Application Note No. 098

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

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Introduction

In cases of water contamination, an important objective for the water industry is to decrease turnaround times of samples and increase capacity. Traditional techniques involve the liquid-liquid extraction (LLE) of the drinking water samples 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 (SPE) with drying of the extract using a Gore-Tex membrane and analysis by GC-TOF-MS; 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 into 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 characterize 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 co eluting 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 co eluting 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 analyze a wide range of different compounds including acids, phenols, triazines, organochlorine and organophosphorous pesticides spiked into tap water at a concentration of 1-10 µg/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

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	á-HCH	Hexachlorobutadiene
Tecnazene	ã-HCH	Hexachlorobenzene
Trifluralin	â-HCH	Propetamphos
Diazinon	ä-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	á-Endosulfan
Dieldrin	p,p-TDE	â-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		

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Acids:

Dicamba	Dichlorprop	2,4-D	MCPP
Trichlorpyr	Bromoxynil	2,4,5-T	MCPB
Ioxynil	Bentazone	PCP	MCPA
Pichloram	Fluroxypur	2,4-DB	Fenoprop
Benazolin	Cloyralid	2,3,6-TBA	

Internal standards:

d_6-Benzene	d_{10}-p-Xylene	d_5-Chlorobenzene
d_6-Phenol	d_{12}-BHT	d_8-Naphthalene

d_{34}-Hexadecane d_{10}-Phenanthrene d_{62}-Squalane

Methods

1 liter of dechlorinated 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 quantization was not possible. The extract was also analyzed following a methylation step. 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 µl 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, acids, organochlorine and organophosphorous pesticides. Even very volatile compounds found in tap water like the THMs: Dibromochloromethane (Figures 1 & 2), tribromomethane and dibromoacetonitrile were extracted through to in volatile compounds like squalane.

The GC-TOF-MS was found to be faster than GC-(quadruple / ion trap)-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, see Figures 4-5.

Difficult compounds like the phenols, dichlorvos and azinphos ethyl and methyl showed good peak shapes even at low-level concentrations, see Figures 6-11.

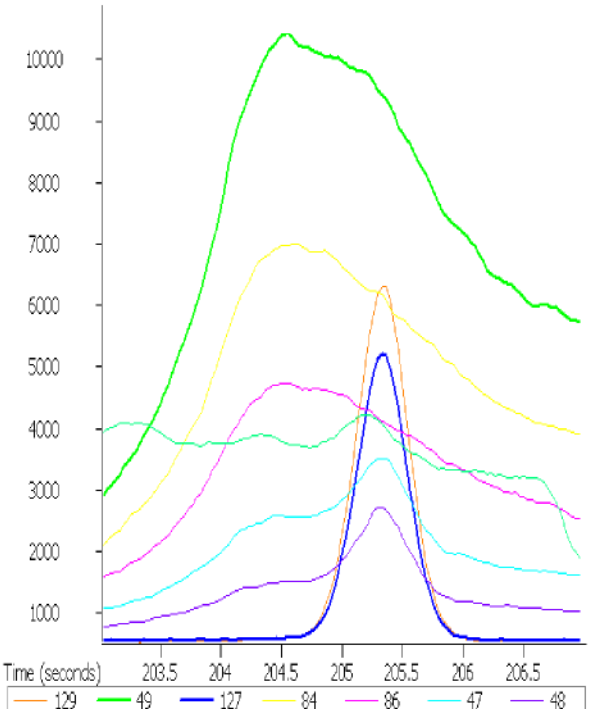
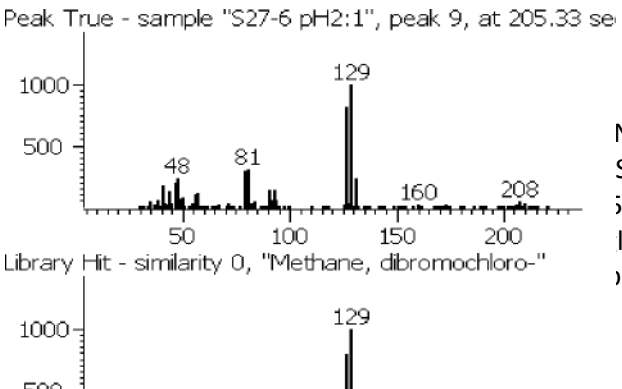


Figure 1: *Dibromochloromethane peak at retention time 205s in dechlorinated pH2 extract spiked at 10 µg/L*



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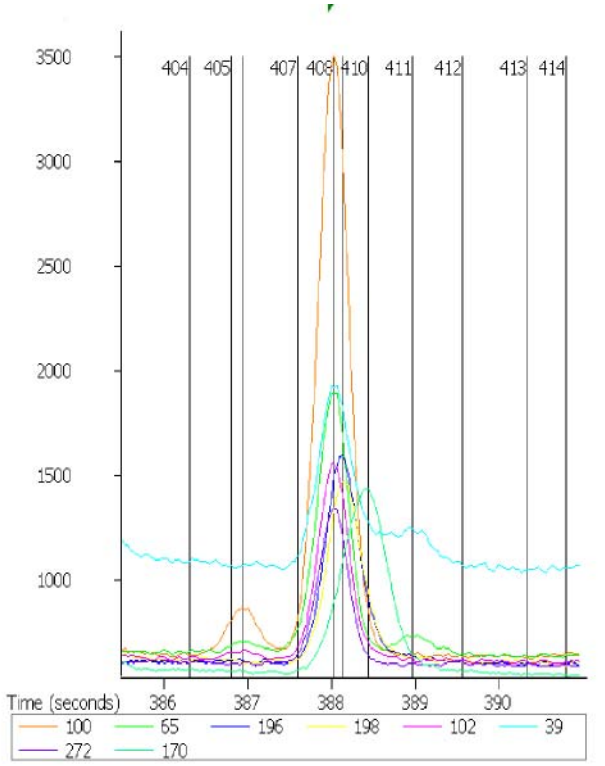

Figure 3: *(406) Ioxynil Me-; (407) PCP Me-; (408) Heptachlor; (409) Picloram Me-ester; (410) Terbutryn; (411) Fenitrothion in dechlorinated pH2 methylated extract spiked at 10 µg/L*

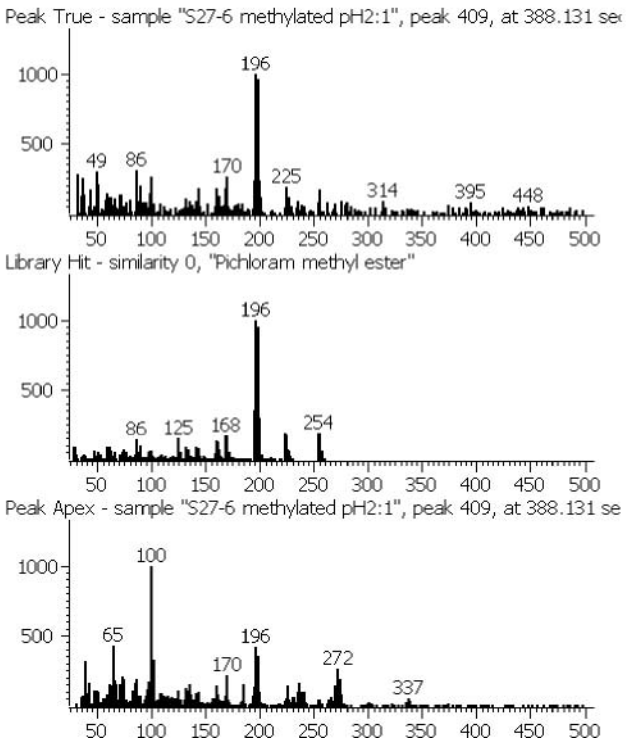

Figure 5: *Deconvoluted mass spectrum (top), library hit (middle) and total ion mass spectrum (bottom) for methylated pichloram*

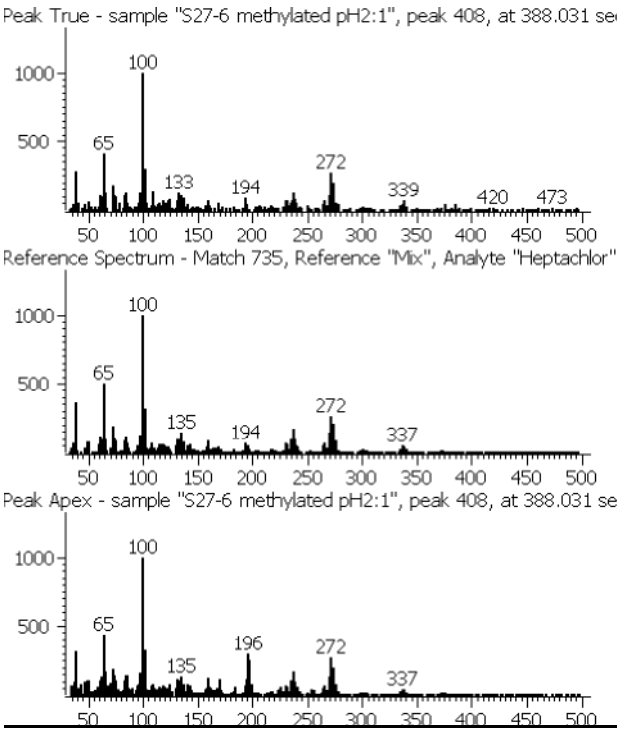

Figure 4: *Deconvoluted mass spectrum (top), library hit (middle) and total ion mass spectrum (bottom) for Heptachlor*

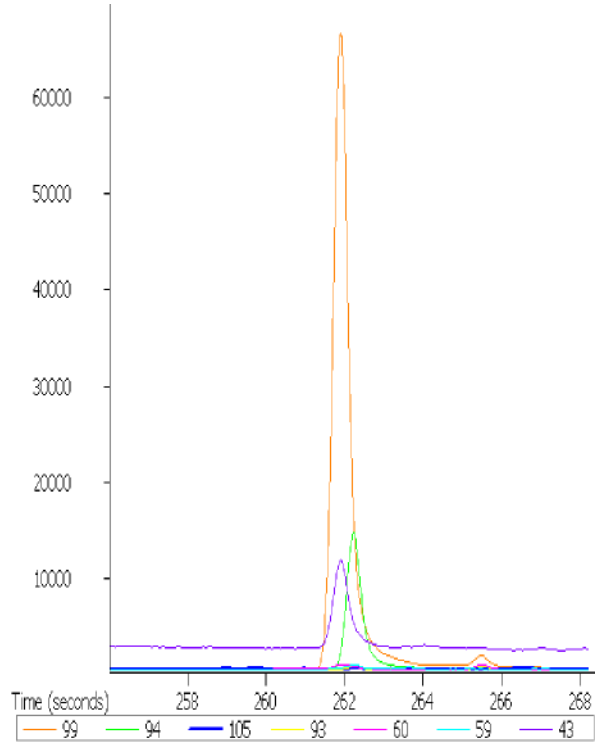

Figure 6: *Phenol-d6 (261.9 s) and phenol (262.2 s) in dechlorinated pH2 extract spiked at 10 µg/L*

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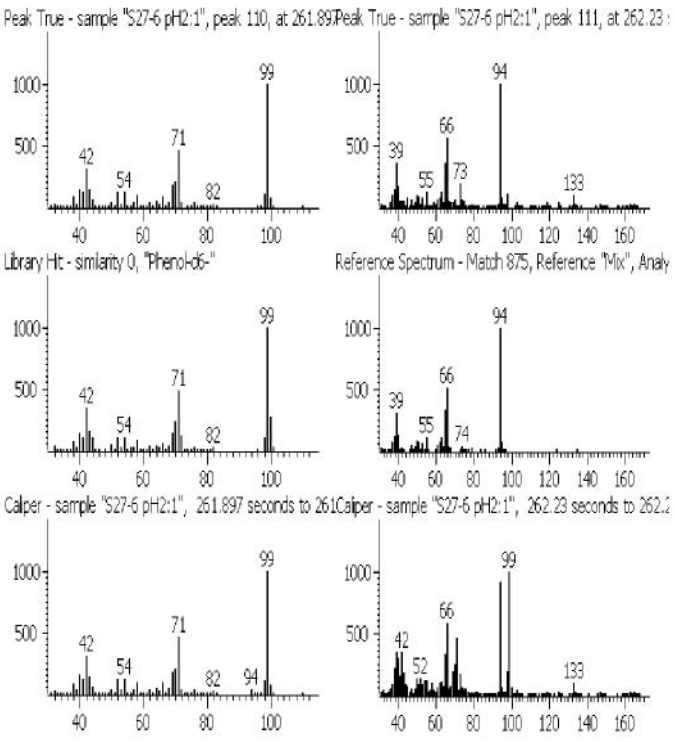

Figure 7: *Deconvoluted mass spectrum (top), library hit (middle) and total ion mass spectrum (bottom) for Phenol-d6 and Phenol with matches of >87%*

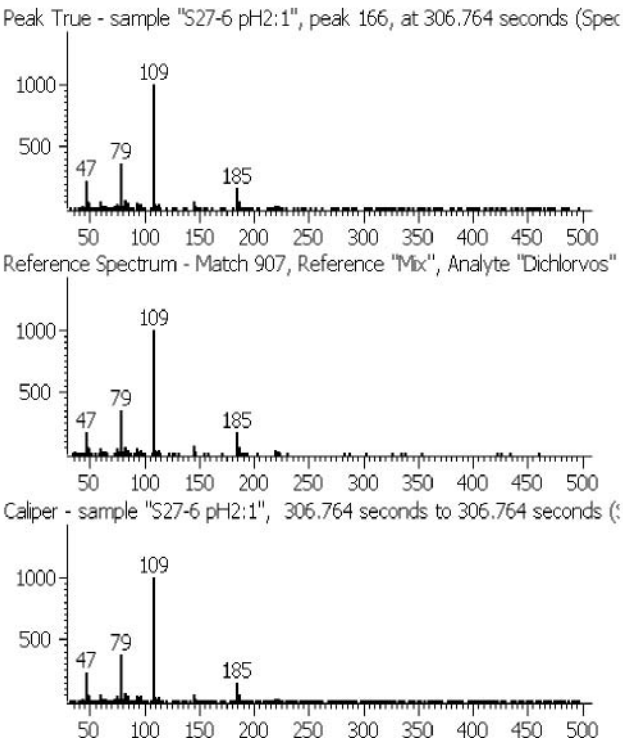

Figure 9: *Deconvoluted mass spectrum (top), library hit (middle) and total ion mass spectrum (bottom) for Dichlorvos with a match of 90%*

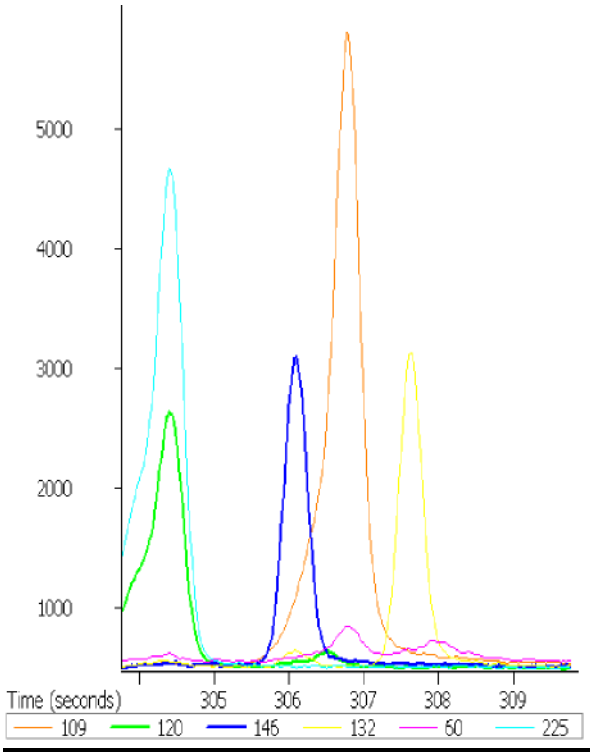

Figure 8: *Dichlorvos (306 s) and HCBD (304 s) in dechlorinated pH2 extract spiked at 10 µg/L*

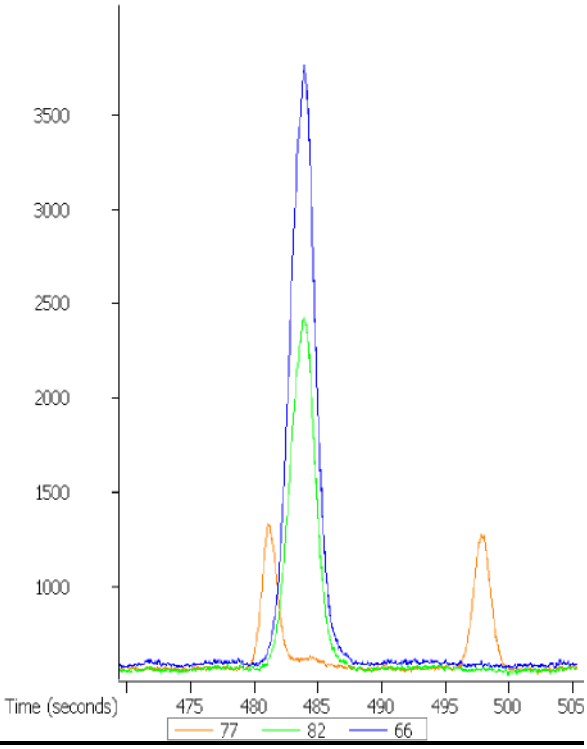

Figure 10: *Azinphos methyl (481 s) and ethyl (497 s) in dechlorinated pH2 extract spiked at 10 µg/L*

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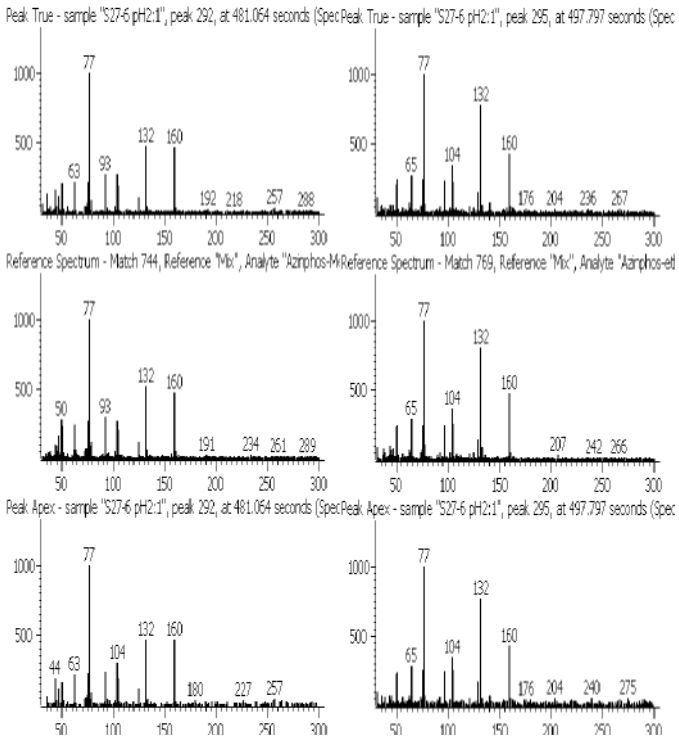

Figure 11: *Deconvoluted mass spectrum (top), library hit (middle) and total ion mass spectrum (bottom) for Azinphos methyl and ethyl with spectral matches of 75%. The large peak on the tail of the Azinphos methyl is the d_{64}-Squalane.*

Conclusion

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 promising, although more work needs to be carried out to assess this approach quantitatively. Difficult compounds like azinphos-ethyl and methyl had good recoveries and peak shapes; this is thought to be due to the fast analysis time so they have little time to break down on the GC column. Even shorter GC columns, for example 10 m, could further reduce analysis times.

Acknowledgements

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