Screening for Pollutants in Water with GC/MSD and MassHunter SureTarget Mass Spectral Deconvolution Workflow

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Introduction

Existing qualitative screening workflows depend on manual screening using the traditional target/qualifier identification, which is extremely time consuming and highly dependent on the analyst's skill. Manual screening processes can lead to overlooked or mis-assigned compounds, potentially due to complex matrices, and result in a significant amount of time exhausted on data analysis. Mass spectral deconvolution analysis separates the complex matrix from the pollutants of interest, and identifies these compounds by comparing the deconvoluted mass spectrum to a reference library.

Using mass spectral deconvolution, Agilent's SureTarget GC/MSD Water Pollutants Screener provides a straight forward and easy data analysis workflow for the qualitative screening of water samples. The GC/MSD screener was utilized to study multiple stages of the waste water treatment process. The samples were analyzed with the SureTarget workflow, using mass spectral deconvolution. Then, the samples were further analyzed in Unknowns Analysis with the NIST library to identify any additional compounds that were not in the water screener library.

Experimental

Water Samples

Water samples were collected from effluents of 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 30mL water sample for a simple liquid-liquid extraction; these DCM extracts were analyzed with GC/MSD.

GC/MSD parameters

The method uses an Agilent 7890B GC and Agilent 5977B InertPlus MSD system. The GC is configured with a CO_2 cooled multimode inlet (MMI) and a HP-5 MS UI 30 m x 0.25 mm id x 0.25 µm capillary column. The 5977B was operated in EI (electron ionization) extractor mode with full scan acquisition. The method is retention time locked with a 10 °C/min oven ramp from 40 °C (hold 2 min) to 300 °C (hold 8 min), and the MMI is temperature programmed at 20 °C (hold 0.5 min) and rapidly ramped to 300 °C.

Data Analysis Workflow

Agilent MassHunter Quantitative Analysis software was utilized to analyze the GC/MSD data with the additional SureTarget workflow for mass spectral deconvolution. Using the automated SureTarget workflow (Figure 1), the mass spectral data is deconvoluted (Figure 1 Step 1) in a compound's retention time window, where background and co-eluting interferences are separated from the compound ions, and the "clean" mass spectrum is compared to the SureTarget water screener library (2). The workflow also automatically searches for alternative peaks in the retention time window with better spectral matches (3). The "clean" mass spectrum is also compared to the NIST14 library for a second identification check (4). The identified compounds are summarized into a batch table with retention times, target and qualifier ion ratios, deconvoluted mass spectra and library match scores. PDF reports were generated to summarize the identified compounds. Data was imported into Unknowns Analysis and compared to the NIST14 library to identify compounds that were not in the SureTarget Water Screener library.

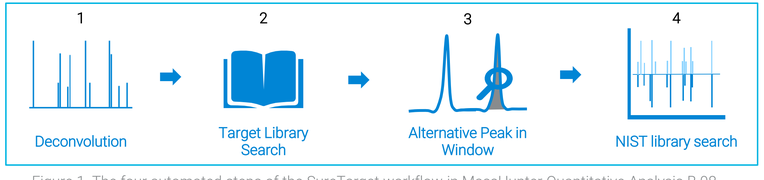

Figure 1. The four automated steps of the SureTarget workflow in MassHunter Quantitative Analysis B.08.

Results and Discussion

SureTarget workflow deconvolution results

Water extract data files were analyzed in MassHunter Quantitative Analysis B.08 with the SureTarget workflow and a target library containing over 1,000 pollutants. A library match score (LMS) threshold of 55 was utilized to minimize the reporting of false positives. The resultant SureTarget identified compounds and alternative peaks were reviewed in Quantitative Analysis. Quantitative Analysis assists in rapid review of compounds by displaying TIC, retention times (RTs), overlaid target and qualifier ions, and deconvoluted spectrum in one layout.

Thirteen compounds were identified in the primary effluent (Table 1), including 1,4-dioxane, phentermine, DEET and codeine. Eight of these compounds persisted through the treatment process and were detected in the final effluent. Bromodichloromethane, a disinfection by-product, also was identified in the final effluent. Summary pdf reports were generated for the effluent results; detailed graphical reports were also generated for select compounds (Figure 2).

Are there additional compounds in the sample?

While the 1,046 compound library contains a fairly comprehensive list of pollutants and other compounds commonly identified in water samples, there are many other compounds that may exist in water samples. To look for additional compounds, the Quantitative Analysis results were imported into MassHunter Unknowns Analysis. Figure 3 highlights an example in which the two of the highest intensity peaks in the TIC are unidentified with targeted analysis.

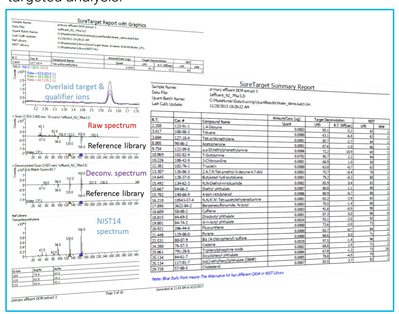

Figure 2. Summary and detailed graphical pdf reports for the primary effluent sample.

Table 1. Compounds identified with SureTarget workflow in the effluents of the waste water treatment process.

RT	Compound Name	SureTarget LMS	
		Primary Effluent	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	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	

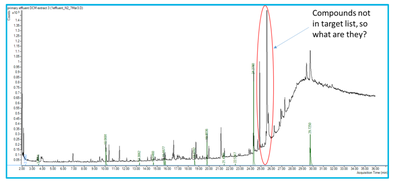

Figure 3. TIC of primary effluent sample. Compounds identified from target library have green traces with RTs. Two, high intensity peaks without green traces, indicating the compounds are still unknown are circled.

References

[1]Smith Henry, Angela; Quimby, Bruce. Application Note: 5991-734EN.

Results and Discussion

Non-targeted analysis in Unknowns Analysis software

Unknown Analysis was used for non-targeted data review, using mass spectral deconvolution analysis on the primary effluent data. Deconvoluted spectra were compared to the NIST14 library with an LMS threshold of 80, since NIST14 library does not contain compound RTs; therefore, RT cannot be utilized as criteria in compound identification. The identified compounds were reviewed and "hits" with less than 4 matching ions between the deconvoluted and reference mass spectra were discarded from the results.

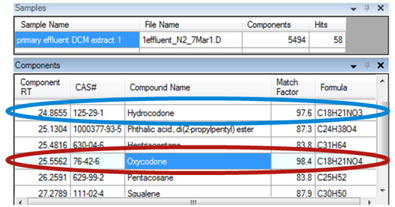

Figure 4. Partial list of compounds identified by non-targeted analysis in Unknowns Analysis for primary effluent sample. The compounds for the two, most intense peaks in Figure 2 were identified and are circled.

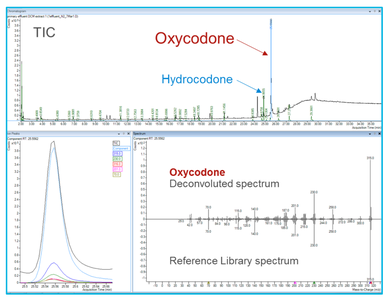

Figure 5. Unknowns Analysis screen shot with oxycodone selected in the TIC. the overlaid component, EICs, and head-to-tail comparison of the deconvoluted spectrum with NIST14 library spectrum.

Fifty-two additional compounds were identified in the non-targeted analysis, including the two most intense peaks in the TIC. These two peaks are hydrocodone at 24.87 min with a LMS of 97 and oxycodone at 25.56 min with a LMS of 98, as indicated in Figures 4 and 5. The TIC, with oxycodone and hydrocodone highlighted, oxycodone deconvoluted mass spectrum, compared to the NIST reference spectrum, and oxycodone extracted ion chromatograms (EICs) are shown in Figure 5.

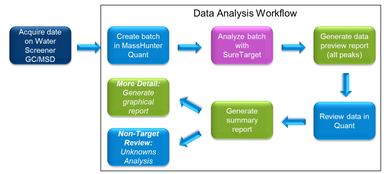

Figure 6. Suggested Data acquisition to data analysis workflow

Data Analysis workflow

Figure 6 contains a suggested data analysis workflow, starting with data acquisition on the water screener GC/MSD. A user will create a batch of samples and run SureTarget (deconvolution) analysis in Quantitative Analysis. The user can review the data and alternative peaks, generate a summary report, and choose to complete non-targeted analysis in Unknowns Analysis and/or generate graphical reports containing detailed information about each compound.

Conclusions

The GC/MSD water pollutants screener with SureTarget workflow offers streamlined data analysis and reporting with additional non-targeted analysis in Unknowns analysis for full understanding of what is in the sample.

- SureTarget – Workflow for deconvolution built into MassHunter Quantitative Analysis with additional features of **alternative peak** in the RT range identification and **NIST search**, and exclusive to the Water Pollutants Screener
- PDF reporting – Customized report templates for summary and detailed, graphical reports
- Unknowns Analysis – Non-targeted, deconvolution analysis platform