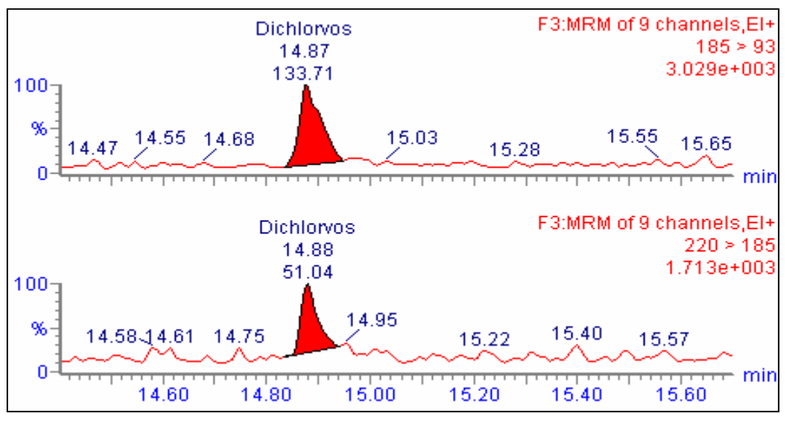

Figure 6, Confirmatory chromatogram for Dichlorvos, at a 0.05µg/L concentration

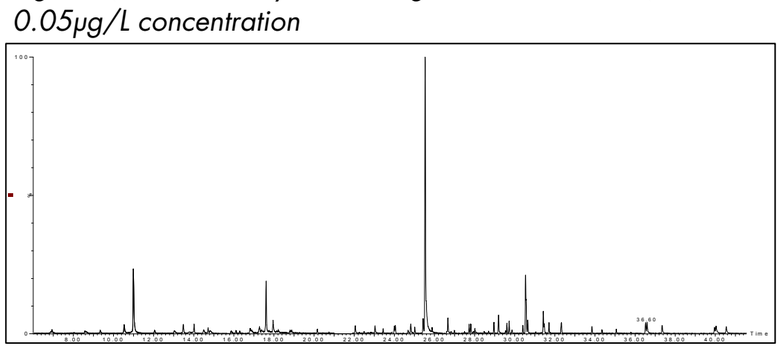

Figure 7, 0.1µg/L spiked canal water reconstructed TIC

CONCLUSIONS

The analysis of pollutants in water requires the laboratory to analyse a large number of samples for a wide range of compounds. The analysis can be time consuming requiring the application of a number of different methods for different compound groups.
The method described here presents the laboratory with the opportunity to combine a number of these class specific analyses into a single method that can result in the reduction of sample turnaround times.
The use of solid phase extraction, combined with GC-MS/MS detection allows the laboratory to achieve much greater confidence in results obtained. The use of solid phase extraction combined with GC-MS/MS detection allows the laboratory to achieve greater confidence in results obtained. Additionally, the laboratory can reduce solvent usage and improve analyte recovery during sample preparation when compared with traditional liquid-liquid techniques.

References

[1]Directive 76/464/EEC, Dangerous Substances Discharged into the Environment, Official Journal of the European Union no. L 129, Brussels, 1976.
[2] Anal. Chem.2000, 72,1430-1440; Broad Spectrum Analysis of 109 Priority Compounds Listed in the 76/464/CEE Council Directive Using Solid-Phase Extraction and GC/EI/MS; Sílvia Lacorte, Ingrid Guiffard,Daniel Fraisse,Damià Barceló
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[4] USEPA method 8270, Semivolatile Organic Compounds by GC/MS, U.S. EPA Office of Solid Waste (OSW) Methods Team, Ariel Rios Bldg. (5307W), 1200 Pennsylvania Ave. NW, Washington, DC 20460
[5] Lacorte, S.; Lartiges, S.; Garrigues, P.; Barcelo´ , D. *Environ. Sci. Technol.,1995, 29* (2), 431-438.

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