

ENVIRONMENTAL ANALYSIS

HIGH SENSITIVITY GC/MS/MS ANALYSIS OF NONPOLAR ORGANIC COMPOUNDS IN WATER USING THE AGILENT 7000 TRIPLE QUADRUPOLE GC/MS

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SOLUTION NOTE

Environmental

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Abstract:

A highly sensitive and reliable method has been developed for 51 nonpolar compounds in potable water, and PBDEs, PAHs, and diazinon in wastewater. Most MRLs in potable water were 2 ng/L or less, and the MRLs for the analytes in wastewater less than 0.2 ng/L for some compounds. Run time is less than 20 minutes, sample preparation is straight forward, and the potable water method is accredited by the UKAS.

Introduction

The environmental analysis of nonpolar organic compounds, including pesticides and polychlorinated biphenyls (PCBs), has traditionally been done using gas chromatography (GC) with electron capture detection (ECD). Two columns with differing modes of separation are often needed to confirm identity of the compounds, since the ECD detector does not provide any structural information. As a result, GC/ECD methods can be time-consuming and tedious due to the use of two columns, and can be sensitive to interferences which can reduce sensitivity and the ability to confirm identity.

The use of GC and tandem mass spectrometry (MS/MS) can eliminate interferences problematic with GC/ECD, while providing the required sensitivity and high-confidence compound identification. Environmental analyses for nonpolar organic compounds can benefit by transitioning to a GC/MS/MS platform.

Severn Trent Services, in the United Kingdom, has successfully made this transition, using the Agilent 7000 Triple Quadrupole GC/MS to provide required limits of detection (LODs) and precision requirements for a suite of 51 nonpolar organic compounds in potable water, including chlorinated pesticides and PCBs.



Using a single DB column and two multiple reaction monitoring transitions per analyte, Severn Trent has developed a method with a 12-minute run time and as little as 15-minute cycle time, better selectivity, enhanced sensitivity and robustness, and easier data processing compared to the previous GC/ECD method. This application note presents the results obtained using this method to analyze both potable water and wastewater.

The highest limit of detection (LOD) in potable water with minimal sample prep was 3 ng/L for captan, all others were 2 ng/L or less, well below the LOD requirement of < 0.025 µg/L. Recoveries ranged from 99.5 to 105.1% for compounds spiked into water of medium hardness (200 mg/L CaCO₃) at the UK prescribed concentration value (PCV), with the majority of the relative standard deviations (RSDs) below 5%. The method has also been used for crude sewage and industrial effluents, with more extensive sample preparation.

These matrices are held to very low detection limits, and this method can provide method reporting limits (MRLs) less than 1 ng/L for some compounds. The method is accredited for potable water by the United Kingdom Accreditation Service (UKAS) and is used routinely at Severn Trent Services for analysis of potablewater.

RESULTS AND DISCUSSION

METHOD DEVELOPMENT

Moving the method from a GC/MS/ECD platform to GC/MS/MS on the Agilent 7890 Series GC and 7000 Triple Quadrupole GC/MS required only a slight modification in the liquid extraction method. A DB1 column provided good separation of DDT isomers, and the multimode inlet enabled large injection volumes, eliminating the need for a time consuming solvent evaporation step. Moving the method to GC/MS/MS made possible cycle times less than 15 minutes with cryocooling, high selectivity through the use of two transitions per compound, and easier data processing through the use of Agilent MassHunter software.

METHOD VALIDATION

The method was validated for the analysis of 51 compounds in five water matrices: soft, medium, and hard potable water; borehole and surface raw water. Most of the compounds contained organochlorine, and they exhibited a large volatility range (Table 1). The laboratory precision target was less than 12.5%.

The UK prescribed concentration values (PCVs) for presence in potable water are 0.1 µg/L for individual pesticides. Method validation with water of medium hardness spiked at PCV levels resulted in recoveries no lower than 98.4% and no higher than 105.1%, with RSDs as low as 2.1% and no higher than 7.1% (Table 2). Over three months, the RSDs ranged from 1.6 to 7.4%, with 43 of the 51 compounds having RSDs below 5%. Figure 1 illustrates some typical results for the hexachlorohexane (HCH) delta isotope over a three month period.

1,2,4-Trichlorobenzene	p,p'-DDE	PCB 28
Hexachlorobutadiene	Dieldrin	PCB 52
Dichlobenil	o,p'-TDE	PCB 101
alpha-HCH	Endrin	PCB 118
beta-HCH	beta-Endosulphan	PCB 153
Hexachlorobenzene	p,p'-TDE	PCB 138
gamma-HCH	o,p'-DDT	PCB 180
delta-HCH	p,p' DDT	Cyfluthrin
Chlorothalonil	Methoxychlor	Cypermethrin
Heptachlor	Captan	Fenvalerate
Aldrin	EPTC	Deltamethrin
Isodrin	Tecnazene	Phorate
cis-Heptachlor Epoxide	Trifluralin	Tri-allate
trans-Heptachlor Epoxide	Disulphoton	Chlorpyrifos-methyl
o,p'-DDE	Fenitrothion	Parathion-ethyl
alpha-Chlordane	cis-Permethrin	Chlorpyrifos-ethyl
alpha-Endosulphan	trans-Permethrin	Carbophenothion

Med. water - PCV spike								
Name	Recovery	RSD	Name	Recovery	RSD	Name	Recovery	RSD
EPTC	105.1%	2.9%	trans-Heptachlor epoxide	104.0%	6.8%	Methoxychlor	100.7%	6.3%
124-TCB	100.3%	3.3%	Dieldrin	100.6%	8.3%	PCB 180	100.9%	4.8%
Hexachlorobutadiene	101.6%	5.2%	Isodrin	101.8%	4.5%	cis-Permethrin	102.2%	3.5%
Dichlobenil	103.1%	3.5%	o,p' DDT	100.7%	3.7%	trans-Permethrin	102.0%	3.3%
Tecnazene	102.7%	5.1%	PCB 101	101.3%	3.7%	Cyfluthrin	99.1%	3.4%
Trifluralin	104.3%	3.8%	alpha-Chlordane	99.5%	4.7%	Cypermethrin	100.6%	3.0%
alpha-HCH	101.6%	2.9%	alpha-Endosulphan	102.3%	3.3%	Fenitrothion	100.6%	4.7%
Hexachlorobenzene	101.7%	4.8%	p,p' -DDE	101.0%	3.5%	Deltamethrin	98.4%	6.9%
gamma-HCH	101.6%	2.6%	OP-TDE	100.7%	4.0%	delta-HCH	102.0%	2.6%
beta-HCH	101.9%	3.0%	PCB 118	100.9%	3.3%	Triailate	104.1%	3.9%
PCB 28	102.9%	4.4%	PP-TDE	100.8%	4.5%	Parathion-ethyl	100.7%	3.2%
Chlorothalonil	107.8%	3.6%	Endrin	98.9%	7.2%	Carbophenothion	101.5%	5.6%
Heptachlor	104.7%	6.0%	op-DDT	102.8%	5.4%	Chlorpyritos-methyl	101.1%	2.4%
PCB 52	100.8%	5.0%	PCB 153	100.5%	3.6%	Chlorpyrifos-ethyl	100.7%	2.7%
Fenitrothion	103.5%	3.9%	beta-Endosulphen	103.1%	3.7%	Captan	101.5%	5.4%
Aldrin	104.2%	5.8%	PCB 138	100.5%	3.1%	Phorate	101.1%	2.5%
cic-Heptachlor epoxide	104.0%	7.1%	pp-DDT	101.1%	2.1%	Disulphoton	102.1%	2.1%

Table 2. Method Validation Results for Potable Water of Medium Hardness

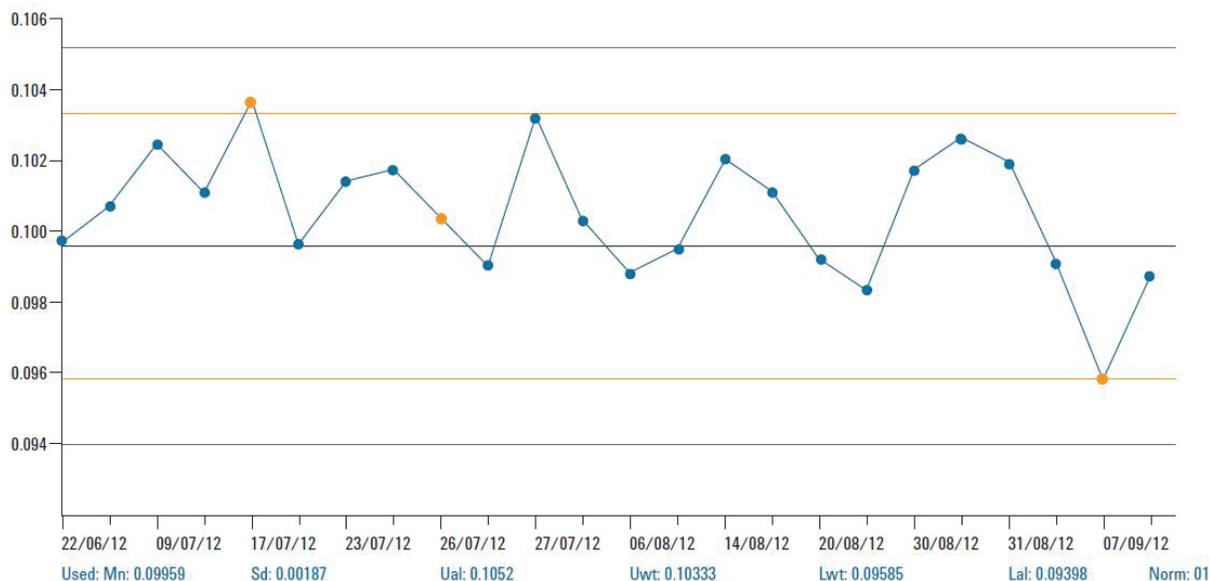


Figure 1. Analytical quality control (AQC) results for analysis of hexachlorocyclohexane (HCH) delta spiked into water at 0.1 µg/L, over a three month period.

METHOD PERFORMANCE

The method routinely provided calibration curves with R² values >0.998 for a concentration range of 10 to 120 ng/L. Chromatographic separation was sufficient to separate the isomers of DDT in potable water for example, as well as the HCH isomers (Figure 2). Applying the method to wastewater specifically for the analysis of PBDEs, PAHs, and diazinon required more extensive sample preparation than was required for the 51 nonpolar organic compounds in potable water. The run time is also slightly longer owing to the need to separate Benzo(b) and (k) Fluoranthene.

This version of the method meets the requirement for low method reporting limits (MRLs) in wastewater for these analytes, with some compounds having MRLs <0.2 ng/L. In these dirty matrices, including crude sewage, the sensitivity and selectivity of GC/MS/MS are essential. For example, the method easily detects cypermethrin in crude sewage at 2.5 ng/L and PBDE 47 at 1 ng/mL (Figure 3). The dynamic range of the method enables detection of diazinon in landfill leachate at 0.7 ng/L, and 1,300 ng/L in effluent from a dyeing plant (Figure 4). The lower MRLs for the wastewater method are due to a greater concentration factor during sample preparation, compared with the potable water method. The sensitivity and selectivity of the 7000 Triple Quadrupole GC/MS enables these LODs across a range of difficult matrix types, which would be impossible with a mass selective detector (MSD) and/or conventional detectors.

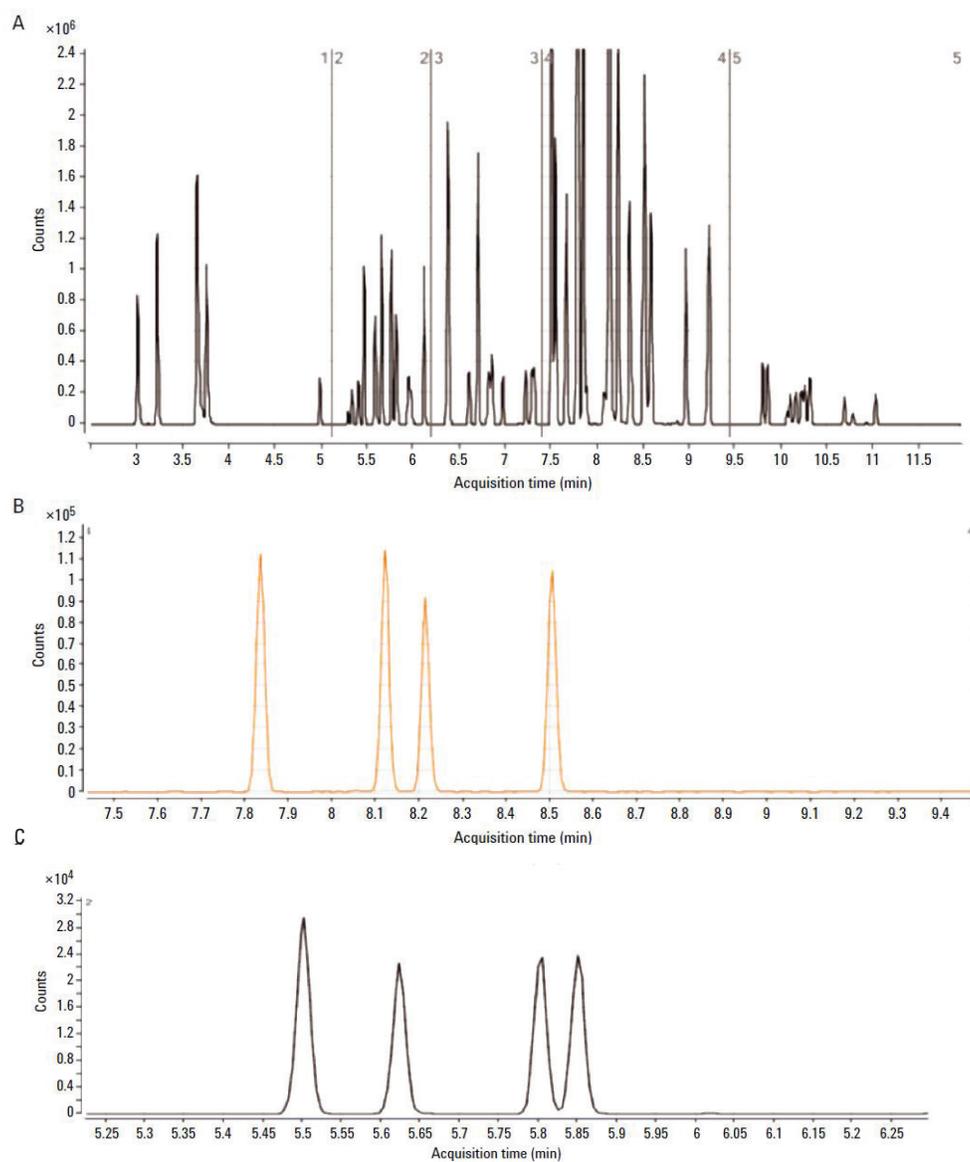


Figure 2. Representative chromatograms for: A. Total ion current (TIC) of 51 nonpolar compounds spiked at 120 ng/L into potable water of medium hardness; B. Extracted ion current (EIC) for DDT isomers spiked at 10 ng/L; C. EIC for four HCH isomers spiked at 10 ng/L.

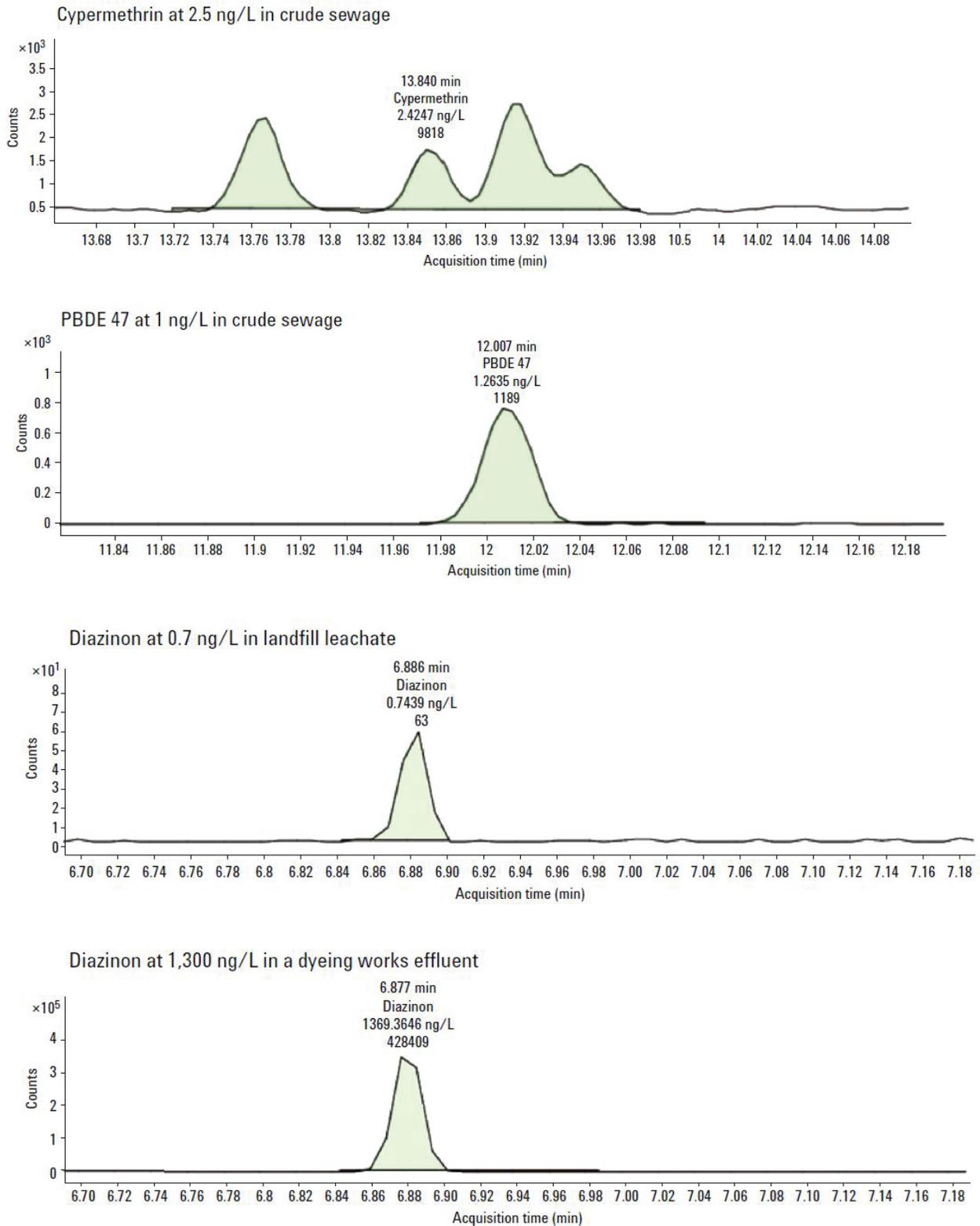


Figure 4. Dynamic range of analysis of diazinon in wastewater.

CONCLUSION

A sensitive and reliable GC/MS/MS method has been developed on the Agilent 7000 Triple Quadrupole GC/MS that provides required LODs and precision for analysis of 51 nonpolar organic compounds in potable water. It also enables detection of as low as sub-1 ng/L (ppt) levels in wastewater for PAHs, PBDEs and organochlorine pesticides. It is rapid and robust, with a cycle time as little as 15 minutes and recovery RSDs that did not exceed 7.4% for all 51 compounds in potable water over a three month period. This method is UKAS accredited for potable water and has been in routine use in this laboratory for several months.

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