ENVIRONMENTAL ANALYSIS

A TURN-KEY ANALYSER SOLUTION FOR THE TARGET BASED SCREENING OF ENVIRONMENTAL WATER SAMPLES ON THE AGILENT 5977 GC/MS

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Solution Note

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Abstract

Agilent is now offering a comprehensive analyser package for the target based, multi-residue screening of environmental waters on the Agilent 5977 GC/MS. This screening method uses Target Deconvolution (TD) on the MassHunter Quantitative software. It is suitable for the analysis of environmental waters as required by the Water Framework Directive (WFD 2000/60/EC). This method uses a target MS library that contains over 1000 compounds, including both volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs), allowing for the rapid identification and reporting of organic pollutants in an extracted water sample.

The entire system is manufactured and supported by Agilent and includes instrument hardware, proven methods conforming to the required Quality standards, the target MS library, as well as operational consumables. Agilent's installation, commissioning and training program with clearly defined timelines means that the receiving laboratory can rapidly plan for routine operation within a matter of weeks. It should be noted that the library is fully customisable to suit the needs of the laboratory.

Introduction

In December 2000, the European Commission introduced a brand new piece of legislation, the Water Framework Directive (WFD 2000/60/EC). The key objective is to provide for the planning and delivery of a better aquatic environment. It is aimed to help protect and further enhance the quality of the water environment across all member states of the European Union. At the heart of the WFD lies the requirement on countries to develop river basin management plans. In England & Wales there are 11 river basins with management plans and these compliment a further 40 international river basin plans across the European Union.

The WFD applies to surface freshwater bodies (including lakes, streams, canals and rivers), groundwaters, transitional water bodies (estuaries) and coastal waters. In contrast to the existing EU directives the WFD now applies to all water bodies. Under the WFD, surveillance, operational and investigative chemical monitoring is required to be undertaken. The Environment Agency (EA) has to consider making this chemical monitoring cost effective. It is not possible to monitor for everything, everywhere.
There is also the need to identify new emerging pollutants that do not exist in current routine suites and to inform of future monitoring priorities.

In order to address part of the chemical challenge of the WFD, the EA commissioned the development of the GC/MS based screening tool. The requirements of which are:

- A screening method capable of detecting a wide range of organic pollutants in a given water body under WFD.
- The ability to identify both VOCs and SVOCs from a single sample.
- Typical Limit of Detection (LOD) of 0.1µg/L.
- Low cost solution for validating the pressures and risks to water bodies.
- As monitoring requirements are constantly changing the provision to add new substances.

GC/MS was chosen as the analytical technique as it is widely applicable for the identification and measurement of a vast range of chemicals.

Originally, the method was developed on an Agilent 5975 GC/MS system using a retention time locked method and Deconvolution Reporting Software (DRS) [1]. Using the Hazardous Industrial Chemicals Database as a starting point, a large target database with over 1000 target compounds was created. This provided the EA with the necessary automation it required, whilst also reducing data interpretation time and increasing the accuracy of chemical identification.

The new system offers significant performance benefits in terms of sensitivity and throughput and is based on the Agilent 5977 GC/MS with the MassHunter Workstation and the new Target Deconvolution software working with the specially produced target database.

Analytical Technique

Sample Preparation

To 1 litre of sample an Internal Standard is added. The sample is extracted with 50mL of Dichloromethane (DCM) solvent for 15 minutes and the solvent is removed. The remaining sample is then acidified and extracted with a further 50mL of DCM for 15 minutes. This solvent is then removed. The extracts are combined and reduced to 1mL, dried with anhydrous sodium sulphate and transferred to an auto-sampler vial ready for analysis by GC/MS.

The liquid/liquid partition method using DCM under neutral and acid conditions was chosen to extract the widest variety of compounds. The extraction is performed on bottle rollers to maximise the solvent/matrix interaction and also to reduce the formation of emulsions. The extracts are concentrated using Zymark Turbo-Vap concentrators, which enables volatiles to be retained through the control of temperature and gas flow.

Instrumentation

Gas Chromatograph	Agilent 7890B
Automatic Sampler	Agilent 7693A Injector and Autosampler
Inlet	Agilent Carbon Dioxide Cooled Multi Mode Inlet (MMI)
Injection Port Liner	Agilent Dimpled, Splitless, Ultra Inert Liner (5190-2297)
Injection Mode	Cold Splitless
Injection Volume	1.5 µL
Inlet Temperature Program	20 °C (0.05 min), 720 °C/min to 300 °C (8 min)
Inlet Gas Flow	Purge flow to split vent, 250 mL/min at 0.8 min
Carrier Gas	Helium, Constant Pressure Mode
Column	30 m x 0.25 mm ID x 0.25 µm HP5-MSUI (19091S-433UI)
Oven Temperature Program	40 °C (2 min), 10 °C/min to 300 °C (8 min)
Retention Time Locking	Fluorene locked at 15.577 min
Run Time	36 min

Mass Selective Detector	Agilent 5977A Extractor Source
EI Tune File	Etune.u
Interface Temperature	280 °C
Source Temperature	250 °C
Quadrupole Temperature	150 °C
Gain Factor	15
Scan Acquisition Range	35 – 566 amu

Results and Discussion

Agilent 5977 GC/MS

The 7890B / 5977 Series GC/MS offers better performance over previous systems. The 5977 MS system features a new inert source with an extractor lens, which provides additional focus to the ion beam into the mass analyser, resulting in a significant increase in the number of ions analysed and better sensitivity of the instrument. Figure 1 shows the increased sensitivity that can be achieved with this new source.

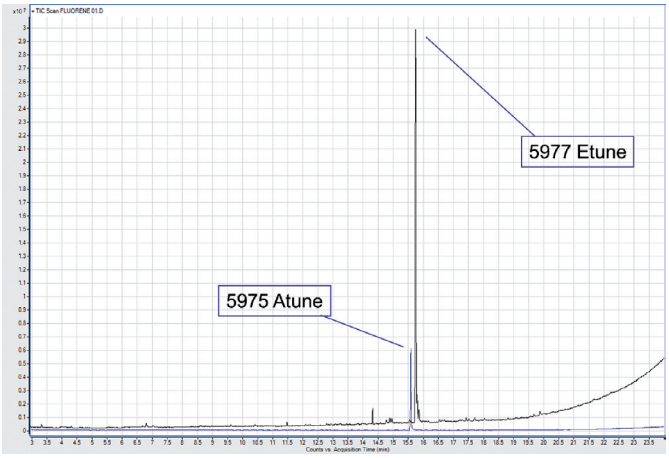


Figure 1. Comparison of responses for Fluorene using Atune on 5975 GC/MS and Etune on 5977 GC/MS.

Development of the Target Deconvolution Method on the Agilent 5977 GC/MS

The Agilent 5977 GC/MS uses MassHunter software. The MassHunter (MH) Acquisition Software (G1701FA) creates data files that are then processed using either the MH Qualitative (Qual) or Quantitative (Quant) software. Target Deconvolution (TD) is a new feature of MH Quant B.06.00 (March 2013). The entire TD process is contained within MH Quant.

A single chromatographic peak may contain multiple components. The deconvolution process pulls out the individual components and their spectra. MH deconvolutes component spectra and performs spectral matching of these spectra against the target MS library. It uses retention time (RT) windows and library match scores (LMS) as qualifiers. This information is combined with the Quantitative results to produce a TD summary report. This process is summarised in Figure 2.

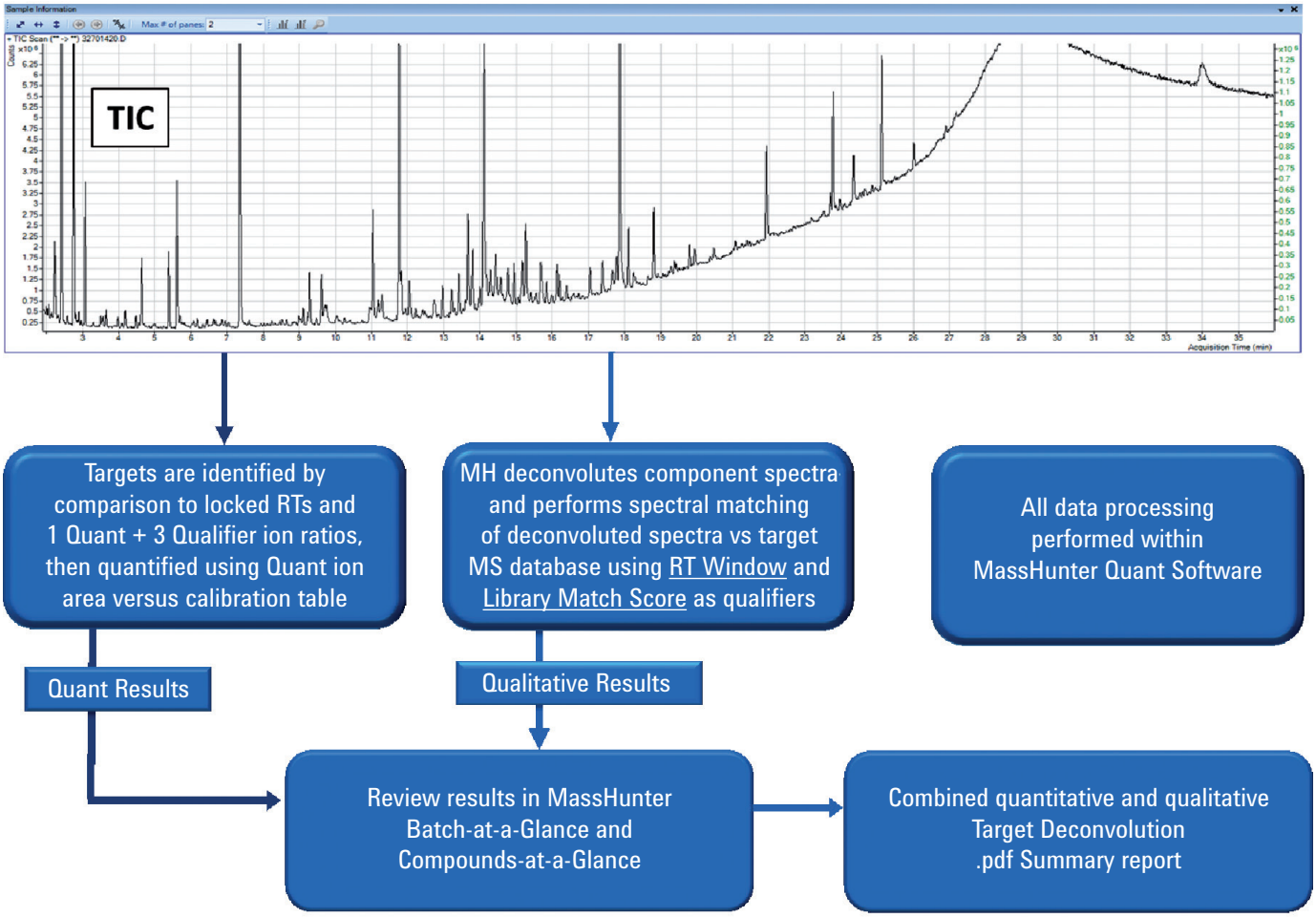


Figure 2. Target Deconvolution (TD) workflow in MassHunter Quant.

Resolution

TD automatically runs the full sample deconvolution at up to four different settings (low, normal, high and very high) and reports the component spectrum that best matches the reference spectrum for the target.

Target RT Window and LMS

The peak apex of the deconvoluted component must be within the RT range of the target peak identified by the Quant engine in order to be used for library matching. This window can be specified in the RT Setup section of the Quant method. For this method, the target window was set to +/- 0.166 minutes for each compound. The minimum LMS can also be adjusted in the Outlier Setup Tasks section of the Quant method.

Target MS Library

The required target reference MS library can be selected in the software. The target MS library that has been created for the EA contains compounds that are relevant to the water industry and WFD [2]. It includes pesticides, fungicides, molluscicides, hydrocarbons & PAHs, emerging pollutants, industrial chemicals, metabolites, volatile solvents as well as pharmaceuticals and personal care products. It presently contains 1040 compounds, but as a living database this will continue to grow. New compounds can be added to this library by running them on the RTL method and then adding them to the MH Quant method and the MH target MS library.

Quantitation and Limits of Detection

The results are semi-quantitative and estimates of concentration are obtained by running a reference standard for each individual compound at a known concentration, typically 1µg/L, to produce a response factor. Fully quantitative analysis is not practical due to the large number of compounds in the library and the requirement to use a set of standards.

The LOD is dependent on compound, sample matrix and sample volume extracted. One of the initial requirements was to achieve a typical LOD of 0.1µg/L and this is achievable for the vast majority of compounds in this method.

Data Analysis

The results can be reviewed either by batch or by compound. Figures 3 and 4 show how the information is displayed using Batch-at-a-Glance, with Figure 4 showing the Compound Information panel in more detail. Figure 5 shows how the information is displayed using Compounds-at-a-Glance. In addition to the target RT window and minimum LMS, a range of other outliers can be applied to speed up the data review process. Figure 5 shows the results for 25 of the target analytes in an extracted water sample. The target results that are highlighted in red are those that have failed on one or more of the applied outliers.

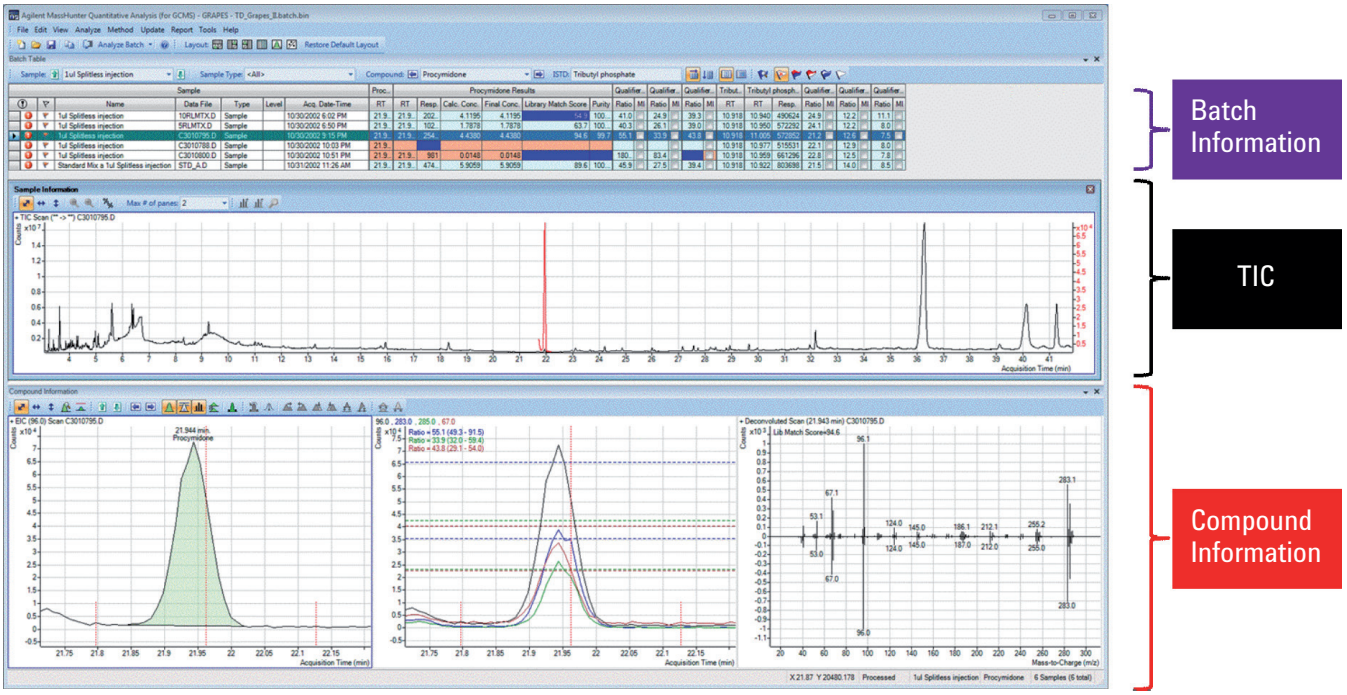


Figure 3. Batch at a Glance Screenshot.

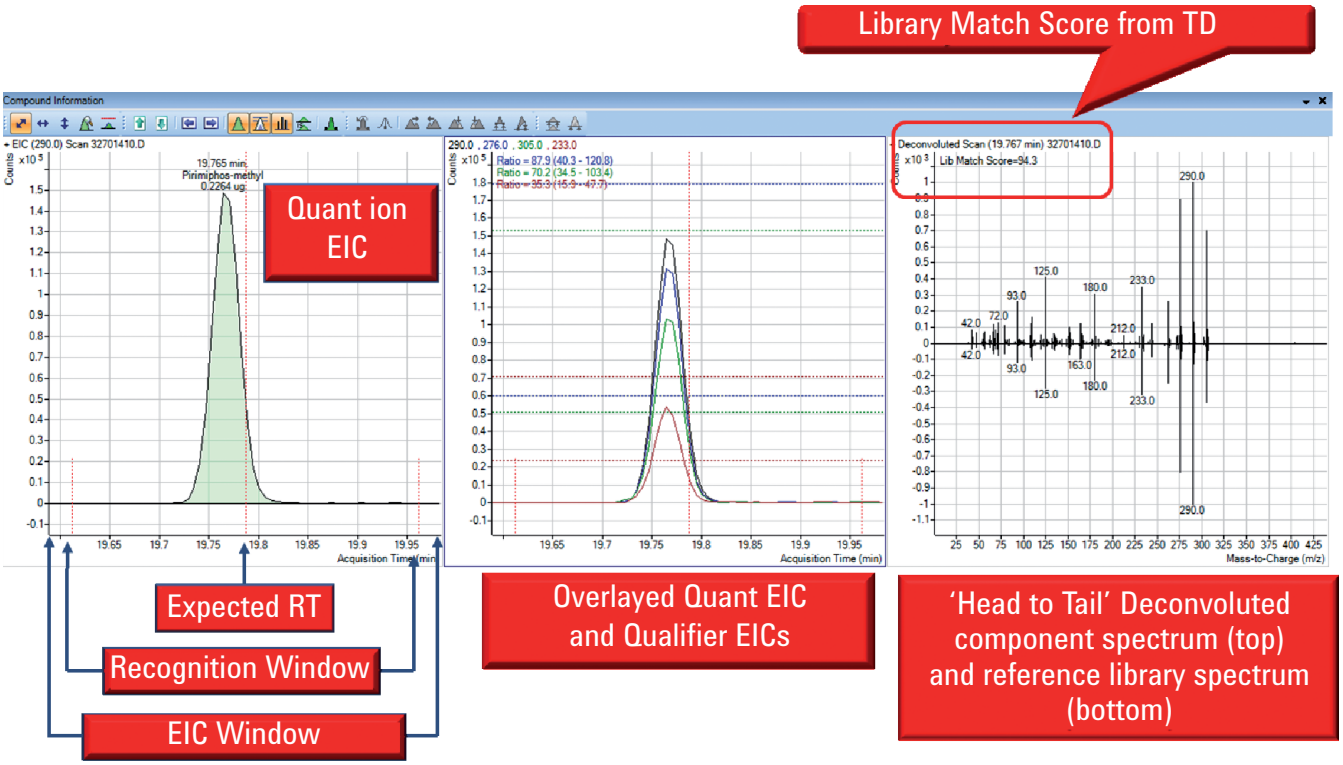


Figure 4. Batch at a Glance Compound Information.

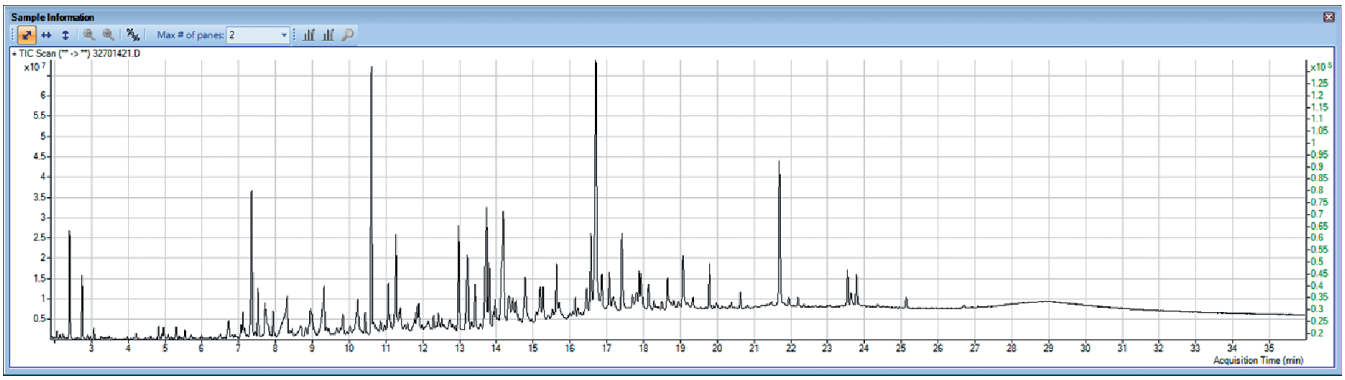
Figure 5. Compounds at a Glance Screenshot.

Extracted Hazardous Waste Landfill Site Water

Figure 6 shows the total ion chromatogram for an extracted hazardous waste landfill site water and the TD results. This chromatogram is complex, containing many overlapping and co-eluting peaks making it ideally suited for the deconvolution process. The TD report lists those target analytes that are within the RT window and possess LMS values greater than the minimum set out in the quant method. The purity value corrects the quantitation result in the event of another deconvoluted compound with the same m/z as the quantitation ion interfering with the peak area of the target compound. Thus, a purity value of 100 denotes that no interference was detected. For this sample, a total of 98 compounds were identified.

Data Processing Times

Another major advantage of TD is the rapid data processing. Data processing times are dependent on a range of factors, including the length of the analytical run and the number of targets. Using this method with over 1000 target compounds, it takes approximately 1 minute to process a single data file.



Targeted Deconvolution Report

Sample Name: 2076207
Data File: 32701421.D
Quant Batch Name: C:\Users\csandy\Desktop\Wayne MH TD Data\QuantResults\Wayne_TD_with_deconv_CAS_numbers.batch.bin
Last Calib Update: 4/22/2013 4:21:41 PM

R.T.	Cas #	Compound Name	Amount/Conc	LMS	R.T. Diff(sec)	Purity
2.4059	123-91-1	1,4-Dioxane	94.5059	84	-2.3	100.0
2.8114	110-86-1	Pyridine	0.2756	97	-2.3	100.0
3.0656	108-88-3	Toluene	2.4674	96	-3.9	100.0
3.3682	123-63-7	Paraldehyde	1.0414	93	0.1	100.0
3.4348	4359-46-0	2-Ethyl-4-methyl-1,3-dioxolane	0.3016	56	0.5	98.7
3.6467	127-18-4	Tetrachloroethylene	0.2378	54	-0.2	100.0
4.2156	108-90-7	Chlorobenzene	1.3325	98	-1.0	100.0
4.4698	100-41-4	Ethylbenzene	0.4074	98	-1.8	100.0
4.6030	106-42-3	p-Xylene	0.6540	98	-2.2	100.0
4.6030	108-38-3	m-Xylene	0.6540	98	-2.5	100.0
5.0085	108-94-1	Cyclohexanone	0.0045	58	-0.9	86.2
4.9903	95-47-6	o-Xylene	0.5275	93	-2.4	100.0
5.5411	98-82-8	Isopropylbenzene	1.7048	96	-0.4	100.0
5.9951	95-49-8	2-Chlorotoluene	0.8895	97	0.0	99.5
6.0496	103-65-1	n-Propylbenzene	0.0643	59	0.0	91.4
5.9951	106-43-4	4-Chlorotoluene	0.8181	94	-5.9	99.5
6.3038	108-67-8	1,3,5-Trimethylbenzene	0.0328	79	0.0	100.0
6.4672	62-53-3	Aniline	0.1452	96	-0.7	100.0
6.5701	108-95-2	Phenol	0.2102	72	1.8	98.4
6.7335	98-06-6	tert-Butylbenzene	0.1722	40	0.4	99.9
6.7335	95-63-6	1,2,4-Trimethylbenzene	1.0966	91	-1.6	100.0
7.0482	106-46-7	1,4-Dichlorobenzene	0.3960	82	-0.9	100.0
7.2843	99-87-6	p-Isopropyltoluene	0.0048	42	0.1	89.2
7.3569	5989-27-5	d-Limonene	41.7104	44	-1.3	100.0
7.4417	95-50-1	1,2-Dichlorobenzene	0.6421	94	0.1	100.0
7.7140	108-62-3	Metaldehyde	33.6191	82	-1.0	100.0
7.8169	95-48-7	o-Cresol (2-methylphenol)	3.0404	91	1.6	100.0
7.9077	1702-17-6	Clopyralid	8.1652	70	-2.0	100.0
8.0046	98-86-2	Acetophenone	0.2141	64	-1.0	100.0
8.1619	95-53-4	o-Toluidine	0.5981	43	5.0	100.0
8.1619	106-44-5	p-Cresol (4-methylphenol)	0.7321	71	2.2	100.0
8.1619	108-39-4	m-Cresol (3-methylphenol)	0.7595	71	1.6	100.0
8.4222	493-01-6	Decahydronaphthalene (cis)	0.0701	51	-7.2	97.9
8.6764	576-26-1	2,6-Dimethylphenol	1.1205	87	0.6	100.0
8.9185	78-59-1	Isophorone	0.1785	51	1.0	99.1
9.1667	3320-83-0	2-Chlorophenyl isocyanate	10.1403	86	-0.4	100.0
9.3664	105-67-9	2,4-Dimethylphenol	0.4945	69	2.1	100.0
9.6630	108-68-9	3,5-Dimethylphenol	1.4116	54	0.7	99.1
9.9354	91-20-3	Naphthalene	0.1309	77	1.1	99.8
10.0140	98-55-5	Terpineol	0.9533	55	-1.7	100.0
10.1593	108-43-0	3-Chlorophenol	0.7783	79	4.0	100.0
10.1593	106-48-9	4-Chlorophenol	1.9097	80	2.9	100.0
10.1956	51000-52-3	Neodecanoic acid-ethenyl ester (Breakdown product)	10.8571	52	1.8	100.0
10.1835	108-42-9	3-Chloroaniline	1.2360	72	-1.6	100.0
10.1835	106-47-8	4-Chloroaniline	1.1075	68	-1.9	100.0
11.2669	1570-64-5	4-Chloro-2-methylphenol	14.6904	98	1.1	100.0
11.5938	680-31-9	Hexametapol	57.4174	47	2.1	100.0
12.5501	759-94-4	EPTC	0.1349	71	1.1	100.0
12.8588	92-52-4	Biphenyl	0.0038	48	-0.8	100.0
13.3248	126-86-3	2,4,7,9-Tetramethyl-5-decyne-4,7-diol	2.0161	80	0.7	99.8
13.9240	122-42-9	Propham	2.2502	78	1.1	99.9
14.6504	128-37-0	Butylated hydroxytoluene	0.1369	67	0.0	100.0
14.7169	132-64-9	Dibenzofuran	0.0246	54	0.2	100.0

Targeted Deconvolution Report

15.0801	150114-71-9	Aminopyralid	5.8310	47	-1.5	100.0
15.2677	7212-44-4	Nerolidol	10.7556	45	-0.4	98.3
15.5219	134-62-3	N,N-Diethyl-m-toluamide	1.9765	96	2.2	100.0
15.5704	86-73-7	Fluorene	0.0402	57	-0.4	99.2
15.6733	84-66-2	Diethyl phthalate	1.1294	69	-0.8	100.0
15.8064	140-66-9	4-tert-Octylphenol	0.7564	73	0.7	99.9
15.9940	15687-27-1	Ibuprofen	0.2745	64	2.5	100.0
16.0183	122-39-4	Diphenylamine	0.0970	63	-0.5	100.0
16.0183	86-30-6	N-nitrosodiphenylamine	0.1003	63	-0.6	100.0
16.1333	119-61-9	Benzophenone	0.3468	64	-1.5	100.0
16.2483	101-42-8	Fenuron	0.5089	55	4.2	100.0
16.1817	1134-23-2	Cycloate	0.3165	73	-0.9	100.0
16.3693	126-73-8	Tributyl phosphate	0.3234	47	3.2	98.1
16.3996	101-21-3	Chlorpropham	0.7944	74	1.5	100.0
16.4419	5825-67-6	2-[3-Chlorophenoxy]propionamide	1.3991	47	1.9	100.0
16.5690	934-34-9	2(3H)-Benzothiazolone	40.7615	95	1.4	100.0
16.7022	93-65-2	Mecoprop	1251.6825	92	5.1	100.0
16.8596	35256-85-0	Tebutam	8.6088	93	-0.8	99.9
17.0654	4602-84-0	Farnesol	4.0159	48	-5.3	100.0
17.6162	76-74-4	Pentobarbital	0.3433	77	-0.8	100.0
17.9248	3622-84-2	Benzenesulfonamide, N-butyl	34.1904	95	0.3	100.0
17.9309	944-22-9	Fonofos	0.2674	43	-0.2	100.0
17.9309	85-01-8	Phenanthrene	0.0442	43	-1.4	100.0
18.0398	120-12-7	Anthracene	0.0118	63	-1.6	99.0
18.2940	110-27-0	Isopropyl myristate	0.0825	53	-1.8	100.0
18.5483	86-74-8	Carbazole	0.0107	42	1.8	99.9
18.9538	68505-69-1	Benfuresate	0.2840	44	2.7	100.0
19.2504	63-25-2	Carbaryl	0.2181	64	-0.8	100.0
19.3654	834-12-8	Ametryn	0.0483	60	2.0	100.0
19.6983	886-50-0	Terbutryne	0.3575	83	3.3	100.0
19.8072	84-74-2	di-n-butyl phthalate	1.2657	80	-2.6	100.0
19.7890	26225-79-6	Ethofumesate	4.8642	96	-4.1	100.0
20.3822	25057-89-0	Bentazone	2.1870	95	-1.5	100.0
20.9209	206-44-0	Fluoranthene	0.0154	49	-3.0	100.0
21.7017	76674-21-0	Flutriafol	14.3106	87	-2.2	100.0
21.8046	15299-99-7	Napropamide	0.2256	78	-3.0	98.5
21.9438	80-05-7	Bisphenol A	3.7023	94	-4.7	100.0
22.1919	5234-68-4	Carboxin	9.9041	97	-2.8	100.0
22.6822	77-90-7	Tributyl acetylcitrate	0.1333	54	-0.3	100.0
23.5235	85-68-7	butyl benzyl phthalate	0.1220	60	-4.1	100.0
23.6264	1698-60-8	Pyrazon	2.0675	97	1.8	100.0
23.5356	2164-08-1	Lenacil	15.4235	90	-5.0	100.0
23.9835	115-86-6	Triphenyl phosphate	0.5111	76	-1.0	100.0
25.1275	84-61-7	Dicyclohexyl phthalate	2.8130	69	-1.7	100.0
25.1275	117-81-7	bis(2-ethylhexyl)phthalate (DEHP)	3.7712	90	-5.3	100.0

Figure 6. Hazardous Waste Landfill Site Water Extract Chromatogram and TD Report.

Conclusions

A target based, multi-residue, retention time locked screening method using the Target Deconvolution feature of MassHunter Quant software was successfully developed on an Agilent 5977 GC/MS system in response to the requirements of the WFD. This method uses a target MS library that contains over 1000 compounds, including both VOCs and SVOCs and has allowed for many of these target compounds to be identified at low levels, below 0.1 µg/L.
The library is fully customisable and the use of Target Deconvolution has resulted in improvements in compound identification, reporting and faster data processing.

Turn Key Package

Agilent's turn-key guaranteed analyser package for the target based screening of environmental water samples comprises the following:

- Complete hardware setup of the Agilent 5977 GC/MS with dedicated analytical column
- Installation of software and libraries
- System checkout with a special reference sample
- Standard operating procedure (SOP) with detailed descriptions of the analysis procedure
- Method of analysis (a DVD/CD containing sample preparation and sample analysis methods, recommended consumables and materials)
- On-site training and full Agilent support

References

1. Wayne Civil, 'Target Based Screening of Environmental Water Samples using Deconvolution Reporting Software on an Agilent 5975 Series GC/MSD and the Creation of a New Screening Database,' Agilent Technologies publication, 5991-1431EN, November **2012**.
2. The Target MS Library can be viewed on the NLS website: www.natlabs.co.uk

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www.solutions-to-win.com

Published in USA, March 14, 2014
5991-4127EN

The Measure of Confidence

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