

Surpassing Detection Limits for 200 Organic Compounds in Water Using EPA Method 525.2 via GC-MS

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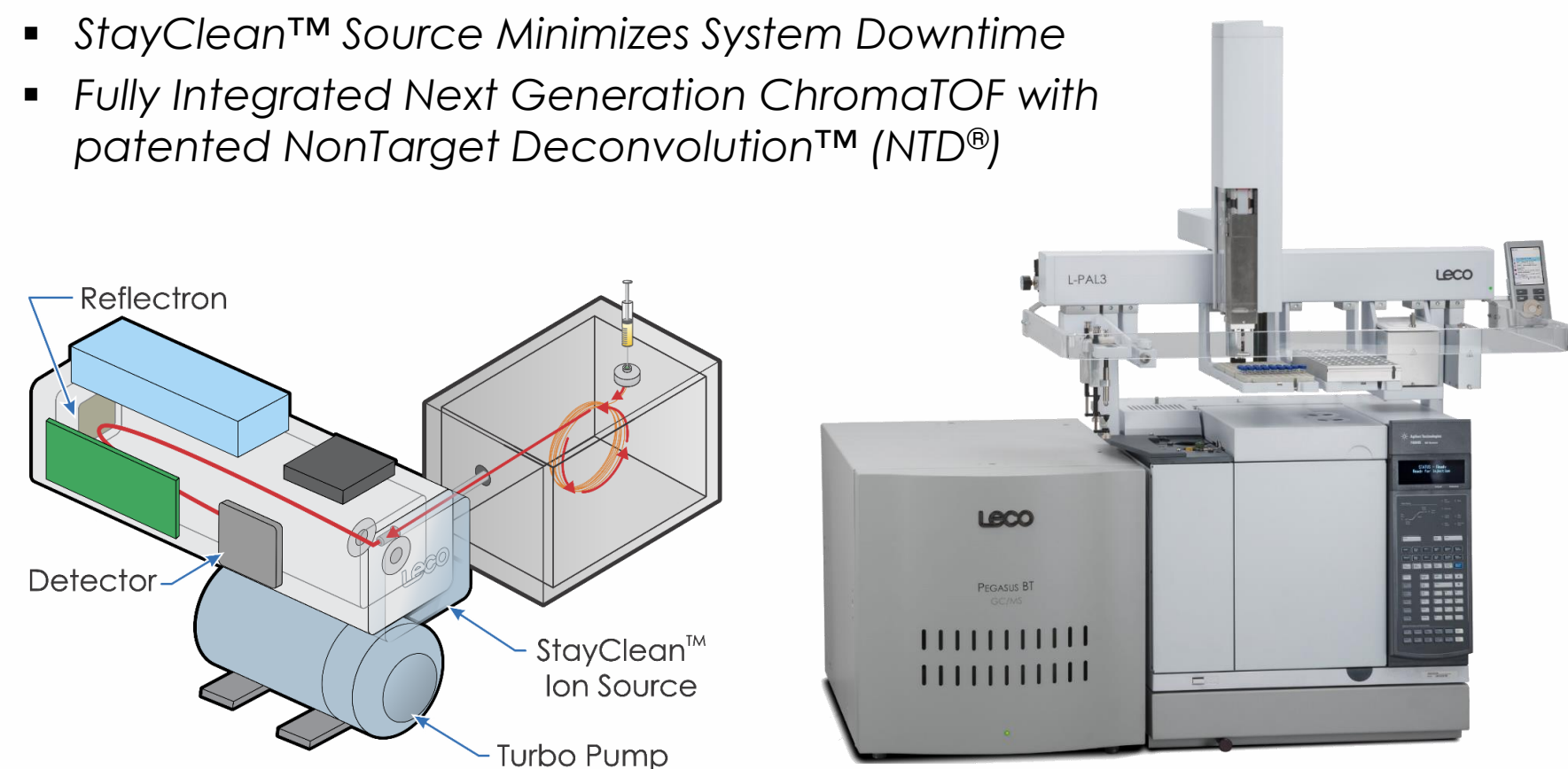
Introduction

The United States Environmental Protection Agency (US EPA) Method 525.2 can be applied for the determination of organic compounds in drinking water, or water in any phase of the drinking water process from source to tap, by liquid-solid extraction and gas chromatography/mass spectrometry.

In this study, EPA Method 525.2 was applied to determine the detection limit of more than 200 organic compounds, namely pesticides and polyaromatic hydrocarbons, in water using gas chromatography with LECO's new benchtop time-of-flight mass spectrometer (GC-MS).

Pegasus® BT GC-TOFMS Design

- SIM-like Sensitivity with Full Mass Range Spectral Data
- Comprehensive Data for Retrospective Analysis
- Targeted and Untargeted Peak Find Options
- StayClean™ Source Minimizes System Downtime
- Fully Integrated Next Generation ChromaTOF with patented NonTarget Deconvolution™ (NTD®)



Method Conditions

MS Method Conditions Pegasus BT-TOFMS	
Transfer Line Temperature	320 °C
EI Source Temperature	280 °C
Acquisition Rate	8 spectra/sec
Mass Range	35 – 645 m/z
Gas Chromatograph & Autosampler Agilent 7890B GC & LECO L-PAL3 ATX	
Injection	1 uL Pulsed Splitless, 20 psi for 1.1min; GC injector 40 °C for 0.1 min, 720 °C/min to 280 °C for 5 min
Column	Rxi-5MS 30 m x 0.25 mm x 0.25 μm
Temp. Program	1.0 min at 40 °C, ramp 60 °C/min to 160 °C, ramp 6 °C/min to 320 °C, hold 2.0 min

Tuning and System Checks

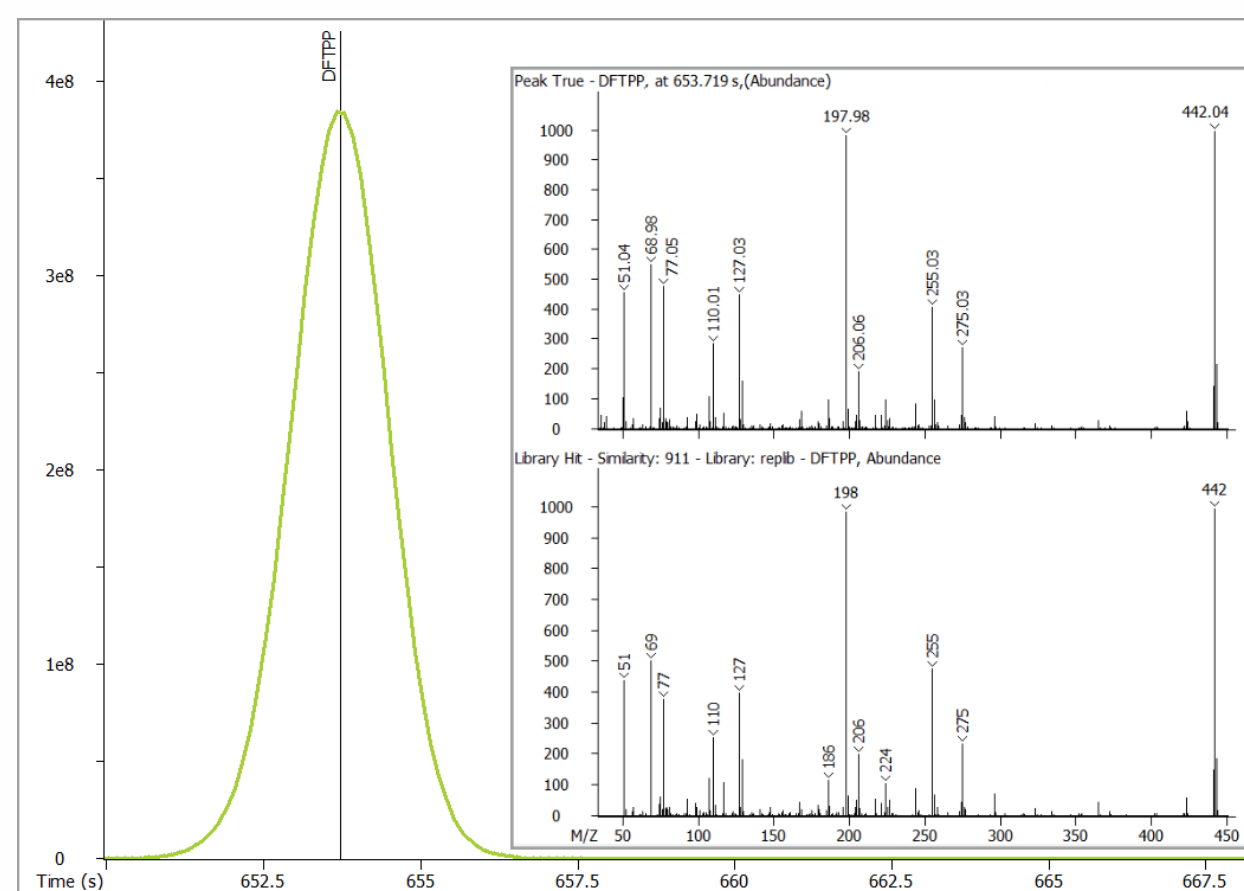


Figure 1. DFTFP 5ppm injection chromatographic peak and spectrum. The Peak True spectrum (top) is comprised of data automatically deconvoluted from any coeluting signals by ChromaTOF®. The Peak True Similarity Score of 911 demonstrates high fidelity to the NIST 14 spectrum (bottom).

DFTFP Tune Criteria			
m/z	Relative Abundance Criteria	Pegasus BT Values	Pass / Fail
51	10-80% of Base Peak	45.9% of Base Peak	Pass
68	<2% of m/z 69	1.45% of m/z 69	Pass
70	<2% of m/z 69	0.72% of m/z 69	Pass
127	10-80% of Base Peak	45.3% of Base Peak	Pass
197	<2% of m/z 198	0.31% of m/z 198	Pass
198	Base Peak or >50% of m/z 442	98.3% of m/z 442	Pass
199	5-9% of m/z 198	7.0 % of m/z 198	Pass
275	10-60% of Base Peak	27.4 % of Base Peak	Pass
365	>1% of Base Peak	2.8% of Base Peak	Pass
441	Present & < m/z 443	66.2% of m/z 443	Pass
442	Base Peak or >50% of m/z 198	Base Peak	Pass
443	15-24% of m/z 442	21.9 % of m/z 442	Pass

Table 1. DFTFP 5 ppm injection Peak True spectrum evaluation against Method 525.2's tuning criteria. All evaluation criteria were well within the method's expected ranges.

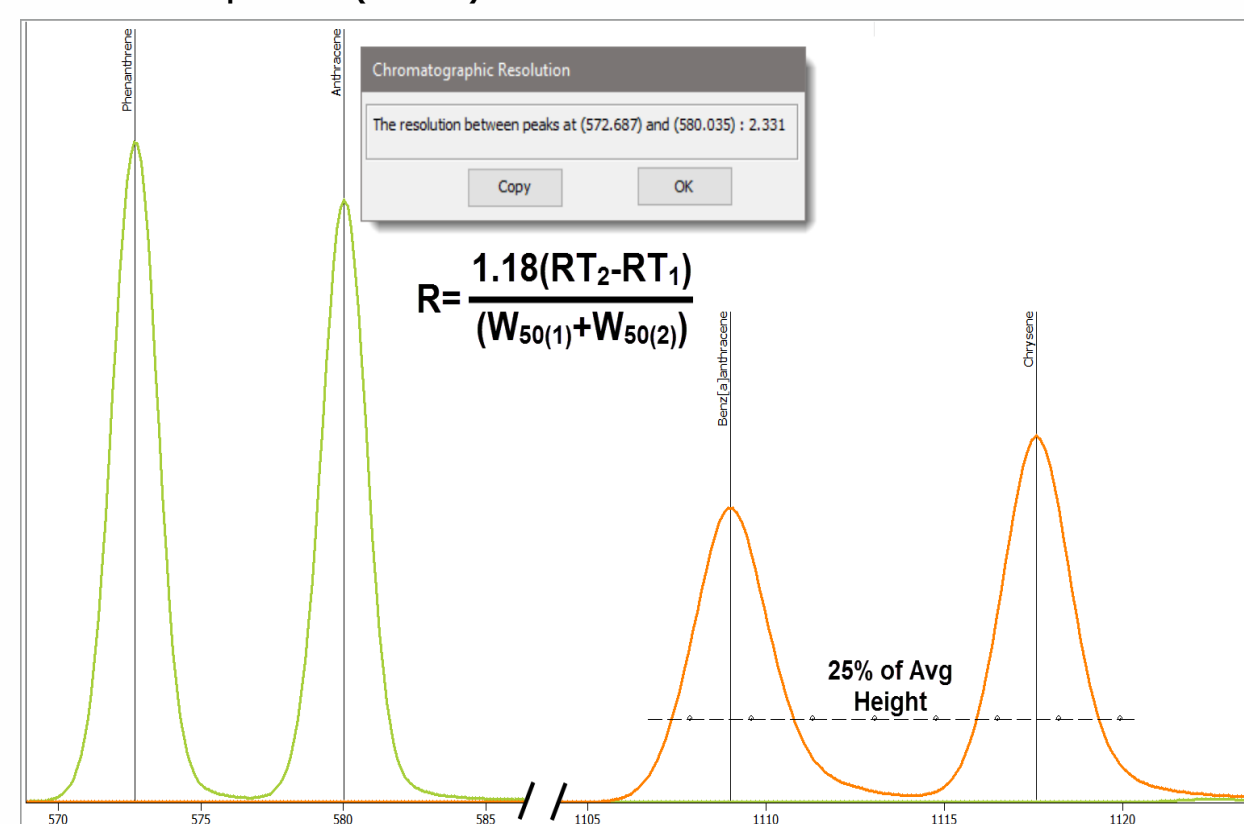


Figure 2. Evaluation of chromatographic separations. Chromatographic resolution is easily calculated within ChromaTOF. R values greater than 1.5 are regarded as being baseline resolved. A constant value trace can be plotted on the chromatogram to easily highlight the valley criteria of Benz[a]anthracene and Chrysene.

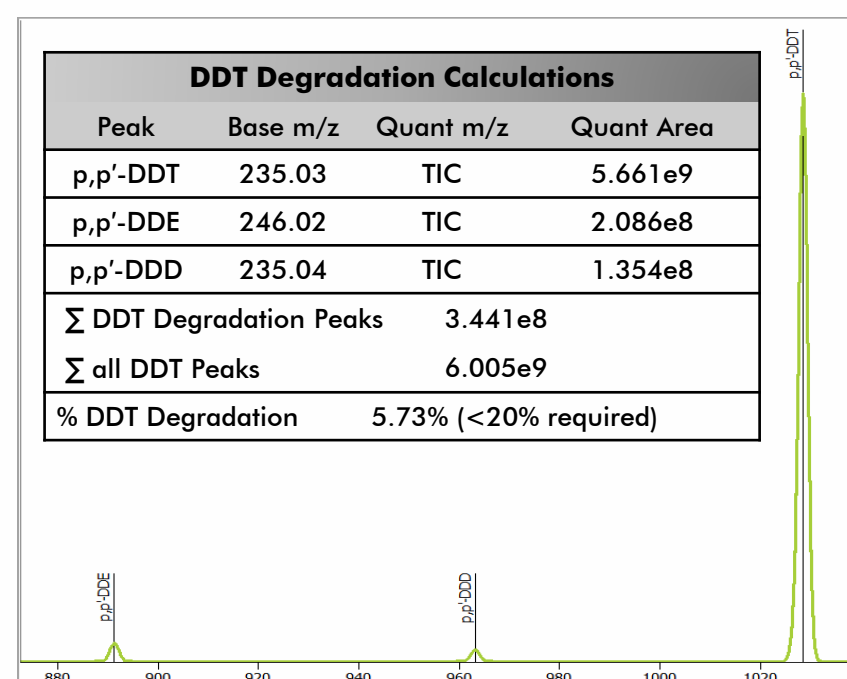


Fig 2. Evaluation of p,p'-DDT degradation. Method 525.2 requires less than 20% of DDT degrade into p,p'-DDE and p,p'-DDD based on each peak's TIC area.

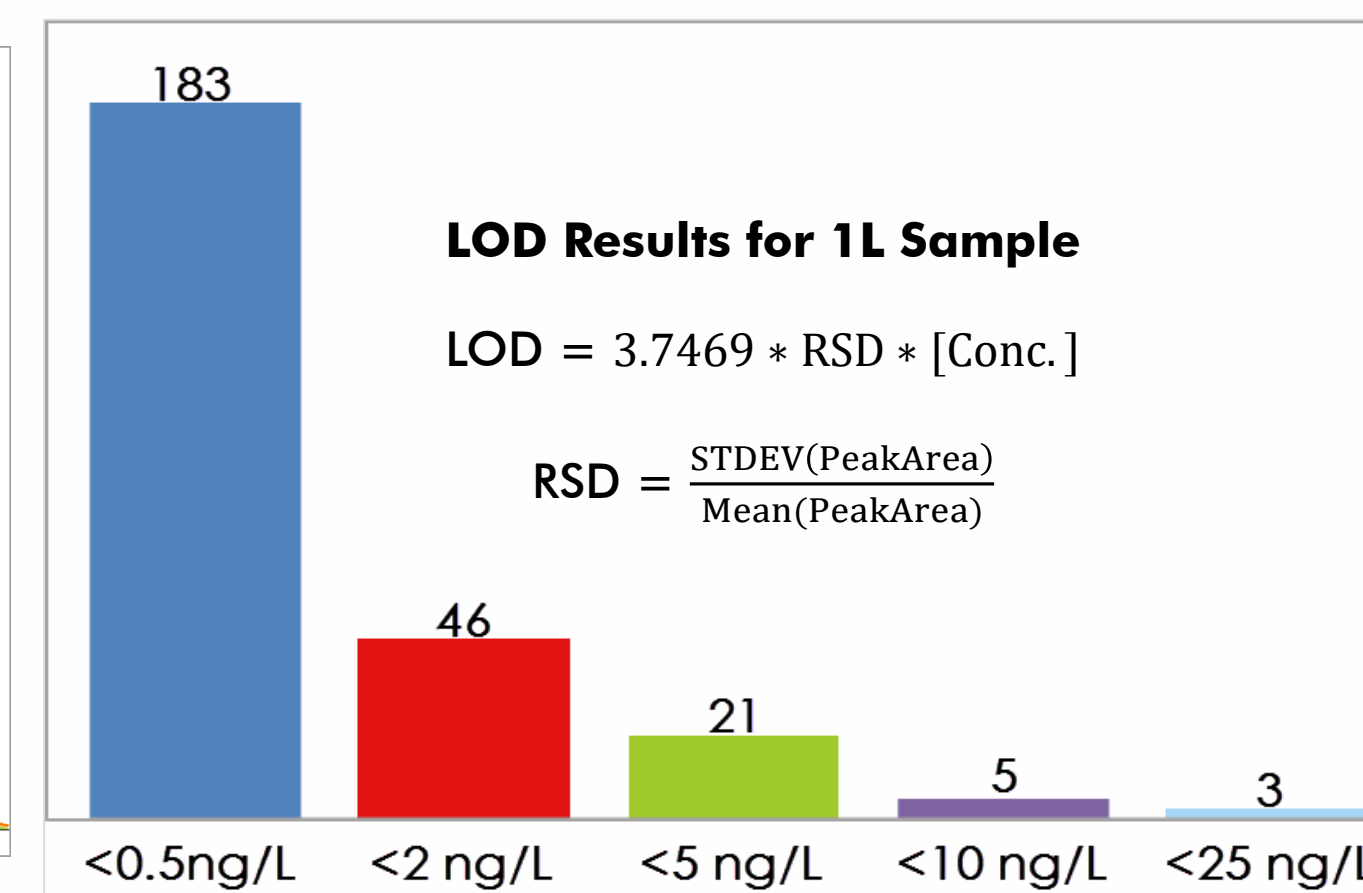


Figure 3. Number of target compounds at different Limits of Detection (LOD). Calculations based on fortified water standards at 1, 2, 5, 10, 20 & 50 ppb. RSD values calculated using 5 replicates per level. EPA 525.2 lists demonstrated MDLs of ~25 to ~2400 ng/L (most compounds 100-500 ng/L).

Selected Target Analytes in 1L River Water Sample

Name	Peak S/N	Conc. (ng/L)
2,4-Dimethylphenol	113	35.7
Diethyl Phthalate	1265	8.7
Atrazine	164	11.6
Anthraquinone	81	2.0
Aldrin	113	6.0
Metolachlor	82	4.4
Fluoranthene	280	2.1
Pyrene	262	1.9
Chrysene	41	1.3
Benzo[b]fluoranthene	138	1.1

Untargeted Peak Identification

River Water Sample – Downstream from Treatment Plant			
Name	Likely Source	Similarity	Peak S/N
Dihydroactinidiolide	Fragrance (tea scent)	853	838
Diethyltoluamide (DEET)	Insect Repellent	867	573
2,6-Dibromohydroquinone	Flame Retardant	830	271
Tri(β,β'-dichloroisopropyl)phosphate	Flame Retardant	756	97
Dehydroabietic acid	Pulp Resin	902	2154

Table 3. Examples of compounds found in a river water sample through ChromaTOF's NTD peak finding algorithms. An example of the deconvolution of DEET is shown below.

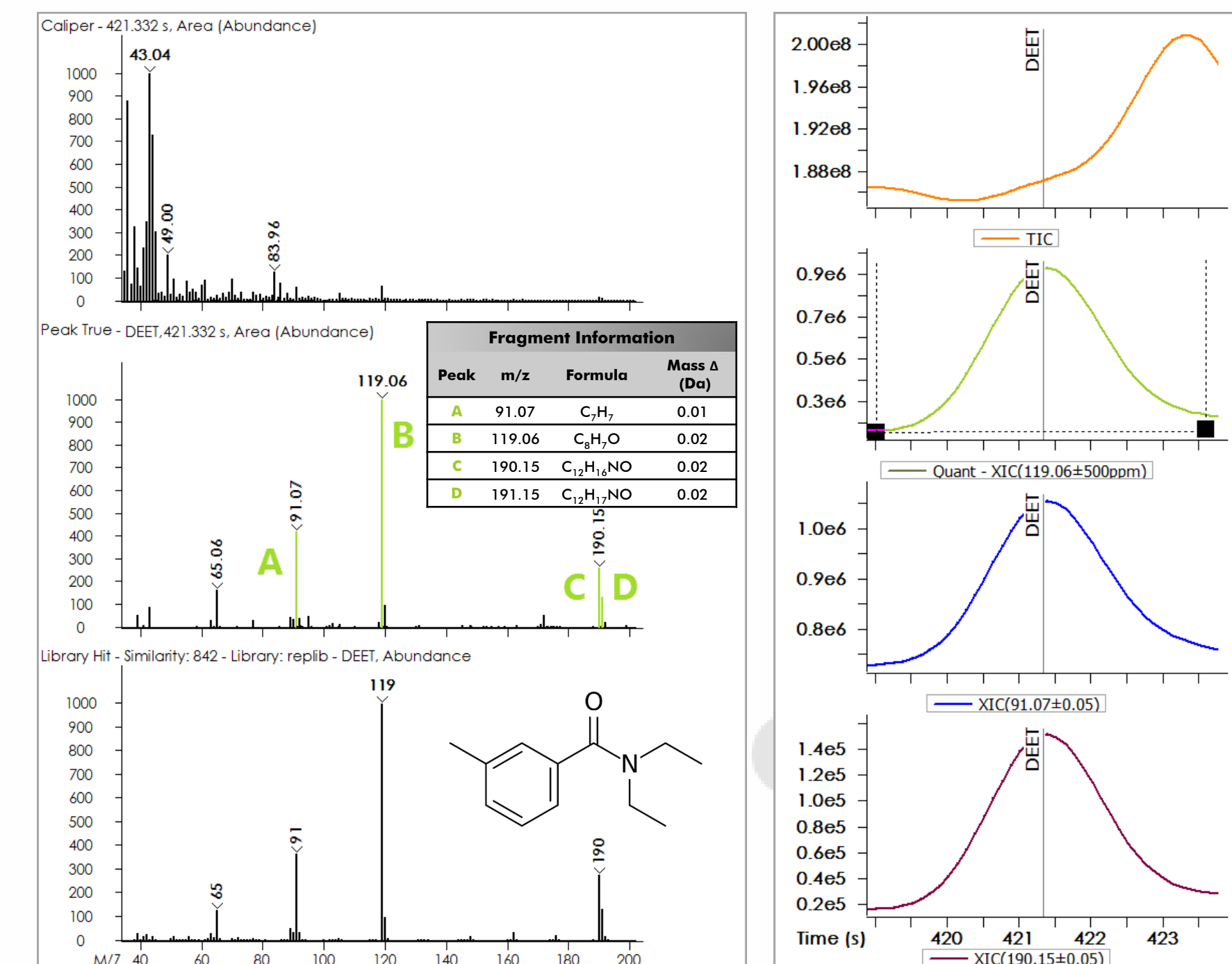


Figure 4. Selected mass traces and fragment calculations of the DEET signal found in a river water sample. Despite its relatively low abundance, ChromaTOF was able to find and deconvolute the related peak information. The top two spectra show the TIC spectra and deconvoluted Peak True spectra at the DEET peak's elution time. The library spectra (bottom) is shown for reference. Fragment ions and formulas calculated within ChromaTOF may be used to help confirm the presumptive library match.

Conclusions

The Pegasus BT's ability to collect full mass range spectral data with SIM level sensitivity allows for monitoring EPA Method 525.2 targets while also providing the ability to effectively detect new and emerging non-targeted contaminants at these same low limits of detection. NonTarget Deconvolution results combined with library and formula searches can lead to accurate identification of untargeted analytes.

Additionally, because you collect the entire mass range, you do not need to store and rerun the sample in order to evaluate historical contaminant trends.