# Screening for Pollutants in Water Using a GC/MSD Extractor Source With MassHunter Deconvolution Software and Customized Reporting

Chris Sandy[1] (chris_sandy@agilent.com), Angela Smith Henry[2] (angela.smith@agilent.com), Bruce Quimby[2] (bruce_quimby@agilent.com), Lei Tao[3] (lei.tao@agilent.com), Sue Zhang[3] (sue_zhang@agilent.com), Vadim Kalmeyer[3] (Vadim_kalmeyer@agilent.com), Sun Li[3] (li_sun@agilent.com), [1]Agilent Technologies, 5500 Lakeside, Cheadle Royal Business Park, Cheshire, SK8 3GR, UK; [2]Agilent Technologies, 2850 Centerville Road, Wilmington, DE 19808, USA; [3]Agilent Technologies, 5301 Stevens Creek Blvd, Santa Clara, CA 95051, USA

ASMS 2016
WP204

Agilent Technologies

## Introduction

The EU has instituted the Water Framework Directive[1] (WFD) as a legal basis to ensure good chemical status of water bodies, from drinking water and rivers to waste water. The WFD introduced environmental quality standards for bodies of water by determining priority substances and priority hazardous substances, and established general observation of other pollutants. Priority substances are categorized as pollutants that present significant risk to the water systems (e.g. dichlorvos); priority hazardous substances are those which are persistent, hazardous, and bio-accumulate (e.g. anthracene), or substances of high concern, such as endocrine disruptors.

The GC/MSD acts as a screener for water samples, where the extractor lens in the mass spectrometer provides greater sensitivity to identify priority substances and non-targeted pollutants with a limit of detection (LOD) of 0.1 µg/L. Water samples, such as waste water, can have complex matrices that can obscure pollutants, which may NOT be identified with a human reviewer using the traditional target/qualifier identification. Deconvolution analysis separates the complex matrix from the compounds of interest and identifies the pollutants by comparing the deconvoluted compound mass spectrum to a reference library spectrum. The MassHunter data analysis package provides a novel algorithm to rapidly deconvolute the spectra and compare the results to a 1000+ pollutant library and the general National Institute of Standards and Technology (NIST) library to produce a customized report in PDF format.

## Experimental

### Water Samples

Water samples were collected from 2 sources: **1.)** unfiltered tap water in Lehigh County, Pennsylvania, USA; **2.)** effluents from the Wilmington, DE, USA wastewater treatment plant. Three samples were drawn from the Wilmington wastewater plant: primary effluent – the sedimentation stage, secondary effluent – biological content degradation, and final effluent – final filtration and disinfection. Three milliliters of dichloromethane (DCM) were added to a 30 mL water sample for a simple liquid-liquid extraction; these DCM extracts were analyzed with GC/MSD.

### AccuStandard Standards

Method 8270 Semi-Volatile by Capillary GC/MS mixtures (Mixes 1, 2, 3, 4A, 4B, 5, and 6) were purchased from AccuStandard and diluted from the stock (2 mg/mL in DCM) to concentrations between 100 ppb and 10 ppm in DCM. Reference Gas Oil mix (RGO) was spiked (1 µL) into the diluted AccuStandard samples to create a complex matrix for rigorous testing of the deconvolution algorithm.

### GC/MSD parameters

The method uses an Agilent 7890B GC and Agilent 5977A Extractor Source MSD system. The GC is configured with a carbon dioxide cooled multimode inlet (MMI) and a HP-5 MS UI 30 m x 0.25 mm id x 0.25 µm capillary column. The 5977A was operated in EI (electron ionization) extractor mode with full scan acquisition, and the method is retention time locked.

MassHunter Quantitative Data Analysis and its SureTarget workflow were used with a 1000+ compound library to analyze the data. Customized PDF reports were produced to summarize the data into a short form report and provide a bookmarked detailed graphical report (Figure 3).

### Data Analysis Algorithm

MassHunter's SureTarget provides improved confidence in compound identification. The SureTarget algorithm automatically removes ions from background and co-eluting peaks to yield a compound spectrum which can be searched against a target library. Furthermore, SureTarget will identify any target analytes with a high library match score in the same retention time (RT) range and present those as Alternative Target Hits. The user can then very quickly evaluate the validity of their search results.

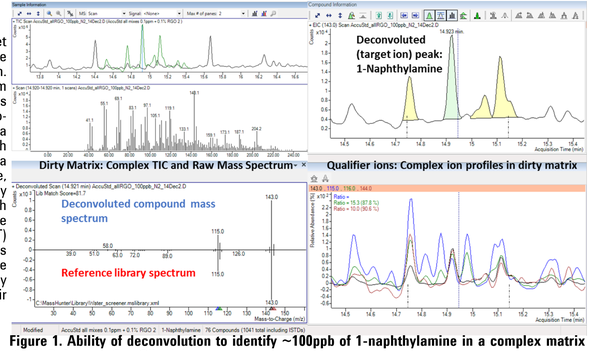


**Figure 1. Ability of deconvolution to identify ~100ppb of 1-naphthylamine in a complex matrix (0.1% Reference Gas Oil mix).**

## Data Analysis

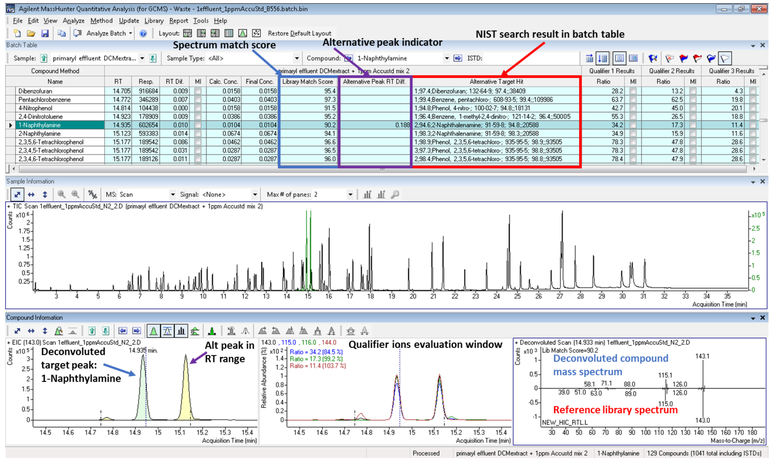


**Figure 2. MassHunter Quantitative Analysis batch table displaying results after SureTarget analysis and highlighting the inclusion of alternative peak and alternative target hit (NIST search) abilities.**

## Results and Discussion

**Table 1. Compounds identified in extracts of primary and final effluents of Wilmington, DE waste water.**

| | | AMDIS Average LMS | | MH Quant B.08.00 Average LMS | |
|---|---|---|---|---|---|
| RT | Compound Name | Primary Effluent | Final Effluent | Primary Effluent | Final Effluent |
| 2.345 | Bromodichloromethane | 51 | 62 | | 58.7 |
| 2.366 | 1,4-Dioxane | 64.2 | 78 | 68.5 | 80.4 |
| **3.606** | **Tetrachloroethylene** | **86.3** | **61.5** | **79.7** | **54** |
| 9.619 | a,a-dimethylphenethylamine | 67.9 | 66.7 | 69.1 | 65.2 |
| 10.031 | Tributylamine | 96.8 | 95.2 | 94.6 | 92.6 |
| 12.383 | Triacetin | 57.8 | | 60.2 | |
| 13.307 | 2,4,7,9-Tetramethyl-5-decyne-4,7-diol | 77.0 | 57.7 | 75.3 | 55.6 |
| 15.500 | N,N-Diethyl-m-toluamide | 90.9 | 57 | 83.8 | |
| **15.776** | **4-tert-Octylphenol** | **90.3** | **64.6** | **84.8** | **60.1** |
| 16.223 | N,N,N',N'-tetraacetylethylenediamine | 65.4 | | 59.1 | |
| 18.610 | Caffeine | 95.1 | | 91.1 | |
| 18.804 | Diisobutyl phthalate | 88.4 | 80.1 | 84.3 | 67.8 |
| 24.278 | Codeine | 98.4 | 88 | 97.2 | 90.1 |
| 29.724 | Cholesterol | 80.1 | | 79.1 | |

**Results in bold** are priority substances in the EU WFD.

### Testing deconvolution algorithm with standards and water samples

SureTarget deconvolution was tested with data from the AccuStandard 8270 standards in DCM (solvent) and with 0.1% RGO spike, as a complex matrix, between 100 ppb and 10ppm. The same data was analyzed with AMDIS, and results of the two deconvolution algorithms were compared (RGO results at 4 Hz in Table 2). Samples were taken at two data rates, 4 Hz and 8 Hz, to compare the effect of data rate (number of points per peak) on peak deconvolution, identification, and library match score (LMS). Analysis results of Lehigh County water (Table 3) indicate sanitation byproducts and select WFD priority substances are found in the unfiltered water.

### Waste Water

Primary and final effluent extracts were analyzed for substances that are not broken down in the waste water treatment plant (Table 1). Codeine survives the treatment processes of waste water, as does 4-tert-octylphenol, an endocrine disruptor and priority pollutant in the WFD.

## Results and Discussion

**Table 2. Number of identified compounds and average library match scores (LMSs) of the AccuStandard 8270 Semi-Volatiles mixture with a 0.1% reference gas oil (RGO) spike per software program.**

| Approximate AccuStandard concentration | Software package | 4 Hz | |
|---|---|---|---|
| | | # compounds found (of 86) | Average LMS |
| 1ppm | AMDIS | 82 | 90.6 |
| | MassHunter Quant B.08.00 | 84 | 89.4 |
| 200ppb | AMDIS | 69 | 80.2 |
| | MassHunter Quant B.08.00 | 72 | 79.3 |
| 100ppb | AMDIS | 59 | 76.0 |
| | MassHunter Quant B.08.00 | 62 | 75.6 |

**Table 3. Extract of Lehigh County, PA, USA tap water (unfiltered). Results in bold** are priority substances in the EU WFD.

| | | 4Hz | |
|---|---|---|---|
| RT | Compound Name | AMDIS Avg. LMS | MassHunter Quant B.08.00 Avg. LMS |
| **2.328** | **Trichloroethylene** | **82.2** | **85.3** |
| 2.388 | Bromodichloromethane | 90.2 | 93.5 |
| 3.419 | Chlorodibromomethane | 92.4 | 92.3 |
| **3.630** | **Tetrachloroethylene** | **87.3** | **79.9** |
| 4.817 | Bromoform | 83.0 | 84.2 |
| 21.986 | Bisphenol A | 59.3 | 64.4 |

## Conclusions

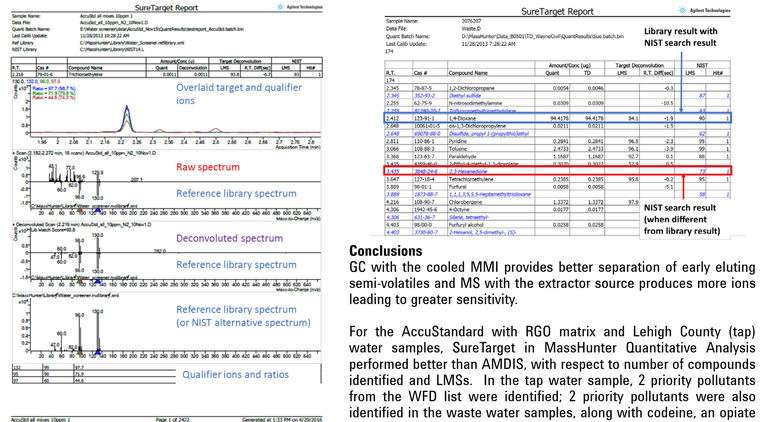


**Figure 3. Examples of PDF reports showing a graphical report (left) and section of a summary report (right).**

### Conclusions

GC with the cooled MMI provides better separation of early eluting semi-volatiles and MS with the extractor source produces more ions leading to greater sensitivity.

For the AccuStandard with RGO matrix and Lehigh County (tap) water samples, SureTarget in MassHunter Quantitative Analysis performed better than AMDIS, with respect to number of compounds identified and LMSs. In the tap water sample, 2 priority pollutants from the WFD list were identified; 2 priority pollutants were also identified in the waste water samples, along with codeine, an opiate that does not degrade in waste water treatment.

Quantitative Analysis – Interactive UI allows individual sample (and compound) review, or batch review to assess compounds identified in multiple files, and brings review of alternative peaks and NIST results into the data analysis program.

SureTarget – Workflow for deconvolution built into MassHunter Quantitative Analysis with additional features:

**Alternative peak** in the RT range identification and **NIST search**

PDF reporting – Customized report templates for summary and detailed, graphical reports with SureTarget deconvolution analysis and NIST search results.

The GC/MSD water screener with SureTarget workflow offers streamlined data analysis and reporting.

### Reference

[1]Directive 2000/60/EC, Official Journal of the European Communities, L 327 (Vol 43), 22 December 2000.