

## High Throughput Multi-Residue Screening of Drinking Water using the SPE-DEX and Pegasus GC-TOF MS

Steve Scott, Thames Water, Reading, UK

Diane Turner, ATAS, Hardwick, Cambridgeshire, UK

### Introduction

In cases of pollution incidents, an important objective for the water industry is to decrease turn around times of samples and increase capacity. Traditional techniques involve the liquid-liquid extraction (LLE) of the drinking water sample with dichloromethane followed by drying with sodium sulphate, a concentration step and GC-MS analysis. The total analysis time is 2-3 hours depending on the number of peaks found and if the peak(s) were identifiable in the database.

A new approach to this analysis has been tried using automated solid phase extraction with drying of the extract using a Gore-Tex membrane and analysis by fast GC-TOFMS. This reduces the total analysis time to 30 minutes.

The Horizon Technology SPE-DEX is a fully automated extraction system providing speed, accuracy and simplicity for aqueous organic extractions. It delivers all necessary solvents, processes the sample directly from the original sample bottle and thoroughly rinses it, extracts the analyte from the SPE disk in a collection vessel then purges the extractor in preparation for the next sample.

Horizon Technology's DryDisk and solvent drying system is a physical separation process for the removal of residual water from organic extractions. It uses a Gore-Tex hydrophobic membrane with selective permeability to remove residual water from solvent extracts without retaining the analytes of interest. More consistent recoveries are obtained and faster, without all the problems of chemical drying.

The Pegasus III Time-of-Flight Mass Spectrometer can collect up to 500 full mass spectra per second, obtaining sufficient data density to accurately characterise even the narrowest peaks and therefore enabling fast GC-MS analyses to be carried out. The Peak Find algorithm automatically locates all peaks in the chromatogram, including coeluting peaks buried beneath the background of the TIC. The Mass Spectral Deconvolution algorithm then automatically extracts the mass spectra for each analyte, free of interferences from the system and matrix backgrounds and coeluting analytes. The automated data processing method quickly and accurately enables the detection and identification of low-level unknown analytes.

Presented here are the initial results from using this system to qualitatively analyse a wide range of different compounds from phenols to triazines to organochlorine and organophosphorous pesticides spiked into tap water at a concentration of 1 ug/L.

### Instrumentation and Conditions

- Horizon Technology SPE-DEX 4790
- Horizon Technology DryDisk
- Optic 2 Programmable Injector
- Focus Robotic Sample Processor
- Agilent 6890 GC
- Leco Pegasus III ToFMS
- Leco ChromaTOF™ software

#### Optic Conditions:

Method: Splitless with an ATAS splitless liner  
Temperature ramp: 35 °C  
8 °C/s to 325 °C  
Pressure profile: 31.3 psi (2.5 mins)  
Initial 31.3 psi to Final 60.4 psi  
Splitless time: 2.5 mins

#### GC Conditions:

Column: DB-5, 20 m x 0.18 mm x 0.18 µm  
Oven program: 40 °C (hold 3 mins)  
80 °C/min to 280 °C (hold 3.5 mins)  
Total run time: 9.5 mins  
Carrier gas: Helium

#### MS Conditions:

Solvent delay: 200 sec  
Mass range saved: 30-500  
Scan rate: 30 spectra/s  
Ion source temperature: 230 °C  
Transfer line temperature: 260 °C

### Compound List

#### Phenols:

Phenol	4-Chlorophenol	4-Chloro-3-Methylphenol
2-Methylphenol	2,5-Dimethylphenol	2,4,5-Trichlorophenol
3-Methylphenol	2,4-Dimethylphenol	2,4,6-Trichlorophenol
4-Methylphenol	3,5-Dimethylphenol	Pentachlorophenol
2-Chlorophenol	2,4-Dichlorophenol	

#### OPPs/OCPs:

Dichlorvos	α-HCH	Hexachlorobutadiene
Tecnazene	γ-HCH	Hexachlorobenzene
Trifluralin	β-HCH	Propetamphos
Diazinon	δ-HCH	Parathion-methyl
Heptachlor	Endrin	Parathion-ethyl
Fenitrothion	Aldrin	Heptachlor epoxide
Cyanazine	Isodrin	cis-Chlordane
Malathion	p,p-DDE	trans-Chlordane

Fenthion	o,p-TDE	$\alpha$ -Endosulfan
Dieldrin	p,p-TDE	$\beta$ -Endosulfan
Methoxychlor	o,p-DDT	Azinphos-methyl
Carbofenothion	p,p-DDT	Azinphos-ethyl

**Triazines:**

Simazine	Chlortoluron	Diuron	Prometryn
Atrazine	Isoproturon	Linuron	Terbutryn
Propazine	Tebuthiuron	Monuron	Ametryn
Propyzamide	Carbetamide		

**Internal standards:**

d <sub>6</sub> -Benzene	d <sub>10</sub> -p-Xylene	d <sub>5</sub> -Chlorobenzene
d <sub>6</sub> -Phenol	d <sub>12</sub> -BHT	d <sub>8</sub> -
Naphthalene		
d <sub>3,4</sub> -Hexadecane	d <sub>10</sub> -Phenanthrene	d <sub>62</sub> -Squalene

**Methods**

1 litre of tap water was spiked with pesticides, acidified to pH2 and loaded onto the SPE-DEX. The system automatically pre-conditioned the 50 mm hydrophilic disk with DCM, acetone and water before extracting the sample through it. The analytes were then eluted from the disk with DCM and the extract dried using the DryDisk, a portion was then transferred to a vial for analysis. The final extract volume was not controlled or concentrated therefore accurate quantitation was not possible.

In one instance, after extracting the water sample through the disk at pH2, the water was collected, the pH adjusted to pH12 and the sample passed through the disk a second time.

A 1 uL cold splitless injection was carried out for analysis of the samples by GC-TOFMS. A fast oven temperature ramp rate was used with a narrow bore column and a fast column flow of 1.8 mL/min.

**Results**

The SPE-DEX was shown to work for all groups of compounds evaluated, including triazines, phenols, organochlorine and organophosphorous pesticides. Even very volatile compounds found in tap water like the THMs: Dibromochloromethane (Figures 1 & 2), tribromomethane and dibromoacetonitrile were extracted together with involatile compounds like squalene.

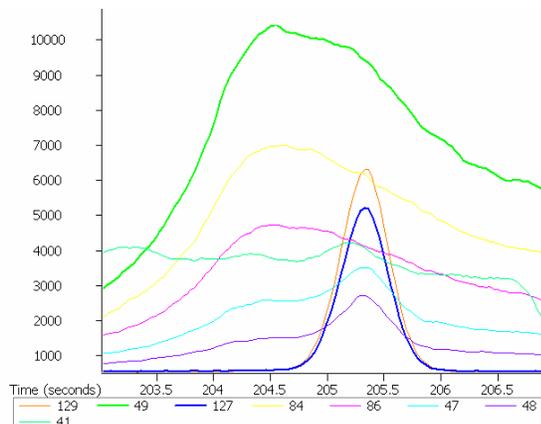


Figure 1: Dibromochloromethane peak at retention time 205s

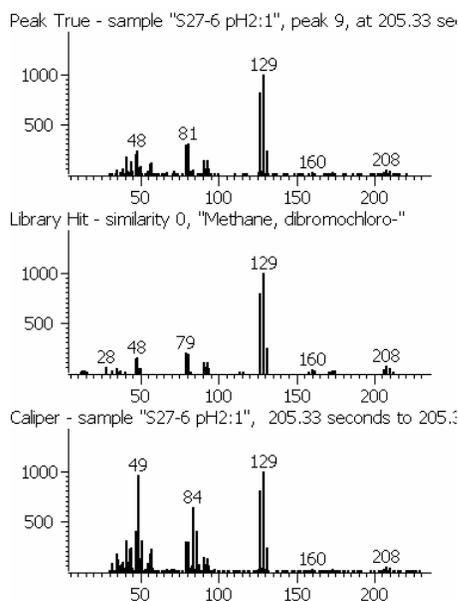
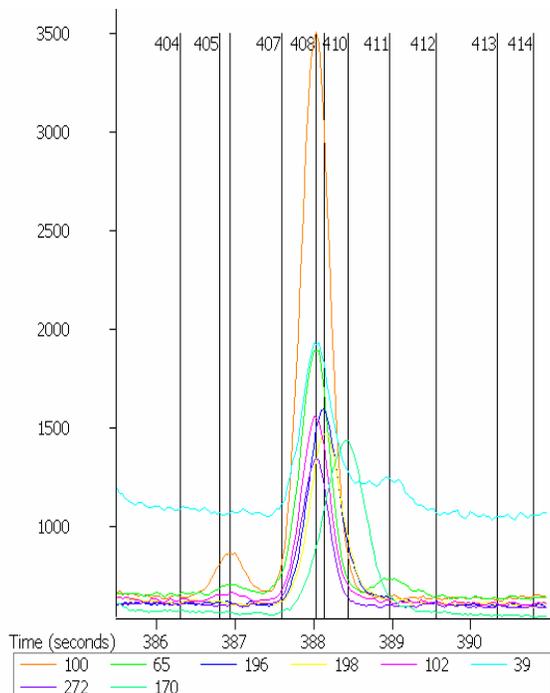
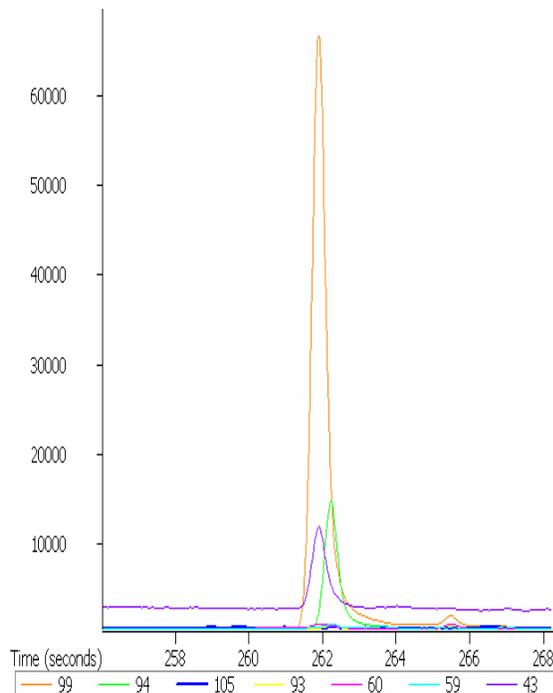


Figure 2: Deconvoluted mass spectrum (top), library hit (middle) and total ion mass spectrum (bottom) for Dibromochloromethane with a similarity hit of 80.4%

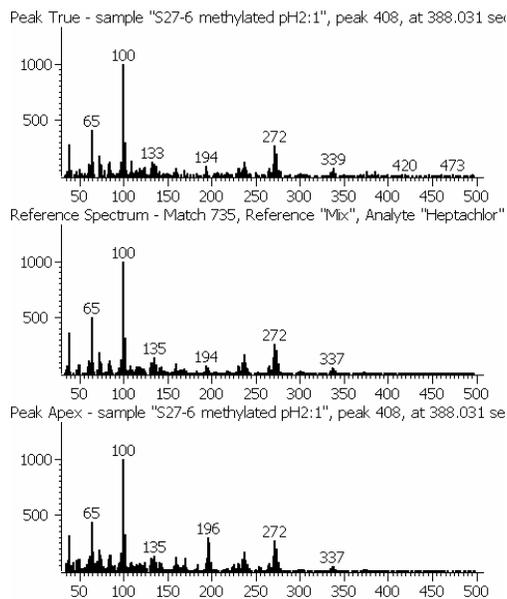
The GC-TOF-MS procedure was found to be faster than conventional GC-MS by an order of magnitude. Analysis of all compounds was completed within ten minutes on a 20 m column and automated data processing took no longer than two minutes. Within a 2 second time window, see Figure 3, 7 pesticides were resolved, had good peak shapes and were correctly identified by the software, Figure 4. Difficult compounds like the phenols and azinphos ethyl and methyl showed good peak shapes even at low-level concentrations, see Figures 5-8.



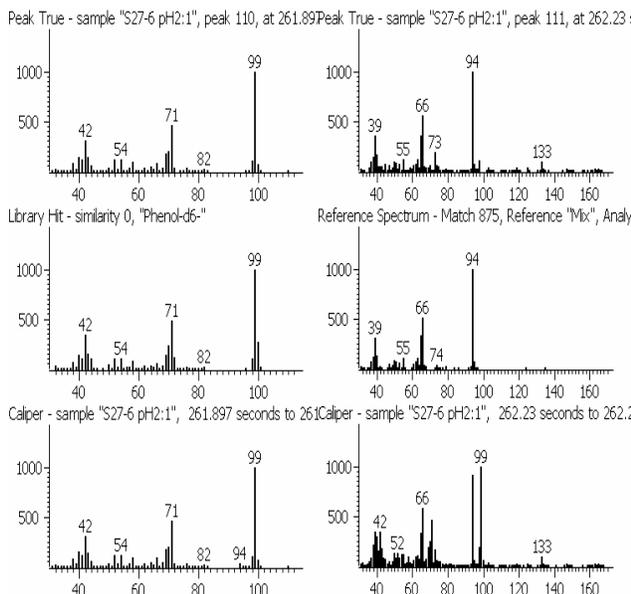
**Figure 3:** (406) Ioxynil Me-; (407) PCP Me-; (408) Heptachlor; (409) Picloram Me-ester; (410) Terbutryn; (411) Fenitrothion



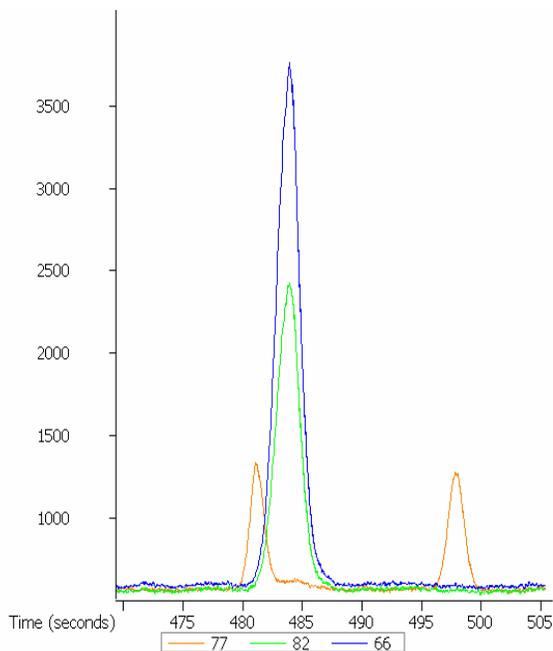
**Figure 5:** Phenol-d6 (261.9 s) and phenol (262.2 s)



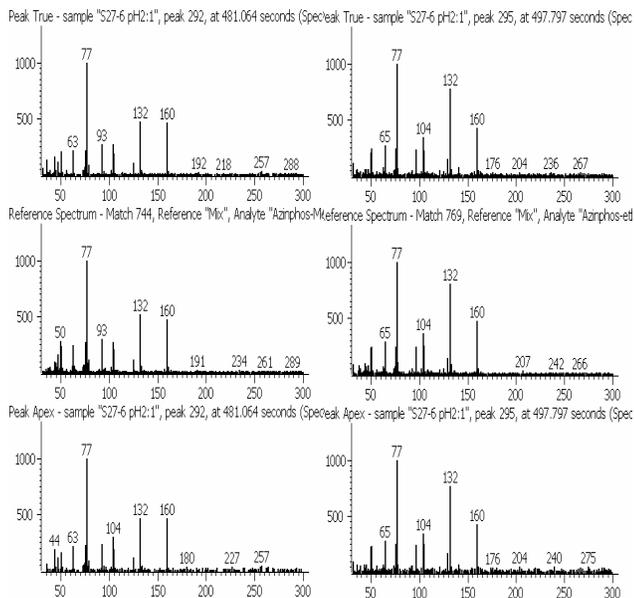
**Figure 4:** Deconvoluted mass spectrum (top), library hit (middle) and total ion mass spectrum (bottom) for Terbutryn



**Figure 6:** Deconvoluted mass spectrum (top), library hit (middle) and total ion mass spectrum (bottom) for Phenol-d6 and Phenol with matches of >87%



**Figure 7:** Azinphos methyl (481 s) and ethyl (497 s)



**Figure 8:** Deconvoluted mass spectrum (top), library hit (middle) and total ion mass spectrum (bottom) for Azinphos methyl and ethyl with spectral matches of 75%

### Conclusions

The use of the SPE-DEX and DryDisk for the extraction and the Pegasus III TOF-MS for the rapid screening and qualitative analysis of contaminants in drinking water down to the required levels looks very promising. Detection limits for a full suite of compounds proved to be more than adequate. Total sample turnaround time was less than 30 minutes.

More work would need to be carried out to assess the value of this approach for quantitative determinations.

### Acknowledgements

We would like to thank Bob Johnson from Horizon Technology and Ray Perkins from ATAS UK for their help with the set-up and running of the samples on instruments used.