Screening for Water Pollutants With the Agilent SureTarget GC/MSD Water Pollutants Screener, SureTarget Workflow, and Customized Reporting

Application Note

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Introduction

Laboratories conducting water analysis increasingly need to screen samples for a large number of compounds prior to performing a full quantitative analysis. The qualitative analysis of extracted water samples with GC/MSD provides the ability to understand what is in the sample at approximate levels.

Existing qualitative screening workflows depend on manual screening, which is extremely time-consuming and highly dependent on the analyst's skill. Manual screening processes can also lead to overlooked or misassigned compounds, potentially due to complex matrices. Additionally, the discrepancy between analysts' results and any bias associated with compound identification can lead to a significant amount of time exhausted on data analysis. Typically, a compound list for manual review is approximately 50 compounds. Since each compound is reviewed and identified by its retention time (RT), mass spectrum, and target and qualifier ion ratios, greatly increasing the number of compounds to review per single sample would multiply the complexities already faced. For example, if an analyst were to screen a sample for 1,000 possible compounds, it could take up to 18 hours to review that single sample.

The Agilent SureTarget GC/MSD Water Pollutants Screener provides a straight-forward and easy analysis workflow for the qualitative screening of water samples. Not only will the Agilent SureTarget analysis workflow allow for the fast screening of a large, wide-reaching compound list, but it will also remove bias and inconsistencies in compound identification. The SureTarget GC/MSD Water Pollutants Screener is preconfigured with the optimal hardware, consumables, software, and analytical methods to allow for the fast implementation of screening methods for pollutants in water.

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Experimental

Water samples were collected from two sources: unfiltered tap water in Lehigh County, Pennsylvania, USA, and effluents from the Wilmington, DE, USA wastewater treatment plant. From the Wilmington wastewater plant, three samples were drawn:

- Primary effluent – Sedimentation stage

- Secondary effluent – Biological content degradation

- Final effluent – Final filtration and disinfection

Sample preparation

Each water sample, including the blanks, were extracted through liquid-liquid extraction (LLE). Three milliliters of dichloromethane (DCM) were added to a 30 mL water sample, shaken for 5 minutes, and the DCM layer was extracted and deposited into 2-mL autosampler vials for analysis.

Reference 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 to concentrations ranging between 100 ppb and 10 ppm in DCM (86 compounds in total). One microliter of the Reference Gas Oil mix (RGO) was spiked into each of the diluted AccuStandard samples to provide a complex matrix.

Instrumentation

All analyses were run on an Agilent 7890B Gas Chromatograph (GC) coupled with an Agilent 5977B InertPlus Mass Spectrometer Detector (MSD). A CO_2-cooled multimode inlet (MMI) was used to temperature program the inlet, which provided additional separation between the DCM solvent peak and some early-eluting semivolatile compounds. Table 1 provides the GC and MSD method parameters for data acquisition.

Data analysis

All samples were analyzed using the SureTarget workflow with deconvolution in Agilent MassHunter WorkStation Software Quantitative Analysis Version B.08.00 for GC/MS. The results of the SureTarget workflow were then compared to the results of the (same) samples analyzed in MSD ChemStation Data Analysis program with Deconvolution Reporting Software (DRS), which uses AMDIS (deconvolution software developed by NIST) as the deconvolution tool.

Table 1. GC and MSD Parameters for Data Acquisition

GC Conditions

Column	Agilent HP-5MS UI, 30 m × 0.25 mm, 0.25 µm		
Injection	1.0 µL cold splitless with CO_2 cooled MMI		
Solvent	Dichloromethane		
Inlet temperature program	Rate (°C/min)	Temp (°C)	Hold time (min)
Initial		20	0.05
Rate	720	300	0
Carrier gas and mode	Helium in constant pressure mode*		
RTL Compound and time	Fluorene at 15.577 minutes		
Oven temperature program	Rate (°C/min)	Temp (°C)	Hold time (min)
Initial		40	2
Rate	10	300	8
MS transfer line temperature	280 °C		

MS Conditions

Solvent delay	1.82 minutes
Scan acquisition range	35–550 amu
Tune	Etune.u
Source temperature	250 °C
Quad temperatures	150 °C

* Final pressure dependent on RT-Locking procedure

The SureTarget workflow is enabled in MassHunter Quantitative Analysis upon installation of the water screener feature disc. When the SureTarget analysis method is used, the deconvolution algorithm will remove the background and interfering mass fragments in the raw mass spectra from an identified compound's mass fragments (Figures 1 and 2). Figure 1A displays a total ion chromatogram (TIC) with an overlaid extracted ion chromatogram (EIC) for 1-naphthylamine in a time window of 14.5 to 15.5 minutes with the 1-naphthylamine peak located at 14.92 minutes. Figure 1B shows the complex raw mass spectrum under the peak selected at 14.92 minutes; the deconvolution algorithm cleans this complex mass spectrum of interferences.

Figure 2 illustrates the result of the deconvolution process, which is a clean, deconvoluted mass spectrum for 1-naphthylamine at 14.92 minutes. The deconvoluted spectrum was compared, in a head-to-tail fashion, with the reference library spectrum of that compound. Next, the software automatically compared the deconvoluted mass spectra to the reference library, and generated a library match score (LMS). This LMS is based on the similarity between the deconvoluted mass spectrum and the library mass
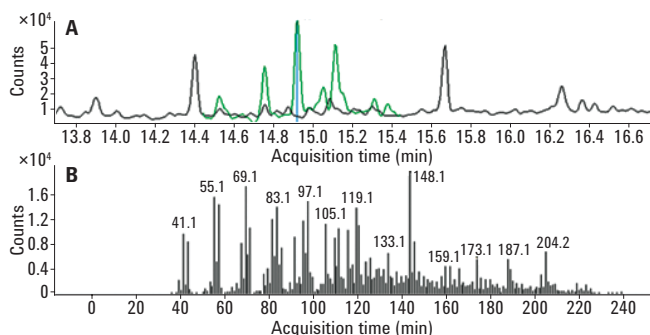
Figure 1. TIC (A) and raw spectrum (B) of 1-naphthylamine (from AccuStandard mixtures) in reference gas oil matrix.
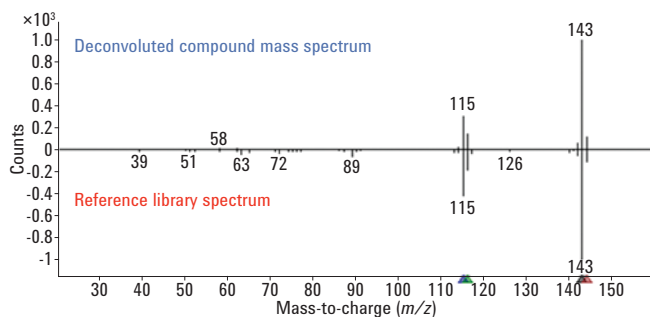

Figure 2. Head-to-tail comparison of the deconvoluted mass spectrum (top) and reference library spectrum (bottom) for 1-naphthylamine. The deconvoluted spectrum is very different from the raw spectrum in Figure 1B, as the software was able to separate out all of the interfering ions.

spectrum of the identified compound. The analysis method also looks for alternative peaks in the retention time window that produce high library match scores. This additional peak search aids in the review of the data, especially when analyzing complex matrices. The software then compares and matches each SureTarget deconvoluted mass spectrum to mass spectra in the NIST library and ranks each of the matches in the NIST hit list; a hit list is generated for each SureTarget identified compound. Figure 3 displays a graphical representation of the SureTarget workflow steps.
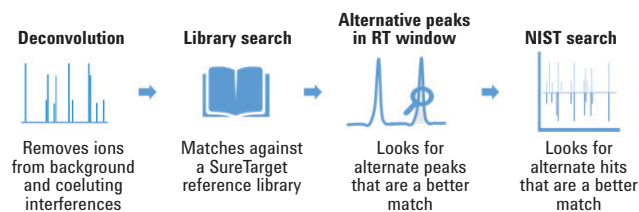

Figure 3. The four major Agilent SureTarget workflow steps include mass spectral deconvolution in the RT window, library search of deconvoluted mass spectrum, identification of alternative peaks (in the RT window), and search of the NIST library.

Results and Discussion

Each prepared AccuStandard mixture included 86 compounds for identification, which are also found in the water screener library. These samples were run at 1 ppm, 200 ppb, and 100 ppb in RGO (complex matrix). After data acquisition, the SureTarget deconvolution workflow was completed on 10 samples per concentration level, and the results (number of identified compounds and LMSs) were averaged. The unfiltered tap water sample (Lehigh County, Pennsylvania), primary effluent, and final effluent of wastewater treatment (Wilmington, Delaware) were each averaged over five replicate runs to provide more analytical data for the deconvolution comparison.

The number of identified compounds and their LMS values at each concentration were observed and documented for all AccuStandard mixtures and real-world water samples. Once the SureTarget workflow on the extracted water samples was complete, the data analysis was repeated with the DRS, which uses AMDIS (NIST software). Both sets of data analysis results were then compared (Table 2 for AccuStandard results, and Table 3 for tap water results).

The data files were analyzed with DRS (AMDIS) and SureTarget to evaluate the ability of SureTarget. At each concentration level for AccuStandard samples (Table 2), both DRS and SureTarget reported a similar number of compounds, within a margin of error (fewer than four compounds difference on average), and similar LMS values (within ~1 point per concentration level). These results indicate that SureTarget performs very well and similarly to DRS (AMDIS), with respect to identified compounds and corresponding LMSs.

Table 2. Number of Identified Compounds and Average Library Match Scores (LMSs) of the AccuStandard 8270 Semivolatiles Mixture with a 0.1 % Reference Gas Oil (RGO) Spike per Software Package

Approximate AccuStandard concentration	Deconvolution tool (software package)	No. of compounds found (of 86)	Average LMS
1 ppm	AMDIS (DRS)	82	90.6
	SureTarget (in Quant B.08)	84	89.4
200 ppb	AMDIS (DRS)	69	80.2
	SureTarget (in Quant B.08)	72	79.3
100 ppb	AMDIS (DRS)	59	76.0
	SureTarget (in Quant B.08)	62	75.6

Table 3. Extract of Lehigh County, PA, USA Unfiltered Tap Water

RT	Compound	AMDIS (DRS) Avg. LMS	SureTarget (Quant B.08) 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

In the unfiltered tap water sample (Lehigh County, Pennsylvania), six compounds were identified by both analysis programs with similar match scores (within five LMS points). Trihalomethanes (sanitation by-products), trichloroethylene, and bisphenol A were identified with high match scores in the tap water by both deconvolution analyses.

With the confidence in the SureTarget deconvolution workflow, the wastewater samples (Wilmington, Delaware; wastewater plant) were examined with the SureTarget workflow in MassHunter Quantitative Analysis. Each wastewater sample was averaged over five replicate runs to achieve more confident results. Several compounds were identified in the primary and final wastewater effluent samples, including a mixture of concerning compounds. These compounds include 1,4-dioxane, tetrachloroethylene, codeine, and 4-*tert*-octylphenol. Other compounds identified in the primary effluent included caffeine, phentermine (weight loss drug), DEET (insect repellant), and cholesterol. Table 4 displays the compounds identified in the primary and final effluent. Table 4 also provides a picture as to what compounds were destroyed, or not destroyed, in the wastewater treatment process. DEET, triacetin, caffeine, TAED, and cholesterol were destroyed in wastewater treatment, while bromodichloromethane was introduced upon sanitation of the wastewater in the final stage. In contrast, several compounds were retained through the wastewater treatment process, including codeine, 1,4-dioxane, 4-*tert*-octylphenol, phentermine, and diisobutyl phthalate.

Table 4. Compounds Identified in Primary Wastewater Effluent (After Solid Separation Phase) and Final Effluent (After Sanitation of Wastewater) with Agilent SureTarget Deconvolution

RT	Compound	Average LMS Primary effluent	Average LMS Final effluent
2.345	Bromodichloromethane		58.7
2.366	1,4-Dioxane	68.5	80.4
3.606	Tetrachloroethylene	79.7	54
9.619	a,a-dimethylphenethylamine (Phentermine)	69.1	65.2
10.031	Tributylamine	94.6	92.6
12.383	Triacetin	60.2	
13.307	2,4,7,9-Tetramethyl-5-decyne-4,7-diol	75.3	55.6
15.500	N,N-Diethyl-m-toluamide (DEET)	83.8	
15.776	4-*tert*-Octylphenol	84.8	60.1
16.223	N,N,N',N'-tetraacetylethylenediamine (TAED)	59.1	
18.610	Caffeine	91.1	
18.804	Diisobutyl phthalate	84.3	67.8
24.278	Codeine	97.2	90.1
29.724	Cholesterol	79.1	

Obtaining the results may be the first part of any water screening analysis, but data reports are needed for communicating the results. The SureTarget GC/MSD Water Pollutants Screener also supplies PDF reports to preview, summarize, and graphically display the data (Figure 4). The data preview report is designed to show the details (compound name, CAS number, RT, and LMS) associated with a primary peak of an identified compound, and any alternative peak in the RT window with a high LMS (greater than minimum) for that compound. The preview report indicates which compounds have alternative peaks (with the alternative RT) for further user review in the Quantitative Analysis batch Table (Figure 4). The summary report is designed to summarize the identified compounds, all compound related details (compound name and CAS number, RT, LMS, approximate concentration, and difference from reference RT in minutes), as well as the rank and score of the compound in the NIST hit list in a tabular view. If the SureTarget identified compound is not found in the NIST list (user-defined list, sized between 1 and 100, and set in method parameters), then the top hit will be recorded on a second line (Figure 4). The detailed graphics report dedicates one page to each identified compound in the sample (Figure 4). Each page will display the overlaid target and qualifier EICs, raw mass spectrum, deconvoluted spectrum, reference library spectrum, and the NIST spectrum (if the NIST hit is different from the identified compound).
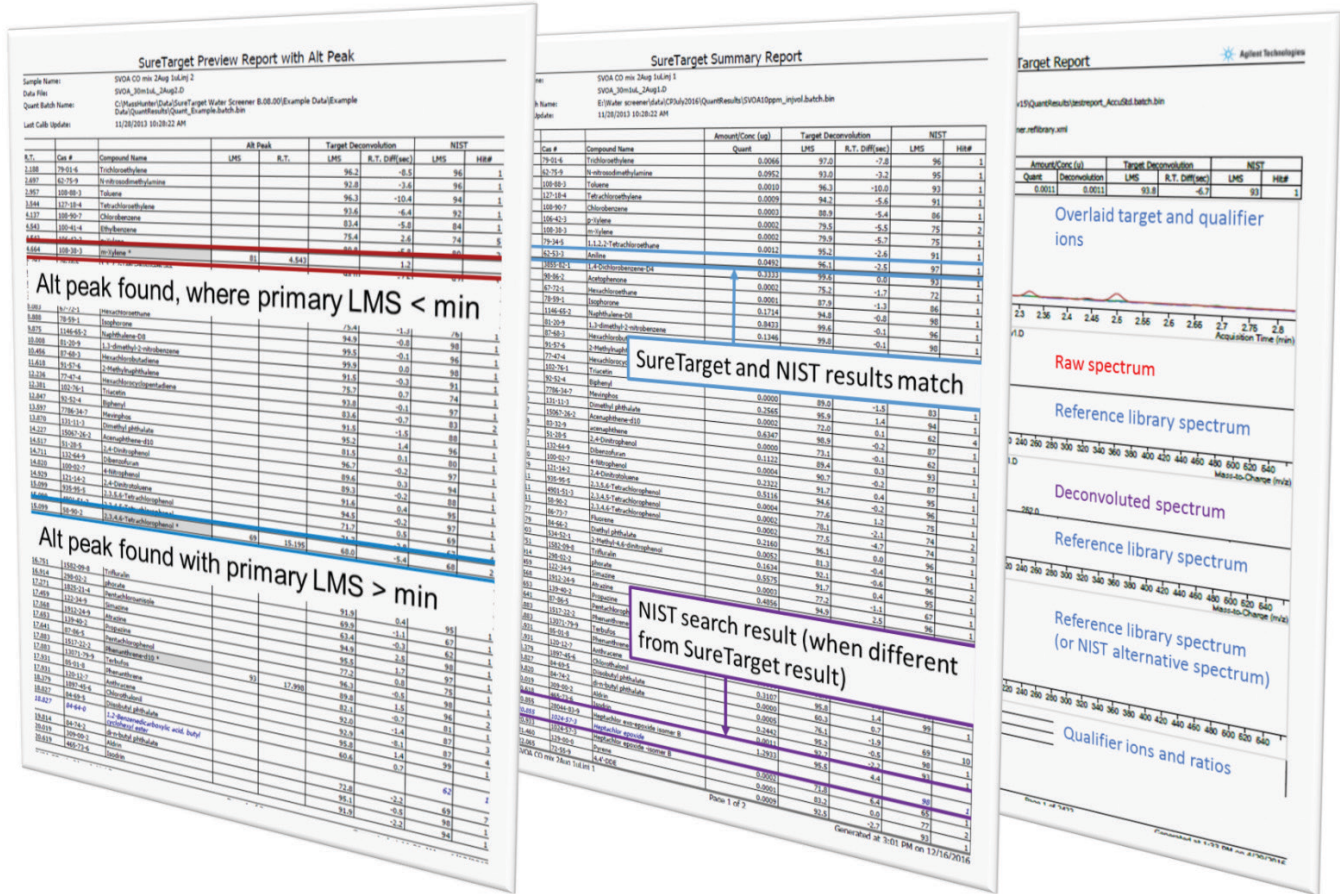
Figure 4.   Examples of PDF reports showing the preview report (left), summary report (middle) and a detailed graphics report page for one compound (right).

Conclusions

The Agilent SureTarget GC/MSD Water Pollutants Screener with the SureTarget deconvolution workflow offers streamlined data analysis and reporting by enabling the automated separation and identification of compounds in complex matrices, such as tap and wastewater samples. The water screener includes the SureTarget deconvolution workflow, which is activated in Agilent MassHunter Quantitative Analysis (B.08.00), with additional features to support the complete optimal solution. These features include alternative peak identification in the RT window, NIST search, and customized report templates (preview, summary, and detailed graphics). The use of automated deconvolution data analysis considerably reduces the manual review time, while increasing the number of reviewable compounds to greater than 1,000. The library match score, generated from the deconvolution analysis, helps to communicate confidence in compound identification along with the ability to visually review a deconvoluted mass spectrum next to the reference library spectrum.

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